Catalyzed N\textsubscript{2}O Activation

Promising (New) Catalysts for Abatement and Utilization

J. Pérez-Ramírez
Stellingen

behorende bij het proefschrift:

Gekatalyseerde N₂O Activering
Veelbelovende (Nieuwe) Katalysatoren voor Bestrijding en Toepassing

door Javier Pérez-Ramírez

1. Een behoorlijke mate van sceptis over de vooruitzichten van combinatoriële methoden wordt niet alleen veroorzaakt door het in hoge mate vertrouwelijke karakter van de vorderingen van het industriële onderzoek, maar wordt ook gevoed door het verlenen van octrooien op instrumenten die allang bestonden en al jaren in gebruik waren.

Hoofdstuk 2 van dit proefschrift.
United States Patent 6 149 882 to Symyx Technologies Inc. Parallel fixed bed reactor and fluid contacting apparatus.

2. Het criterium voor katalysatorbedverdunning zoals voorgesteld door Sofekun et al. lijdt aan 'het kip of het ei' probleem, aangezien het kennis vereist over de reactiesnelheidsconstante en de reactieorde, die beide nog onbekenden zijn in kinetiek onderzoek.

Hoofdstuk 3 van dit proefschrift.

3. De mogelijkheid om in situ spectroscopische analyses te verrichten tijdens de thermische ontleding van hydrotalcieten is cruciaal om fysisch-chemische omzettingen van chemische species en hun onderlinge interacties te bestuderen, evenals de fasedoorgangen tijdens de ontleding.

Hoofdstuk 4 van dit proefschrift.

4. Voltammetrie is een krachtige techniek om een 'vingerafdruk' te krijgen van de verschillende aanwezige species in ijzerkatalysatoren.

Hoofdstuk 6 van dit proefschrift.

5. Sporen van extra-framework ijzer-species in commerciële H-ZSM-5 leiden tot een hoge activiteit voor het activeren van het N₂O molecuul, terwijl andere extra-framework species slechts een bijrol vervullen.

Hoofdstuk 9 van dit proefschrift.

6. Toepassing van EXAFS voor de bepaling van de ijzer-coordinatie in ijzer-zeolieten wordt beperkt door het heterogene karakter van deze systemen.

Hoofdstukken 5, 6, en 9 van dit proefschrift.
7. Beweringen betreffende het creëren van poriën met een uniforme afmeting van ~4 nm in poreuze vaste stoffen vinden vaak hun oorsprong in een verkeerde interpretatie van gasadsorptie isothermen.


8. Wetenschappers die IR spectroscopie toepassen moeten collega’s zorgvuldiger citeren. Zo kende Lezcano et al. een absorptieband bij 1840 cm⁻¹ toe aan NO geadsorbeerde op ijzer(oxide) clusters in FeZSM-5, refererend aan Joyner and Stockenhuber, terwijl in de originele publicatie Joyner and Stockenhuber deze band toekenden aan NO op geïsoleerde ijzer(II) ionen.


9. De rol van lachgas (N₂O) in het milieu is om te huilen.

10. Eco-etiketten op alle produkten waarin N₂O (E-942) gebruikt wordt, bijvoorbeeld als drijfgas in slagroomspuitbussen, moeten direct verboden worden aangezien deze foutieve informatie bij consumenten misleidende associaties oproept.

Research Note of this thesis
Stelling 9

11. Eén tot twee jaar van een promotieonderzoek bezig zijn met het bouwen van een experimentele opstelling verschaf de benodigde tijd te verwerken wat anderen reeds gedaan hebben en om de juiste experimenten te bedenken.

12. Voor velen is geloof een prettig substituut voor kennis, zoals de dood is voor een moeilijk leven.

13. De opvatting over NO als zijnde een schadelijke vervalster is gewijzigd door het gebruik als signaalmolecuul in biologie en geneeskunde. Gecontroleerde doses van dit gas (<25 ppm per &-urige dag) zijn uitermate bevorderlijk voor verschillende fysiologische processen in levende wezens.


14. Atheïsme is een ‘non-prophet’ organisatie.

15. Een goede wetenschapper weet wat hij/zij zegt, terwijl een gemiddelde wetenschapper slechts zegt wat hij/zij weet.
Propositions

belonging to the Ph.D. thesis:

Catalyzed N₂O Activation
Promising (New) Catalysts for Abatement and Utilization

by Javier Pérez-Ramírez

1. A major source of skepticism about the future prospects of combinatorial methods stems not only from the highly confidential character of the progress accomplished by industrial research, but is also fed by patent granting on instruments that were already existing and used for years.

Chapter 2 of this thesis.
United States Patent 6 149 882 to Symyx Technologies Inc. Parallel fixed bed reactor and fluid contacting apparatus.

2. The criterion for bed dilution developed by Sofekun et al. suffers from 'the chicken and the egg' problem since it requires the rate coefficient and reaction order, which are beforehand unknown in kinetic investigations.

Chapter 3 of this thesis.

3. The ability to perform in situ spectroscopic (infrared and Raman) analyses during thermal decomposition of hydrotalcites is crucial to investigate physico-chemical transitions of single chemical species and the interactions between them, as well as phase transition upon decomposition.

Chapter 4 of this thesis.

4. Voltammetric response is a powerful technique to generate a fingerprint of the various species in iron-based catalysts.

Chapter 6 of this thesis.

5. Traces of extra-framework iron species in commercial H-ZSM-5 lead to high activities in the activation of the N₂O molecule, while other extra-framework species play only a secondary role.

Chapter 9 of this thesis.

6. Application of EXAFS for the determination of the Fe coordination in iron-zeolites is limited by the heterogeneous nature of this system.

Chapters 5, 6, and 9 of this thesis.
7. Statements regarding the creation of pores with a uniform size of ~4 nm in porous solids are often due to the wrong interpretation of the gas adsorption isotherms.


8. Scientists that apply IR spectroscopy should cite their colleagues more carefully. Lezcano et al., referring to Joyner and Stockenhuber, attributed an absorption band at 1840 cm\(^{-1}\) to NO adsorbed at iron(oxide) clusters in FeZSM-5, while in the original publication Joyner and Stockenhuber assigned it to NO adsorbed at isolated iron(II) ions.


9. The environmental role of laughing gas (N\(_2\)O) is not a laughing matter.

10. Eco-labels in all products using N\(_2\)O (E-942), e.g. as propulsor gas in whipped cream cans, should be immediately forbidden, since they are misleading to the customer.

Research Note of this thesis.
Proposition 9.

11. Spending 1-2 years of a Ph.D. research in building an experimental set-up provides the essential time to assimilate what others have already done and to think about the right experiments.

12. For many, faith is a suitable substitute for knowledge, as death is for hard life.

13. The perception of NO as a noxious pollutant has been altered by its use as signal molecule in biology and medicine. Indeed, controlled doses of this gas (< 25 ppm per 8-h day) are extraordinarily beneficial for different physiological processes in living creatures.


14. Atheism is a non-prophet organization.

15. A good scientist knows what he/she says, while an average scientist just says what he/she knows.
Catalyzed N\textsubscript{2}O Activation

Promising (New) Catalysts for Abatement and Utilization
Catalyzed $\text{N}_2\text{O}$ Activation

Promising (New) Catalysts for Abatement and Utilization

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. dr. ir. J.T. Fokkema,
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Javier Pérez-Ramírez

Master of Sciences in Chemical Engineering
geboren te Benidorm, Spanje
The research reported in this thesis was carried out at the Industrial Catalysis section, DelftChemTech, Faculty of Applied Sciences, Delft University of Technology (Julianalaan 136, 2628 BL, Delft, The Netherlands) with financial support by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO). The author can be contacted by e-mail: javier.perez.ramirez@hydro.com.
To My Parents Mariano and Rosario,
To Whom I Owe Everything

To Amalia, For Her Love,
Patience, and Dedication

"Humanity needs practical men, who get the most out of their work, and, without forgetting the general good, safeguard their own interest. But humanity also needs dreamers, for whom the disinterested development of an enterprise is so captivating that it becomes impossible for them to devote their care to their own material profit.

Without doubt, these dreamers do not deserve wealth, because they do not desire it. Even so, a well-organized society should assure to such workers the efficient means of accomplishing their task, in a life free from material care and freely consecrated to research."

Marie Sklodowska (1867-1934)
In Madame Curie, Pocket books,
Simon and Schuster, New York, 1946
Nitrous oxide (N$_2$O), also known as laughing gas, has been long considered as a relatively harmless species and has suffered from a lack of interest from scientists, engineers, and politicians. However, during the last decade a growing concern can be noticed since N$_2$O is a harmful gas in our atmosphere, contributing to the greenhouse effect and ozone layer depletion. Until recently, strategies for addressing climate change have principally been focused on reducing emissions of the main greenhouse gas carbon dioxide, but the importance of other greenhouse gases and opportunities for their abatement have been more and more recognized in the last years. This culminated in an agreement at the Third Conference of the Parties (COP-3) to the United Nations Framework on Climate Change in Kyoto (Japan) in December 1997 to set legally binding targets for reducing greenhouse gas emission based on a “six gas basket”, including carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), hydrofluorocarbons and perfluorocarbons (HFCs and PFCs), and sulfur hexafluoride (SF$_6$). As a result, the EU agreed to reduce emissions of the six-gases by 8% of 1990 levels by 2010 (1995 levels for HFCs, PFCs, and SF$_6$). Reduction of N$_2$O emissions plays an important role in reaching this target, as shown in Fig. 1. N$_2$O is the third most important greenhouse gas after CO$_2$ and CH$_4$. Due to its long life-time of approximately 150 years in the atmosphere, N$_2$O has 310 times the greenhouse potential of CO$_2$ (on a weight basis and when calculated over a 100-year time horizon). This makes that a relatively limited emission (compared to other greenhouse gases) is equivalent to about 10% of the CO$_2$ emission. Furthermore, N$_2$O plays a significant role in the stratosphere, because it is broken down by photolysis and oxidation, and initiates a chain of cyclic reactions leading to stratospheric ozone destruction. In spite of the “well-documented” environmental role of N$_2$O, several aspects regarding its use in today’s society are still being neglected (see Research Note).

Fig. 1. Relative importance of the greenhouse gases in the EU for the fulfillment of the Kyoto target. Others: HFCs, PFCs, and SF$_6$. The pie chart shows the distribution of the anthropogenic N$_2$O emission per sectors in the EU, averaged for the period 1990-1998 (European Environmental Agency, 2000).

Biological processes in soils and oceans are the primary natural source of N$_2$O. Human activities are believed to be responsible for half or more of the total annual generation of N$_2$O. Agriculture, through soil cultivation and the use of nitrogen-fertilizers, contributes to 57% of the total emission in the EU (see Fig. 1). Chemical production and the burning of organic material and fossil fuels are also important sources. A rapidly increasing source that
also doubled between 1990 and 1998 is the transport sector, as a side-effect of the introduction of the catalytic converter to control NO₂. Due to the large uncertainty in the emission estimates, it is not possible to firmly conclude anything.

Control of N₂O emissions from agriculture is difficult to assess due to large uncertainties of emission factors, on how various parameters affect emissions, and scarce data on efficacy of options to reduce emissions. N₂O emissions that can be reduced in the short term are associated with chemical production and the energy industry (~35% in the EU, see Fig. 1). Emissions from chemical industry mainly apply to adipic acid and nitric acid production plants. Other “newly identified” sources are production plants of caprolactam, glyoxal, acrylonitrile and, in general, processes using nitric acid as oxidizing agent or involving ammonia oxidation. Even though specific emission levels for N₂O have not been yet approved in the EU countries, stringent limits probably will be imposed in the near future. Prior to legislation, a number of industries have voluntarily initiated efforts to reduce N₂O from adipic acid production (global reduction from 600 to <100 kton N₂O per year) by development of thermal and catalytic technologies. Nitric acid production plants are currently the major N₂O source in the chemical industry, with a global annual emission of 400 kton N₂O. The large N₂O emission reduction potential (125 Mton CO₂-eq.) combined with the limited number of well-established sources makes N₂O abatement in the nitric acid industry a very attractive means to meet the targets set in the Kyoto agreements. This applies also to other sources in the chemical industry, although emissions are less significant. Combustion processes of coal, biomass, and waste in fluidized-bed reactors also contribute significantly to N₂O emissions, although quantification is less accurate. Most challenging, however, is the reduction of N₂O emissions from vehicles. Only in the particular case of adipic acid production, technologies are commercially available, but their application in other sources is not feasible, due to the characteristics of the tail-gas:

- Diluted N₂O streams (in the 0.05-0.5 vol.% range),
- Relatively low temperature (typically < 800 K), and
- Presence of catalyst inhibitors (O₂, H₂O, NOₓ, and SO₂).

Catalytic decomposition of N₂O into N₂ and O₂ is an attractive and cost-effective end-of-pipe technology to reduce N₂O emissions, but none of the catalysts proposed in the literature show a good activity and stability in N₂O conversion under realistic conditions of feed composition and space velocities. To improve stability and to lower the light-off temperature of certain catalysts, co-addition of reducing agents, like light hydrocarbons or ammonia to the feed mixture has been applied for catalytic N₂O reduction. This option is less attractive in stationary sources, due to the increased operating costs of the after-treatment and the potential source of other undesired emissions, i.e. NH₃ slip, unburnt hydrocarbons, CO, and CO₂. A novel process used in adipic acid plants, taking advantage of the high N₂O concentration, is based on the reuse of N₂O in the tail-gas as valuable oxidant to produce phenol from benzene, but in “diluted” tail-gases this alternative is unfeasible.

The work presented in this thesis focuses on the development of active and stable catalysts for N₂O abatement in tail-gases from different sources, with an open eye towards options for using N₂O as selective oxidant. Major attention is paid to nitric acid plants, the largest industrial source, and stationary combustion processes. Other sources analyzed are related to chemicals production and mobile combustion. The simulated tail-gases investigated largely vary in temperature (523-1223 K), total pressure (1-13 bar), space velocities (up to ~10⁶ h⁻¹), and concentration of N₂O (0.05-40 vol.%) and other components (O₂, NO, H₂O, SO₂). Development of such versatile formulations, applicable in the various sources, is challenging. Primary requirements for suitable catalyst formulations are activity at low temperature and especially resistance towards deactivation (chemical stability).
Different levels of catalyst development have been carried out. In the microlevel (catalyst selection), the most important part in this thesis, several stages of catalyst development have been performed, involving an iterative sequence of activities: extensive catalyst preparation, efficient testing under realistic conditions, identification of promising formulations, and catalyst and process optimization. Catalyst optimization refers to (i) the development of new preparation or activation routes, (ii) development of (novel) characterization procedures and to analyze promising formulations, (iii) stability tests, (iv) quantitative testing and kinetic studies, and (v) in situ mechanistic investigations. The successful identification of potentially applicable catalysts leads to scale-up in the mesolevel, i.e. putting the catalyst in practice (reactor selection). This level aims at the minimization of the pressure drop and reactor volume, with a high catalyst effectiveness, resistance to attrition, etc. The macrolevel accounts for the selection of the abatement option and the integration of the catalytic reactor in the entire plant (process integration). The location of the catalytic unit is determined by the flexibility of the plant/process with respect to space, heat exchange, interference with other reactions, etc., but should also confirm to optimized operation conditions of the catalyst.

Outline of the thesis

Chapter 1 reviews the environmental role of N₂O. Current strategies to control emissions in different sources are briefly summarized. The main industrial source of N₂O, i.e. the manufacture of nitric acid, is described in detail as a case study. For each location in the plant the potential N₂O abatement options are presented, including a process description, advantages, and disadvantages. The different abatement technologies proposed are rated based on a cost estimation for new or existing plants. This chapter gives a good impression of the different levels in catalyst development and the complexity of process selection. Prospects for future regulations of N₂O emissions and trends for implementation of efficient technologies are evaluated. Those interested mainly in scientific aspects should start reading this thesis from Chapter 2.

Chapter 2 reviews current trends in catalyst testing and describes the six-flow reactor set-up as a valuable tool for secondary catalyst screening in catalyst development, which is crucial for high-throughput screening and optimization of promising formulations (quantitative screening, kinetic studies, and stability tests). Criteria for ideal behaviour in reactor models and transport phenomena, crucial in order to achieve intrinsic catalyst activity and kinetic data are presented. The versatility, accuracy, and reproducibility of the six-flow reactor was proven in a detailed investigation related to transport phenomena in diluted fixed-bed laboratory reactors in Chapter 3. The influence of catalyst-diluent distribution and the degree of dilution on the conversion in catalyst testing are studied both experimentally and by means of simulations. A revised general criterion for maximum allowance of diluent based on observable quantities is derived.

For optimization purposes, two catalytic systems are mainly investigated: mixed oxides from hydrotalcites, and Fe-based catalysts (mainly MFI zeolites). Controlled decomposition of hydrotalcites is crucial to optimize the performance of the so-formed mixed oxide catalysts. In Chapter 4, in situ infrared and Raman vibrational spectroscopies are for the first time used to investigate the thermal decomposition and reconstruction of promising catalytic systems: Co- and Ni-hydrotalcites. Based on the application of these and other in situ techniques, a detailed mechanistic model has been proposed.

In Chapter 5 the characterization of FeZSM-5, prepared via a novel ex-framework route, is presented. Chapter 6 focuses on the development of a novel and efficient electrochemical method to characterize heterogeneous catalysts. This technique, which is based on
voltammetric response of electro-active species in the solid catalyst, is applied to determine the nature of the iron species in isomorphously substituted FeZSM-5 and their products of activation by calcination and steam treatment.

Chapter 7 reports on the superior performance of the ex-framework FeZSM-5 catalysts for direct N₂O decomposition in simulated tail-gases from chemical production plants and combustion processes. This catalyst has been compared with noble metal-based catalysts on different supports and FeZSM-5 catalysts prepared by other methods. The versatility of ex-framework catalyst is remarkable, and the application to other processes of industrial or environmental relevance is discussed. These control options include:

- Direct decomposition of N₂O in tail-gases from nitric acid plants and stationary combustion processes.
- Selective reduction of N₂O with hydrocarbons in mobile combustion sources (lean de-NOₓ catalyst) or low temperature tail-gases.
- Utilization of N₂O as valuable chemical, in the selective oxidation of benzene to phenol.

N₂O and NO go together in tail-gases and their formation/removal are strongly linked. A great advantage of Fe-based catalysts is the promotion effect of NO in the N₂O decomposition. In Chapter 8 the NO-assisted N₂O decomposition over these catalysts is elucidated. Based on steady-state and transient kinetic studies, a mechanism for the promotion is proposed. The promotion is observed for zeolitic as well as for non-zeolitic Fe-based catalysts and the mechanism depends on the operation temperature for N₂O decomposition. Several mechanistic aspects of various N₂O-related reactions and the parallelism with other NO-catalyzed processes are discussed.

In Chapter 9, the nature of the active sites for N₂O decomposition over FeMFI zeolites is discussed: Is the presence of iron essential in the catalysis? What form of iron is active/inactive? Are other species, e.g. Lewis acid sites, participating? These questions are approached by extending the ex-framework route introduced in Chapters 5 and 6 to synthesize zeolites with different framework compositions (combinations of Si, Al, Ga, and/or Fe), followed by a detailed characterization and catalyst testing. Special attention is paid to the optimization of the steam activation treatment, which determines the catalyst constitution with respect to iron, and ultimately the catalytic performance. This, together with preparation of zeolites with different crystal size, and application of an alkaline post-treatment, provides structure-activity relationships, and yields valuable information on the nature of the active species in the catalysts.

In Chapter 10 the conclusions of this thesis are summarized. Different aspects relevant to the integration of the macro-, meso-, and microlevel in the development and implementation of suitable (active, selective, and stable) catalysts for N₂O control in different sources are discussed. The implication of the research work carried out for catalysis is emphasized.

At the end of this thesis, a Research Note warns on the impact of N₂O in today’s society, not only in the environment, but also due to its increasing use as drug.

J. Pérez-Ramírez

Delft, February 2002

Each chapter of this thesis is partially written based on one or more separate publications, and can be read independently. Therefore, some overlap between the chapters may occur.
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Control of N\textsubscript{2}O in Nitric Acid Production
Technical and Economical Aspects

Nitric acid production represents the largest source of N\textsubscript{2}O in the chemical industry, with a global annual emission of 400 kton N\textsubscript{2}O. The high impact of N\textsubscript{2}O on the environment as greenhouse gas and stratospheric ozone depletor, and the ongoing agreements and prospective regulations calls for the development of efficient and economical systems for N\textsubscript{2}O mitigation, but no mature commercial technology is yet available. In this chapter, the current state-of-the-art for N\textsubscript{2}O control in the nitric acid manufacture is reviewed. The formation of N\textsubscript{2}O in the process is analyzed and several abatement options are presented, depending on the position in the process. Primary abatement options deals with modifications in the ammonia oxidation catalyst, secondary abatement with options between the ammonia converter and the absorber, tertiary abatement with options in the tail-gas upstream of the expander, and quaternary abatement with options in the tail-gas downstream of the expander (end-of-pipe). The implementation of abatement technologies is evaluated based on the technical advantages and disadvantages, and cost efficiency.
1. Environmental role of N₂O

Nitrous oxide (N₂O) had until recently, largely escaped attention, but with increasing concerns about global warming and ozone depletion in the upper atmosphere, the environmental role of this gas is coming under scrutiny. The atmospheric concentrations of N₂O have been relatively constant for many centuries (~270 ppbv). The present-day N₂O atmospheric concentration is 310 ppbv, which means a 9% increase from pre-industrial levels (285 ppbv) at an annual growth rate of 0.2-0.3% (Fig. 1). This mismatch between N₂O sources and sinks is due to anthropogenic practices, especially during the second part of the 20th century.¹⁴

![Graph showing the evolution of atmospheric N₂O concentration](image)

**Fig. 1.** Evolution of the atmospheric N₂O concentration.³

N₂O as ozone depletor. N₂O is the major source of NOₓ in the stratosphere, and therefore an important natural regulator of stratospheric ozone.⁵⁷ The overall influence of N₂O on the ozone layer is complex and very different from that of substances covered by the Montreal protocol (chlorofluorocarbons (CFCs), halons, carbon tetrachloride, and methyl chloroform).⁸ A great deal of uncertainty exists regarding the chemical reactions involved. At this time, there are no doubts on the negative effect of N₂O on the ozone layer, but there is no consensus on a quantitative value for its ozone-depleting potential.⁹

N₂O as greenhouse gas. N₂O contributes to the greenhouse effect, a phenomenon caused by strong absorbance of infrared radiation in the atmosphere.¹⁰¹¹ Although N₂O is not the major contributor to global warming (~6%),⁹ it is much more potent than either of the other two most common anthropogenic greenhouse gases, CO₂ and CH₄. Due to its long life-time of approximately 150 years in the atmosphere, N₂O has 310 and 21 times the global warming potential (GWP) of CO₂ and CH₄, respectively.¹²¹³ The Kyoto protocol (December, 1997) sets legal binding targets for reducing emissions of 6 greenhouse gases (CO₂, CH₄, N₂O, HFC, PFC, SF₆) to be realized in the period 2008-2012.¹⁴ The European Community committed itself to reducing its emissions of greenhouse gases by 8% during the period 2008-2012 in comparison with their levels in 1990. The reduction targets in the different EU countries are shown in Table 1. N₂O emissions account for 10% of the total greenhouse gas emissions in the EU (Fig. 2), so its reduction plays an important role in reaching the global 8% target. Emissions targets for other industrialized nations are 6% for Japan and Canada and 7% for United States.¹⁴
2. Sources of N₂O and emission control

N₂O is produced by both natural (65%) and anthropogenic (35%) sources (Table 2). Biological processes in soils and oceans are the primary natural sources of N₂O. Agriculture is a major anthropogenic source, but control of these emissions is difficult due to its very diffuse nature. N₂O emissions that can be reduced in the short term are associated with chemical production and energy industry (~35% in the EU, Fig. 2). This emission is concentrated in a limited number of large N₂O sources, which holds promise for an economic and efficient reduction strategy to fulfill the Kyoto commitment. Nowadays, the major sources of N₂O in the chemical industry are the production of nitric acid and adipic acid. N₂O is also produced in general organic synthesis using HNO₃ as the oxidant or reactions involving ammonia oxidation, e.g., during manufacture of glyoxal, caprolactam, and acrylonitrile. Emissions from the latter N₂O sources are less significant and not quantified as yet. Stationary combustion of fossil fuels, biomass, and municipal and industrial waste also involves a significant N₂O emission, although quantification is less accurate. An increasing contribution of N₂O stems from the catalytic converters in motor vehicles, N₂O being formed during NOₓ control.

![Diagram showing relative importance of greenhouse gases in the EU for the fulfillment of the Kyoto target. Others: HFCs, PFCs, and SF₆. The pie chart shows the distribution of the anthropogenic N₂O emission per sector in the EU, averaged for the period 1990-1998.]

Different (catalytic and thermal) abatement technologies have been successfully developed for adipic acid plants, due to the high N₂O concentration in the tail-gas (25-40 vol.%). Due to the exothermicity of the decomposition reaction, a large increase in the temperature occurs within the catalyst bed. For instance, the decomposition of 35 vol.% N₂O in air leads to an adiabatic temperature rise of the gas of 920 K. In this temperature
window, a large number of catalysts exhibit considerable activity. So, in this case the activity of the catalyst is not a critical factor for the effectiveness of the technology.

An attractive variant of this abatement technology is the integration of adipic acid and nitric acid plants (Fig. 3). In this case, HNO₃ is piped from the nitric acid plant into the adipic acid plant. The adipic acid tail-gas, containing around 20 vol.% of N₂O and 20 vol.% NO₂ (plus CO₂, O₂, and N₂) are pumped back into the nitric acid plant. The loop is closed by absorbing NO₂ with water in the absorption column, recovering nitric acid. What is left is a gas which is almost free from NO and NO₂ but still contains all of the N₂O formed in the adipic acid process, which can be (catalytically or thermally) decomposed in a unit integrated in the nitric acid plant (see Fig. 3), downstream of the nitric acid absorption column. This system has been successfully implemented in the BASF’s adipic acid and nitric acid plants in Ludwigshafen (Germany).

Table 2. Global N₂O emissions.¹⁶,¹⁷

<table>
<thead>
<tr>
<th>Type of source</th>
<th>N₂O emissions / Mton N₂O y⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td>~13</td>
</tr>
<tr>
<td>Soils</td>
<td>10</td>
</tr>
<tr>
<td>Oceans</td>
<td>2.9</td>
</tr>
<tr>
<td>Atmospheric chemistry</td>
<td>0.2</td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>~7</td>
</tr>
<tr>
<td>Agriculture (including fertilizers)</td>
<td>3.5</td>
</tr>
<tr>
<td>Nitric acid production</td>
<td>0.4</td>
</tr>
<tr>
<td>Adipic acid production</td>
<td>&lt;0.1 (reduced from 0.6)</td>
</tr>
<tr>
<td>Fossil-fuel combustion (stationary)*</td>
<td>0.2-0.5</td>
</tr>
<tr>
<td>Fossil-fuel combustion (mobile)*</td>
<td>0.4-0.9</td>
</tr>
<tr>
<td>Biomass combustion</td>
<td>1.0</td>
</tr>
<tr>
<td>Sewage treatment</td>
<td>1.5</td>
</tr>
<tr>
<td>Total of all sources</td>
<td>~20</td>
</tr>
</tbody>
</table>

* emission is uncertain.

Fig. 3. Integration concept of adipic acid plants and nitric acid plants for HNO₃ recovery and N₂O abatement, after Kuhn.²¹
Only in the particular case of adipic acid production, technologies are commercially available, but their application (extrapolation or adaptation) in other sources, e.g. (single) nitric acid plants and stationary combustion processes, is not feasible, due to the presence of diluted N₂O streams (in the 0.05-0.5 vol.% range) at a relative low temperature (typically < 800 K), and the presence of catalyst inhibitors (O₂, H₂O, SO₂, and NO₃).¹³,¹⁸,¹⁹

A novel process in adipic acid plants, jointly developed by Solutia and the Boreskov Institute of Catalysis, consists in the reutilization of N₂O as a valuable oxidant to oxidize benzene to phenol (Fig. 4)²⁴ This process also takes advantage of the high N₂O concentration in the tail-gas. The process has been successfully tested in a pilot plant facility erected by Solutia in Pensacola. The new system is meant to replace the thermal off-gas treatment currently used in this adipic acid plant. This application is unfeasible in diluted tail-gases. Attempts to concentrate these streams by selective adsorption using metal-exchanged zeolites has led to N₂O concentrations of 5 vol.%,²⁵ still insufficient to satisfy practical requirements.

![Chemical Diagram](image)

**Fig. 4.** The AlphOx™ process for N₂O reuse as selective oxidant in the benzene-to-phenol process, after Panov.²⁴

### 3. Reducing N₂O emissions from nitric acid production

During the manufacture of nitric acid, N₂O is produced as an unwanted by-product of the catalytic oxidation of ammonia. N₂O is currently emitted via the tail-gas stack. Adipic acid producers have led the way in making and fulfilling a voluntary commitment to reduce N₂O emissions from 600 kton N₂O y⁻¹ in 1994 to 100 kton N₂O y⁻¹ currently (see Table 2). Now nitric acid plants around the world collectively represent the largest single source of N₂O in the chemical industry (400 kton N₂O y⁻¹), and producers of weak nitric acid (Table 3) can come under pressure to develop and implement abatement technology.

In connection to the fulfillment of the Kyoto agreement, the contribution of non-CO₂ greenhouse gases, especially N₂O, PFCs, and HFCs is relatively high due to the promising cost efficiency of the control measures. For example, the cost of CO₂ reduction measures by changing coal-fired to gas-fired electricity plants is 23 € per ton CO₂-eq. removed, while the cost efficiency of reduction of HFC is about 11 € per ton CO₂-eq.²⁶,²⁷ The cost of N₂O reduction measures at nitric acid plants is between 0.3 and 3 € per ton CO₂-eq. (see §6.1). This cost advantage of N₂O-control technology offers a clear benefit and a great market potential.

In several European countries, e.g. Germany, United Kingdom, and The Netherlands, reduction of N₂O emissions from nitric acid plants would effectively contribute or even fulfill their Kyoto commitments (see Table 1), which represents an extramotivation for development of technology. For instance, total N₂O emission of the nitric acid plants in the Netherlands is ~8.5 Mton CO₂-eq., representing one of the largest contributions to the total
N₂O emission in the country. There are only 6 plants, owned by 2 companies (DSM and Norsk Hydro) (Table 4). The large N₂O (and thus CO₂) reduction potential combined with the limited number of sources and the potential cost efficiency makes N₂O abatement in the nitric acid industry a very attractive means to meet the targets set in the Kyoto agreements and prospective regulations.

Table 3. Major licensors of weak nitric acid production.²⁶

<table>
<thead>
<tr>
<th>Licensor (former name)</th>
<th>Country</th>
<th>No. of plants in Europe⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technip (Grande Paroisse)</td>
<td>France</td>
<td>30</td>
</tr>
<tr>
<td>Technip USA (KTI-Chemico)</td>
<td>USA</td>
<td>8</td>
</tr>
<tr>
<td>Krupp Uhde</td>
<td>Germany</td>
<td>51</td>
</tr>
<tr>
<td>Stamicarbon (DSM)</td>
<td>Netherlands</td>
<td>14</td>
</tr>
<tr>
<td>Giovanola (Bagmag)</td>
<td>Switzerland</td>
<td>15</td>
</tr>
<tr>
<td>GIAP</td>
<td>Russia</td>
<td>6 (&gt; 300 in Russia)</td>
</tr>
<tr>
<td>Norsk Hydro</td>
<td>Norway</td>
<td>6</td>
</tr>
<tr>
<td>Montedison (Montecatini)</td>
<td>Italy</td>
<td>4</td>
</tr>
</tbody>
</table>

Other known licensors, but with a small contribution (<4 plants) to the European market: Técnicas Reunidas, Spain (former Espindesa); Jacobs Engineering, UK (former Humphreys & Glasgow); Sumitomo Chemicals, Japan; Chematur Engineering, USA (former Weatherly); Aventis, France (former Rhône-Poulenc); Dupont, USA.

²⁶ capacities not considered; ⁶ excluding former Russia.

Table 4. Potential market volume in the Netherlands.²⁶

<table>
<thead>
<tr>
<th>Owner / location</th>
<th>Plant capacity</th>
<th>N₂O emission</th>
<th>N₂O emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ton HNO₃ per day</td>
<td>ton N₂O per day</td>
<td>kton CO₂-eq. per day</td>
</tr>
<tr>
<td>Hydro Agri / Sluiskild</td>
<td>1620</td>
<td>12.2</td>
<td>3.8</td>
</tr>
<tr>
<td>Hydro Agri / Sluiskild</td>
<td>2030</td>
<td>15</td>
<td>4.7</td>
</tr>
<tr>
<td>DSM / Geleen</td>
<td>580</td>
<td>16.6 - 22.2</td>
<td>5.1 - 6.9</td>
</tr>
<tr>
<td>DSM / Geleen</td>
<td>1390</td>
<td>16.6 - 22.2</td>
<td>5.1 - 6.9</td>
</tr>
<tr>
<td>DSM / IJmuiden</td>
<td>710</td>
<td>16.6 - 22.2</td>
<td>5.1 - 6.9</td>
</tr>
<tr>
<td>DSM / IJmuiden</td>
<td>680</td>
<td>16.6 - 22.2</td>
<td>5.1 - 6.9</td>
</tr>
<tr>
<td>Total</td>
<td>7010</td>
<td>54.1 - 59.7</td>
<td>16.8 - 18.6</td>
</tr>
</tbody>
</table>

²⁶ figures based on production (not on capacity).

4. N₂O formation in nitric acid production

In order to develop N₂O reduction technologies in nitric acid plants, it is important to analyse the causes for formation of this gas in the overall process. Nitric acid is mostly produced as weak acid (concentration of 50-65%) for production of nitrogen fertilizers like ammonium nitrate and super phosphates, but also as oxidizing agent for the production of adipic acid and other organic compounds (in which N₂O is also produced). A smaller amount is produced as concentrated nitric acid (> 70%) for production of explosives, use in the metallurgical industry and production of rocket fuels. As the production of concentrated nitric acid by either concentrating weak acid or direct synthesis from air does not significantly contribute to the N₂O production, this review focuses on the production of weak nitric acid.

Production of weak nitric acid is based on the Ostwald process and consists of the following basic chemical operations:²⁸

1. Catalytic oxidation of ammonia with air into nitric oxide
2. Oxidation of nitric oxide into nitrogen dioxide
3. Absorption of nitrogen dioxide in water to produce nitric acid
Two main process configurations can be distinguished:

- **Mono-pressure** design is generally used in smaller plants, or in larger plants where minimization of capital is a critical design consideration. NH₃ oxidation and absorption of NO₂ occur at the same relative pressure. This reduces the complexity and capital cost of the dual-pressure plant (see below), but at the cost of efficiency loss, potentially for both the front and back ends of the plant. Mono-pressure plants can be designed to operate at low to medium pressure to favor the NH₃ oxidation reaction or at high pressure to favor the absorption reactions (or at any operating pressure in between).

- **Dual-pressure** design is generally used in larger plants, or in midsize plants where higher utility/raw material costs dictate a minimization of operating expenses as a critical design consideration. NH₃ oxidation occurs at low pressure. This decreases the gas density and the nitrogen loading on the gauze. This results in an increase in efficiency of the NH₃ oxidation reaction and minimization of platinum catalyst loss. Absorption of NO₂ occurs at high pressure to maximize the partial pressure of the gas phase reactants. The result is an increase in the rate of NO oxidation and in the solubility of O₂ and NO₂ in the aqueous solution. A nitrous gas compressor boosts the pressure from the front-end of the process (ammonia oxidation) to the back-end (absorption). The production of weak nitric acid according to the dual-pressure configuration is schematically shown in Fig. 5 and is discussed below. An example of characteristic data and operating conditions for the various design types is given in Table 5, and more specifically of dual-pressure plants in Table 6.

### Table 5. Specific consumption figures of various process variants.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>H&amp;H</th>
<th>M&amp;M</th>
<th>M&amp;H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating pressure / bara&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11</td>
<td>9</td>
<td>4.5 / 12</td>
</tr>
<tr>
<td>Typical run time / days</td>
<td>70</td>
<td>120</td>
<td>210</td>
</tr>
<tr>
<td>NH₃ usage&lt;sup&gt;b&lt;/sup&gt; / ton NH₃ per ton HNO₃</td>
<td>0.291</td>
<td>0.285</td>
<td>0.279</td>
</tr>
<tr>
<td>Pt usage&lt;sup&gt;c&lt;/sup&gt; / mg Pt per ton HNO₃</td>
<td>50</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>Power usage / kWh per ton HNO₃</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>HP steam import&lt;sup&gt;d&lt;/sup&gt; / ton HzO per ton HNO₃</td>
<td>0.51</td>
<td>0.60</td>
<td>0.54</td>
</tr>
<tr>
<td>LP steam export&lt;sup&gt;e&lt;/sup&gt; / ton HzO per ton HNO₃</td>
<td>0.27</td>
<td>0.21</td>
<td>0.06</td>
</tr>
<tr>
<td>Cooling water&lt;sup&gt;f&lt;/sup&gt; / m³ HzO per ton HNO₃</td>
<td>130</td>
<td>120</td>
<td>110</td>
</tr>
</tbody>
</table>

H&H and M&M: high and medium mono-pressure plants, M&H: dual-pressure plant.

<sup>a</sup> absolute pressure; <sup>b</sup> including NH₃ for catalytic NO₂ abatement (to 200 ppm); <sup>c</sup> described as net of platinum recovery systems; <sup>d</sup> steam conditions: 42 kg cm² g⁻¹ and 673 K; <sup>e</sup> steam conditions: saturated at 3.5 kg cm² g⁻¹; <sup>f</sup> at 284 K temperature rise and 2.5 kg cm² pressure drop allowance.

### Table 6. Data of two dual-pressure nitric acid plants in Austria.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Plant A</th>
<th>Plant B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity&lt;sup&gt;a&lt;/sup&gt; / ton HNO₃ y⁻¹</td>
<td>300 000</td>
<td>180 000</td>
</tr>
<tr>
<td>NH₃ input 1998 / ton</td>
<td>91 700</td>
<td>52 330</td>
</tr>
<tr>
<td>HNO₃ production&lt;sup&gt;a&lt;/sup&gt; / ton HNO₃</td>
<td>321 400</td>
<td>183 430</td>
</tr>
<tr>
<td>Ammonia oxidation</td>
<td>4.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Temperature / K</td>
<td>1168</td>
<td>1113 - 1123</td>
</tr>
<tr>
<td>Pressure / bara</td>
<td>9</td>
<td>4.8</td>
</tr>
<tr>
<td>Temperature / K</td>
<td>298</td>
<td>298</td>
</tr>
<tr>
<td>Tail-gas flow / Nm³ h⁻¹</td>
<td>112 000</td>
<td>65 500</td>
</tr>
<tr>
<td>NO₂ reduction process</td>
<td>SCR</td>
<td>SCR</td>
</tr>
<tr>
<td>NO₂ concentration after SCR&lt;sup&gt;b&lt;/sup&gt; / ppm</td>
<td>180 - 190</td>
<td>320 - 330</td>
</tr>
<tr>
<td>NH₃ slip / ppm</td>
<td>0.26 - 2.6</td>
<td>0.05 - 0.10</td>
</tr>
<tr>
<td>N₂O concentration / ppm</td>
<td>1960 - 2750</td>
<td>1180 - 1570</td>
</tr>
</tbody>
</table>

<sup>a</sup> related to 100% HNO₃; <sup>b</sup> as NO₂.
4.1. Catalytic oxidation of ammonia

Liquid ammonia is filtered and vaporized before injection in the catalytic ammonia converter (Fig. 6a). Filtered and compressed air is added to obtain an ammonia air ratio of 1:10 in order to stay below the lower explosion limit. In the catalytic converter the ammonia is mainly converted to NO and water (eq. (1)) using a platinum-rhodium gauze with a composition of 90% Pt and 10% Rh (Fig. 6b). Rhodium is added to the catalyst formulation for strength and to reduce the amount of platinum lost during conversion of the process gas.

Operating temperatures may vary between 1073-1223 K and pressures between 1-6.5 bara (for mono-pressure: 1-13 bara). The NO yield depends on the pressure and the temperature, as indicated in Table 7.

**Table 7. Dependence of the NO yield with the pressure and temperature in the NH₃ converter.**

<table>
<thead>
<tr>
<th>P / bara</th>
<th>T / K</th>
<th>NO yield / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 1.7</td>
<td>1083 - 1123</td>
<td>97</td>
</tr>
<tr>
<td>1.7 to 6.5</td>
<td>1123 - 1173</td>
<td>96</td>
</tr>
<tr>
<td>Above 6.5</td>
<td>1173 - 1213</td>
<td>95</td>
</tr>
</tbody>
</table>

The remainder of ammonia is either converted to N₂ or N₂O (eqs. (2) and (3)). The reactions are exothermic. Air pollution or contamination from the ammonia can poison the catalyst. This effect, as well as poor ammonia-air mixing and poor gas distribution across the catalyst gauze, may reduce the yield by 10%.

\[
\begin{align*}
4\text{NH}_3 + 5\text{O}_2 & \rightarrow 4\text{NO} + 6\text{H}_2\text{O} & \text{(1)} \\
4\text{NH}_3 + 4\text{O}_2 & \rightarrow 2\text{N}_2\text{O} + 6\text{H}_2\text{O} & \text{(2)} \\
4\text{NH}_3 + 3\text{O}_2 & \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O} & \text{(3)}
\end{align*}
\]

Lower catalyst temperature for a certain pressure tends to be more selective towards unwanted products (eqs. (2) and (3)). Due to the harsh operating conditions, the catalyst ages due to evaporation of platinum as PtO₂. A catchment facility made of Pd recovers 60-80% of
the evaporated platinum, following the principle schematically represented in Fig. 6c. The catalyst gauzes have to be replaced up to 4 times per year.

Further undesired consecutive reactions the decomposition of NO, which is metastable at the converter temperature, and the reaction of ammonia with nitric oxide (eqs. (4) and (5)), also reduce the effective ammonia conversion efficiency, and can lead to the additional formation of N₂O. Palladium in the catchment packs catalyses the latter reactions.¹⁷

\[
\begin{align*}
2\text{NH}_3 + 8\text{NO} & \rightarrow 5\text{N}_2\text{O} + 3\text{H}_2\text{O} \quad (4) \\
4\text{NH}_3 + 4\text{NO} + 3\text{O}_2 & \rightarrow 4\text{N}_2\text{O} + 6\text{H}_2\text{O} \quad (5)
\end{align*}
\]

4.2. Oxidation of nitrogen dioxide

After formation of NOₓ the nitrous gases are cooled to promote further oxidation to NO₂. NO reacts non-catalytically with residual oxygen to form NO₂ and its liquid dimer, N₂O₄ (eq. (6). As this reaction is also exothermic, continuous cooling is required. Operating at low temperatures and high pressures promotes maximum production of NO₂ within a minimum reaction time. Continuous cooling is obtained by a train of heat exchangers producing high-pressure steam, and heating tail-gas, and the use of cooling water. Condensed water, forming a weak acid solution, is separated and transported to the absorption column. High-pressure steam is used to produce electricity in a steam turbine.

\[
2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4 \quad (6)
\]

4.3. Absorption in water

The final step for the production of weak nitric acid introduces the nitrogen dioxide/dimer mixture into an absorption process after being cooled. The gas mixture is pumped into the bottom of the absorption tower (Fig. 7), while liquid N₂O₄ is added at a higher point. Deionized process water enters the top of the column. Both liquids flow countercurrent to the nitrogen dioxide/dimer gas mixture. Oxidation takes place in the free space between the trays, while absorption occurs on the trays (eq. (7)). The absorption trays are usually sieve or bubble cap trays.

\[
3\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{NO} \quad (7)
\]

Absorption of NO₂ in water is promoted at elevated pressure, resulting in tail-gases containing less than 200 ppmv of NOₓ. Therefore, in dual-pressure systems the nitrous gases are compressed to pressures up to 13 bara and cooled to a typical temperature of 323 K. In mono-pressure systems, compression and further cooling is omitted. The cooled nitrous gases are led into an absorber column in counter current with process water to form a nitric acid solution, containing dissolved NOₓ. This gas is removed in a bleacher column using a counter current flow of air. Evaporated nitrogen dioxides are recycled to the inlet of the nitrous gas compressor (or the absorber column).

4.4. Emissions and control

Tail-gas containing N₂O and traces of NOₓ leaves the absorber column at a temperature of 293-303 K. The tail-gas is used for heat recovery and is heated up to temperatures ranging from 523 K up to 773 K at pressures of typically 10 bara (in dual-pressure plants). The heated tail-gas is used in a tail-gas expander for energy recovery. Expanded tail-gas at atmospheric pressure and a temperature of 373-473 K is subsequently vented. The composition of the tail-gas at the outlet of the NO₂ absorber during stable operation may vary within the limits
Fig. 6. (a) NH₃ burners of the dual-pressure plant built in 1990 for Abu Quir Fertilizers & Chemical Industries, Egypt (courtesy of Krupp-Udhe⁹), (b) operation during replacement of the Pt-Rh(-Pd) gauzes, and (c) principle of recovery of PtO₂ (as Pt) in the Pd-catchment.

Fig. 7. Absorption tower (courtesy of Monsanto Enviro-Chem⁸⁹).

Fig. 8. NH₃- SCR unit for NOₓ abatement (courtesy of Monsanto Enviro-Chem⁸⁹).
shown in Table 8. Typical values are shown between brackets. The temperature and pressure of this stream depends on the process variant and the position in the tail-gas train (see Fig. 5).

Table 8. Composition of the tail-gas at the outlet of the NO$_2$ absorber (N$_2$ balance gas) for a nitric acid plant of 1500 ton HNO$_3$ per day and a tail-gas flow of 2.10$^5$ Nm$^3$ h$^{-1}$.32

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>100 - 3500 ppm (200 ppm)</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>300 - 3500 ppm (1500 ppm)</td>
</tr>
<tr>
<td>O$_2$</td>
<td>1 - 4 vol.% (2.5 vol.% )</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.3 - 2 vol.% (0.5 vol.% )</td>
</tr>
</tbody>
</table>

4.4.1. Nitrogen oxides (NO$_x$)

The NO$_x$ concentration is directly related to the kinetics of the nitric acid formation reaction and absorption tower design.34 NO$_x$ emissions increase when there is:

- low pressure in the absorber
- insufficient air supply to the oxidizer and absorber
- high temperatures in the cooler-condenser and absorber
- production of an excessively high-strength product acid
- operation at high throughput rates
- start-up and shut-down periods
- faulty equipment (compressor or pumps), leading to lower pressures and leaks

The two most common techniques used to control NO$_x$ emissions are extended absorption and catalytic reduction. Non-selective catalytic reduction (NSCR) systems are not competing with SCR systems anymore, due to the high capital and operation costs. Furthermore, cross-media effects occur, such as high secondary emissions (fuel slip and CO) and high fuel consumption levels.12 Extended absorption reduces NO$_x$ emissions by increasing the efficiency of the existing absorption tower or incorporation of an additional absorption tower. An efficiency increase can be achieved by increasing the number of absorber trays, operating the absorber at higher pressures, or cooling the weak acid liquid in the absorber. The existing tower can also be replaced with a single tower of a larger diameter and/or additional trays. For reduction of NO$_x$, most nitric acid plants are equipped with tail-gas de-NO$_x$ units (Fig. 8). The selective catalytic reduction with ammonia (NH$_3$-SCR) is state-of-the-art technology for the reduction of NO$_x$ emissions, achieving up to 95% reduction. The extent of this reduction is a function of plant design, operating temperatures and pressure, space velocity through the catalytic reactor, type of catalyst, and reactant concentration. An extra-advantage of this technology is the fact that ammonia is readily available in the plant.

Monsanto Enviro-Chem systems for NO$_x$ removal include the use in series of high efficiency absorption (HEA) and catalytic reduction (SCR) facilities, enabling the optimization of the operating conditions and operation cost (Fig. 9).34 The HEA column removes a large fraction of NO$_x$ (by recovery of HNO$_3$) and stabilizes the NO$_x$ content of the tail-gas, which is further destroyed by the de-NO$_x$ catalyst (licensed from Rhodia) as required to meet the emission limits. In this technology, the catalytic reduction of NO$_x$ takes place at 450 K without measurable ammonia in the tail-gas. A comparison of the various NO$_x$ abatement configurations can be found in Table 9.
Fig. 9. Combined high efficient absorption (HEA) and catalytic reduction (SCR) for NO\textsubscript{x} abatement.\textsuperscript{34}

Table 9. NO\textsubscript{x} abatement system comparison (see Fig. 9).\textsuperscript{34}

<table>
<thead>
<tr>
<th></th>
<th>SCR only</th>
<th>HEA + SCR</th>
<th>HEA only</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO\textsubscript{x} to HEA / ppmv</td>
<td>-</td>
<td>3500</td>
<td>3500</td>
</tr>
<tr>
<td>NO\textsubscript{x} to SCR / ppmv</td>
<td>3500</td>
<td>700</td>
<td>-</td>
</tr>
<tr>
<td>NO\textsubscript{x} to turbine / ppmv</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{3} recovered / kg per ton H\textsubscript{2}O\textsubscript{3}</td>
<td>-</td>
<td>27</td>
<td>31</td>
</tr>
<tr>
<td>NH\textsubscript{3} consumed / kg per ton H\textsubscript{2}O\textsubscript{3}</td>
<td>8.5</td>
<td>1.3</td>
<td>-</td>
</tr>
<tr>
<td>Capital cost (relative to SCR only)</td>
<td>1</td>
<td>2.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

4.4.2. Nitrous oxide (N\textsubscript{2}O)

The emission of N\textsubscript{2}O depends exclusively on the ammonia combustion process. Once formed, N\textsubscript{2}O passes unreacted through the plant and is not affected by the operating condition in the absorber or the SCR after-treatment in the tail-gases. There is a considerable variation of the emission of N\textsubscript{2}O per ton of nitric acid produced, as the current internationally accepted IPCC (Intergovernmental Panel on Climate Change) guideline figures for estimating national N\textsubscript{2}O emissions indicate (Table 10).\textsuperscript{35} Generally, the amount of N\textsubscript{2}O formed depends on combustion conditions, catalyst composition and state (age), and burner design. Fig. 10 can be used to convert between various ways of expressing levels of N\textsubscript{2}O emission as a function of the yield of eqs. (2) and (5). Contrary to the well-developed technology for de-NO\textsubscript{x} (recovery and abatement) presented above, no technology for N\textsubscript{2}O abatement has been installed as yet. However, prospective environmental demands concerning this gas call for the urgent development of efficient abatement options, which are presented in the next section.

Table 10. IPCC emission factors for N\textsubscript{2}O from H\textsubscript{2}O\textsubscript{3} production.\textsuperscript{35}

<table>
<thead>
<tr>
<th>Source</th>
<th>Type of plant</th>
<th>Emission factor / kg N\textsubscript{2}O per ton H\textsubscript{2}O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA</td>
<td></td>
<td>2 - 9</td>
</tr>
<tr>
<td>Norway</td>
<td>Modern (high pressure)</td>
<td>&lt; 2</td>
</tr>
<tr>
<td></td>
<td>Atmospheric</td>
<td>4 - 5</td>
</tr>
<tr>
<td></td>
<td>Medium pressure</td>
<td>6 - 7.5</td>
</tr>
<tr>
<td>Japan</td>
<td></td>
<td>2.2 - 5.7</td>
</tr>
</tbody>
</table>
Fig. 10. Different ways to express the N₂O emission in nitric acid plants for different ammonia oxidation efficiencies, after Schwefer et al.¹⁶

5. N₂O abatement options during nitric acid production

Development of N₂O abatement systems aims at the achievement of high efficiency (> 90% N₂O conversion) and selectivity (< 0.2% NO loss). The approaches followed by industry, research institutes and universities can be classified in four groups, according to the position in the process (see different locations in Fig. 5):

- **Primary abatement measures** aim at preventing N₂O being formed in the ammonia burner. This involves modification of the ammonia oxidation catalyst.
- **Secondary abatement measures** remove N₂O from the valuable intermediate stream, i.e. from the NO₃ gases between the ammonia converter and the absorption column. Usually this will mean intervening at the highest temperature, immediately downstream of the ammonia oxidation catalyst.
- **Tertiary abatement measures.** The tail-gas leaving the absorption column is treated to destroy N₂O. The most promising position for nitrous oxide abatement is upstream of the tail-gas expansion turbine.
- **Quaternary abatement measures** are the pure end-of-pipe solution, where the tail-gas is treated downstream of the expander, on its way to the stack.

5.1. Primary abatement measures

Production of N₂O can be minimized by optimizing the catalytic oxidation of NH₃ to NO (position 1 in Fig. 5). The conversion of this process is well optimized (95-97%, see Table 7) and further prevention of unwanted N₂O production by improved catalyst performance is expected to be limited. Two options are considered here: improvement of the geometry of Pt-Rh gauzes to optimize the NO yield or replacement of the Pt-Rh gauzes by Co₃O₄. On the long-term improved reactor design (e.g. reverse flow) could reduce N₂O formation, but this will be applied only in new plants due to the high retrofit costs.¹⁷

5.1.1. Modification of the Pt-Rh gauzes

Every additional mol of NH₃ converted to NO in the ammonia burner is a mol less that can be converted to N₂O. Thus measures that increase the conversion efficiency of the catalyst gauzes will reduce N₂O formation. The use of Pt and later Pt-Rh alloys as a catalyst
changed little between 1909 and 1990. The catalyst was originally manufactured as woven gauzes (Fig. 11a). Johnson Matthey introduced knitted gauzes in 1990, which have practically displaced the traditional woven gauze from the market, and has now become the standard in industry (95% of the total production). Manufacturers claim that the use of knitted gauzes lead to the following benefits:

- Increased NO conversion efficiency (no quantification available)
- Reduced RhO₂ formation and lower Pt losses
- Higher surface area
- Longer catalyst life
- Improved resistance to contamination
- Lower pressure drop
- Increased mechanical strength

Several knitted gauzes with different geometry can be seen in Figs. 11b-d, which are recommended by the manufacturer for specific applications. As there are many varieties of knitting stitch, without a doubt all the possibilities for improvement have not yet been exhausted and thus the potential N₂O reduction factor is still uncertain. The composition of the sub-surface layers of the platinum gauze and changes in the surface structure by activation with e.g. H₂O₂, HCOOH, CH₃COOH, CO₂, or H₂ can also lead to improved NO yields, being subject of current investigations.

![Fig. 11. Commercial Pt-Rh catalysts of different geometries for NH₃ oxidation: (a) woven gauze, (b-d) knitted gauzes (adapted from ref. 33).](image)

5.1.2. Replacement of the Pt-Rh gauzes

Transition metal oxides catalyse the oxidation of NH₃ to NO. Since the 1970s cobalt oxide (Co₃O₄) has been used in nitric acid plants as an alternative to Pt-Rh gauzes. Co₃O₄ catalysts offer the advantages of lower investment and longer campaign length compared to precious metal catalysts. Another reason for the revival of interest is the low N₂O emission generated over this catalyst, since Co₃O₄ is highly active in decomposing it. A recent publication reported a conversion rate of NH₃ to N₂O as low as 0.5% over Co₃O₄.

There are serious drawbacks of the cobalt oxide catalyst that inhibit the replacement of the well-established and proven Pt-Rh catalyst. A crucial aspect is the lower ammonia conversion efficiency of Co₃O₄ (88-92% in high-pressure plants) compared with the Pt-Rh gauzes (95-97%). Another disadvantage is the reversible deactivation of Co₃O₄ due to the
reduction to CoO in the upper parts of the bed. Furthermore, the optimal operating temperature of CoO is 70-80 K lower than for Pt-Rh catalysts, which could result in difficulties with the steam balance in a revamped plant.

5.2. Secondary abatement measures

The process options described here focus on the decomposition of N₂O, either by thermal decomposition or by catalytic decomposition, in the high-temperature zone immediately downstream of the ammonia burner (position 2 in Fig. 5).

5.2.1. Homogeneous decomposition (extended chamber concept)

The extended chamber concept is based on the thermal decomposition of N₂O in the hot zone downstream of the ammonia combustion Pt-Rh gauzes at temperatures ranging from 1023 K to 1223 K and pressures of 1-13 bara (Fig. 12). This involves a novel design of the ammonia oxidation unit so that the residence time of the process gas in the burner is extended (1-2 s) and the N₂O, which is metastable at these temperatures, may decompose. This technology, developed and patented by Norsk Hydro, was successfully implemented in the latest nitric acid plant of this company in Porsgrunn (Norway) in 1990, resulting in an N₂O level in the tail-gas of about 200 ppmv (70% N₂O reduction).

![Fig. 12. Extended reaction chamber for homogeneous N₂O decomposition.](image)

The increased residence time in the reaction chamber for decomposition requires extended space between the gauzes and the superheater. This process option leads to increased capital costs of the plant by about 5-6%, with no increase in operational costs. However, it appears to be prohibitive for retrofitting, due to the high costs involved in the redesign of the existing ammonia burners. It is highly unlikely that any new nitric acid plant will be built in Europe before 2010, so this option will not be implemented in this decade. In the longer term, however, it could ensure that all new plants have low levels of N₂O emissions.

Fig. 13 shows the simulated N₂O concentration profile in the decomposition chamber for the case of an ideal adiabatic reactor (no heat loss, dashed profile) and for the more realistic case of a temperature gradient along the decomposition chamber. Operational input conditions (gas flow, pressure, temperature, and temperature gradient) used in this simulation are representative for modern dual-pressure plants (see Tables 5 and 6). It is evident that high conversion levels (> 90%) are difficult to achieve. In addition, the method is
not suited for atmospheric pressure plants as shown in the figure, due to the low residence time of the gas in the reactor.

5.2.2. Catalytic decomposition

Instead of increasing the reactor chamber, the reduction of $\text{N}_2\text{O}$ can be promoted using a catalyst for selective $\text{N}_2\text{O}$ decomposition. The homogenous decomposition is a rather slow reaction under the practical conditions in the ammonia chamber (see Fig. 13). This process can be accelerated by introducing a catalyst behind the Pt-Rh gauze and the Pd catchment, which enhances the reaction rate substantially such that the necessary reactor volume can be reduced compared to the extended reactor concept (Fig. 14). The inert Raschig rings, typically supporting the Pt-Rh gauzes, can be replaced by the catalyst. Some plants do not have a Raschig ring support, and baskets for the catalyst have to be installed at minor costs.

In principle, this cost-efficient process option can be easily applied in existing plants. The catalyst can be introduced without making noticeable modification to the existing burner. However, there are challenges for the development and application of an in process-gas catalyst:

- **Catalyst activity.** The volume of the Raschig ring layer in the space beneath the Pt-Rh gauze (Fig. 14) determines the available catalyst volume and thus the $\text{N}_2\text{O}$ reduction. This volume depends on the specific burner design. A typical catalyst bed height range from 5 to 20 cm, which can be translated into a gas-hourly space velocity ($GHSV$) in the order of 14–50 s$^{-1}$. The figure means that in 1 s a gas volume is passing through the catalyst bed with corresponds up to 50 times the volume of the catalyst bed. Since the reactor volume and gas flow are given (and thus $GHSV$), the effective rate constant $k_{\text{eff}}$ (assuming plug-flow behaviour and first-order kinetics) is a function of the required $\text{N}_2\text{O}$ conversion ($X(\text{N}_2\text{O})$):

$$k_{\text{eff}} = GHSV \ln \left( \frac{1}{1-X(\text{N}_2\text{O})} \right)$$

(8)
Since the target conversion is typically set to $> 90\%$, an effective rate constant in the order of 100 s$^{-1}$ is required. At the high temperature of the ammonia burner, the catalytic N$_2$O decomposition reaction will be highly mass-transfer controlled. The high-pressure drop will rule out the application of a packed bed. Monolithic catalysts pair a low-pressure drop to a high catalyst effectiveness (see Chapter 7). Even under mass-transfer controlled conditions, the high effective rate constant, $k_{\text{eff}} (= k_f a')$, required can be achieved under gas-phase operation. In this expression, $k_f$ is the external mass transfer coefficient (m s$^{-1}$) and $a'$ the specific surface area of the catalyst (m$^2$).

![Diagram of ammonia burner with Pt-Rh-(Pd) gauzes, Raschig rings, and monolithic catalyst](image)

**Fig. 14.** In process-gas catalytic N$_2$O decomposition.

- **Catalyst selectivity.** An important issue concerning process economy of the secondary catalytic abatement is the potential loss of product (HNO$_3$) through the catalytic decomposition of NO in the ammonia burner. The in process-gas N$_2$O decomposition catalyst should be inert towards the decomposition of NO. This is however unlikely because NO is, as N$_2$O, thermodynamically unstable with respect to decomposition into N$_2$ and O$_2$ (eqs. (9) and (10)).

\[
\begin{align*}
2\text{N}_2\text{O} & \rightarrow 2\text{N}_2 + \text{O}_2 \\
2\text{NO} & \rightarrow \text{N}_2 + \text{O}_2
\end{align*}
\]

(9) (10)

The importance of product loss is exemplified in Fig. 15 for a nitric acid plant of 1000 ton HNO$_3$ per day. Due to normal changes in operational conditions, it is difficult to identify NO losses below 0.5%, with an annual economical loss of 250 k€. In order to properly evaluate the feasibility of this abatement option, it is essential to know the exact NO losses for a given catalyst, since this will determine its impact on the process economy.

- **Pressure drop, catalyst (mechanical) stability, and product quality.** The low catalyst utilization obtained with catalyst particles in fixed beds calls for small catalyst particles, but these would lead to a severe pressure drop at the high gas-hourly space velocities applied. The mechanical construction may set some hard-limits in this respect, since the pressure drop generates an extra-load in addition to the weight of the catalyst. The particles should also have a minimum mechanical stability (crush-strength) in order to be properly handled during installation and operation (thermal expansion or contraction of the burner during plant shut-down and start-up). Breakage or abrasion of particles may also lead to an increased pressure drop and dust formation, resulting in the contamination of the acid
product. This could eventually lead to serious safety problems. These operational constraints can be effectively tackled by using a monolithic-type reactor. Due to its open structure, pressure drop is minimal, providing also remarkable mechanical properties.

- **Catalyst (chemical) stability.** The chemical stability affects the level of \( \text{N}_2\text{O} \) reduction and the NO selectivity. High-temperature catalytic processes such as the catalytic reaction exhibit sintering phenomena, which reduce the available surface area for the chemical reaction resulting in a decrease of activity over time. The challenge is to develop materials with are stable under the severe reaction conditions (no chemical phase segregation). Efforts regarding catalyst development are concentrated on low-surface area perovskite or spinel-like mixed oxides.

![Graph showing annual economical losses vs. % NO losses](image)

**Fig. 15.** Annual losses in k€ for a nitric acid plant of 1000 ton HNO\(_3\) per day as a function of the NO losses in the in-process-gas \( \text{N}_2\text{O} \)-decomposition catalyst.\(^{39}\)

**Status of the secondary catalytic technology**

Several companies have made several proposals to install a catalyst in the space beneath the ammonia oxidation gauzes in the converter. Building on their success in the catalytic abatement of \( \text{N}_2\text{O} \) emissions from adipic acid plants, BASF has evaluated promising catalyst to the conditions in nitric acid plant ammonia converters. A Cu-Zn-Al spinel is currently undergoing tests in production plants.\(^{40}\) In October 2000, BASF were able to report an 80% reduction in \( \text{N}_2\text{O} \) from 1000 down to 200 ppm in an atmospheric combustion plant in Ludwigshaven (Germany) and a 70% reduction down to 350 ppm in the 5.5 bara combustion section of their dual-pressure plant in Antwerp (Belgium).\(^{22}\) The high temperature and water vapor content of the \( \text{NO}_2 \) gas put severe demands on the catalyst, and thus more catalytic tests are required to determine the long-term mechanical stability, activity and selectivity. In 2000, the German company L&C Heinmuller, well-known as a supplier of waste heat boilers for nitric acid plants, patented the installation of a wide range of \( \text{N}_2\text{O} \) abatement catalysts below the ammonia oxidation gauzes,\(^{41}\) while DuPont claims a high catalytic activity of \( \text{ZrO}_2 \) in the form of cylindrical pellets installed as a fixed bed beneath the gauzes and catchment system.\(^{42}\)

Norsk Hydro is also active in the development of a highly active (\( \text{N}_2\text{O} \) conversion > 90%), selective (NO loss < 0.5%), and stable in process-gas catalyst.\(^{39}\) More than 600 formulations based on spinel and perovskite materials were tested in a multi-flow laboratory reactor
under realistic conditions. One of the formulations (with secret composition) satisfied the R&D criteria, and was implemented in a medium-sized plant of the company in March 2000. The pilot-plant results were completely transferable to the real reactor in the process, with a remarkable high activity and stability. A catalyst lifetime of > 5 years has been estimated for this catalyst, and no adverse impact on the plant operation and plant performance was found. Norsk Hydro's second generation of catalysts, aiming at lower NO losses (< 0.2%) and improved mechanical stability, is currently being developed.

Most of the patents and process proposed in this application are concerned with fixed-bed reactors, but in view of the features of the process gas and the feature of structured catalysts discussed above, monolithic reactors are the most logical solution. This indicates options for process development and optimization.

5.3. Tertiary abatement measures

Implementation of \( \text{N}_2\text{O} \) abatement measures between the \( \text{NO}_2 \) absorption section and the tail-gas expander (position 3 in Fig. 5) offers the great advantage of not influencing the heart of the nitric acid plant, i.e. the ammonia burner and the absorber, and can be compared with the implementation of a de-\text{NO}_x, SCR unit. Tertiary measures are more flexible with respect to the size of the reactor than secondary measures, enabling the achievement of high levels of \( \text{N}_2\text{O} \) removal (> 99%). A producer might also decide to install a more generously sized reactor than that immediately required, allowing for the addition of extra-catalyst to cope with prospective \( \text{N}_2\text{O} \) emission regulations, or to optimize the catalyst requirement against the level of a potential greenhouse gas tax. The implementation of a tertiary abatement upstream of the expander can be limited by available space, maximum allowable pressure drop (especially if fixed-bed reactors are used), and requirements of the tail-gas expander with respect to inlet temperature.\textsuperscript{17,26,27}

Technologies that can be (in principle) applied at this level of the plant are:

- Thermal decomposition
- Non-selective catalytic reduction (NSCR)
- Selective catalytic reduction (SCR)
- Catalytic decomposition

The pressure and especially temperature of the tail-gas are essential parameters to determine the optimal process option for tertiary \( \text{N}_2\text{O} \) abatement. This is mainly influenced by the process variant and the operating conditions in the NH\textsubscript{3} burner. The temperature also depends on the position in the tail-gas train, due to the various heat recovery stages of the tail-gas on its way to the expander (see Fig. 5). Typical tail-gas temperatures range from 523 to 773 K at elevated pressures (3-13 bara). Low-temperature tail-gases are present in (old) low-pressure plants (mono or dual). High pressures in the ammonia burner lead to a high tail-gas temperature. Accordingly, large dual-pressure or modern high-(mono)pressure

<table>
<thead>
<tr>
<th>Plant</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2\text{O} ) concentration / ppm</td>
<td>1250</td>
<td>1500</td>
<td>1150</td>
<td>1250</td>
<td>920</td>
<td>1500</td>
</tr>
<tr>
<td>Capacity / kton H\textsubscript{2}O \textsuperscript{1}</td>
<td>584</td>
<td>500</td>
<td>210</td>
<td>730</td>
<td>255</td>
<td>245</td>
</tr>
<tr>
<td>Emission / kton ( \text{N}_2\text{O} ) \textsuperscript{1}</td>
<td>4.4</td>
<td>4.5 - 6</td>
<td>1.5 - 2</td>
<td>5.4</td>
<td>1.7</td>
<td>2</td>
</tr>
<tr>
<td>Process variant</td>
<td>Dual</td>
<td>Mono</td>
<td>Mono</td>
<td>Dual</td>
<td>Mono</td>
<td>Dual</td>
</tr>
<tr>
<td>( P ) upstream of the expander / bara</td>
<td>10</td>
<td>11</td>
<td>5</td>
<td>11</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>( T ) upstream of the expander / K</td>
<td>?</td>
<td>773</td>
<td>723</td>
<td>?</td>
<td>673</td>
<td>?</td>
</tr>
<tr>
<td>( T ) downstream of the expander / K</td>
<td>?</td>
<td>220</td>
<td>220</td>
<td>?</td>
<td>220</td>
<td>?</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) concentration / vol.%</td>
<td>?</td>
<td>0.5</td>
<td>1</td>
<td>?</td>
<td>1</td>
<td>?</td>
</tr>
</tbody>
</table>
plants lead to temperatures in the range of 673-773 K (and even higher). Table 11 exemplifies the tail-gas characteristics of the six nitric acid plants operating in the Netherlands. In this case, high-temperature tail-gases are generally present, which facilitates the development of tertiary treatments for N₂O abatement (see below).

5.3.1. Thermal decomposition

Thermal decomposition of N₂O is, at least in theory, not restricted to secondary abatement measures only. A process based on raising the temperature of the tail-gas to the required 1023-1273 K in a recuperative heat exchanger has been proposed to treat off-gas streams containing at least 1500 ppm N₂O. The exothermal decomposition of 1500 ppm N₂O causes only a small rise in temperature (10 K), so a continuous heat supply from an external source to compensate for heat losses, e.g. by injection of fuel (natural gas, methane) is required. This process option seems to be prohibitive, in view of the large investment which can be expected for a high-temperature recuperative heat exchanger and the additional equipment required to obtain the temperature at plant start-up. Thermal decomposition could be applicable in specific situations, e.g. if the tail-gas of the nitric acid plant could be mixed with other high-temperature gases (or highly concentrated in N₂O) from other nearby industrial processes, which would result in net N₂O destruction.

5.3.2. Non-selective catalytic reduction (NSCR)

NSCR has been developed for NOₓ removal and has shown to be capable of reducing N₂O as well. A reducing agent like hydrogen, natural gas, or naphtha is added to the tail-gas. First all O₂ in the tail-gas is consumed, followed by oxygen in components like NOₓ and N₂O. Typical conversion efficiencies are about 90% for NOₓ and 70% for the N₂O, although under pilot plant trials, conversion efficiencies of 90% have been achieved for N₂O. Depending on the type of catalyst (typically Pd/Al₂O₃) and fuel used, the process requires an ignition temperature of 473-573 K (with H₂) up to 723-753 K (with CH₄). This might need preheating of the tail-gas when the tail-gas temperature is too low.

When the oxygen content in the tail-gas is less than 3 vol.%, a single stage catalytic reactor can be used. For handling higher oxygen concentrations, a two stage catalytic reactor is required to enable intermediate cooling (Fig. 16). Due to the strong exothermal reaction, the outlet temperature can exceed 1073 K. Additional cooling is required before the existing

![Diagram of Dual-staged NSCR system](image-url)

Fig. 16. Dual-staged NSCR system.
expander, since replacing the expander is not economical. The surplus heat recovered from (intermediate) cooling is converted to steam.

NSCR is a proven technology for N₂O reduction, commercialized by GIAP, and has been applied in several nitric acid industries of Russia and USA. However, the replacement of NSCR systems by SCR for NO₂ reduction has a negative side effect on its application for N₂O reduction. NSCR is most likely not a viable option anymore, due to the high fuel consumption levels and high secondary emissions. In most of the cases slip of fuel occurs and when using CH₄ as a reductant, large amounts of CO are produced.¹⁷,²⁶,²⁷,₃₂ These negative effects increase the operational costs.

5.3.3. Selective catalytic reduction (SCR)

The schematic flowsheet of this abatement option is visualized in Fig. 17. A reducing agent, e.g. propane, propene, natural gas, LPG (a mixture of propane and butane), or ammonia, is added to the tail-gas leaving the NO₂ absorber. Depending on the operating pressure, the type of reductant and the catalyst used, the ignition temperatures vary in a wide temperature range (573-773 K).²⁶ A high ignition temperature of the catalyst requires preheating of the tail-gas. The SCR process is exothermic but the amount of heat generated is limited compared to NSCR. Most revamp cases also require extra-cooling due to the limited allowable increase of the inlet temperature of existing tail-gas expanders. For new plants the tail-gas expander can be designed for higher inlet temperatures, thus avoiding the installation of the tail-gas cooler.

SCR of N₂O with hydrocarbons has been extensively investigated over Fe-based zeolites (mainly ZSM-5 and eventually Beta).⁴⁴,⁵³ However, a quantitative comparison of activity data from different authors can not be made because of the different (laboratory) conditions of feed composition, space velocity, and total pressure (Table 12). In addition, experiments on the pilot-scale are hardly available. Co-addition of hydrocarbon to the tail-gas mixture reduces the temperature for N₂O decomposition over FeZSM-5 approx. 100 K with respect to direct N₂O decomposition, leading to operation temperatures of 573-648 K for high N₂O decomposition rates. Furthermore, a higher stability in the presence of inhibitors like H₂O is also achieved.⁴⁵,⁴⁷ This behaviour strongly contrasts with other metal-zeolites (e.g. Cu-ZSM-5) or different catalytic systems, which are inhibited or unaffected by the hydrocarbon.⁴⁵,⁴⁹

![Fig. 17. SCR upstream of the tail-gas expander.](image-url)
Table 12. Reported performances of Fe-zeolite catalysts for catalytic N₂O abatement (reduction and decomposition).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reductant</th>
<th>GHSV, P</th>
<th>Feed composition</th>
<th>T, X(N₂O)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeZSM-5</td>
<td>C₃H₈</td>
<td>18000 h⁻¹</td>
<td>500 ppm N₂O, 2 vol.% O₂, 3 vol.% H₂O, 1000 ppm C₃H₆ in He</td>
<td>625 K, 80%</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 bar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeZSM-5</td>
<td>C₃H₈</td>
<td>50000 h⁻¹</td>
<td>500 ppm N₂O, 1000 ppm C₃H₆, 5 vol.% O₂ in He</td>
<td>650 K, 90%</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 bar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeZSM-5</td>
<td>C₃H₈</td>
<td>20000 h⁻¹</td>
<td>1500 ppm N₂O, 1900 ppm C₃H₆, 2.5 vol.% O₂, 100 ppm NO, 0.5 vol.% H₂O in N₂</td>
<td>625 K, 95%</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 bar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeZSM-5</td>
<td>C₃H₈</td>
<td>60000 h⁻¹</td>
<td>1500 ppm N₂O, 1500 ppm C₃H₆, 2.3 vol.% O₂, 330 ppm NO, 0.5 vol.% H₂O in He</td>
<td>650 K, 100%</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 bar</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-Zeta</td>
<td>CH₄</td>
<td>60000 h⁻¹</td>
<td>950 ppm N₂O, 500 ppm CH₄ in He</td>
<td>575 K, 100%</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 bar</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

GHSV = gas-hourly space velocity, P = total pressure, T = temperature, X(N₂O) = N₂O conversion.

Depending on the operating conditions and amount of catalyst, N₂O reductions ranging from 70% to > 99% can be obtained in the desired temperature range. In general, the reduction efficiency increases with (i) a higher operation temperature, (ii) a higher total pressure, (iii) a higher reductant concentration, and (iv) a lower gas-hourly space velocity. Increased total pressure is beneficial for N₂O destruction, lowers the slip of hydrocarbon and also the emission of CO. However, at increased pressure the reducing agents are partly oxidized by oxygen instead of N₂O, rendering the catalyst less selective than at atmospheric pressure. This leads to an increased reagent consumption for a required N₂O reduction. Propane, propene, and LPG are the most effective reductants to achieve a low-temperature activity over FeZSM-5. The use of CH₄ shifts the N₂O reduction to higher temperature and the hydrocarbon slip is substantial. This can be remedied enhancing the oxidation performance of the catalyst by impregnation of noble metals like Pd or Pt. The major drawback of this process option is the high cost associated with the permanent consumption of reductant, which contributes importantly to the total cost of the abatement unit (20 to 60%), and thus to the cost efficiency of the process.

N₂O abatement with ammonia as the reducing agent, has been realized using different Fe-zeolites (BEA, MFI, FAU, FER). Mauvezin et al. reported a temperature of 750 K for 95% N₂O conversion (in the absence of H₂O and NO) over Fe-BEA, the most promising formulation. Although ammonia is readily available in a nitric acid plant, the high operation temperature compared with the reduction by light hydrocarbons, makes it non-competitive for N₂O reduction.

5.3.4. Direct catalytic decomposition

Direct catalytic decomposition of N₂O without addition of reducing agents is an attractive and economical option to reduce N₂O emissions in nitric acid plants (Fig. 18), since the high cost of the reductant and the emissions involved (slip or undesired combustion products) are avoided. However, none of the catalysts proposed in the literature show a good activity and stability in N₂O conversion under realistic conditions of feed composition and space velocities. Although there are numerous papers and patents regarding catalytic systems for direct N₂O decomposition, laboratory results often deviate from what is normally met within industrial practice, and in most cases severe stability tests under realistic conditions have not been taken into consideration.
Fig. 18. Direct catalytic decomposition system upstream of the tail-gas expander.

Transition (Cu, Co, Ni) and noble-metal based catalysts (Rh, Ru, Pd) on different supports (ZnO, CeO₂, Al₂O₃, TiO₂, ZrO₂, calcined hydrotalcites, and perovskites) are very active for N₂O decomposition in N₂O-He feeds, but the presence of other gases in the feed (O₂, NOₓ, H₂O) leads to strong inhibition and/or deactivation and very low reaction rates under practical conditions. ¹⁶,¹⁹,⁵⁵-⁶²

From an extensive screening program it was concluded that no catalyst shows reasonable activities under realistic conditions of temperature, pressure, space velocity and feed composition below 700 K, ⁵² which limits the application of this process option to nitric acid plants with high-temperature tail-gases (700-773 K). FeZSM-5 operates in this temperature range for direct N₂O decomposition (see Table 12) and is also a very attractive system. This catalyst shows no inhibition by oxygen and an improved activity in the presence of NOₓ. ⁶³-⁶⁶ In addition, the hydrothermal stability is improved with respect to noble metal-based catalysts. Only 1/3 of the nitric acid plants in Europe have tail-gases of these characteristics, but since they are dual-pressure or high-pressure plants with large productions, the contribution to the capacity is certainly > 60%, with equal contribution to N₂O emission.

5.4. Quaternary measures

Finally, the N₂O abatement process can be located downstream of the tail-gas expander in the way to the stack (position 4 in Fig. 5). These end-of-pipe applications would not require modifications of the tail-gas expander in the existing plant. The low temperature (473-573 K) and pressure (~1 bara) in this location makes the development of a catalytic abatement very challenging. In this case, the use of preheating equipment and/or reductants is inevitable, which makes the cost efficiency of the abatement option less favourable. In spite of these difficulties, ECN claims feasibility for this option. ²⁶

5.4.1. Non-selective catalytic reduction (NSCR)

For NSCR, the heating capacity of the preheater shown in Fig. 16 has to be enlarged due to the lower inlet temperature. As this preheater is a gas-gas heat exchanger operated at atmospheric pressure, the volume required (and investment cost) will be higher. Also the amount of heat produced has to be efficiently recovered, possibly in the form of high-pressure steam.

5.4.2. Selective catalytic reduction (SCR)

Due to the relatively low ignition temperature for FeZSM-5, during N₂O reduction by hydrocarbons (~623 K) the extra-heat generated can be used to preheat the tail-gas leaving the expander, thus limiting the amount of utilities used, and production of excess steam. ²⁶-²⁷
However, an optimised heat recovery system does increase the investment costs. A flowsheet of this process is shown in Fig. 19. The tail-gas is preheated using the heat generated in the catalytic reactor. A start-up in-line burner is required to start the reaction and to correct for fluctuations in the tail-gas flow and composition. As discussed in §5.3.3, natural gas is not suitable as reducing agent for use in an atmospheric pressure environment due to the large hydrocarbon slip. Therefore natural gas is only used as fuel in a burner for start-up. An N₂O reduction efficiency of at least 70% is claimed by using C₃H₆. Higher efficiencies can be obtained by increasing reactor sizing or increased addition of reducing agent. However, consumption of utilities has to be minimized.

![Diagram](image)

**Fig. 19.** SCR system downstream of the tail-gas expander.

### 5.4.3. Catalytic decomposition

This process is schematically shown in Fig. 20. As the ignition temperature of the catalyst (typically > 673 K) is well above the tail-gas temperature, preheating is required. Heat recovery can be applied in combination with additional firing, with e.g., natural gas. A decomposition level of 70% seems feasible. Using a larger catalytic reactor and/or a higher operating temperature can increase the conversion levels, at the expenses of increased pressure drop and/or fuel consumption.

![Diagram](image)

**Fig. 20.** Catalytic decomposition downstream of the tail-gas expander.
6. Evaluation of potential technologies

6.1. Cost estimation of the different options

Table 13 summarizes the different measures to reduce N₂O emissions in nitric acid plants, with advantages, drawbacks, and costs for abatement per ton of CO₂-eq. The economic feasibility study of these N₂O removal strategies has been assessed by Stork Engineering Consultancy B.V. To enable cost comparison of the different N₂O abatement techniques, all known costs have been extrapolated to a base case. As base case a nitric acid plant with a production capacity of 1500 ton nitric acid (as 100 wt.%) per day, a tail-gas flow of 2.10⁸ Nm³ h⁻¹ and a N₂O concentration of 1500 ppmv in the tail-gas has been used. A distinction is made for new and existing nitric acid plants. For evaluation purposes the production cost of nitric acid has been valued on 70 € per ton of 100 wt.% nitric acid. An operating time of 8000 h per year has been used. Investment and operation costs, and cost efficiency are indicative only to enable qualitative comparison of the defined N₂O reduction techniques. For smaller plants it is expected that investment costs will be lower but that the cost efficiency will decrease due to scaling effects. An overview of the cost of the most promising options is shown in Fig. 21. Alternatives in an exploratory state (e.g. optimization of the Pt-Rh gauzes) are very unfavorable in economic terms and are not considered in this estimation. It should be noted that even for the most expensive method the specific abatement cost per ton CO₂-eq. is one order of magnitude lower than those costs reported for the removal of CO₂ from combustion processes.

Table 13. Summary of available techniques for the N₂O abatement from nitric acid plants. More details regarding this assessment can be found elsewhere.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Cost efficiency</th>
<th>€ per ton CO₂-eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PRIMARY MEASURES</strong></td>
<td></td>
<td></td>
<td>New</td>
<td>Existing</td>
</tr>
</tbody>
</table>
| 1. Improvement of Pt-Rh gauzes | • Simple to install  
• Increase in NO yields | • Uncertain technology  
(Exploratory state) | n.a. | n.a. |
| 2. Alternative (CoOx) catalyst | • Low catalyst cost | • NO yield reduction, especially at high combustion pressures  
• Strong deactivation | n.a. | n.a. |
| **SECONDARY MEASURES** | | | | |
| 3. Extended reactor chamber | • Simple process optimization  
• No consumption of utilities  
• No catalyst use  
• Operating experience available in commercial scale plant | • Possible nitric acid production losses due to NO₃ decomposition in extended reactor chamber  
• High investment cost  
• Severe retrofit limitations for existing plants, including downtime during construction  
• Limited N₂O conversion | 0.3 - 1.1 | 0.9 - 2.0 |
| 4. Catalytic decomposition in reaction chamber | • Retrofit in existing reactor chamber possible (replacement catalyst support)  
• Less catalyst required due to increased reaction kinetics at high temperatures  
• First tests on commercial scale have been completed | • Possible HNO₃ production losses due to catalytic NO₂ decomposition  
• Retrofit might be limited or impossible due to lack of available space for catalyst placement and design of the burner | 0.1 - 0.7 | 0.2 - 0.8 |

25
### TERTIARY MEASURES

<table>
<thead>
<tr>
<th>No.</th>
<th>Operation</th>
<th>Description</th>
<th>Benefits</th>
<th>Cost Range</th>
</tr>
</thead>
</table>
| 5.  | NSCR upstream of the expander | • Proven technology  
• Combined NO<sub>x</sub>/N<sub>2</sub>O reduction  
• No influence on production capacity | • Consumption and slip of fuel  
• Production of CO/CO<sub>2</sub>  
• Heat production  
• Life time of catalyst  
• Not suitable as end-of-pipe option | 1.6 - 1.9  
1.9 - 2.5 |
| 6.  | SCR upstream of the expander | • Suitable for lower tail-gas temperatures (> 573 K)  
• Possible combined NO<sub>x</sub>/N<sub>2</sub>O reduction  
• No influence on production capacity  
• Catalyst is exposed to milder conditions compared to NSCR, resulting in expected higher stability and lower catalyst costs | • Consumption of reducing agent  
• Retrofit limitations  
• Slip when using natural gas as reducing agent  
• Increased pressure drop and surplus steam production due to steam cooler if compared with direct decomposition  
• Not yet proven on commercial scale | 1.4 - 2.4  
1.9 - 2.5 |
| 7.  | Direct decomposition upstream of the expander | • No consumption of utilities  
• Simple process set-up  
• No influence on production capacity  
• Catalyst is exposed to milder conditions compared to in-process decomposition, resulting in expected higher stability and lower catalyst costs | • Relative high tail-gas temperature. Tail-gas temperature < 675 K requires preheating  
• Retrofit limitations  
• Not proven on commercial scale | 0.3 - 0.4  
0.4 - 1.0 |

### QUATERNARY MEASURES

<table>
<thead>
<tr>
<th>No.</th>
<th>Operation</th>
<th>Description</th>
<th>Benefits</th>
<th>Cost Range</th>
</tr>
</thead>
</table>
| 8.  | SCR downstream of the expander | • Simple end-of-pipe use in existing plants  
• Possible combined NO<sub>x</sub>/N<sub>2</sub>O reduction  
• No influence on production capacity  
• Catalyst is exposed to milder conditions compared to NSCR, resulting in expected higher stability and lower catalyst costs | • Consumption utilities / reducing agent (LPG)  
• Pressure drop  
• Not yet proven on commercial scale  
• Fuel consumption for heating | n.a.  
1.4 - 1.5 |
| 9.  | Decomposition downstream of the expander | • Simple end-of-pipe use in existing plants  
• No influence on production capacity  
• Catalyst is exposed to milder conditions compared to NSCR, resulting in expected higher stability and lower catalyst costs | • fuel consumption required for preheating (> 675 K)  
• increased reactor size compared to 7 (increased catalyst cost and pressure drop)  
• not yet proven on commercial scale | n.a.  
1.4 - 1.6 |

1 The cost efficiency is influenced by the nitric acid production losses. The low range figure excludes production losses, the high figure range assumes 2% production losses.

2 The cost efficiency is influenced by the LPG price (0.3-0.4 € per kg).
6.2. In process-gas vs. tail-gas catalytic $\text{N}_2\text{O}$ decomposition

Catalytic $\text{N}_2\text{O}$ decomposition directly after the ammonia oxidation catalyst in the converter or in the tail-gas upstream of the expander are the most attractive options from an technical and economical point of view in existing nitric acid plants. The NO loss and the catalyst lifetime are decisive factors in determining the optimal solution for a specific application, as concluded from the comparison below.

**Influence of the NO loss.** Based on data of Krupp-Uhde, the amount of NO loss that could be tolerated in a secondary abatement system can be determined. The results are shown in Fig. 22. The cumulative cost of a secondary in process-gas catalytic abatement with different level of NO losses (0, 0.25, and 0.5%) has been compared to a tertiary tail-gas catalytic abatement (catalytic $\text{N}_2\text{O}$ decomposition). The calculations are based on a 1500 ton $\text{HNO}_3$ per day plant and the same price per ton was assumed for both catalysts. A catalyst life of 1 and 3 years was considered for the secondary and tertiary catalyst, respectively. Losses of NO were translated into wasted $\text{NH}_3$ and rated at January 2000 prices. The secondary abatement measure provides the more economic solution if there are no losses of NO over the catalyst. If there is only 0.25% NO loss, the costs of secondary catalyst and tertiary abatements coincide in the long term, although in the beginning the secondary treatment is more economic (due to the initial investment for the reactor in the tertiary measure). If NO losses amount to 0.5% the tertiary abatement method is more economical after 5 years operation.

**Influence of the catalyst lifetime.** A similar calculation with the same assumptions as above was carried out to investigate the effect of the catalyst lifetime. Fig. 23. shows a single dashed curve for the secondary abatement catalyst, with a lifetime of 1 year and NO losses of 0.25%. The three solid lines represent the total cumulated costs for tertiary $\text{N}_2\text{O}$ abatement catalysts with lifetimes of 1, 3, and 5 years respectively. It can be seen that a tertiary catalyst with a 3-year life is in the long term comparable in cost to the secondary catalyst at the assumed rate of NO loss. The short-lived, 1-year tertiary abatement catalyst is not able to
Fig. 22. Cumulative total costs vs. time in operation for (●) N₂O tertiary catalytic abatement (catalyst lifetime 3 y) and N₂O secondary catalytic abatement at different three different NO loss rates (□) 0%, (◇) 0.25%, and (○) 0.5%.

compete, because the volume of catalyst required per catalyst change is larger for the tertiary catalyst. On the other hand, a 5-year catalyst life for the tertiary catalyst would give it a clear edge over the secondary abatement catalyst.

It should, of course, be emphasized that the calculations behind these curves involve a number of assumptions and are therefore indicative only. However, it is clear that the NO loss in the secondary, and the catalyst lifetime in the tertiary catalytic abatement can dramatically influence the economics of the chosen process option. A possible future greenhouse tax has not been considered in these calculations, but if there turns out to be a difference between competing technologies in the N₂O reduction level (higher in the tertiary abatement), this aspect needs to be entered into the assessment of the most economic solution.

Fig. 23. Cumulative total costs vs. time in operation for N₂O tertiary catalytic abatement at three different catalyst lifetimes: (▲) 1 y, (●) 3 y, and (●) 5 y, and (○) NO loss of 0.25% is assumed for secondary abatement catalyst.
6.3. Evaluation

From the technical data and cost figures presented Table 13, the following evaluation can be put forward:

**New nitric acid plants.** Based on cost efficiency, an extended reactor chamber, catalytic decomposition in the reactor chamber, and catalytic decomposition upstream of the expander are preferred. From these three options the homogeneous decomposition of N₂O in the process gas has the lowest risk for a negative impact on process performance and leads to no additional operational costs. However, because of the heat loss in the extended chamber, high reduction levels (> 80%) are difficult to achieve. If the catalyst in the reactor chamber proves to be stable enough with only a minor effect on NOₓ decomposition, this technology is preferred on the basis of high cost efficiency. If maintenance has to be minimised, the extended reactor chamber may be preferred. Costs for catalytic decomposition in the reaction chamber can be in the order of magnitude of 0.1-0.7 € per ton CO₂-eq., but can increase dramatically for applications in the reactor chamber when NOₓ also decomposes. Also the lifetime of the catalyst in the ammonia burner has a large effect on the operating costs. Therefore, for stable operation reasons catalytic decomposition upstream of the expander is preferred (no influence on NOₓ decomposition and nitric acid production), with 0.3-0.4 € per ton CO₂-eq. A new plant can be designed in such a way that the temperature before the expander allows catalytic decomposition of N₂O (673-723 K).

**Existing nitric acid plants.** Cost efficiency decreases for an existing nitric acid plant. Only catalytic decomposition in the reactor chamber could result in costs well below 0.45 € per ton CO₂-eq., but this is strongly depending on lifetime and selectivity of the catalyst. Furthermore, not every nitric acid plant has available space for catalyst placement. Using an extended reactor chamber causes a drastic interference with the production process, besides the uncertainties defined above (high operational risks) and production losses during construction (not incorporated in the assessment of cost efficiency). Another option is catalytic decomposition upstream of the expander, with costs of 0.4-1.0 € per ton CO₂-eq. Application is however limited to a minimum tail-gas inlet temperature of 673-723 K. Only 1/3 of all nitric acid plants fall into this category, but they are responsible for a larger part of the capacity (> 60%). Otherwise, SCR and catalytic decomposition upstream of the expander should be applied, with related costs of 1.9-2.5 € per ton CO₂-eq., due to investment and operational costs, which makes the method less attractive, even if the operational risks can be considered as low.

**Cost efficiency.** The costs for N₂O reduction is in most cases for a considerable part determined by depreciation of the investment. Due to scale effects, the impact of depreciation will increase for smaller units. Therefore, application of N₂O reduction measures in nitric acid plants with a considerable production capacity (new plants) will be more cost-effective than application in nitric acid plants with a relatively low production capacity (mainly old plants).

**Cost impact.** Up to now the emission of N₂O is hardly restricted. Initiatives of nitric acid producers to limit N₂O emissions are driven by individually set targets. Based on economics of the fertilizer branch, costs for autonomous application of de-N₂O technology have to be reduced below a maximum of about 0.13 € per ton CO₂-eq. (equivalent to about 0.36 € per ton nitric acid produced). Therefore, most of the techniques mentioned above will only be applied when other driving forces (legislation or joint implementation to reduce CO₂ emission) are introduced.
7. Concluding remarks

Nitric acid production is the largest source of N₂O in the chemical industry (400 kton y⁻¹). Emissions of this gas require urgent reduction due to its role as a strong greenhouse gas (310 times stronger that CO₂) and as ozone layer depletor. Although no governmental legislation has been officially issued with respect to N₂O emission, the voluntary commitment of adipic acid producers to reduce emissions has put pressure on nitric acid producers. The large N₂O (and thus CO₂) reduction potential combined with the finite number of nitric acid plants makes N₂O abatement in this source a very attractive means to meet the ongoing process of new agreements and regulations, in particular the Kyoto Protocol on greenhouse gas emissions. However, no mature technology to reduce N₂O emissions from this source has been installed as yet.

The European market for de-N₂O in nitric acid production will concentrate on existing installations (124 plants), since installation of new plants is not likely is not expected in the next 10 years. Currently, two de-N₂O technologies are available at commercial scale: homogeneous decomposition in the enlarged chamber and NSCR in the tail-gas. Homogeneous decomposition in the reactor chamber can be effectively used for new plants, but it is not competitive for existing plants due to high retrofit costs, while NSCR is regarded as being outdated. A number of de-N₂O technologies are currently under development. The choice of a system depends on the plant characteristics, on the location in the process, and on the technical requirements of the abatement option. The catalytic decomposition inside the reaction chamber and the direct decomposition upstream of the tail-gas expander show the highest cost efficiency (0.2-1.0 € per ton CO₂-eq. in existing plants) and are expected to play a major role on the future de-N₂O market. The influence of the in-process-gas catalytic decomposition on the nitric acid production capacity, strongly affects the cost efficiency of this abatement option, and is not yet well established. Catalytic N₂O decomposition upstream of the tail-gas expander may yield a high N₂O reduction levels at moderate costs, but it can not be applied in low-temperature tail-gas facilities (T < 673 K). Selective catalytic reduction upstream of the tail-gas expander can be applied for low temperature tail-gases, but operation costs are prohibitive due to the permanent consumption of the reductant. If SCR of N₂O can be combined with SCR of NOₓ, the SCR technology will gain attractiveness. The cost efficiency of the abatement options downstream of the tail-gas expander (end-of-pipe options) is even less favourable, due to inevitable use of preheating equipment and/or reductants.

References


Catalyst testing in laboratory reactors requires careful experimentation and data interpretation. Classical methods of catalyst development tend to be slow, laborious, and incapable of addressing most complex, multi-component chemical systems challenges. In order to speed up this process in an efficient way and on a quantitative basis, the six-flow parallel reactor technology is used. This enables quantitative parallel catalyst testing, which enhances the number of catalysts tested significantly and reduces the time for kinetic studies. Thus, operation costs are lowered and the success rate for important breakthroughs is increased. The six-flow set-up allows a proper catalyst testing, under more realistic and accurate conditions than in conventional “combinatorial” techniques, especially when the catalyst development stage is advanced and quantitative data are required. The application of this technology in different catalytic processes is reviewed and combined with criteria for ideal behaviour in reactor models and transport phenomena, crucial in order to achieve intrinsic catalyst performance data.
1. State-of-the-art in catalyst development

The experimentation with a laboratory-scale reactor is, now more than ever, a prerequisite in the development of catalysts for a new process or the improvement of existing processes.\textsuperscript{1-3} Discovering, developing, and optimizing new catalytic materials using current approaches is predominantly a process of trial and error, sequentially generating data from one experiment to another. This process yields low success rates, and requires long timelines and large expenditures, especially as desired materials increase in complexity.

The catalyst development work required before a new or modified process is introduced, consists of many stages. Fig. 1 schematically indicates the order of activities, initialized by the new idea for a process or catalyst: (i) catalyst preparation, (ii) catalyst screening, (iii) establishing reaction networks, (iv) kinetic studies, (v) stability tests, and (vi) scale-up on pilot plant level. During the advancement of the development there will be a continuous feedback from one to other activities to optimize the catalyst and/or the catalytic process. Two different objectives can be distinguished during the catalyst development program: primary screening and secondary screening.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{catalyst-development-process.png}
\caption{Stages in a catalyst development program.}
\end{figure}

High-Throughput Experimentation or Screening (HTE or HTS) represents nowadays a paradigm shift in the management and execution of research and development work. For drug screening in the pharmaceutical industry, HTS technology has been rapidly developed and applied since the end of the nineteen-eighties.\textsuperscript{4,5} The application of this technology has been focussed on the automated synthesis and fast screening of large libraries of target drug molecules. The basic concepts of this technology are equally well and much broader applicable to other areas of both product and process research and development, like in catalysis and materials science.\textsuperscript{6} Over the past 5 years, the number of publications dealing with a combinatorial approach applied to heterogeneous catalysis has been steadily increasing.\textsuperscript{6-11} There is a growing interest of the scientific community for this new methodology. Examples of catalytic reactions studied by combinatorial methods are: dehydrogenation of cyclohexane,\textsuperscript{8} oxidation of methane and CO,\textsuperscript{11} oxidative dehydrogenation of lower alkanes,\textsuperscript{12} selective oxidation of alcohols,\textsuperscript{13} and NO reduction with C\textsubscript{3}H\textsubscript{6}.\textsuperscript{14} However, a major source of disagreement about the future prospects of combinatorial methods emanates from the highly confidential aspect of the progress accomplished by industrial research.
1.1. Primary catalyst screening

In the combinatorial stage or primary screening many catalyst formulations need to be prepared, investigated, and roughly compared on activity and selectivity. High-throughput synthesis and screening of the activity of these samples in a qualitative sense allow a rapid identification of potential "lead" catalysts. By combining microreactor technology with high speed performance analysis, informatics, simulation and also library synthesis, a virtuous circle of technology is created, reducing the scale, increasing the speed of execution and broadening the knowledge base of R&D. Optical methods and mass spectrometry have been the most commonly used methods in catalyst screening became of their broad applicability and relative high speed compared to other techniques. The successful implementation of combinatorial approaches will require that all of the components shown in Fig. 2 must be in place and function smoothly, otherwise "bottlenecks" will limit the throughput.

Without any doubt, primary screening accelerates development due to a high efficiency and level of automation. Although the preparation of solid-state libraries of catalytic materials by thin film deposition and solution-based methods (e.g. by coprecipitation, sol-gel, or impregnation) have been successfully miniaturized, there is an important issue in library synthesis. Since the ultimate goal of catalysis research is to develop industrial catalysts, it is desirable that each step of the combinatorial effort lends itself to large-scale production, which is not often the case. The screening of libraries of catalytic materials continues to be a challenging task because of the dynamic i.e. the time dependent nature of catalytic function.8

Furthermore, the activity of most catalytic materials changes with time on stream (stability). Most catalysis deactivates with time, and some exhibit significant induction periods before they become active. Consequently, to truly assess the value of new materials developed, their reaction performance must be extended to longer reaction times, which lowers the efficiency of the primary screening of large libraries.

Furthermore, screening systems mimicking the multi-cup principle operate under poorly defined conditions and are limited to mild experimental conditions of pressure and temperature. In this area, in particular, testing conditions may exert a decisive role on the observed activity. This can be exemplified by the mass spectrometer screening technique reported by different authors.15,17 In one of these cases, the library consisted of an open structure where catalyst powders, prepared for example by the sol-gel method, were placed in a spatially addressable configuration on a heated substrate. Library screening tool was achieved by sequentially flowing the feed gas onto the surface of a particular site through a capillary feed line and by withdrawing the products through another capillary (Fig. 3). The capillary bundle, containing both the feed and sampling lines, was then moved from site to site by using a robotic movement mechanism. The utility of this system as a valuable catalyst screening was demonstrated by determining different products in the partial oxidation of propylene as a function of catalyst formulation.16 These screening systems cannot efficiently address issues related to the time-dependent behaviour of materials because they were designed to provide reactant-catalyst contact only for a short period of time, i.e. about 1 min.
Fig. 3. Spatially resolved mass spectrometer system to screen catalysts; (a) photograph of the open reactors with a mounted library of 69 catalysts, (b) schematic drawing of the system.\textsuperscript{15,16}

In array microreactors containing the catalyst pellets in wells (Figs. 4 and 5), it is possible to test a large numbers of catalysts in parallel and for extended periods of time. thereby identifying leads that have greater chances of becoming practical catalysis. However, as in the former case, this configuration does not have a well-defined flow pattern (hydrodynamics), nor heat and mass-transfer characteristics, which should be carefully considered in order to interpret the measured data properly. In this sense, conventional combinatorial methods are of limited value and only serve as a qualitative indication. In addition, ‘cross-over’ effects (e.g. local heating) are not excluded, which may lead to a falsified measured catalyst performance.

1.2. Secondary catalyst screening

The above-mentioned points remain bottlenecks in HTS R&D. The development and application of miniaturized and parallel flow reactor systems with identification of reaction products, promises to ease this bottleneck. This is so-called secondary screening or quantification stage. This stage targets the optimization of already-existing formulations, without necessarily excluding the discovery of new materials. The testing of potentially interesting catalysts from the former stage on a more quantitative basis is performed, consisting of determining the reaction kinetics and obtaining a first insight into the catalytic stability. This stage follows a more rational approach, which orients the investigation along predetermined paths.\textsuperscript{10} The techniques are usually considerably slower than primary screening techniques, but more accurate or more detailed information can be obtained. Secondary screening can be achieved by employing continuous flow parallel reactors with identification of reaction products (Fig. 6).\textsuperscript{8,10,19-23}
The quantification stage also includes time-consuming kinetic studies, which are indispensable for the development of the design, operation, and process control of a large-scale catalytic reactor. They require an exhaustive description of the catalytic rate as a function of the process variables, such as temperature, pressure, space time, and composition of the reaction mixture. The basis for the kinetic modeling studies is obtained by investigating the catalytic reaction mechanism and establishing the reaction network. Stability studies, in which the catalyst is tested for a longer period on-stream, should be carried out to evaluate the practical application of the new catalyst before scale-up is initiated. In current practice, however, these studies are usually performed during the bench or pilot scale testing with real feed and recycle streams and catalysts in its practical shape. These allow investigation of the effect of trace impurities or accumulated components, not observed in laboratory-scale experiments.

Reducing the scale of experimentation (downscaling) for stability studies offers many advantages although it can never completely replace larger-scale testing. Micro- and nanoflow units have been generally used in exploratory studies, and nowadays they are also increasingly applied in development studies on more established processes. The incentives behind downscaling may include: (i) cheaper equipment to construct and install, (ii) fewer materials to consume, store, and dispose of, (iii) fewer demands on laboratory infrastructure, (iv) lower utility requirements, (v) intrinsically safer (reduced hazards of toxic emissions, explosions or fires), and (vi) high accuracy in experimentation and the use of representative samples. The increase in research productivity resulting from catalyst testing on a smaller scale is illustrated by Fig. 7. It can be inferred that the more modern, automated micro- or nanoreactor units operating without human attention require at least one order of magnitude less manpower than the traditionally large pilot plants.
Obviously, the number of catalysts will decrease during the progress of catalyst development (Fig. 1), but the complexity, the time taken, and size increase and, consequently, the costs involved. This demands an efficient and proper approach for laboratory scale experimentation.

In this chapter, the past and present of the six-flow technology as secondary screening tool are reviewed. The six-flow set-up is proposed to be a proven technology for secondary screening, being an efficient tool as laboratory reactor allowing integration of the different stages involved in a general catalyst development program. The paper focuses on the description of the features, advantages, and operation of this system, as an innovative and attractive approach compared to other catalyst screening techniques. This set-up was applied in the development of catalytic system for different processes. Current investigations deal with N₂O decomposition and NO₃ reduction, as well as Fischer-Tropsch synthesis. General recommendations for proper catalyst testing and design criteria to avoid non-idealities in the catalyst bed are also emphasized to achieve accurate and intrinsic data on the catalyst performance.

Fig. 6. Examples of multiple-tube reactor for secondary screening.²⁰⁻²³
2. Laboratory reactors

Many different types of reactors can be applied for catalyst testing, and it is of primary importance to select the proper reactor configuration to obtain the required information. Several overviews of test reactors and recommendations for a proper reactor selection in the laboratory, as well as in an industrial application, have been published.\textsuperscript{25-36}

In order to obtain intrinsic catalyst properties (activity, selectivity, deactivation, and reaction kinetics) from experimental data, the following criteria should be fulfilled:

- Sufficient contact between the reactants and the catalyst
- Absence of mass and heat transport limitations inside and outside the catalyst particles
- Availability of a good description of the reactor characteristics, with well-defined residence time distributions under isothermal conditions. The criteria generally imply the use of ideal reactor types such as the plug-flow reactor (PFR) or the continuously-stirred tank reactor (CSTR).

The choice of the reactor is usually made via the following scheme:

1) Determine which type of information is required from the experiments
2) Define the performance factors that determine the selection to be made, e.g. experimental conditions, catalyst shape, reaction features, and complexity of reaction network
3) Choose the type of reactors that should be considered
4) Rank the choices available on the basis of the performance factors for each reactor.

A classical and complete reactor classification based on the operation can be found in ref. 1. Reactors operating at steady state, and in particular packed-bed reactors, are most widely applied in catalyst testing, due to the ease of operation and the low costs. Transiently operated reactors, however, are used much less for the mere goal of catalyst testing. Batch operation has the disadvantage that possible deactivation during the progress of the experiment cannot be observed directly and should be verified afterwards, e.g. by repeating the experiment. Pulse reactors, such as the TAP,\textsuperscript{37} operate at catalyst conditions that are usually quite different from those at steady-state operation. However, this disadvantage does not apply for transient operation in the case of switching between isotopically labelled species at steady-state conditions.\textsuperscript{38} Transient operation is mainly applied for obtaining mechanistic information and to establish reaction networks.\textsuperscript{39}

Kapteijn and Moulijn\textsuperscript{2} have reviewed advantages and drawbacks of frequently used laboratory reactor types. Based on these guidelines and on the general requirements for catalyst testing, the fixed-bed reactor is commonly applied in the parallel-flow technology. The fixed-bed reactor is simple, cheap, easy to handle, and applicable for both gas and liquid phase systems and, with some caution, also for three phase systems. Moreover, the reactor requires relatively small amounts of catalyst and deactivation is noted directly if the reactor is operating at steady-state conditions. Drawbacks are that (i) the plug-
flow reactor experiments yield conversions rather than rates, (ii) low flow rates can lead to concentration and temperature gradients over the stagnant layer surrounding the catalyst pellets, and (iii) care must be taken to ensure plug-flow behaviour. Integral operation (high conversion) is adopted for most activity and stability tests, as well for kinetic studies (scanning the whole range of conversions).

3. Six-flow technology

3.1. General description

The basic principle of the six-flow reactor can be seen in Fig. 8. The operation principle of the system is similar to that of a single-flow reactor system. Three different sections can be distinguished: gas mixing section, reactor section, and analysis section. The set-up contains six small easily accessible fixed-bed reactors that run in parallel. The flow rate, the composition of the catalyst bed, and the reactor pressure can be selected independently, whereas the feed composition and the temperature are the same in all reactors. Nowadays, mass-flow controllers for both liquid and gas streams are capable to provide stable molar flow rates, ideal for kinetic studies. This largely improved former systems where the flow was determined by capillaries in front of the reactor inlet. Mass-flow controllers are used to synthesize a desired flow mixture for the six reactors. A back-pressure regulator serves to maintain the feed pressure for the six distributing mass-flow controllers to the individual reactors. The excess of the mixture, needed to maintain the pressure, is vented. Downstream back-pressure regulators maintain the pressure in each reactor or the feed mixture. A selection valve sequentially selects the product mixture of a reactor to be send to the analysis section. Various methods of product analysis are available and depend highly on the system under investigation. Usually analysis techniques are sufficiently fast compared to the time needed to reach a stable catalyst activity. The set-up is PC-controlled and runs unattended. All these features facilitate and accelerate catalyst testing and kinetic investigations. Further reduction of the experimental effort can be obtained by sequential experimental design, carefully planning new experimental conditions, based on previous results.\textsuperscript{35,40,41}

Fig. 8. Basic scheme of the six-flow reactor system for fast catalyst screening and kinetic studies.\textsuperscript{21}
Of course, the number of six parallel reactors is not a hard, fixed value. More or less reactors can be put in parallel, depending on the demands. The oven containing the various reactors then needs to be adapted and space restrictions will have to be considered. More reactors also put more demand on the speed of the analysis method. Mass spectrometry is very fast, but cannot always be used. Gas chromatography, which is preferentially used in many cases such as in Fischer-Tropsch synthesis product analysis, is inherently much slower. Nevertheless even in this case six reactors were chosen, since the catalysts and equipment need a long time to stabilize, which outweighs the longer analysis time.

An interesting idea that was recently put forward in relation to PC-controlled equipment is the Temperature Scanning Reactor (TSR) for kinetic studies. The conversion levels at various experimental settings of temperature and space time are investigated by temperature-programmed experiments. Generally, one is only interested in a limited temperature range of about 100 K. In this technique, the data collection grid is so dense that an even isothermicity along the reactor axis is in principle not a strict requirement anymore. Generation of data sets of conversion and exit temperatures as a function of the space time \( W_{\text{cat}} / F(t)_W \) at the same inlet temperature is possible. By polynomial interpolation one can numerically differentiate the \( X \) vs. \( W_{\text{cat}}/F(t)_W \) curve to obtain the reaction rate at different values of the corresponding space time. The corresponding reaction temperature is derived from the temperature - space time correlation. This can be repeated for several pressures and compositions. Finally one obtains a large data set of \( (W_{\text{cat}}/F(t)_W, X, r, T) \) points, that can be used for a thorough kinetic analysis. In principle this seems a promising approach, especially when combined with the six-flow set-up, provided that the catalyst does not suffer from deactivation during the whole experimentation.

3.2. Operation modes

Fig. 9 shows different possibilities for experiments carried out in a six-flow set-up. Generally, for screening purposes, the reactors can be filled with the same amount of five different catalysts (Fig. 9a), and for kinetic studies with different amounts of the same catalyst (Fig. 9b). It is recommended to use always one reactor as reference, filled with inert material, e.g. SiC (blank runs). Activity and stability tests with the same set of catalysts can be carried out in a single experimental run. Variation of \( W_{\text{cat}}/F(t)_W \) by changing the amount of catalyst \( W_{\text{cat}} \) or \( F(t)_W \) allows a broad range of conversions to be covered in a single run. The six-flow set-up also offers the possibility to investigate the stability of six different catalysts at identical conditions or six samples of the same catalyst at different conditions simultaneously. If both the temperature and the feed composition have to be varied, it was experienced that it is often faster to vary the temperature at a given feed composition and repeat that for different compositions than the other way around. Linear or step-wise temperature programmed experiments are usually carried out during screening and many kinetic experiments.

Finally, it is worthwhile to note the flexibility and convenience of the six-flow reactor in comparison with a single-flow set-up for performing diagnostic experimental tests to verify the presence or absence of transport limitations, which are described in §4. Figs. 9c and 9d show typical results when checking the influence of the particle size (effect of intraparticle limitation) or the effect of the gas flow rate at constant space time (effect of extraparticle limitation) in the observed reaction rate.
Fig. 9. Operation modes in the six-flow reactor set-up: (a) activity tests and life-time experiments; (b) kinetic studies; (c) and (d) diagnostic experimental tests for the presence of intraparticle limitations and extraparticle limitations, respectively.

One of the strongest advantages of the six-flow reactor as a laboratory reactor is the accuracy and reproducibility of the screening and kinetic measurements. This is crucial for a suitable comparison between catalyst formulations and to develop kinetic models based on experimental results. The flow and pressure system is robust and the analytical unit has a high accuracy. Fig. 10 shows a typical activity curve for N₂O decomposition over ex-FeZSM-5 (described in Chapters 5-9 of this thesis). N₂O conversion was measured as a function of temperature. The reproducibility achieved is remarkable. The same reactor, prepared by carefully weighing a certain amount of catalyst, was tested in the six different positions of the reactor oven (Fig. 10a). Analogously, the conversion levels are also very similar for the three different bed preparations of the sample holder in the same position of the reactor oven (Fig. 10b). Conversions are always determined by putting a reference reactor (filled with an inert material, SiC) in the corresponding run.

3.3. Evolution and evaluation of the six-flow technology

The six-flow system has been successfully applied in catalyst testing and kinetic studies in our group.⁴⁴⁻⁵⁸ Plug-flow reactors have been used in all cases. The reactor oven in the set-ups for Diesel soot oxidation and Fischer-Tropsch are appropriately configured to insert also a monolithic reactor. Table 1 summarizes the past and the current catalytic systems studied and developed in our laboratory. A remarkable example of a successful implementation of some of these ideas was the kinetic study of the selective catalytic reduction of NO over alumina-supported manganese oxide.⁴⁹ Product analysis was performed by a mass
spectrometer. This yielded data at five different space-times (the sixth reactor served as a blank reference). In one month all kinetic data had been collected. Analogously, we have recently performed quantitative kinetic studies regarding N₂O decomposition over different formulations. One recent example of the high throughput of the six-flow reactor for kinetic studies is presented in Fig. 11. The influence of temperature, partial N₂O and O₂ pressures on the N₂O conversion over a Co-based mixed oxide was collected and processed in 3 weeks. A kinetic model is currently being developed. The tremendously increased speed of data generation (5-6 times faster than with a single flow set-up) with this parallel testing system completely outweighs the relatively small additional investment compared to a single-flow set-up. In fact, this investment only accounts for the addition to the system of the flow distribution and product selection in the reaction section. An extra-cost is also involved in the automatization of the equipment, being indispensable for an efficient operation.

Fig. 10. Reproducibility studies in the six-flow reactor system. N₂O conversion vs. temperature over ex-FeZSM-5 is presented: (a) the same catalyst sample with holder in the six positions (Pos.) of the reactor oven (Fig. 6, top right) and (b) different catalyst sample bed preparations (Prep.) in the same position of the reactor oven. Conditions: 4.5 mbar N₂O in He; P = 3 bar; GHSV = 60000 h⁻¹. Conversions were calculated based on the analytical results using one of the reactors filled with SiC (reference material).
Fig. 11. Kinetic study: N₂O decomposition over a Co-based mixed oxide derived from the thermal decomposition of the corresponding hydrotalcite. Effect of (a) temperature, (b) partial N₂O pressure, and (c) partial O₂ pressure on the N₂O conversion; \( W_{in}/F(N_2O)_in = 8.05 \times 10^5 \) g s mol⁻¹.
Table 1. Utilization of the six-flow technology in catalyst development: screening and kinetic studies.

<table>
<thead>
<tr>
<th>Process</th>
<th>Catalytic system</th>
<th>Product analysis</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO oxidation</td>
<td>Cu/Cr/activated carbon</td>
<td>GC</td>
<td>44-46</td>
</tr>
<tr>
<td>NO₂ reduction with CO</td>
<td>Cu/Cr/activated carbon</td>
<td>NO₂-analyser</td>
<td></td>
</tr>
<tr>
<td>Water-gas shift reaction</td>
<td>Cu/Cr/γ-Al₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cu/Cr/activated carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂ reduction with ammonia (NH₃-SCR)</td>
<td>Cu/activated supported</td>
<td>MS</td>
<td>47-50</td>
</tr>
<tr>
<td></td>
<td>Mn oxides/activated carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn oxides/γ-Al₂O₃</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Modified activated carbons</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Mn₃O₆-WO₇/γ-Al₂O₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soot oxidation*</td>
<td>Ag/Mn/ZrO₂</td>
<td>NDIR</td>
<td>51-53</td>
</tr>
<tr>
<td></td>
<td>Cu-V/Al₂O₃</td>
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</tr>
<tr>
<td></td>
<td>Cu/K/Mo/(Cl)/ZrO₂</td>
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<td></td>
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<td></td>
<td>V/ZrO₂</td>
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<tr>
<td></td>
<td>Cs₈MoO₄-V₂O₅</td>
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<tr>
<td></td>
<td>CsVO₄-MoO₃</td>
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<tr>
<td></td>
<td>CsSO₄-V₂O₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorofluorocarbons (CFC) hydrogenolysis</td>
<td>[Rh, Ru, Re, Pt, Pd,Ir]/activated carbon</td>
<td>GC</td>
<td>54,55</td>
</tr>
<tr>
<td></td>
<td>Pd/activated carbon</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-zeolite Y</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pd-Mordenite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂O decomposition*</td>
<td>Mixed oxides from hydrotalcites</td>
<td>GC</td>
<td>56-58</td>
</tr>
<tr>
<td>NO₂ reduction with hydrocarbons (HC-SCR)</td>
<td>Fe-based catalysts</td>
<td>NO₂-analyser</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-based catalysts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fischer-Tropsch synthesis**</td>
<td>Co/SiO₂, Co/Al₂O₃</td>
<td>GC</td>
<td>-</td>
</tr>
</tbody>
</table>

GC: Gas chromatography; NO₂: nitrogen oxides; MS: mass spectrometer; HC: hydrocarbons; NDIR: non-dispersive infra-red; *: current applications; **: operation in both fixed-bed and monolithic reactors.

3.4. Case study: removal of nitrogen oxides

The work presented in this thesis was aimed at the development of catalysts for direct N₂O decomposition in tail-gases from nitric acid plants and fluidized-bed combustors. In view of the extensive amount of catalyst formulations to be tested, an automated six-flow reactor set-up was designed. A general view of the set-up is depicted in Fig. 12. The experimental set-up is versatile and is used in parallel for selective catalytic reduction of NO₂ with hydrocarbons and oxidative dehydrogenation of hydrocarbons. Other processes, such as selective reduction with ammonia or selective oxidations can also be performed. Fig. 13 shows the detailed flow-sheet of the set-up. The amount of equipment and instrumentation gives an idea of the magnitude of the experimental system. Several improvements have been made to the six-flow set-up compared to the original ones (see references in Table 1):

- The mixing of the feed gases is done in a manifold, which consists of different modules (one for each feed gas). Each module consists of a system of two open-close valves, which allow either the entrance of the gas to the reactor or the purge to the vent. This system produces an optimal mixture of the gases involved, decisive for homogeneity, and minimizes the dead volume.
- Liquid reactant (water in this case) is stored in a stainless steel reservoir, and is fed to the
system by means of a liquid mass-flow controller. After mixing with the carrier gas, the stream enters the evaporation chamber unit. Subsequently, the vapor is mixed with the stream coming from the above-mentioned manifold.

- The entire reactor section furnace is placed in an oven maintained at 333-343 K to avoid the need for a separate heat tracing of the lines (Fig. 14a). The maximum allowed temperature of the reactor section is 343 K due to the presence of electronic parts in the digital mass-flow controllers and back-pressure regulators.

- The reactor furnace (Fig. 14b) is made of brass (alloy of copper and zinc with a high thermal diffusivity) although also silver or aluminum may be considered, and tightly fixed to the reactors for an efficient heat exchange.

- Each reactor outlet is equipped with a back-pressure regulator, enabling an independent control of the reactor pressure.

- One of the reactors is always used as a reference to check for any undesired homogeneous reaction, and the activity of the wall or diluent.

- The stream to be analyzed is selected with a manifold of two-way valves and not by means of a multi-position valve as suggested in Fig. 8. The main advantage of the manifold is the possible extension when more reactor outlets need to be analyzed, by simply addition of new modules (see Fig. 12). In addition, versatility should be pointed out too, by independent operation of each module. The dead volume of this device is minimized and no stagnant regions are developed.

- The excess flow stream, vended by the back-pressure regulator before the reactor feeding mass-flow controllers is also analyzed in order to check the exact composition of the feed.

- The set-up is fully PC-controlled and predesigned kinetic runs (pressure and temperature variation) could be carried out automatically within a short period of time. Automation comprises the use of ADAM modules and a LabView software. Compared to automation packages previously used in our laboratory, LabView is easier to use and does not require specific programming knowledge. Different sub-routines (VI's) can be used for interfacing hardware. The automation of the set-up was completed in six weeks. The data generated during the experiment is automatically saved, being readable with standard software. Data mining requires special attention for a successful experiment. Design of template spread-sheet is advisable, enabling efficient data handling and avoiding human mistakes in inputting data.

Fig. 12. Photograph of the six-flow system for catalytic removal of nitrogen oxides (N₂O-NOₓ).
Fig. 13. Detailed flowsheet of the six-flow set-up for catalytic removal of NO and N₂O.
During the first stage of catalyst development, this set-up was used to test numerous catalysts in order to identify promising formulations for direct N₂O decomposition in simulated tail-gases from nitric acid production. The catalysts include supported oxides, zeolites, and mixed oxides derived from hydroalumino-silicates. Around 100 catalyst were synthesized and tested within 1 month under representative tail-gas conditions.

Primary evaluation of catalytic performance was made after testing the catalyst in a broad temperature range (from 0 to 100% N₂O conversion) and upon increasing-decreasing reaction temperature cycles. These points are crucial for a proper and efficient evaluation, as shown in Figs. 15 and 16. In the literature comparisons of catalysts based on the temperature at which a certain reactant reaches 50 or 100% conversion (so-called T₅₀ and T₁₀₀).
Fig. 15. Typical activity curves for direct N₂O decomposition over four different catalysts.

respectively), are often found. Also, simply comparing activities at one or two temperatures is common practice. Fig. 15 shows two examples where these criteria can lead to misinterpretation of data for typical N₂O conversion vs. temperature curves. In Fig. 15a, comparison of catalysts A and B according to the T₅₀ criterion will lead to an identical performance. However below T₅₀ catalyst A is significantly more active than catalyst B, and above T₅₀ the opposite holds. This is simply due to the high activation energy of formulation A, which makes the reaction rate over this catalyst more sensitive to temperature. A similar argument holds for Fig. 15b, where the T₁₀₀ criteria was used to compare catalyst C and D. Indeed, both catalysts reach 100% conversion at the same temperature, but below T₁₀₀, catalyst C is superior to catalyst D. With this illustrative example it is concluded that in general the operating temperature range and estimation of the activation energy from the experimental data is crucial for a proper evaluation of catalyst performance in a specific application, in this case the direct N₂O decomposition.

Measuring conversion vs. temperature curves upon increasing and decreasing reaction temperature was also found an important check for catalyst evaluation. This provides information on the short-term stability of the catalyst formulation. In the examples shown in Fig. 16, the activity curve of Co,Pd-La,Al mixed oxide for N₂O decomposition in simulated

Fig. 16. N₂O conversion vs. T over (▲, △) Co,Pd-La,Al mixed oxide and (●, ◊) PdZSM-5. Feed composition: 4.5 mbar N₂O, 75 mbar O₂, 0.6 mbar NO, and 15 mbar H₂O, P = 3 bar, GHSV = 13000 h⁻¹. Solid symbols: increasing temperature. Open symbols: decreasing temperature.
tail-gases of nitric acid plants follows the same path at increasing or decreasing reaction temperature, while a significant decrease in conversion was observed over PdZSM-5 during the cooling branch. This indicates severe deactivation after 10 h, which ruled out further evaluation of this formulation (e.g. kinetic studies), since one of the primary requirements, i.e. stability, is not fulfilled. Analogously activation of the catalyst in heating-cooling cycles can also occur.

3.5. Summary of features of the six-flow set-up

The six-flow reactor system integrates both screening and quantification functions, necessary for a catalyst development program, and is therefore considered as a powerful tool for efficient and high throughput catalyst screening and kinetic studies. Typical features of the set-up are:

- Enhancement of the throughput of catalysts to be tested
- Remarkable accuracy and reproducibility
- Use references for reliability
- Decrease of time required for kinetic studies and diagnostic experimental tests
- Individual flow and pressure control in each reactor
- Moderately increased cost compared to a single reactor set-up

4. Analysis of fixed-bed reactors: a summary of testing criteria

The parallel-flow technology as an efficient tool in procuring data on catalyst activity, stability, and kinetics is not effective if no precaution is taken to avoid various phenomena of non-ideal reactor behaviour, mass and heat transport limitations on the reactor scale and on the catalyst particle scale, that disguise intrinsic catalytic activities and selectivities. Therefore, the related criteria are briefly reviewed in this paper. The discipline *Catalytic Reaction Engineering* covers the description of these phenomena since it integrates catalysis, reactor analysis and transport phenomena.40,59-64

For a fixed-bed reactor operated under steady conditions, the most important scaling factors are the dimensions of the catalyst bed and the catalyst particles.24 Usually, hydrodynamics play a less relevant role than chemical kinetics, and intraparticle diffusion in determining the conversions and the selectivities in most fixed-bed processes is of practical interest. However, hydrodynamics are important in relation with the pressure drop, several heat transport phenomena, the hold-up in multiphase flow systems, and the distribution of fluids over the reactor cross section. A series of recommendations and criteria to ensure accurate determination of intrinsic reaction rates are given in eqs. (1)-(9). The background of some of these equations is briefly considered hereafter. If otherwise stated, these criteria were checked and fulfilled in the activity experiments reported in this Ph.D. research.

1. Minimum bed length (to neglect effect of axial dispersion):

\[
\frac{L_b}{d_p} > \frac{20 n}{Bo} \ln \left( \frac{1}{1 - X} \right)
\]  

(1)

2. Minimum reactor diameter (to neglect wall effects in gas-solid operation)

\[
\frac{d_r}{d_p} > 10
\]

(2)
3. Pressure drop in the catalyst bed (Ergun)

\[
\frac{\Delta P_b}{L_b} = \frac{150 \mu_g (1-\varepsilon)^2}{d_p^2} \frac{1}{\varepsilon^3} \frac{u}{u^2} + \frac{1.75 \rho_g (1-\varepsilon)}{d_p} \frac{1}{\varepsilon^3} u^2 < 0.2 \frac{P_{tot}}{L_b}
\]  

(3)

4. Extraparticle mass transfer (to neglect extraparticle mass transfer limitation)

\[
Ca = \frac{r_{e,obs}}{a' k_f C_b} < \frac{0.05}{|n|}
\]

(4)

5. Extraparticle heat transfer (to neglect extraparticle heat transfer limitation)

\[
\gamma \beta_c Ca = \left( \frac{E_a}{R T_b} \right) \left[ \frac{(-\Delta H_r)}{h T_b} \right] \left( \frac{r_{e,obs}}{a' k_f C_b} \right) < 0.05
\]

(5)

6. Intraparticle mass transport (to neglect intraparticle diffusion limitation)

\[
\Phi = \eta \varphi^2 = \left( \frac{r_{e,obs} L^2}{D_{eff} C_b} \right) \left( \frac{n+1}{2} \right) < 0.15
\]

(6)

7. Intraparticle heat transport (to neglect intraparticle heat transport limitation, assuming spherical particles)

\[
\gamma \beta_i \left( \eta \varphi^2 \right) = \left( \frac{E_a}{R T_b} \right) \left[ \frac{(-\Delta H_r)}{\lambda_{eff,p} T_b} \right] \left( \frac{r_{e,obs} L^2}{D_{eff} C_b} \right) < 0.1
\]

(7)

8. Radial temperature gradient (to neglect effect of radial temperature gradient on reactor scale)

\[
\left( \frac{E_a}{R T_w} \right) \left[ \frac{(-\Delta H_r)}{\lambda_{eff,b} T_w} \right] \left( \frac{r_{e,obs} L^2}{D_{rad} C_b} \right) \left( \frac{1}{8} + \frac{1}{B_{tw} d_f} \right) < 0.05
\]

(8)

9. Bed dilution (to neglect effect of bed dilution on the conversion)

\[
\left( \frac{b}{1-b} \right) \frac{d_p X}{2 L_b} n < 0.05
\]

(9)

4.1. Assumption of ideal plug-flow behaviour

In an ideal plug-flow reactor, the fluidum can be assumed to flow as a straight front through the reactor. Diffusion and local flows around the catalyst particles and along the wall, however, may cause a disturbing axial dispersion.\textsuperscript{65} If the maximum allowed deviation from plug-flow reactor is set at 5%, a criterion can be set for the minimum ratio of bed length and particle, see eq. (1).\textsuperscript{66,67}

The difference between the packing density in the interior and that near the wall and the flat surface of the wall may also cause a deviation from ideal plug flow. This wall effect causes a higher local velocity near the wall, resulting in a non-flat radial velocity profile, and possibly also bypass of gas along the wall. For gases, the wall effect can be neglected if the ratio between bed diameter and particle diameter is larger than 10 (eq. (2)).\textsuperscript{68}
4.2. Pressure drop

The pressure drop over the catalyst bed can be estimated using the Ergun equation, eq. (3). The first term in this equation represents the Blake-Kozeny equation for laminar flow and forms the major contribution in laboratory reactors. A rule of thumb is that the pressure drop should be lower than approximately 20% of the total operation pressure in the reactor. Alpay et al. give a method to correct rate coefficients for the effect of the pressure drop.

4.3. Mass and heat transport limitations

Effects of transport limitations in heterogeneously catalyzed reactions have been studied extensively. It is of utmost importance to check for their presence or absence, in particular before performing an extensive kinetic investigation. For laboratory-scale gas-solid operation the following order in relative importance of the various gradients is usually valid:

\[(T - \text{grad})_{\text{bed}} > (T - \text{grad})_{\text{extra}} > (C - \text{grad})_{\text{intra}} > (T - \text{grad})_{\text{intra}} > (C - \text{grad})_{\text{extra}}\]

The temperature gradients on reactor scale and those due to extraparticle heat transfer are usually the most critical transport phenomena because of the poor heat conductivity of gas-solid fixed-beds. In the case of liquids, however, concentration gradients are usually the most important because liquids have a much higher density and heat conductivity and lower diffusivities. Although several of the above-mentioned concentration and temperature gradients may occur simultaneously, the proposed criteria are derived neglecting the effects of a combination of gradients.

A highly exothermic or endothermic reaction in combination with a low thermal conductivity of the catalyst bed may cause significant temperature gradients within the particle (intraparticle), at its interface with the external fluid phase (extraparticle), and in the radial and axial direction of the reactor.

For extraparticle mass transfer eq. (4) applies as criterion, where the Carberry number relates the concentration difference over the film to procurable quantities. For extraparticle heat transfer eq. (5) applies as criterion. For the heat and mass transfer coefficients in fixed-beds there are correlations available in terms of dimensionless numbers.

The criterion for intraparticle mass transport for an n-th order reaction under isothermal operation is given by the so-called Wheeler-Weisz modulus, eq. (6), which also gives a procurable and observable quantity. Mears analyzed the problem of intraparticle heat transport limitation and obtained an approximate solution for the maximum temperature rise in the catalyst bed. Based on this result a criterion for a less than 5% deviation from the isothermal rate can be given by Taylor series expansion of the rate, considering the whole cross section of the reactor for an average reaction rate, see eq. (7).

A criterion for the radial temperature gradient in a plug-flow reactor has also been derived, see eq. (8). The first term represents the dimensionless activation energy, based on the reactor wall temperature; the second term represents the ratio of the heat production rate and the heat conduction rate in radial direction; the last term accounts for the relative contributions of the radial conductivity and the heat transfer at the reactor wall. The latter contains the particle to bed radius ratio and the Biot number for heat transport at the wall. Different correlations can be used for the calculation and estimation of the different parameters involved in the former expression. From eq. (8) follows that dilution of the catalyst bed with inert solids and the use of small tube diameters favour the radial isothermicity. More discussion concerning the use of bed dilution follows in §4.5.
4.4. Experimental checks for the presence of transport limitations

Any of the preceding criteria should be considered at best only as a preliminary check, to be confirmed through proper experimental test runs. Additionally, experimental checks may indicate the presence of other effects for which no criterion exits, such as the formation of preferential routes through the catalyst bed (channelling).

Different diagnostic experimental tests have been described elsewhere. For the extraparticle concentration gradients, it consists of varying the flow rate and the amount of catalyst simultaneously, while keeping the space time $W_{int}/F(i)_o$ constant (Fig. 17a). If no limitations exist, the resulting conversions should be the same. If temperature effects also interfere, however, these might (over)compensate the concentration effects. This method should therefore be used with caution.

Fig. 17. Experimental check for the absence of (a) intraparticle and (b) extraparticle diffusion limitations in FeZSM-5. Conditions: 1.5 mbar N$_2$O in He, $P = 1$ bar, $W_{int}/F(N_2O)_o = 8.65 \times 10^5$ g s mol$^{-1}$.

For the intraparticle concentration gradients, variation of the particle size, e.g. by crushing and sieving the catalyst, and tests under identical conditions should indicate whether internal diffusion interferes (Fig. 17b). At small particle sizes the reaction is chemically controlled and independent of the particle size. Only for larger particles a decrease in the observed rate occurs. In particular, at a low-Reynolds-number, i.e. at flow rates typically occurring in laboratory exploratory reactors, the method can fail if the check is performed over a too narrow range of flow rates. Hence the range explored should be sufficiently large (i.e. 1 to 2 orders of magnitude).

The best experimental way to investigate the presence of temperature gradients on the reactor scale is to dilute the catalyst bed with an inert and good heat conducting material. If gradients are present, lower conversions should result for exothermic reactions and higher for endothermic reactions. Fig. 18 shows
an example where almost no difference was found between the pure and diluted catalyst bed in direct N₂O decomposition. The presentation of crude rate data in ‘Arrhenius plots’ to inspect the temperature behaviour can give indications of the presence of limiting transport processes by a changing slope (< activation energy). However, one should be aware of the fact that other phenomena can also induce this: change of the rate determining step, catalyst deactivation or fouling, approach of thermodynamic equilibrium, ignition phenomena, and even improper bed dilution.

4.5. Catalyst bed dilution

The application of catalyst-bed dilution considerably improves the catalyst testing process since it acts upon different aspects such as the dispersion and heat transfer limitation. This dilution technique has been successfully applied in hydrotreating research using trickle-flow reactors. Low surface area materials such as quartz, α-alumina, glass, and especially silicon carbide (SiC) are preferred as diluting solids because of their relative inertness.

Bed dilution of the catalyst bed results in the following decisive positive effects (Fig. 19):

- heat conduction in the bed is improved
- heat production (or consumption) is spread over a larger volume
- enlarged heat exchange area
- effect of axial dispersion is decreased by increasing the catalyst bed
- complete catalyst bodies can be investigated, when using fine inert particles, decoupling hydrodynamics and kinetics.

![Diagram](image)

Fig. 19. Testing of complete catalyst bodies by dilution with small inerts.

One should be aware that a very high degree of dilution may result in a disturbing sample inhomogeneity, causing an uneven distribution and also bypassing of the catalyst. This problem was originally evaluated by van den Bleek et al., who developed a criterion, which applies for an inert bed fraction b and a 5% maximum acceptable deviation from the ideal situation. We have recently considered this aspect thoroughly both experimentally and by means of simulations, arriving at an improved criterion based on observable parameters (eq. (9)). This point is further discussed in Chapter 3.

5. Concluding remarks

The six-flow set-up is a powerful tool for efficient and high throughput catalyst screening and kinetic studies. However, several recommendations and design criteria should be fulfilled in order to allow easy and accurate interpretation of the extensive data measured.

Acknowledgements. J.P.R. acknowledges the contribution of Dr. ir. R.J. Berger to this chapter.
Notation

\[ \begin{align*}
\dot{a} & = \text{specific external surface area of catalyst particle} = \frac{6}{d_p} \text{ for spherical particles} \\
b & = \text{inert volume fraction of the bed} \\
1-b & = \text{catalyst fraction of the bed} \\
C & = \text{concentration} \\
d_p & = \text{particle diameter} \\
d_r & = \text{reactor diameter} \\
D_{\text{eff}} & = \text{effective diffusivity in particle} \\
D_{\text{rad}} & = \text{diffusivity in the radial direction} \\
D_{\text{ax}} & = \text{dispersion in the axial direction} \\
E_a & = \text{activation energy} \\
F(i) & = \text{molar feed flow of component i} \\
h & = \text{gas-solid heat transfer coefficient} \\
k_f & = \text{mass transfer coefficient} \\
L & = \text{characteristic catalyst dimension} (= \frac{d_p}{6} \text{ for spherical particles}) \\
L_b & = \text{bed length} \\
n & = \text{reaction order} \\
P_{\text{tot}} & = \text{total pressure} \\
r_n, \, v & = \text{observed reaction rate per unit particle volume} \\
R & = \text{universal gas constant} \\
SV & = \text{space velocity} \\
T & = \text{temperature} \\
u & = \text{superficial velocity} \\
W_{\text{cat}} & = \text{catalyst mass} \\
X & = \text{conversion} \end{align*} \]

Dimensionless numbers

\[ \begin{align*}
Bo & = \text{Bodenstein (or Péclet particle) number} = \left( \frac{u d_p}{D_{\text{ax}}} \right) \\
Ca & = \text{Carberry number} = \left( \frac{r_{n, \text{obs}}}{k_f} \frac{a^t c_b}{C_b} \right) \\
Bi_e & = \text{Biot number at the reactor wall} = \left( \frac{h_e d_p}{\lambda_{\text{eff}}} \right) \\
Re_p & = \text{Reynolds number (particle)} = \left( \frac{\rho_g u d_p}{\mu_g} \right) \\
\end{align*} \]

Greek

\[ \begin{align*}
\Delta H_r & = \text{reaction enthalpy} \\
\Delta P_b & = \text{pressure drop over the catalyst bed} \\
\epsilon & = \text{void bed fraction} \\
\eta & = \text{effectiveness factor} \\
\phi & = \text{Thiele modulus} = L \sqrt{\frac{k_c}{D_{\text{eff}}}} \\
& \quad (k_c = \text{rate constant per unit volume expressed in s}^{-1}) \\
\lambda_{\text{eff}} & = \text{effective thermal conductivity} \\
\lambda_g & = \text{gas thermal conductivity} \\
\mu_g & = \text{(dynamic) gas viscosity} \\
\rho_g & = \text{gas density} \end{align*} \]

\[ \begin{align*}
\text{J mol}^{-1} & \\
\text{Pa} & \\
- & \\
- & \\
- & \\
- & \\
- & \\
\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1} & \\
\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1} & \\
\text{kg m}^{-1} \text{s}^{-1} & \\
\text{kg m}^{-3} & \\
\end{align*} \]
\[ \Phi = \text{Wheeler-Weisz modulus} \quad (= \eta \phi^2 = \frac{r_{\text{obs}} L^2}{D_{\text{eff}} C_b}) \]

Subscripts

- \( b \) = in bulk phase; also bed
- \( \text{eff} \) = effective
- \( g \) = gas
- \( \text{obs} \) = observed
- \( p \) = particle
- \( s \) = at external particle surface
- \( t \) = tube
- \( \text{tot} \) = total
- \( w \) = at the reactor wall

References

Catalyst Bed Dilution in Laboratory Microreactors: Friend or Foe?

The influence of dilution of catalyst particles by inert particles has been investigated in a gas-solid laboratory micro-reactor for a first-order irreversible reaction, viz. catalyzed \( \text{NO}_2 \) decomposition, using two different catalysts: FeZSM-5 and Co-La,Al mixed oxide. Vertically and horizontally segregated beds, as well as mixed beds with different degrees of dilution were considered. If the catalyst and the diluting particles are not well-mixed, the conversion reduces significantly due to bypassing and axial dispersion. Also apparent activation energies are reduced. The effects are stronger at high conversions (> 0.4). Even over perfectly mixed catalyst-inert beds the conversion may be negatively affected by the dilution. Application of a Random Particle Distribution (RPD) model to the segregated bed enables the estimation of the axial and radial dispersion coefficients, as well as bed tortuosity. The relative deviation in conversion caused by the dilution, which is approximately proportional to the reaction order, can be well estimated from observable parameters, i.e. the conversion, the volume fraction of bed dilution, the bed height, and the particle diameter. A simple criterion for this deviation is established. The combination of a high degree of dilution and high conversion should be avoided in the evaluation of catalytic activity and in kinetic studies.
1. Introduction

Many activity measurements of heterogeneous catalysts are carried out in a fixed-bed reactor. Usually, the reactor is operated in the integral mode and the reactor model to describe the performance is based on plug-flow behaviour. Gas-flown catalyst beds are often diluted with inert particles in order to improve the isothermicity of the bed and to suppress other potentially disturbing effects such as axial dispersion and bypassing. Low-surface-area materials such as glass, quartz, α-alumina, and especially silicon carbide (SiC) are preferred as dilution because of their relative inertness and good heat transfer properties. Bed dilution does not primarily reduce the temperature gradients around the catalyst particles, but only the temperature gradients on reactor scale; i.e. the radial and axial temperature gradients in the packed bed, which are generally the largest. If the aim is to determine intrinsic kinetics, it is in any case recommended to perform a complete check concerning mass and heat transport limitations. There is extensive literature related to this subject.\textsuperscript{1,2}

Inert bed dilution is now increasingly applied by many researchers\textsuperscript{3,5} and the increasing use of parallel catalyst testing units may even further enhance this.\textsuperscript{2} Dilution of a bed consisting of complete catalyst bodies with fine inert particles is also applied in laboratory gas-liquid-solid trickle-bed reactors but for different reasons: to increase catalyst wetting and liquid hold-up and to suppress axial dispersion and wall-effects.\textsuperscript{6-8}

![Fig. 1. Effect of different distributions of inert diluent in catalyst beds on the conversion for an irreversible 1st order reaction.](image)

However, bed dilution may also negatively influence the reactant conversion due to local bypassing of the catalyst. The extent of the negative effect depends on \(i\) the amount of dilution, \(ii\) the reaction kinetics, \(iii\) the particle and reactor geometry, and \(iv\) the degree of segregation of catalyst and diluent. A simple example, taken from van den Bleek et al.\textsuperscript{9} demonstrates the negative effect of bed dilution on the conversion. A first-order irreversible reaction is carried out in three fixed beds with identical total amounts of catalyst and dilution but with a different distribution, as shown in Fig. 1. If plug-flow behavior is assumed, the conversions \(X_1\), \(X_2\), and \(X_3\) can be calculated as follows and the results are shown graphically in Fig. 1.

\[
\begin{align*}
X_1 &= 1 - \exp(-kC_o\tau) \\
X_2 &= 1 - 0.5 \left[ \exp(-2kC_o\tau) + 1 \right] \\
X_3 &= 1 - 0.25 \left[ \exp\left(-\frac{1}{2}kC_o\tau\right) + \exp(-kC_o\tau) + \exp(-2kC_o\tau) + \exp\left(-\frac{3}{2}kC_o\tau\right) \right]
\end{align*}
\]  
(1)

60
Conversion $X_2$, which corresponds to the case that all dilution is located at one side of the reactor, is significantly less than if the dilution is more homogeneously distributed. A large amount of diluent tends to increase the inhomogeneity of the distribution and consequently the deviation. If the fractional conversion in the bed is low (i.e. less than ca. 0.15), however, the effect of dilution on the conversion is in absolute and also in relative sense much smaller.

If the catalyst and the diluent are well-mixed, the distribution of the diluent will be much less inhomogeneous than in the example and the effect on the conversion will be smaller. In fact $X_1$ and $X_3$ are the two extremes. If the reaction order is positive, the deviation of the conversion due to the presence of diluent is always negative. This example shows that inert bed dilution does not lower the activity homogeneously throughout the bed. Catalyst particles keep their intrinsic activity, but they are dispersed in an inert surrounding, giving rise to a discrete particle problem, i.e. locally in the bed reaction takes place or not. Hence, catalyst-diluent particle distribution and radial bed transport seem to be important parameters.

In practical applications, the distribution of catalyst particles and inert particles that is obtained may be worse than expected. Besides insufficient attention to the mixing procedure, this may be due to a non-ideal behaviour of the particles (e.g. particles which tend to agglomerate) or non-equal size distributions or different shapes of the particles. Additionally, in particular when using a high inert bed dilution, the assumption of plug-flow behaviour is often not allowed. Radial dispersion will decrease the concentration differences in radial direction and consequently increase the conversions $X_2$ and $X_3$ in the example given above. Axial dispersion may also influence the results.

With respect to the degree of dilution, van den Bleek et al. also showed that the influence on the conversion as a consequence of applying dilution cannot be completely eliminated by perfect mixing of the catalyst and the diluent particles. These authors introduced the 'dilution effect' $\Delta$ as a relative measure of the deviation in the conversion:

$$\Delta = \frac{X_{\text{und}} - X_{\text{ed}}}{X_{\text{und}}}$$  \hspace{1cm} (2)

The conversion in the undiluted bed ($X_{\text{und}}$) is the conversion that would be obtained in the ideal case if the catalyst activity would be homogeneously distributed over the entire catalyst bed volume and if plug-flow behaviour can be assumed. The following equation was proposed in the case of an irreversible 1st order reaction:

$$\Delta = \frac{0.6 \sqrt{3} d_p b}{4 h_{\text{bed}} (1-b)}$$  \hspace{1cm} (3)

A major drawback of this equation is that the effect of the conversion is not incorporated. Sofekun et al. extended the calculations of van den Bleek et al., and derived the following expression:

$$\Delta = 0.4315 b \left(\frac{d_p}{h_{\text{bed}} (1-b)}\right)^{1.01} \left(\frac{(k\tau)^2 e^{-k\tau}}{1-e^{-k\tau}}\right)^{1.02} n^{0.37}$$  \hspace{1cm} (4)

This equation has the disadvantage that it requires the rate coefficient and reaction order, which are beforehand unknown in kinetic investigations. It would be useful to have a generally applicable relation containing observable quantities to estimate the maximum allowed amount of dilution and to account for the effect of radial dispersion more properly.
In this chapter a comprehensive investigation of the influence of applying dilution on the conversion for single phase (apart from the solid catalyst) systems is given. The effect of improper mixing at the macro-scale and the degree of dilution on the conversion have been studied both experimentally and by simulations. Dispersion coefficients and bed tortuosities were derived from our experiments, and a simple and generally applicable criterion for the maximum allowed amount of bed dilution is presented. Additionally, the effect of the reaction order is considered.

2. The Random Particle Distribution (RPD) model

In order to model the reactor performance and to estimate the effect of bed dilution on the conversion, the fixed bed is described using a rectangular shape, consisting of small cubes corresponding with a single catalyst or diluent particle (Fig. 2). The influence of using a rectangular shape instead of a circular shape is very small if the number of cells in radial direction is sufficient large (> 10), since the effect of radial dispersion is largely limited to adjacent cells and the cells around these. The catalyst and diluent particles are stochastically distributed over the entire bed. The fraction of cells filled with catalyst particles equals to 1-b. If the influence of axial dispersion is neglected, the performance of the reactor can be simulated layer by layer. All cells are assumed to act as small continuously stirred tank reactors (CSTRs). The concentrations in the adjacent cells in horizontal direction influence the mass balance via (radial) dispersion terms. This dispersion is described like Fickian diffusion using a concentration gradient equal to the ratio of the concentration difference between the two adjacent cells and the cell size (d_cell). For an irreversible 1st order reaction, the mass balance in a cell is given by:

\[
C_{i,j,k-1} - C_{i,j,k} + \frac{D_{\text{rad}}}{u d_{\text{cell}}} (C_{i-1,j,k} + C_{i+1,j,k} + C_{i,j-1,k} + C_{i,j+1,k} - 4C_{i,j,k}) - q k c_{\text{cat}} C_{i,j,k} = 0
\]  

(5)

Van den Bleek et al. and Sofekun et al. used a simpler approach in which the radial mass transfer was effectuated between this layer and the subsequent layer instead of in the same layer. This results in a significant underestimation of the effect of radial mass transfer, in particular at high radial dispersion coefficients. As a consequence of this, their simulation results will overestimate \( \Delta \).

The space time in a cell containing a catalyst particle \( (\tau_{\text{cell}}) \) depends on the amount of bed dilution \( (b) \) and the total number of layers \( (N_{ax}) \) according to eq. (6). In this expression, the term \( (1-b) \) is introduced to take into account that all the catalyst activity is located in the \( (1-b) \)th part of the total number of cells.

\[
\tau_{\text{cell}} = \frac{W}{W_{\text{cell}}} = \frac{1-b}{F(i)_{\text{cell}}} = \frac{N_{ax}^2 N_{\text{rad}}^2}{F(i)_{\text{cell}}} = \frac{W_{\text{cell}}}{N_{ax}(1-b)}
\]  

(6)

If the mass balance is applied for all cells in a single layer, a set of \( N_{\text{rad}} \) linear equations with \( N_{\text{rad}} \) unknowns (i.e. the concentrations in all cells) appears, which can be solved directly. This was done using the LSLRG routine in Visual Fortran. Of course, the cells at the edge of the reactor should be described with taking into account that there is no dispersion from or towards cells located outside the reactor.
The reaction term in eq. (5) differs from that used by van den Bleek et al.\textsuperscript{9} and Sofekun et al.\textsuperscript{10} who described the reaction term using a plug-flow approach. The radial dispersion $D_{\text{rad}}$ could be calculated using a Péclet number for mass transfer in the radial direction (eq. (7)) equal to $\sim 10$, which is reported as a typical value for fixed beds.\textsuperscript{12}

$$Pe_{\text{mr}} = \frac{u d_p}{D_{\text{rad}}} = 10$$

(7)

![Diagram of rectangular reactor](image)

**Fig. 2.** Rectangular reactor used in the simulations with the Random Particle Distribution (RPD) model. In this case $N_{\text{rad}} = 6$ and $N_{\text{ax}} = 15$. Any light-grey cell contains a catalyst particle, any dark-grey cell contains an inert SiC particle.

The effect of axial dispersion can be incorporated in a similar way as was done for the radial dispersion. If the radial dispersion is not included, the mass balance for a cell becomes:

$$C_{i,j,k-1} - C_{i,j,k} + \frac{D_{\text{ax}}}{u d_{\text{cell}}} \left( C_{i,j,k-1} + C_{i,j,k+1} - 2C_{i,j,k} \right) - q k \tau_{\text{cell}} C_{i,j,k} = 0$$

(8)

If both axial and radial dispersion are included in the model, a set of $N_{\text{ax}} N_{\text{rad}}^2$ linear equations should be solved. Although this is easy in mathematical terms, the numerical solver may encounter difficulties at large values of $N_{\text{ax}}$ and $N_{\text{rad}}$ due to the increased number of equations to be solved.

3. Axial and radial dispersion in fixed-bed reactors

The axial dispersion in a fixed-bed reactor represents the transport that occurs in axial direction superimposed on that due to the convection. At low gas velocities, \textit{i.e.} in the laminar flow regime, the dispersion is mainly caused by diffusion. At higher gas velocities, \textit{i.e.} in the turbulent flow regime, the dispersion is enhanced. The radial dispersion also contains a contribution from diffusion and a contribution due to turbulence, although the latter is generally smaller compared to that in axial dispersion.

The axial dispersion in fixed beds has been investigated in detail. Wakao \textit{et al.}\textsuperscript{14} reported relations for both the axial and the radial dispersion coefficients ($D$):
\[
\frac{D}{\epsilon_{\text{bed}}} = \frac{D_m}{\tau_{\text{bed}}} \quad \text{for } Re < 1
\]  
\[\]  
\[
\frac{D}{\epsilon_{\text{bed}}} = \frac{D_m}{\tau_{\text{bed}}} + m d_r u \quad \text{for } Re > 5
\]  
\[
(9b)
\]

For radial dispersion \( m = 0.1 \), and for axial dispersion \( m = 0.5 \). In most laboratory micro-
scale gas-solid fixed-bed experiments, \( Re \) is less than 1. In all experiments discussed in this paper \( Re \) amounts to approximately 0.1 and therefore the dynamic term present in eq. (9b) is not taken into account. The static term consists of the bulk diffusivity \( (D_m) \) and tortuosity of the bed \( (\tau_{\text{bed}}) \). According to Wakao et al.,\(^{14}\) this tortuosity typically ranges from 1.25 to 1.67. Edwards and Richardson\(^{15}\) reported a similar value: 1.37, while Suzuki and Smith\(^{16}\) reported a slightly higher value (2.3). Puncochar and Drahos\(^{17}\) found a correlation between the bed porosity and the bed tortuosity according to eq. (10). Obviously, the dispersion is also directly influenced by the bed porosity \( (\epsilon_{\text{bed}}) \).

\[
\tau_{\text{bed}} = \frac{1}{\sqrt{\epsilon_{\text{bed}}}}
\]  
\[\]  
\[
(10)
\]

As mentioned above, the use of the plug-flow model to describe the reactor performance may give erroneous results if the axial dispersion becomes significant. Mears\(^{18}\) derived the following criterion to determine if the effect of axial dispersion may be neglected (within 5% deviation):

\[
\frac{h_{\text{bed}}}{d_p} > \frac{20}{Bo} \ln \left( \frac{1}{1-X} \right)
\]  
\[\]  
\[
(11)
\]

where \( Bo = \) Bodenstein’s number for axial mass transport:

\[
Bo = \frac{u d_p}{D_{ar}}
\]  
\[\]  
\[
(12)
\]

\( Bo \) is the same dimensionless number as \( Pe_p \), the Pécelet number referring to the particle. Gierman\(^{19}\) refined this criterion and concluded, based on their practical experience, that this could be relaxed by using a factor of 8 instead of the factor 20.

4. Experimental

4.1. Catalysts

The effect of the catalyst distribution and the degree of dilution on the conversion was investigated experimentally by means of a first-order irreversible reaction, i.e. the catalytic decomposition of \( \text{N}_2\text{O} \) into \( \text{N}_2 \) and \( \text{O}_2 \). Two catalytic systems were used: FeZSM-5 and Co-
La,Al mixed oxide (denoted hereafter as Co-La,Al-ox). FeZSM-5 was prepared by an ex-
framework method and Co-La,Al-ox was obtained from the thermal decomposition at 723 K of a hydrotalcite containing these metals. Details on the preparation and characterization of the catalysts have been reported elsewhere.\(^{20,21}\) Both catalysts show a high activity and a stable performance in \( \text{N}_2\text{O} \) decomposition in a wide range of temperatures.\(^{22,23}\) All the characteristics of these catalytic systems are summarized in Table 1. The porosity of the catalyst particles \( (\epsilon_p) \) was determined using mercury porosimetry and nitrogen physisorption at 77 K. The bed porosity \( (\epsilon_{\text{bed}}) \) (the interparticle void space) was calculated from the bed heights obtained in the reactor tubes.
4.2. Bed configurations

Different bed configurations were prepared with the catalyst and the diluent (SiC). Fig. 3 shows the different bed configurations for the FeZSM-5 system, including a well-mixed bed (no. 7), a poorly-mixed bed (no. 6), vertically segregated beds (nos. 2, 3, and 5), and horizontally segregated beds (nos. 4 and 8). The difference between the configurations 4 and 8 is the presence of a thin wall of non-porous quartz (thickness 0.3 mm) between the catalyst and the SiC compartments in no. 8, eliminating the transverse diffusion of gas between them. A thin (0.3 mm) stainless steel foil was used during loading of the samples. All the samples were captured between two quartz-wool plugs and positioned on a quartz frit located in the middle of the quartz reactor tubes having an internal diameter of 4.0 mm. Experiments with Co-La,Al-ox were carried out only with configurations 4 and 7. The required amounts of catalyst and the dilution were weighed and loaded into the reactor. In all beds a plug of quartz wool was placed over the sintered quartz frit located near the bottom of the reactor tube. The well-mixed diluted bed was prepared carefully by placing another plug of quartz wool in the top of the reactor and subsequently rotating the reactor around its axis in horizontal orientation while tilting it up and down in vertical direction, leading to a visible homogeneous distribution of catalyst particles.

The experiments to investigate the influence of varying amounts of dilution in well-mixed beds were carried out with the Co-La,Al-ox catalyst. The catalysts were tested using different degrees of dilution \( b = \frac{V_{\text{cat}}}{V_{\text{cat}} + V_{\text{dil}}} \), keeping the total mass of the bed constant at 400 mg. The space velocity \( \left( W_{\text{cat}}/F(\text{N}_2\text{O})_a \right) \) was kept constant at 5.58·10⁵ g s mol⁻¹ by adjusting the flow rate. The dilution fraction \( b \) was varied between 0.87 to 0.98. The bed height in all reactors was about 18 mm. More experimental details regarding the reactor configuration can be found in Table 1.

Table 1. Data on the catalysts, catalyst bed, and experimental conditions during the activity tests.

<table>
<thead>
<tr>
<th>Catalyst bed</th>
<th>FeZSM-5</th>
<th>Co-La,Al-ox</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_r ) / mm (i.d.)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>( d_p ) / ( \mu m )</td>
<td>125 - 200 a)</td>
<td>106 - 212 a)</td>
</tr>
<tr>
<td>( \rho_{\text{cat,solid}} ) / kg m⁻³</td>
<td>1780</td>
<td>5150</td>
</tr>
<tr>
<td>( \rho_{\text{SiC}} ) / kg m⁻³</td>
<td>3200</td>
<td>3200</td>
</tr>
<tr>
<td>( \varepsilon_{\text{f}} ) -</td>
<td>0.3</td>
<td>0.68</td>
</tr>
<tr>
<td>( \rho_{\text{cat}} ) / kg m⁻³</td>
<td>1246</td>
<td>1627</td>
</tr>
<tr>
<td>( \varepsilon_{\text{bed}} ) -</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>( W_{\text{cat}} ) / mg</td>
<td>50</td>
<td>20</td>
</tr>
<tr>
<td>( W_{\text{SiC}} ) / mg</td>
<td>150</td>
<td>40</td>
</tr>
<tr>
<td>( b ) (well-mixed case) / -</td>
<td>0.54</td>
<td>0.50</td>
</tr>
<tr>
<td>( h_{\text{bed}} ) / mm</td>
<td>13</td>
<td>5.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Activity evaluation</th>
<th>FeZSM-5</th>
<th>Co-La,Al-ox</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T ) / K</td>
<td>600 - 875</td>
<td>600 - 875</td>
</tr>
<tr>
<td>( P ) / bar</td>
<td>1</td>
<td>2.5</td>
</tr>
<tr>
<td>( p(\text{N}_2\text{O}) ) / mbar</td>
<td>1.55</td>
<td>1.0</td>
</tr>
<tr>
<td>( \phi ) / cm³ (STP) min⁻¹</td>
<td>50</td>
<td>120</td>
</tr>
<tr>
<td>( u ) / m s⁻¹</td>
<td>0.195</td>
<td>0.189</td>
</tr>
<tr>
<td>( R_p ) -</td>
<td>0.051</td>
<td>0.129</td>
</tr>
<tr>
<td>( W_{\text{cat}}/F(\text{N}_2\text{O})_a ) / g s mol⁻¹</td>
<td>8.65·10⁵</td>
<td>5.58·10⁵</td>
</tr>
</tbody>
</table>

a) SiC of the same particle size range was introduced as diluent.
   A: influence of the catalyst bed distribution; B: influence of the amount of diluent.
4.3. Experimental set-up

Evaluation of the catalytic activity of the different bed configurations described above was carried out in a fully automated six-flow reactor system (Fig. 4). This set-up has been described in Chapter 2. Five reactors were filled with the samples to be tested whereas the sixth reactor was filled with SiC dilution material only to serve as a reference. The flow direction was downwards. Before the reaction, the catalysts were heated in He at 10 K min⁻¹ up to 773 K and maintained for 1 h at this temperature. After decreasing the temperature to the desired value, the N₂O-He mixture was introduced. The thermocouples were directly inserted in the top of the catalyst beds. The temperature differences between the six reactors were always less than 1.5 K, and the axial temperature difference in each reactor was less than 0.5 K. The experimental conditions used in the activity measurements are shown in Table 1.

The product gases were analyzed by gas-chromatographic analysis (Chrompack CP 9001) equipped with a thermal conductivity detector, using a Poraplot Q column (for separation of N₂O) and a Molsieve 5Å column (for separation of N₂ and O₂). The reactors were allowed to stabilize for 1 h before the analysis of the product gases was started. Each experiment lasts around 30 h. In none of the beds the catalyst showed a measurable deactivation. The mass balance for N and O closed within less than 1% and 2%, respectively; only in the experiments with the Co-La₂Al-ox catalyst at 700 K both closed within less than 2% and 5%, respectively. The ratio N₂/O₂ (formed) was always 2.0, thus indicating steady-state operation. The selectivity of the reaction to N₂ and O₂ was 1.0 in all experiments. The N₂O conversions were calculated according to:

\[
X(\text{N}_2\text{O}) = 1 - \frac{A(\text{N}_2\text{O})}{A(\text{N}_2) + A(\text{N}_2\text{O})}
\]

(13)

where \(A\) is the GC peak area corrected for the response of the different gases in the GC analysis.
5. Results and discussion

5.1. Influence of bed distribution

5.1.1. Activity tests

The conversion-temperature plots over FeZSM-5 obtained with the different catalyst-diluent distributions are shown in Fig. 5. According to what might be expected, the highest conversions are obtained if the catalyst and the diluent are well mixed (open squares). If the catalyst and the diluent are not mixed but inserted in separate horizontal layers, the conversion is slightly lower (dots). Applying the catalyst layer on top of the diluent layer, the other way around, and applying two catalyst layers and two diluent layers instead of one (reactors nos. 3, 2, and 5 in Fig. 3, respectively) yielded the same results. The difference in conversion with respect to that obtained in a well-mixed bed is due to back-mixing of the reactants and products as a consequence of axial dispersion. The sample referred to as 'poorly mixed' yields a significantly lower conversion (solid triangles) due to bypassing; the number of catalyst particles that are 'met' by the gas packages flowing in axial direction through the reactor is not independent of the entrance position. An even lower conversion is obtained if the catalyst and the diluent are placed completely in parallel to each other ('half-half' distribution; indicated by the open circles). In that case, 50% of the flow bypasses the catalyst (see Fig. 1, X5). Nevertheless, the conversion becomes higher than 50% due radial dispersion, which counteracts the bed non-uniformity. If the effect of radial dispersion is eliminated by applying a non-porous quartz wall between both halves, the conversion decreases and the maximum attained conversion amounts to 50%. This is a clear indication of equal flow resistance of both bed halves.

Although the different catalyst-diluent distributions strongly affect the conversion above 0.5, there are hardly any visible differences at conversions below 0.3. This is explained by the fact that the exponential concentration profile in the reactor reduces to a linear function of the axial coordinate at low conversion.
Fig. 5. N₂O conversion vs. temperature for different distributions of FeZSM-5 (indicated in the schematic pictures with light gray) and SiC diluent (indicated dark gray). Conditions: \(p(\text{N}_2\text{O}) = 1.55\) mbar in He, \(P = 1.0\) bar, \(W_{\text{cat}} = 50\) mg, \(W_{\text{cat}}/F(\text{N}_2\text{O})_0 = 8.65 \times 10^{-5}\) g s mol⁻¹.

5.1.2. Activation energies

For an irreversible 1st order reaction, such as the reaction in this study, the observed reaction rate constant \(k^{\text{obs}}\) can be calculated from the conversion using eq. (14):

\[
k^{\text{obs}} = \frac{F(\text{N}_2\text{O})_0}{W_{\text{cat}} p(\text{N}_2\text{O})_0} \ln \left( \frac{1}{1 - X(\text{N}_2\text{O})} \right)
\]  

(14)

The \(k^{\text{obs}}\)-values calculated from the data in Fig. 5 were used to construct the Arrhenius plot shown in Fig. 6. In the absence of transport limitations and if the kinetics follow an Arrhenius' behaviour, such plots should result in straight lines of which the slope corresponds with the apparent activation energy divided by the universal gas constant \((-E_\text{app}/R)\). This applies for the well-mixed case, except for some values at the highest temperatures, which slightly deviate from the straight line that was fitted through all the available data within the conversion range 0.01-0.8. The fitting resulted in an apparent activation energy of 137 kJ mol⁻¹ and a \(k\) value at 580 K equal to 5.4 \times 10⁻⁷ mol bar⁻¹ g⁻¹ s⁻¹. For the other samples, in which the catalyst and the diluent are segregated or improperly mixed, the slope tends to decrease significantly at higher temperatures. The apparent activation energies derived from the slopes within Range II of Fig. 6 are significantly lower than 137 kJ mol⁻¹, which is elaborated in Fig. 7. The results are spectacular. As long as one uses only the data at conversions below 0.25 (corresponding with Range I in Fig. 6), all the samples do yield the same apparent activation energy. However, the data at high temperature are very much dependent on the configuration of the bed.

This decrease of the slope at high temperatures is not identical with that due to diffusion limitations in and around a single catalyst particle. This latter case is extensively discussed in the Catalysis Engineering literature.⁷ If there is pore-diffusion limitation only, the slope is reduced by a factor of two; if diffusion limitation through the film surrounding the catalyst particles is dominant, the slope decreases to almost zero. The phenomenon here is due to a
combined effect of particle segregation in the bed, resulting in a kind of diffusion limitation on the bed level (radial dispersion), and the incorrect plug-flow assumption for data contaminated with axial dispersion.

Fig. 6. Arrhenius plots obtained from the data shown in Fig. 5. The bold line represents the Arrhenius fit of the data obtained with the well-mixed bed (open squares); the slope corresponds with an apparent activation energy of 137 kJ mol\(^{-1}\).

Fig. 7. Apparent activation energies \(E_{\text{app}}\) derived from the Arrhenius plot in Fig. 6. Ranges I and II are defined in Fig. 6. The dashed horizontal line corresponds with the apparent activation energy derived for the well-mixed bed.
5.1.3. Estimation of dispersion coefficients and bed tortuosity

The activity results obtained with the different bed distributions give information on the axial and radial dispersion. The difference between the conversion vs. temperature curves obtained with the vertically segregated beds (reactors no. 2, 3 and 5) and that obtained with the well-mixed bed can be used to estimate the axial dispersion coefficient. The difference between the curves obtained with the two horizontally segregated beds (reactor no. 4 and reactor no. 8) can be used to estimate the radial dispersion coefficient.

**Radial dispersion coefficient**

The results obtained with the 'half-half' sample (i.e. no. 4 in Fig. 3) can be used to estimate the radial dispersion coefficient. For the simulation of the reactor the Random Particle Distribution model was used. If the effect of axial dispersion is neglected, the reactor can be simulated layer by layer using the model equation for each cell shown in eq. (5).

The influence of axial dispersion can be also incorporated in a similar way, resulting in a set of $N_{ax} N_{rad}^2$ linear equations to be solved. Some test calculations using a larger particle size and smaller numbers of $N_{ax}$ and $N_{rad}$ than the appropriate values showed that if axial dispersion is taken into account, the conversions decrease slightly, but not more than up to 0.01 at the highest values for the radial dispersion coefficient value used. Since this effect is very small in comparison with that due to radial dispersion, axial dispersion was not included in the calculations of which the results are shown in Figs. 8 and 10.

At the low $Re$ numbers applied in the experiments (~ 0.1), both the axial and the radial dispersion coefficient follow from eq. 9a, yielding:

$$D = \frac{\varepsilon_{bed}}{\tau_{bed}} D_{N_{ax}He}$$  \hspace{1cm} (15)

**Fig. 8.** Experimental (solid circles) and simulation results (lines) obtained for the half-half bed in comparison with the data (open squares) and fit (top curve) for the mixed bed (FeZSM-5 catalyst, $p(N_{2}O) = 1.55$ mbar in He, $P = 1.0$ bar, $W_{cat} = 50$ mg, $W/P(N_{2}O)_{0} = 8.65\times10^6$ g s mol$^{-1}$, $N_{rad} = 24$, $N_{ax} = 76$). The solid simulation lines are obtained assuming an exact half-half distribution ('0-100' distribution), the dashed lines are obtained assuming the '0-25-50-50-75-100' distribution at the interface (see Fig. 9).
Fig. 9. Catalyst-diluent distributions in horizontal direction used to simulate the results obtained with the 'half-half' samples for \(N_{set} = 12\) (sample no. 4 in Fig. 3).

The bed porosity \(\varepsilon_{bed}\) was measured experimentally and the molecular diffusivity of \(\text{N}_2\text{O}\) in He was estimated using the correlation from Fuller, Schettler and Giddings,\(^\text{24}\) which for example yields a value of \(1.61\times10^{-4}\) m\(^2\) s\(^{-1}\) at 1.0 bar and 800 K. This leaves the bed tortuosity \(\tau_{bed}\) as the unknown parameter to be estimated from the results. Fig. 8 shows the simulation results for FeZSM-5 at different values of \(\tau_{bed}\). The numbers of cells used in the simulations in axial and radial direction were 76 and 24, respectively. These numbers were calculated from the volume-averaged particle size 172 \(\mu\)m (calculated by assuming a homogeneous distribution in the range 125-200 \(\mu\)m), the bed diameter (4 mm) and the measured bed height (13 mm).

The solid curves in Fig. 8 are the results obtained when an exactly half-half distribution ('0-100' distribution) is used. Since it is more probable that a little mixing of catalyst and diluent particles has occurred at the interface during preparation, the simulations were repeated using a distribution in which some exchange of catalyst and diluent particles in the four vertical interface layers between both bed halves was included, as shown in Fig. 9. This catalyst distribution is referred to as the '0-25-50-50-75-100' distribution and the results obtained with this distribution are indicated in Fig. 8 by dashed curves. The differences between the results obtained with both distributions are systematic but not large, which implies that the results allow a reasonable estimation of the radial dispersion coefficient. As expected, the maximum conversion is limited to 0.5 if the radial dispersion is neglected (setting \(\tau_{bed}\) equal to infinity). At lower values of \(\tau_{bed}\) the conversion curves approach the one obtained for the well-mixed bed (open squares). The experimental results obtained with the half-half sample are indicated by symbols. These are well described using a \(\tau_{bed}\) value equal to approximately 1.8 or 2, when assuming the exact half-half distribution or the '0-25-50-50-75-100' distribution, respectively. Since the exact cell size to be used is uncertain because in reality a rather broad range of particle sizes were used, the cell size was varied from 143 to 222 \(\mu\)m. The effect of the size appeared to be negligible because in these experiments the effect of radial dispersion is a reactor-scale effect rather than a particle-scale effect.

The same experiment was carried out using the Co-La,Al-ox catalyst (Fig. 10). The data for the well-mixed bed were fitted to the Arrhenius equation, which yielded an apparent activation energy of 65 kJ mol\(^{-1}\) and a \(k^{\text{app}}\) value at 580 K equal to 6.6\times10^{-5} \text{ mol bar}^{-1} \text{ g}^{-1} \text{ s}^{-1}. The numbers of cells in axial and radial direction used in the simulations were 22 and 31, respectively. These numbers were calculated from the volume-averaged particle size 180 \(\mu\)m (calculated by assuming a homogeneous distribution in the range 106-212 \(\mu\)m), the bed diameter (4 mm) and the measured bed height (5.6 mm).
The experimental results obtained with the half-half sample are indicated by solid dots, and these dots are fitted well using an \( \theta_{\text{ref}} \) value equal to approximately 1.2 or 1.8, when assuming the exact half-half distribution or the '0-25-50-50-75-100' distribution, respectively. These values are slightly lower than those found with the FeZSM-5 catalyst.

![Graph](image)

**Fig. 10.** Experimental (soild circles) and simulation results (curves) obtained for the half-half bed in comparison with the data (open squares) and fit (top curve) for the mixed bed (Co-La,Al-ox catalyst, \( p(N_2O) = 1.0 \text{ mbar in He}, P = 2.5 \text{ bar}, W_{\text{cat}} = 20 \text{ mg}, W_{\text{cat}}/F(N_2O) = 5.58 \times 10^{-5} \text{ g s mol}^{-1}, N_{\text{rad}} = 22, N_{\text{ax}} = 31 \). The continuous simulation lines are obtained assuming an exact half-half distribution ('0-100'), the dashed lines are obtained assuming the '0-25-50-50-75-100' distribution at the interface.

**Axial dispersion coefficient**

The results obtained with two and four horizontal layers of catalyst and diluent, which are available for FeZSM-5 only, can be used to estimate the axial dispersion coefficient. For the simulation of the reactor again the random particle distribution model was used. The model equation for each cell is shown in eq. (8). The term accounting for the radial dispersion could be removed since the geometry of the catalyst-diluent distribution excludes any effect of radial dispersion.

Fig. 11 shows the simulation results at different values of \( \theta_{\text{ref}} \). Since the differences in conversion obtained with the different configurations and \( \theta_{\text{ref}} \) values are much smaller than in the investigation of the radial dispersion, only the data at high conversion are shown. The experimentally found differences in conversion between the four layered beds are very small. The simulations also yielded almost identical conversions. Slightly higher conversions were obtained for the four-layer configuration, but since the difference in conversion never exceeded 0.001 these simulation results were not included in the figure. The results obtained with all three configurations can thus be combined and used to estimate the axial dispersion coefficient. Although the uncertainty is larger than in the case of the radial dispersion, it can be concluded that the \( \theta_{\text{ref}} \) value for axial dispersion lies around 1.

These values are lower than those estimated for radial dispersion, which may be due to agglomeration. Moulijn and van Swaaij\textsuperscript{25} showed that agglomeration is a typical phenomenon in fixed beds with particles smaller than 2 mm. It is due to a non-uniform distribution of the fine particles, as a consequence of large interaction forces between the particles compared to the gravity forces. It results in channeling, the gas mainly flows

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through specific routes and hardly flows through the higher-density areas ('agglomerates'), and enhances the axial dispersion. As a consequence, the apparent $\tau$ will become smaller (see eq. 15). This phenomenon may have influenced the results.

**Bed tortuosity**

For both catalysts tested, the $n_{ed}$ values for the radial dispersion are within the range 1.2 - 2. These values agree very well with the values reported in the literature, which were discussed in §2.

![Graph](image)

**Fig. 11.** Experimental (open symbols) and simulation results (curves) obtained for the layered beds in comparison with the data (open squares) and fit (top curve) for the mixed bed (FeZSM-5 catalyst, $p(N_2O) = 1.55$ mbar in He, $P = 1.0$ bar, $W_{in} = 50$ mg, $W_{in}/P(N_2O)_0 = 8.65 \times 10^6$ g s mol$^{-1}$, $N_{in} = 76$).

### 5.2. Influence of well-mixed catalyst-diluent on the conversion

**5.2.1. Activity tests**

The conversions measured for the Co-La,Al-ox catalyst at 700 and 770 K with five different degrees of dilutions ($b$, see Table 1) varying from 0.875 to 0.975 were used to calculate the fractional deviations in the conversions according to eq. (2). The deviations are shown in Fig. 12 as small circles with addition of the error bars. The results show that $\Delta$ depends on the conversion: at 70% $N_2O$ conversion $\Delta$ is about two times higher than at 34% conversion. It also appears that $\Delta$ increases with the dilution fraction $b$, and to an increasing extent when $b$ approaches 1.

Fig. 12 also shows the deviation calculated using the equation van den Bleek *et al.*, which was presented in the Introduction of this chapter. This equation does not incorporate the conversion level, which is of major importance. Accordingly, at high dilutions it under- or overestimates the deviation, depending on the conversion level. The equation derived by Sofekun *et al.* (see Introduction, eq. (4)) also gives reasonable fits of the experimental data (not shown in Fig. 12), but it suffers from 'the chicken and the egg' problem since it requires the rate coefficient and reaction order, which are beforehand unknown in kinetic investigations. Additionally, Fig. 6 contains the curves calculated using the following expression:
\[ \Delta = \left( \frac{b}{1-b} \right) \frac{X_{\text{dil}} d_p}{2 h_{\text{bed}}} \]  

(16)

This equation adequately incorporates the effect of the conversion, does not need any input of \textit{a priori} unknown reaction kinetic parameters, and describes the experimental trend well. The equation, which is applicable at conversions \( \leq 0.4 \) was derived by analytically modeling the conversion obtained if all the catalytic activity would be homogeneously distributed over the catalyst bed and that obtained in the presence of dilution (see Appendix). The effect of radial dispersion, which could not be incorporated in the analytical derivation to estimate \( \Delta \), was implemented by means of a fit parameter in the denominator equal to 2, which represents the number of particles in a single cell used to describe the fixed bed.

![Graph](image)

\textbf{Fig. 12.} Experimentally observed deviations in the conversion (\( \Delta \)) as a function of the fraction of diluent (\( b \)) in the well-mixed catalyst bed at 700 K (conversion without dilution effect = 0.34), the lower curve and symbols, and 770 K (conversion without dilution effect = 0.70), the upper curve and symbols. The dashed curve is obtained using the equation from van den Bleek \textit{et al.}\textsuperscript{9} for both conversions (Co-La,Al-ox catalyst, \( p(N_2O) = 1.0 \) mbar in He, \( P = 2.5 \) bar, \( W_{\text{cat}} + W_{\text{dil}} = 400 \) mg, \( W_{\text{cat}}/P(N_2O) = 5.58 \times 10^3 \) g s mol\(^{-1}\)).

The reactor performance obtained in the well-mixed diluted bed was also simulated numerically using the RPD model, which takes into account the effect of radial dispersion and applies different, randomly generated, catalyst-diluent distributions. The reactor model used describes the fixed bed as a stack of layers comprising cubic cells containing a single catalyst or diluent particle, as described in §2. Although the model described the tendencies well, the values of \( \Delta \) obtained using a bed tortuosity of 1.8 are approximately 2 times lower than the ones experimentally found. This factor 2 is in fact already incorporated in eq. (16) as a fit factor. Recent simulations showed that this difference can be overcome by using a cell size of 0.3 mm, which is a factor of 5/3 larger than the average particle size (0.18 mm).

Several reasons can be suggested to explain this discrepancy. In practice particles are not spheres of identical diameter, but they exhibit a size distribution and the shape will be non-uniform. Additionally, the average particle size that was estimated by volume-averaging the
particle size range used (106-212 μm) may be a too low estimate. Crushing of pellets and subsequent sieving usually yields a significant fraction of oblong-shaped particles having a size in the longest direction that is larger than the mesh size. The size of oblong particles obtained by sieving is determined by the size in the direction in which it is the smallest. Another possible cause of the discrepancy may be that the bed is highly non-ideal, for instance due to particle agglomeration,\(^26\) implying that cells in the simulations contain more than one particle.

Although several phenomena influencing the deviation of the conversion in well-mixed diluted beds are not yet well understood, the simple eq. (3) that requires only observable parameters can be recommended for practical use since it has a fundamental basis and it properly describes the experimental data obtained at different conversions (X) and dilution degrees (b). Additional confidence in eq. (3) is obtained from the sensitivity analysis performed using the complete model, which showed that \(\Delta\) increases proportionally with particle size \((d_p)\) and decreases proportionally with increasing bed height \((h_{bed})\).

### 5.2.2. Influence of the reaction order on \(\Delta\)

The Random Particle Distribution model was used to investigate the influence of the order of the reaction on the deviation in the well-mixed case. It was found that the deviation is approximately proportional with the value of the reaction order. Therefore eq. (16) can be generalized to:

\[
\Delta = \left( \frac{b}{1-b} \right) \frac{X_{dil} d_p}{2 h_{bed}} n \tag{17}
\]

For zero-order reactions the deviation \(\Delta\) appears to be equal to zero, as long as there does not exist an area (cells) where total conversion is attained. This can be easily understood since for zero-order reactions the reaction rate does not depend on conversion; and only at complete conversion the reaction drops suddenly to zero. In agreement with the discussion on the first order reaction the deviation is always negative if the order is positive. For negative order by-passing is favorable and the observed conversion exceeds that for an ideal plug-flow reactor with a homogeneous activity.

It is emphasized that the dilution effect discussed here is a systematic type of error that always decreases the conversion. It should not be interpreted as a random type of error that may both increase or decrease the conversion. The maximum allowed error as a consequence of the dilution should therefore not be directly related to the measurement error, as it has been done in the literature.\(^9\,10\) Instead, it should be treated in a way similar as e.g. the maximum allowed negative effect of external transport limitation through the gas film surrounding the particles (i.e. the Carberry number), which is usually set at 0.05 (i.e. 5% deviation).

### 5.2.3. Effect on rate constant

In kinetic investigations, the measured conversions are used to calculate the rate coefficient, e.g. to determine the apparent activation energy of the catalytic reaction. For an irreversible 1st order reaction, the observed rate constant can be calculated directly from the conversion using eq. (14).

Therefore it is in most cases more useful to calculate the deviation of this \(k\) instead of the deviation of \(X\). If this is done using eq. (2), the following expression for the fractional deviation of the rate constant \((\Delta k)\) is obtained (with \(\Delta\) according to eq. (2)):
\[
\Delta_k = \frac{k_{\text{und}} - k_{\text{dil}}}{k_{\text{und}}} = \frac{\ln \left(\frac{1-X}{1-\Delta} \right)}{\ln \left(\frac{1}{1-X}\right)}
\] (18)

Fig. 13 shows the results of this calculation for several values of \( \Delta_k \) as a function of the dilution and the conversion for a constant \( h_{\text{bed}}/d_p = 100 \). The figure should be read as follows: an experiment at \( X(\text{N}_2\text{O}) = 0.5 \) and \( b = 0.95 \) (and \( h_{\text{bed}}/d_p = 100 \)) will result in a deviation of the calculated rate constant due to the dilution (\( \Delta_k \)) between 5% and 10% (approximately 7%). The shaded area in Fig. 13 represents the region of conditions where the deviation exceeds the criterion of 5% deviation. This region should be avoided in particular if the aim is to measure intrinsic reaction kinetics. The figure clearly illustrates that the experimental data at high conversions, although all of them satisfy the 5% criterion for \( \Delta_k \), introduce considerable errors in the calculated rate constant. Therefore, one should always try to avoid the combination of high degree of bed dilution and high conversion levels. It is noted that eq. (16) and thus also eq. (17) have not been validated at conversion levels above 0.75 and dilutions below 0.8, but they can be used as a safe rule of thumb.

The plug-flow criterion for 1% and 5% deviation of the conversion due to axial dispersion (eq. (11)) is also included in Fig. 13. The small dark shaded area corresponds to conditions where this deviation exceeds the criterion of 5%. The curves tend to lower conversions at high dilutions due to the decrease of the flow rate in order to keep \( W_{\text{cat}}/F(\text{N}_2\text{O})_0 \) constant. The criterion is easily satisfied due to the high \( h_{\text{bed}}/d_p \) ratio used as a consequence of the application of a high degree of dilution. This is not generally valid; dilution is used amongst other to satisfy the axial dispersion criterion, but on the other hand it creates a deviation in the observed conversion. So there will be a dilution degree at which both criteria will yield similar constraints. This dilution degree depends strongly on the system under consideration.

![Fig. 13. Calculated effect of conversion and dilution on \( \Delta_k \), the relative deviation in the 1st order rate constant calculated from the observed conversion, using eq. (18) for \( h_{\text{bed}}/d_p = 100 \). Dashed lines represent the criterion for neglecting the effect of axial dispersion at \( W_{\text{cat}}/F(\text{N}_2\text{O})_0 = 5.58 \times 10^6 \) g s mol\(^{-1}\) and \( W_{\text{cat}} + W_{\text{ref}} = 400 \) mg. Symbols (\( \times \)) represent the conditions used in the dilution experiments.](image-url)

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6. Conclusions

The frequently applied dilution of catalyst beds by inerts in laboratory micro- or nano-flow reactors should be applied with caution. Care should be taken to achieve a homogeneous mixture between catalyst and diluent in the bed. Improper mixing inevitably results in bypassing of the catalyst-rich zones, thus decreasing the overall conversion. The decrease of conversion is larger if the segregation between catalyst and diluent increases. Vertical layering has a stronger influence than horizontal layering. These effects are far from negligible: the decrease can be as large as that due to internal and external transport limitations for catalyst particles. Since a completely homogeneous distribution of catalyst and diluent is hard to achieve, the use of data obtained at high conversions with highly diluted fixed beds should preferably be avoided. It can affect the observed catalyst activities and lead to a wrong interpretation of the kinetic data derived from these, e.g. the apparent activation energy may vary from the intrinsic value even down to zero.

It was found that the degree of bed dilution in perfectly mixed beds also influences the conversion significantly. This is due to the same phenomenon, bypass of catalyst particles, but then on the particle scale instead of reactor scale. Eq. (17) can be used to estimate the deviation of the conversion caused by the dilution. The deviation is approximately proportional to the reaction order; it is negative for positive reaction orders and positive for negative reaction orders. Eq. (18) and Fig. 13 can be used to get insight in the effect of dilution on the calculated rate constant for a 1st order reaction.

If one aims to measure intrinsic kinetics, significant deviations of the conversion due to the dilution should be avoided. It is therefore recommended to avoid combining high conversion levels and high dilutions, and to pay particular attention to a proper mixing of catalyst and diluent.

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Notation

- \( A \) = area of peaks in GC analysis
- \( b \) = volume of inert material as fraction of total volume of solids
- \( Bo \) = Bodenstein number
- \( C \) = concentration
- \( d \) = size or diameter
- \( D \) = dispersion coefficient or molecular diffusivity
- \( E_a \) = activation energy
- \( F(i) \) = molar flow of component \( i \)
- \( h \) = height
- \( k \) = rate constant
- \( n \) = reaction order
- \( N \) = total number of cells
- \( P(i) \) = partial pressure of reactant \( i \)
- \( P_{cat} \) = Péclet number for mass transfer in radial direction
- \( q \) = stochastic factor (\( q = 1 \) for cell containing catalyst particle and \( q = 0 \) for cell containing diluent particle)
- \( r \) = reaction rate
- \( T \) = temperature
- \( u \) = superficial gas velocity at reaction conditions
- \( V \) = volume
- \( W_{cat} \) = catalyst weight

- \( m^2 \) = dil m^3 _{dil+cat}
- \( m \) = mol m^3
- \( m \) = m^2 s^{-1}
- \( kJ \) mol^{-1}
- \( mol \) s^{-1}
- \( m \)
- \( m^3 g_{cat}^{-1} s^{-1} \) or \( mol \) bar^{-1} g_{cat}^{-1} s^{-1}
- \( bar \)
- \( mol \) g_{cat}^{-1} s^{-1}
- \( K \)
- \( m \) s^{-1}
- \( m^3 \)
- \( g_{cat} \)
Chapter 3

\[ W_{\text{cat}} = \text{weight of one catalyst particle} \]
\[ X = \text{conversion} \]
\[ g_{\text{cat}} \]

Greek

\[ \Delta = \text{deviation of the conversion due to the dilution} \]
\[ \varepsilon = \text{porosity} \]
\[ \phi = \text{volumetric flow} \]
\[ \tau = \text{space time } (= W_{\text{cat}}/F(t)_{o}) \]
\[ \tau_{\text{bed}} = \text{tortuosity of the bed} \]
\[ \tau_{\text{cell}} = \text{space time in one cell } (= W_{\text{cell}}/F(t)_{\text{cell}}) \]
\[ m^{3}_{\text{void}}, m^{3}_{\text{bed}} \]
\[ m^{3} s^{-1} \]
\[ g_{\text{cat}} s \text{ mol}^{-1} \]
\[ g_{\text{cat}} s \text{ mol}^{-1} \]

Subscripts and superscripts

\[ \text{app} = \text{apparent} \]
\[ \text{ax} = \text{axial (in axial direction)} \]
\[ \text{bed} = \text{bed} \]
\[ \text{calc} = \text{calculated} \]
\[ \text{cat} = \text{catalyst} \]
\[ \text{cell} = \text{cell} \]
\[ \text{dil} = \text{diluent or diluted bed} \]
\[ \text{het} = \text{heterogeneous (discrete catalyst and diluent particles)} \]
\[ \text{hom} = \text{homogeneous (assuming that the catalytic activity is homogeneously distributed)} \]
\[ i,j = \text{counters for cell in horizontal direction} \]
\[ \text{layer} = \text{layer} \]
\[ k = \text{counter for cells in vertical direction} \]
\[ m = \text{molecular} \]
\[ \text{obs} = \text{observed} \]
\[ p = \text{particle} \]
\[ \text{rad} = \text{radial (in radial direction)} \]
\[ \text{tot} = \text{total} \]
\[ \text{und} = \text{undiluted bed} \]
\[ o = \text{reactor feed (reactor inlet)} \]

References

Appendix. Derivation of approximation for $\Delta$

The problem faced in this chapter is one of a discrete catalyst particle distribution. Catalyst particles with their original activity are embedded in a surrounding of an inert material by dilution, i.e. a heterogeneous case. This should be compared with the performance of a catalyst bed of increased size with a homogeneously lower activity. The conversion of the heterogeneous case may deviate from the homogeneous case by the introduced relative deviation $\Delta$ due to this difference. The example in the introduction shows that bypassing of catalyst particles may lead to important deviations in a plug-flow model. Radial mixing of the fluid phase will lower this effect.

In order to derive a relation for $\Delta$, the following model is considered. Originally the considered catalytic system comprises $W_{ca}$ kg catalyst, total molar reactant feed rate $F(i)_o$ and a first-order rate constant $k$ based on the amount of catalyst. The related space time $\tau$ equals $W/F(i)_o$. By dilution the bed length is increased to $N_{ax}$ layers of $N_{layer}$ particles. The catalyst bed is modeled as a tanks-in-series model for each layer. For a sufficient number of layers this approaches the plug-flow model. Within each layer each particle is described as an individual CSTR in parallel to the other. In between the layers the fluid is assumed to be completely mixed and equally distributed over the cells in the next layer.

For the homogeneous case the amount of catalyst has increased by dilution to $W_{ca}/(1-b)$, while the catalyst activity has been lowered to $k^{hom} = k(1-b)$. The space time for one layer and one (particle) cell of a layer is then:

$$\frac{W}{F(i)_o} \frac{1}{N_{ax}} \frac{N_{layer}}{N_{ax}} = \tau$$

$$\frac{W}{F(i)_o} \frac{1}{N_{layer}} = \frac{\tau}{(1-b) N_{ax}}$$

(1)

(2)

Considering layer one of the bed the conversion of one cell modeled as a CSTR reads:

$$X^{hom}_{cell} = 1 - \frac{1}{1 + \frac{k^{hom}}{F(i)_o N_{layer}}} = 1 - \frac{1}{1 + \frac{kr}{N_{ax}}} = X^{hom}_{layer}$$

(3)

The latter equality holds since all cells yield the same conversion.

In the heterogeneous case the amount of catalyst has remained the same and these particles have kept their original activity. The catalyst particles are assumed to be distributed equally throughout the bed, so all layers contain equal amounts of particles and a single layer contains $N_{layer}(1-b)$ catalyst particles. For a cell containing a catalyst particle the corresponding space time is now:

$$\frac{W}{F(i)_o} \frac{1}{N_{layer}} = \frac{N_{ax}}{N_{layer}} \frac{N_{ax}}{(1-b)} = \frac{N_{ax}}{(1-b)}$$

$$\frac{W}{F(i)_o} \frac{1}{N_{layer}} = \frac{\tau}{N_{ax}(1-b)}$$

(4)

The conversion of one cell containing a catalyst particle in the first layer is:
\[ X_{\text{cell}}^{\text{het}} = 1 - \frac{1}{1 + k_{\text{cell}}^{\text{het}}} = 1 - \frac{1}{1 + \frac{k}{N_{ax} (1-b)}} \] (5)

Since only a fraction \((1-b)\) of the cells are active, the averaged conversion of layer one is then:

\[ X_{\text{layer}}^{\text{het}} = (1-b) \left[ 1 - \frac{1}{1 + \frac{k}{N_{ax} (1-b)}} \right] \] (6)

For these two conversions the following relation can be derived:

\[ X_{\text{layer}}^{\text{hom}} = \frac{(1-b) X_{\text{layer}}^{\text{het}}}{1-b - b X_{\text{layer}}^{\text{het}}} \] (7)

For \(N_{ax}\) CSTRs in series the overall conversion becomes

\[ X^{\text{het}} = 1 - \left( 1 - X_{\text{layer}}^{\text{het}} \right)^{N_{ax}} = 1 - \left( 1 - N_{ax} X_{\text{layer}}^{\text{het}} \right) = N_{ax} X_{\text{layer}}^{\text{het}} \] (8)

and similarly for the \(X^{\text{hom}}\). This simplification is acceptable at low conversions only \((< \sim 0.4)\).

For the deviation between the homogeneous and heterogeneous case this results in:

\[ \Delta = \frac{X^{\text{het}}}{X^{\text{hom}}} = \frac{X_{\text{layer}}^{\text{het}}}{X_{\text{layer}}^{\text{hom}}} = \frac{b}{(1-b) N_{ax}} X_{\text{layer}}^{\text{hom}} \] (9)

At high total conversions the simplification thus induces an underestimation of \(\Delta\). However, this may be compensated by the effect that at high conversions the increase of \(\Delta\) with increasing conversion becomes less due to the approach to complete conversion.

For practical application the parameter \(N_{ax}\) is replaced by the ratio of bed height \(h_{\text{bed}}\) and particle diameter \(d_r\), while \(X^{\text{het}}\) represents the observed conversion of the diluted bed \(X_{\text{dil}}\).

\[ \Delta = \left( \frac{b}{1-b} \right) \frac{d_r}{h_{\text{bed}}} X_{\text{dil}} \] (10)

This equation should finally be corrected for the effect of radial dispersion, which reduces the fractional deviation \(\Delta\). One way to do this is by using cells containing two particles instead of one particle. For high values of \(b\), this results in a reduction of \(\Delta\) by a factor 2. \(\Delta\) further decreases when three or more particles are used per cell. This correction factor yields the best correspondence with the experimental results. It is noted that the uncertainty in the number of layers in the bed, due to the used value of the particle size \((d_r)\), is also reflected in this factor. Using this correction factor finally yields:

\[ \Delta = \left( \frac{b}{1-b} \right) \frac{X_{\text{dil}} d_r}{2 h_{\text{bed}}} \] (11)
In situ Spectroscopic Study of the Thermal Decomposition of Hydrotalcites

In situ infrared spectra and in situ laser Raman spectra of Co-Al and Ni-Al hydrotalcites (HTIcs) have revealed several novel aspects of the structure, and physico-chemical transformations upon thermal decomposition of these materials in air. The infrared spectra of the Co-Al hydrotalcite at room temperature reveal the presence of a fraction of the carbonate in a low symmetry, which was not observed for Ni-Al hydrotalcite. Furthermore, compared to Co-Al hydrotalcite, a relatively smaller ratio of carbonate over hydroxyls is present in the as-synthesized Ni-Al hydrotalcite, as revealed by the infrared and Raman spectra. This is in agreement with a mass spectrometric analysis of the as-synthesized materials upon thermal decomposition, and the relatively small c parameter determined from the XRD pattern of the as-synthesized sample. An extraordinary stability of interlayer water in Ni-Al-HTIc was found, which was only completely removed above 300°C, a temperature 100°C higher than found for Co-Al-HTIc. Dehydroxylation of the octahedral layers and carbonate reorganization and decomposition also require higher temperatures for Ni-Al-HTIc (500-350°C and > 550°C) than for Co-Al-HTIc (150-200°C and 450-500°C). The low thermal stability of Co-Al-HTIc is attributed to the oxidation of Co²⁺ to Co³⁺, which was investigated by HT-XRD and UV-Vis spectroscopy. Raman spectra indicate the presence of an intermediate CoO₂ phase upon decomposition of Co-Al-HTIc in the temperature range of 175-250°C, before formation of a solid solution of cobalt spinels (Co(Co,Al)₂O₄). Highly dispersed NiO strongly interacting with the Al₂O₃ support was identified after decomposition of Ni-Al-HTIc at 550°C. The spectroscopically determined transition temperatures are in excellent agreement with X-ray diffraction, thermogravimetric, and mass spectrometric analyses.
1. Introduction

Synthetic hydrotalcite-like compounds (HTLcs), also referred to as anionic clays or Feitknecht’s compounds, are mixed hydroxides of lamellar structure with a general formula $[\text{M}^{2+}\text{X}^{n-}]_{\nu}^n\text{M}^{3+} (\text{OH})_2\text{H}_2\text{O}$. These materials can be visualized as brucite-type octahedral layers, in which $\text{M}^{3+}$ cations partially substitute for $\text{M}^{2+}$ cations. The positive charge resulting from this substitution is balanced by anions (often carbonate) and water molecules arranged in interlayers alternating with the octahedral layers. The structure as outlined above was first described by Allman and Taylor and is schematically represented in Fig. 1.

![Schematic representation of the hydrotalcite-like structure.](image)

HTLcs have attracted much attention in recent years as catalyst precursors and catalyst support due to the ability of these materials to accommodate a large variety of divalent and trivalent cations, and the formation of high-surface area and well-dispersed mixed oxides upon controlled thermal decomposition. These characteristics are due to the nature of the precursor and the thermal decomposition mechanism. Co-Al and Ni-Al-HTLcs are mainly synthesized as precursors of oxide catalysts, generally expressed as CoO/Al$_2$O$_3$ and NiO/Al$_2$O$_3$. The catalytic properties of the HTLc-derived mixed oxides largely depend on the activation procedure. Monitoring structural changes during thermal decomposition of HTLcs has been the aim of numerous studies. The interpretation of the decomposition process is often based merely on the information obtained from X-ray diffraction and thermal analysis (TGA combined with DTA or DSC). An integration of suitable techniques and experimental procedures is usually not applied. Furthermore, most of the studies published on thermally decomposed hydrotalcites are carried out at room temperature. Ex situ studies have the disadvantage that mixed oxides derived from HTLcs may rehydrate and reconstruct to the original structure at ambient temperatures in air. HT-XRD has been used as one of the few in situ techniques to investigate the decomposition and reconstruction mechanism over Mg-Al-HTLc. Other in situ techniques like Neutron Diffraction and EXAFS have been applied during the decomposition of HTLcs, although in lesser extent. A recent study using Mg and Al K-edge XAFS has provided valuable information of the changes of the metal coordination on calcination and rehydration of Mg-Al-HTLc, and also claims the necessity of application of true in situ techniques when structural changes during the activation of hydrotalcites are investigated.

Vibrational spectroscopies have been rarely used to investigate the thermal decomposition mechanism of hydrotalcites. Infrared spectroscopy has been mainly used to identify exchange of compensating anions in the interlayer space in hydrotalcites, while decomposition studies were either performed in vacuum or ex situ. Infrared spectroscopy can be used in situ, and provides structural information on the dehydroxylation and decarbonation processes. Klopproeger and Frost have introduced the application of in situ...
IES (Infrared Emission Spectroscopy) to assess the spinel formation upon decomposition of Mg, Co, and Ni-HTlc, but the low temperature range (<200°C) could not be assessed due to the intrinsic nature of the IES technique. The limitations of this technique have been recently discussed.\textsuperscript{28}

Laser Raman spectroscopy is complementary to infrared spectroscopy and enables the analysis of framework vibrations of the layered structure and the oxide phases. The application of Raman spectroscopy for the analysis of the decomposition of hydrotalcites has to the best of our knowledge never been reported in the literature. Raman spectra of as-synthesized Mg-Al-HTlc was successfully recorded by Kagunya \textit{et al.}\textsuperscript{21} and Kloprogge and Frost\textsuperscript{29} at room temperature. The last authors were not able to record spectra of Co-Al-HTlc and Ni-Al-HTlc under the same conditions, due to extensive fluorescence.

In this paper we will show that \textit{in situ} FT-IR spectroscopy, using a DRIFT accessory, is a powerful tool to investigate the thermal decomposition mechanism of Co-Al and Ni-Al hydrotalcites. Furthermore, for the first time, \textit{in situ} laser Raman spectra of hydrotalcite-like compounds and their thermally decomposed products will be presented. Transitions of the single groups (water, hydroxyls, carbonates) and phases upon thermal decomposition will be discussed. X-ray diffraction, thermal analysis, and mass spectrometry were additionally used to interpret the spectroscopic results.

2. Experimental

2.1. Materials

Co-Al and Ni-Al hydrotalcite were prepared by co-precipitation at constant pH and temperature at low supersaturation conditions, as described elsewhere.\textsuperscript{8,28} The experimental set-up used is shown in Fig. 2. A flow (21 h\textsuperscript{-1}) of an aqueous solution of the respective metal nitrates Co(NO\textsubscript{3})\textsubscript{2}-6H\textsubscript{2}O, >99.0%, Merck; (Ni(NO\textsubscript{3})\textsubscript{2})-6H\textsubscript{2}O, >99.0%, Merck; Al(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O, >99.0%, Fluka) with a total cation concentration of 1.5 M was mixed slowly at 22°C under vigorous agitation with an alkaline solution of Na\textsubscript{2}CO\textsubscript{3} (Alfa, >99.0%) and NaOH (Alfa, 98.5%). The carbonate concentration was adjusted to obtain a molar CO\textsubscript{3}\textsuperscript{2-}/Al\textsuperscript{3+} ratio of 2. The pH of the precipitates was kept at 9.5, by adjusting the flow rate of the alkaline solution. After addition of the reactants the slurry was aged at 65°C for 18 h under mild stirring. A reflux unit was mounted on top of the vessel to prevent water evaporation (not shown in Fig. 2). Finally, the material was cooled to room temperature, filtered, washed with a large amount of warm (30°C) deionized water, and dried at 90°C for 12 h.

![Fig. 2. Co-precipitation set-up used to prepare the hydrotalcite samples.](image-url)
2.2. Techniques and procedures

The chemical composition of the as-synthesized hydrotalcite-like materials was determined by Inductive Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) (PerkinElmer Plasma 40 (Si) and Optima 3000DV (axial)).

X-ray diffraction (XRD) patterns of the as-synthesized materials and the calcination products at 550°C for 3 h were measured in a Bruker AXS diffractometer with Bragg-Brentano geometry, using Cu Kα radiation (λ = 0.1541 nm) and a diffracted beam graphite monochromator. Data were collected in the 2θ range of 5 to 75° with a step size of 0.1° 2θ and a counting time of 8 s. The parameter a of the layered structure corresponds to the average cation-cation distance within the brucite-like layers and was calculated as a = 2 d(110). The c parameter, which is related to the thickness of the brucite-like layer and the interlayer distance, is commonly calculated as c = 3 d(003), assuming a 3R polytypism for the hydrotalcite. This computation is applicable if the d(001) reflections are sharp. However, if the peaks are somewhat broad, it has been proposed that c can be better determined by averaging the position of the diffraction peaks corresponding to planes (003) and (006), according to the formula: c = 3/2 d(003) + 2 d(006). The (440) and (220) reflection planes in the pattern of the thermally decomposed Co-Al and Ni-Al-HTIcs at 550°C, respectively, were used to determine the a parameter of the cubic mixed oxide structure. The observed interplanar d spacings used for the determination of the cell parameters were corrected using Si as an external standard (ICPDS 27-1402), using the Si(111) plane for the (003) and (006) reflections and the Si(400) plane for the (110), (440), and (220) reflections (see Table 1 for more details).

![Diagram of HT-XRD set-up]

Fig. 3. Photograph and schematical representation of the HT-XRD set-up.

The oxidation process of Co²⁺ to Co³⁺ in Co-Al-HTIc was investigated by means of high-temperature X-ray diffraction (HT-XRD) and diffuse reflectance ultraviolet visible (UV-Vis) spectroscopy. HT-XRD was carried out in a STOE diffractometer. A high-temperature cell was installed (Fig. 3), enabling in situ experiments under controlled atmosphere. The measurements were performed under a flowing air or N₂ (50 ml (STP) min⁻¹). The patterns were measured after 1 h equilibration at each temperature, in the range of 30-500°C. The heating rate used was 10°C min⁻¹. Measurement conditions were 2θ range 5-70°, step size 0.034° 2θ, and step counting time 2 s. UV-Vis spectra were recorded on a Shimadzu UV-2010 PC spectrophotometer with a diffuse reflectance accessory, using MgO (Alfa, > 99.95%) as the background. Co₃O₄ (Alfa, > 99.7%) was used as reference.

Thermal Analysis (TGA-DSC) was carried out in a Thermal Sciences STA 1500H apparatus. The solid (10 mg sample with SiC dilution until 50 mg, particle size 75-100 µm)
was placed in an alumina sample crucible (70 µl), and α-Al₂O₃ was used as a reference. Analyses were performed in dry air flow of 100 cm³ (STP) min⁻¹. The temperature was increased from 25°C to 1000°C with a heating rate of 10°C min⁻¹.

The evolution of the gases during the decomposition of Co-Al-HTlc and Ni-Al-HTlc in air were analyzed on-line by a computer-controlled quadrupole mass spectrometer (MS) (Balzers Quadstar 421). 50 mg of the as-synthesized material (particle size 75-100 µm) was decomposed in air (100 cm³ (STP) min⁻¹) in a quartz-tube fixed-bed reactor of 5 mm inner diameter. The temperature was raised from room temperature to 700°C at 10°C min⁻¹. Masses analyzed were m/e 18 (H₂O) and m/e 44 (CO₂).

The in situ Fourier Transform Infrared (FT-IR) spectra were recorded on a Nicolet Magna 550 Fourier transform spectrometer using a Spectratech diffuse reflectance (DRIFT) accessory, equipped with a high-temperature cell. This set-up has been described elsewhere. The transitions during thermal activation of 20 mg of hydrotalcite were studied in situ in air (25 cm³ (STP) min⁻¹). The spectra were collected in the range 25-550°C at intervals of 50-75°C using a heating rate of 10°C min⁻¹. The spectra were acquired by coaddition of 256 scans (scanning time ~300 s), with a nominal resolution of 4 cm⁻¹.

The in situ laser Raman spectra were obtained using a Renishaw Raman Imaging Microscope, system 2000, which is shown in Fig. 4. The green (λ = 514 nm) polarized radiation of an argon ion laser beam of 20 mW was used for excitation. A Leica DMLM

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Fig. 4. Top: Photograph of the Raman set-up (left) with a detail of the in situ cell (right). Bottom: General drawing of the different components of the Raman Imaging Microscope.
3. Results and Discussion

3.1. Chemical composition

Elemental chemical analysis data (Table 1) indicate that the molar metal ratios of Co/Al and Ni/Al in the as-synthesized materials (2.9:1 and 2.8:1, respectively) were close to the value in the parent solutions (Co/Al and Ni/Al = 3:1). This indicates that the precipitation step was carried out effectively.

3.2. X-ray diffraction

Fig. 5 shows the XRD patterns of the as-synthesized Co-Al and Ni-Al-HTTcs. Both patterns show the hydrotalcite structure as the only crystalline component (JCPDS 22-700), exhibiting sharp and symmetric reflections for the basal (003), (006), and (009) planes, and broad and asymmetric reflections for the non-basal (012), (015), and (018) planes. The overlap of the (009) and (012) reflections results in a broad signal between 32 and 38° 2θ. The (110) and (113) reflections can also be clearly distinguished. The cell parameters in Table 1 were calculated according to the procedure described in §2.2. Ni-Al-HTTc has a smaller a parameter than Co-Al-HTTc. This result is not expected, because the ionic radius of Ni (0.72 Å) is very close to that of Co (0.74 Å). Nevertheless, the calculated cell parameter of the samples is in agreement with that reported in the literature. The c parameter of Ni-Al-HTTc is also smaller than that of Co-Al-HTTc. The difference in the c parameter can be related to the amount of water and carbonates in the interlayer space, which is apparently affected by the divalent metal present in the octahedral layers of the hydrotalcite structure. This will be further discussed in the next sections.

By calcination of the Co-Al and Ni-Al hydrotalcites at 550°C for 3 h different oxide phases are formed (Fig. 6). The cell parameters of the formed cobalt and nickel oxide phases are also presented in Table 1. Thermal decomposition in air of Co-Al-HTTc leads to a cobalt spinel phase. Due to the similar reflection angles and intensities in XRD, it is not possible to distinguish between Co₃O₄ (JCPDS 43-1003), CoAl₂O₄ (JCPDS 44-160), and Co₂AlO₄ (JCPDS 38-814). Based on the molar Co/Al ratio of the as-synthesized material, a solid solution of Al³⁺ ions in Co₃O₄ is likely to be formed, as previously proposed by us. In the case of the Ni-Al system, the single oxide NiO (cubic structure, JCPDS 4-835) is the only crystalline phase identified after thermal decomposition. NiAl₂O₄ is only formed as a crystalline phase above 800°C. The Al³⁺ ions can either be incorporated in an amorphous nickel aluminate phase, or in a separate amorphous alumina phase (Al₂O₃).
Table 1. Data on the materials used in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic molar ratio</th>
<th>Phases\textsuperscript{b}</th>
<th>Cell parameters / nm</th>
<th>Phases\textsuperscript{b}</th>
<th>Cell parameter / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In solution</td>
<td>In solid</td>
<td>\textit{a}\textsuperscript{d}</td>
<td>\textit{c}\textsuperscript{e}</td>
<td></td>
</tr>
<tr>
<td>Co-Al-HTlc</td>
<td>3/1</td>
<td>2.9/1</td>
<td>HT\textsuperscript{c}</td>
<td>0.3076 ± 0.0002</td>
<td>2.279 ± 0.008</td>
</tr>
<tr>
<td>Ni-Al-HTlc</td>
<td>3/1</td>
<td>2.8/1</td>
<td>HT</td>
<td>0.3035 ± 0.0002</td>
<td>2.253 ± 0.008</td>
</tr>
</tbody>
</table>

\textsuperscript{a} after thermal treatment of the as-synthesized hydrotalcites in air at 550°C for 3 h.
\textsuperscript{b} crystalline, as determined from XRD; \textit{c} HT: hydrotalcite.
\textsuperscript{d} from the (110) reflection of the XRD patterns (see text), corrected by Si (\textit{d}(400) = 0.13579 nm, JCPDS 27-1402).
\textsuperscript{e} from the averaged (003) and (006) reflections of the XRD patterns (see text), corrected by Si (\textit{d}(111) = 0.31379 nm, JCPDS 27-1402).
\textsuperscript{f} from the (440) and (220) reflections of Co- and Ni-oxides of the XRD patterns, respectively (see text), corrected by Si (\textit{d}(400) = 0.13579 nm, JCPDS 27-1402).
3.3. Thermal analysis and mass spectrometry

The decomposition profiles of Co-Al-HTlc and Ni-Al-HTlc as determined by TGA-DTG-DSC in air, as well as the analysis of the evolved decomposition products by mass spectrometry are presented in Figs. 7 and 8, respectively. Two endothermal transitions can be observed in the DSC profiles (I and II in Fig. 7), associated with a two-stage weight loss in the thermogravimetric profiles. This behaviour is typically observed in decomposition profiles of layered materials.12-14,23,28 The maximum peaks of the DSC profiles (T<sub>DSC</sub>) and of the derivative of the weight loss (T<sub>DTC</sub>) are in excellent agreement, as is shown in Table 2. The total weight loss of Ni-Al-HTlc after thermal decomposition at 550°C was slightly higher than that of Co-Al-HTlc (32.3 wt.% and 29.1 wt.%, respectively). Interpretation of the TGA-DSC analysis is based on the MS analysis of the evolved gases (Fig. 8). Two m/e 18 signals can be observed in the decomposition profiles of Co-Al-HTlc and Ni-Al-HTlc. The first signal is attributed to the removal of interlayer water (transition I in the DSC profile), whereas the second transition is likely to involve further dehydration, as well as dehydroxylation. In Co-Al-HTlc, the two transitions occur in a narrow temperature window, indicating a relatively low stability of the partially dehydrated phase and explaining the apparent single step of weight loss in the TGA profile.

Table 2. Transition temperatures and weight losses during decomposition of Co-Al-HTlc and Ni-Al-HTlc in air, as determined by TGA-DTG-DSC and MS analyses. I and II are shown in Fig. 7 and defined in the text.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Co-Al-HTlc</th>
<th>Ni-Al-HTlc</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA / wt.%</td>
<td>I: 15.1</td>
<td>II: 10.1</td>
</tr>
<tr>
<td>DTG / °C</td>
<td>I: 192</td>
<td>II: 234</td>
</tr>
<tr>
<td>DSC / °C</td>
<td>I: 193</td>
<td>II: 234</td>
</tr>
<tr>
<td>MS / °C</td>
<td>I: 230</td>
<td>II: 264</td>
</tr>
</tbody>
</table>

90
For both samples, CO$_2$ evolution also occurs in different stages. The first minor CO$_2$ evolution (<100°C) is related to physically adsorbed CO$_2$. A m/e 44 signal of high intensity (transition II) is observed around 265°C and 330°C in the profiles of Co-Al-HTlc and Ni-Al-HTlc, respectively, indicating extensive decarbonation. For both hydrotalcites, this process occurs simultaneously with the coupled dehydration and dehydroxylation processes. The ratio of the m/e 44 signal over the m/e 18 signal is significantly higher for Co-Al-HTlc, suggesting that the as-synthesized sample contained relatively more carbonates and less hydroxyls than Ni-Al-HTlc. At higher temperatures an additional broad m/e 44 signal appears around 450°C and 375°C for the Ni-Al-HTlc and Co-Al-HTlc, respectively. This corresponds to the weak and broad endothermal transition in the DSC profiles (indicated as III in Fig. 7), and is explained by residual carbonate decomposition. The weight loss associated with transition III was higher for Ni-Al-HTlc (5.1 wt.%) than for Co-Al-HTlc (3.5 wt.%).

3.4. In situ Infrared and Raman spectroscopies

Infrared spectra recorded at room temperature, as well as during the decomposition of Co-Al and Ni-Al hydrotalcites in the temperature range of 25-550°C are presented in Fig. 9. The corresponding in situ laser Raman spectra are shown in Fig. 10. The various absorption bands and physico-chemical transformations are summarized in Scheme 1.
3.4.1. As-synthesized samples

**Water and hydroxyl vibrations.** In the infrared spectrum at room temperature of the as-synthesized Co-Al and Ni-Al-HTLcs, broad adsorption bands at 3545 cm\(^{-1}\) and 3590 cm\(^{-1}\), respectively, and at 3050 cm\(^{-1}\) (shoulder) are observed, which can be attributed to OH stretching vibrations of hydroxyl groups, water molecules in the interlayer, and physically adsorbed water (Scheme 1a). The shoulder present at 3050 cm\(^{-1}\) is induced by hydrogen bonding of H\(_2\)O to CO\(_3^{2-}\) ions in the interlayer space.\(^{34,36}\) The corresponding HOH bending vibration of interlayer water is located at 1750 cm\(^{-1}\),\(^{25,28}\) while the 1650 cm\(^{-1}\) band is mainly due to HOH bending of physically adsorbed water. It is proposed that the relatively high frequency of the 1750 cm\(^{-1}\) band is due to symmetry restrictions induced by interactions with the CO\(_3^{2-}\) ions (see Scheme 1a), and hydroxyl groups of the brucite-like layers. The 1750 cm\(^{-1}\) band can also be observed in the spectra recorded by Labajos and Rives\(^{37}\) for Ni-Cr-HTLc, but was not specifically mentioned or assigned. A similar vibration was observed by Klopproge and Frost\(^{29}\) in the infrared spectrum of takovite at room temperature. These authors attributed this band to a small amount of water strongly coordinated to a cation not incorporated in the hydrotalcite structure. Since no additional phases were observed in our XRD patterns, this assignment is not very likely. Furthermore, infrared spectra recorded at higher temperatures indicate that both bands at 1750 cm\(^{-1}\) and 3050 cm\(^{-1}\) follow a similar decreasing trend, suggesting that both vibrations are related to water in the interlayer space.

Analogous to the infrared spectra, the broad absorption band around 3500-3600 cm\(^{-1}\) in the Raman spectra of the as-synthesized materials is assigned to stretching vibrations of water molecules. Stretching frequencies of hydroxyl groups are located at Raman shifts of 3680 cm\(^{-1}\) and 3690 cm\(^{-1}\) for Co-Al-HTLc and Ni-Al-HTLc, respectively. The MOH bending vibrations are located at Raman shifts of 1046 cm\(^{-1}\) (Co-Al-HTLc) and 1049 cm\(^{-1}\) (Ni-Al-HTLc) (Scheme 1a). These assignments will be further discussed later.

Remaining Raman bands at 521 cm\(^{-1}\) and 462 cm\(^{-1}\) in Co-Al-HTLc (545 cm\(^{-1}\) and 482 cm\(^{-1}\) for Ni-Al-HTLc) are both assigned to hydroxyl groups associated with mainly Al, both also influenced by probably one divalent cation in its coordination.\(^{23}\) The band at 462 cm\(^{-1}\) is only Raman active while the bands at 521 cm\(^{-1}\) in Co-Al-HTLc and at 545 cm\(^{-1}\) in Ni-Al-HTLc have an equivalent in the infrared spectrum at 625 cm\(^{-1}\) and at 640 cm\(^{-1}\), respectively.

**Carbonate vibrations.** In the carbonate region of the spectra of Co-Al and Ni-Al-HTLcs, bands are located around about 1414-1420 cm\(^{-1}\) (v\(_3\), asymmetric stretching) and 818-833 cm\(^{-1}\) (v\(_2\), out-of-plane deformation). Several authors have observed the v\(_3\) vibration of the carbonate at frequencies ranging from 1360 to 1400 cm\(^{-1}\).\(^{3,25,34,42}\) One could speculate that the high molar CO\(_3^{2-}/\text{Al}^{3+}\) ratio of 2 used in the preparation of the hydrotalcites leads to symmetric carbonate outside the HTLc structure, explaining the relatively high frequency of 1414-1420 cm\(^{-1}\). However, there is no clear correlation between the molar CO\(_3^{2-}/\text{M}^{2+}\) ratio in the synthesis gel and the position of the v\(_3\)(CO\(_3^{2-}\)) vibration. Jiitanu et al.\(^{42}\) observed this vibration at 1360 cm\(^{-1}\) in Ni-Al-HTLc using excess carbonate in the hydrotalcite synthesis, while Klopproge and Frost\(^{29}\) identified the v\(_3\) carbonate band at 1402 cm\(^{-1}\) in Mg-Al-HTLc using a stoichiometric amount of carbonates (CO\(_3^{2-}/\text{Al}^{3+} = 0.5\) in the preparation. During preparation of hydrotalcites, many authors have used co-precipitation conditions in excess carbonate.\(^{25,28,32,42,45}\) It is generally accepted that the carbonates which do not take part in the generation of the interlayer space are removed by the washing procedure. If remaining carbonates would segregate this should be observed in XRD analyses, as well as in TGA-DSC and MS profiles, which is not the case. The differences in carbonate frequencies reported for room temperature spectra in the literature are related to the relative amount of carbonate residing in a high and low symmetry. This is likely to be dependent on the preparation.
Fig. 9. In situ FT-IR spectra for the thermal decomposition of (a) Co-Al-HTlc and (b) Ni-Al-HTlc in air at different temperatures, as indicated in figures.
procedure (mainly ageing conditions) and nature of the divalent ion. In fact, the presence of 
a shoulder at 1350 cm$^{-1}$ in the room temperature spectrum of Co-Al-HTlc (Fig. 9a) is 
indicative of the presence of a fraction of the carbonate in a lower symmetry of C$_3$ or C$_2$.$^{35,40}$ 
The corresponding C=O vibration should be located at approximately 1570 cm$^{-1}$, but is hard 
to identify due to overlap of the 1414 cm$^{-1}$ band in the room temperature spectrum. Miyata$^{34}$ 
explained that both a monodentate or bidentate conformation in the interlayer give rise to 
splitting of the carbonate vibrations,$^{46}$ and a priori it cannot be ascertained, from the analysis 
of the number of bands, which type of interaction is actually present. This aspect will be 
further addressed in §3.4.2. The amount of carbonates in a low symmetry in the as-
synthesized material depends on the size of the trivalent cation. This correlation has been 
associated to the lower amount of water in the interlayer space upon increasing the cation 
size. This facilitates the direct interaction of carbonate groups and hydroxyls in the brucite-
like layers and thus the splitting of the $\nu_3$ mode.

The bands at 1059 and 1062 cm$^{-1}$ in the Raman spectra of Co-Al and Ni-Al hydrotalcites, 
respectively, are assigned to the symmetric stretching vibrations of carbonate in a high 
symmetry (see §3.4.2). It should be noted that the intensity ratio of the Raman bands 
assigned to carbonates and hydroxyls is significantly higher in the spectrum of Co-Al-HTlc 
(11059 cm$^{-1}$/11046 cm$^{-1}$) than that of Ni-Al-HTlc (11062 cm$^{-1}$/11049 cm$^{-1}$) at room temperature. This 
suggests that the as-synthesized Co-sample contains a higher concentration of carbonate 
groups in the interlayer than the Ni-sample, which is in agreement with the higher intensity 
 ratio of the $m/e$ 44 over the $m/e$ 18 responses in the MS profiles presented in Fig. 8, and the 
relatively high intensity of the carbonate bands in the infrared spectrum of Co-Al-HTlc. This 
suggests that in the interlayer of Ni-Al-HTlc both carbonate and hydroxyls are compensating 
the positive charge of the brucite-like sheets. Obviously the size of the hydroxyl is smaller 
than the size of the carbonate, explaining the relatively smaller c parameter deduced from 
the XRD pattern of Ni-Al-HTlc, compared to Co-Al-HTlc.

Framework vibrations. In the low-wavenumber region of the infrared spectra 
(< 1000 cm$^{-1}$), hydrotalcite framework vibrations are located. The band centered at 625 cm$^{-1}$ is 
assigned to O-O stretching in the brucite-like layer, while the band at 471 cm$^{-1}$ is due to Al-
O stretching.$^{29,35}$ The band at 955 cm$^{-1}$ is assigned to an Al-OH deformation.$^{29}$ The bands at 
150 cm$^{-1}$ and 270 cm$^{-1}$ in the Raman spectra of the samples at room temperature have not 
been formerly assigned but are likely related to framework vibrations, since they disappear 
at the temperature where the layered-double hydroxide structure collapses (see next section). 
The band at 270 cm$^{-1}$ was only observed for Co-Al-HTlc.

3.4.2. Thermal decomposition

Removal of interlayer water and dehydroxylation. The first change in the infrared spectra 
of both hydrotalcites occurs upon increasing the temperature from 25 to 100°C. For Co-Al-
HTlc, a decrease in intensity of the bands centered at 3545 and 1650 cm$^{-1}$ is observed, which is 
related to a loss of physically adsorbed water. In this temperature range, there is also a slight 
decrease in intensity of the shoulders at 1750 and 3050 cm$^{-1}$ indicating partial removal of 
interlayer water. The bands at 1650, 1750, and 3050 cm$^{-1}$ disappear completely at 200°C. The 
spectra of Ni-Al-HTlc show the same trend, although interlayer water has a higher thermal 
stability. Disappearance of the shoulders around 1750 and 3050 cm$^{-1}$ was only observed at 
350°C. This is in agreement with the Raman spectra. The shoulder at 3550 cm$^{-1}$ can be 
oberved in the Raman spectra of the Ni-Al-HTlc up to 250-300°C, while the Raman spectra 
of Co-Al-HTlc did not show any features in the 3000-4000 cm$^{-1}$ range above 175°C. Also the
Fig. 10. In situ Raman spectra for the thermal decomposition of (a) Co-ALH\textsubscript{14} and (b) Ni-ALH\textsubscript{14} in air at different temperatures, as indicated in figures.
hydroxyl groups appear much more stable in the Ni-Al-HTlc than in the Co-Al-HTlc, since the Raman bands at 1049 and 3650 cm\(^{-1}\) still have a high intensity at 300°C. In fact the concurrent decrease of the 3650 and 1049 cm\(^{-1}\) bands (from 300-350°C) is evidence for the assignment of the 1049 cm\(^{-1}\) band to an OH vibration. The decomposition temperatures of interlayer water and hydroxys observed in infrared and Raman are in good agreement with thermogravimetry and mass spectrometric analyses. A significant amount of H\(_2\)O was evolved at temperatures of 310-340°C for Ni-Al-HTlc and 190-220°C for Co-Al-HTlc (Fig. 8). These results suggest that removal of interlayer water and hydroxys from the brucite-like layers strongly depends on the divalent metal (Co or Ni) in the HTlc formulation.

**Carbonate reorganization and decomposition.** At 200°C the \(v_3\) mode of the carbonate in the as-synthesized Co-Al hydrotalcite (at 1414 cm\(^{-1}\)) splits into two new bands, located at 1350 cm\(^{-1}\) and 1570 cm\(^{-1}\). These new spectral features indicate the reorganization of the carbonate anion in the structure of the hydrotalcites starting at 150°C. A similar splitting was found in Co-hydrotalcites with different trivalent cations.\(^{27}\) The reorganization of the carbonate species leads to either a mono or bidentate configuration, interacting with the hydroxyl groups of the interlayer. The band at 1350 cm\(^{-1}\), also present in the as-synthesized Co-Al sample, is attributed to the C-O vibration interacting with OH groups of the octahedral layers, whereas the band at 1570 cm\(^{-1}\) is attributed to the C=O vibration.

**Scheme 1.** Assignments during thermal decomposition of Co-Al and Ni-Al hydrotalcites (a) water, hydroxyl, and carbonate vibrations in the layered structure in the as-synthesized material, (b) bidentate and (c) monodentate carbonate coordination to hydroxyl groups in the brucite-like layers after removal of interlayer water, (d) bidentate and (e) monodentate carbonate coordination to metal ions in the decomposed material (oxidic phase). Position of the relevant absorption bands (in cm\(^{-1}\)) derived from the infrared and Raman (R) spectra of the Co-Al and Ni-Al systems are shown in the scheme.
(Scheme 1b). Again, a priori it is not possible to assign the bands specifically to a mono or bidentate configuration. In Co-Al-HTlc, the intensity of the doublet in the carbonate region rapidly decreases in the temperature range of 200-250°C. A new doublet is formed at somewhat lower frequencies and with a high degree of splitting. It is illustrated in Schemes 2b and 2d that these spectral changes are related to the transition of groups associated with OH groups to groups directly coordinated to the metal ions. In view of the extensive splitting of the carbonate doublet in Co-Al-HTlc (240 cm\(^{-1}\) at 250°C), a bidentate coordination to the metal ions is most likely to occur at these high temperatures (Scheme 1d). Since a transition from monodentate hydroxylic interactions, to a bidentate metal coordination is less likely than bidentate-bidentate transitions, it appears that the hydroxylic conformation was also in the bidentate form (Scheme 1b). The carbonate bands disappear at 450-500°C in Co-Al-HTlc.

In the case of Ni-Al-HTlc, the carbonate band appears to split in an overlapping quartet. It can be envisaged that both mono and bidentate configurations exist in Ni-Al-HTlc (Schemes 1b and 1c), with corresponding frequencies at 1560 and 1370 cm\(^{-1}\) and 1590 and 1290 cm\(^{-1}\), respectively. In view of the effect of the hydroxyl group on one carbonate C-O bond (monodentate), or two C-O bonds (bidentate), the doublet with a high degree of splitting (1590 and 1290 cm\(^{-1}\)) should be related to the bidentate configuration (Scheme 1b). It should be mentioned that the pattern at 250°C is affected by carbonate remaining in a higher symmetry, as a consequence of the high stability of interlayer water. The stability of the interlayer water in Ni-Al-HTlc might also cause narrowing of the doublet at 350-400°C, before a quartet can be distinguished at 550°C, assigned to carbonate coordination to the Ni ions (Schemes 1d and 1e). Summarizing, a high stability of the carbonate groups and the presence of both bidentate (1333 and 1590 cm\(^{-1}\)) or monodentate (1360 and 1430 cm\(^{-1}\)) coordinated carbonate were observed. Comparing the Raman and infrared spectra of Co-Al and Ni-Al hydrotalcites, suggests that the 1059 and 1062 cm\(^{-1}\) bands in the Raman spectra are related to carbonate present in a high symmetry induced by the presence of interlayer water (\(v_{\text{L}}\) symmetric stretching, Scheme 1a). The concurrent decrease of the 3556 cm\(^{-1}\) (interlayer water) and 1062 cm\(^{-1}\) in the Raman spectra of Ni-Al-HTlc confirms this assignment and the contribution of symmetric carbonate to the infrared pattern at 250°C. Interaction of the carbonate to hydroxyls or coordination to metal ions changes the symmetry, as previously discussed, and apparently renders the 1062 cm\(^{-1}\) vibration to become Raman inactive in the temperature range of 175-200°C for Co-Al-HTlc and 250-300°C for Ni-Al-HTlc. The intensities of Raman-allowed frequencies of the carbonate species in a low symmetry are apparently very low and not observed in our Raman spectra.

**Phase transitions.** Besides information regarding the transitions of interlayer water and carbonate, important information on the formed oxidic phases can also be derived from the Raman spectra in the region where lattice vibrations occur. In the Raman spectra of Co-Al-HTlc at 175-200°C, the characteristic bands of the hydrotalcite phase are overlapped by a strong band at 590 cm\(^{-1}\), which should be related to an emerging oxide phase. This band was previously assigned to dispersed surface cobalt oxide in a Co\(_5\)O\(_4\)-V\(_2\)O\(_5\)/Al\(_2\)O\(_3\) catalyst.\(^{47}\) The spectral changes suggest an additional feature in the mechanism of the formation of the oxide phase in Co-Al-HTlc. Apparently, the layered hydrotalcite loses hydroxyls upon heating, leading to a first (preliminary) oxide phase, where the cobalt oxide (probably as CoO) is dispersed on the emerging cobalt aluminate (Scheme 2a). The bands at 150 cm\(^{-1}\) and 270 cm\(^{-1}\), related to framework vibrations of the layered structure are no longer visible at 200°C, indicating the collapse of the HTlc structure. The intensity of the band at 590 cm\(^{-1}\) in the Raman spectra progressively decreases with increasing temperature and a new band appears at 680 cm\(^{-1}\). In general this band matches that of crystalline Co\(_3\)O\(_4\), although it has
slightly shifted to lower Raman shift and became somewhat broader. This is indicative of a small particle size. The shift to lower wavenumbers is also related to the presence of a solid solution of cobalt spinels, i.e. Co₉O₄ and CoAl₂O₄, as was suggested by Payen et al. At higher temperatures, the cobalt oxide phase (as Co₉O₄) sinters and the aluminium Al³⁺ ions dissolve in the oxide phase, forming a solid solution (denoted as Co(Co,Al)₉O₄). This has been previously described for a CoO/Al₂O₃ system. Generally, the spectral features observed in Raman are confirmed by the infrared spectra. At 250°C a doublet at 725 cm⁻¹ and 610 cm⁻¹ appears, typical of a normal II-III spinel compound, indicating the loss of lamellar arrangement in the layered structure. The bands observed are shifted with respect to the data reported for pure spinel compounds, due to the co-existence of different oxide-related phases in the samples.

The appearance of the intermediate oxide phase observed in Co-Al-HTlc (Raman shift at 590 cm⁻¹) was not observed in Ni-Al-HTlc. At 300°C, the framework vibrations in Ni-Al-HTlc tend to overlap, announcing the collapse of the layered structure. This leads to the appearance of a single band at 550 cm⁻¹. The Raman band at 550 cm⁻¹ is different from the Raman band for crystalline NiO (460, 500 cm⁻¹) and NiAl₂O₄ (200, 375, 600 cm⁻¹). The position of this band corresponds to that observed by Chan and Wachs for a NiO-V₂O₅/Al₂O₃ catalyst, and was assigned to a surface nickel (II) oxide phase with nickel incorporated into the sub-surface of the alumina support. This suggests that the nickel oxide is strongly interacting with the emerging alumina support upon hydrotalcite decomposition, forming a surface spinel NiAl₂O₄ (Scheme 2b). This is in agreement with spectroscopic studies of a NiO/Al₂O₃ catalyst reported elsewhere, which revealed that nickel oxide diffuses into the surface octahedral and tetrahedral sites of γ-alumina to form stoichiometric or non-stoichiometric surface spinel compounds.

![Diagram](attachment:image.png)

**Scheme 2.** Schematic representation of the oxidic phases formed after decomposition of (a) Co-Al-HTlc and (b) Ni-Al-HTlc.

In the infrared spectra a broad absorption band with a maximum around 860 cm⁻¹ was identified above 350°C. This band corresponds to the oxide phase and can be assigned to an average vibration between the stretching vibrations of AlO₆ and NiO₆ octahedra. This band shifts to higher wavenumbers at higher temperatures (880 cm⁻¹ at 550°C). The shoulder around 600 cm⁻¹ is characteristic of a NiAl₂O₄ spinel structure and supports the high dispersion and strong interaction of Ni and Al in the oxidic phase. Apparently, the low concentration of the NiAl₂O₄ phase and probably its amorphous nature did not allow the identification of this phase in XRD.

### 3.5. Evaluation of the spectroscopic techniques

Table 3 summarizes the temperatures for the decomposition stages of Co-Al and Ni-Al hydrotalcites, as derived from in situ infrared and in situ laser Raman spectrocopies. For both Co-Al and Ni-Al-HTlcs complete dehydroxylation and decarbonation was observed at
somewhat lower apparent temperatures in Raman spectroscopy. Carbonates in low symmetry are not detected by Raman spectroscopy, while they are well identified by infrared. This limits the comparison between decomposition temperatures by the two spectroscopies. An explanation for the different temperature for dehydroxylation could be additional heating of the sample by the laser, despite the low laser power applied. The transition temperatures obtained by vibrational spectroscopies agree well with other in situ techniques (high-temperature X-ray diffraction, thermal analysis, and mass spectrometry). Vibrational spectroscopies are complimentary and provide substantial information on different aspects of the decomposition mechanism:

- symmetry of carbonate groups in the as-synthesized material and changes during thermal decomposition,
- dehydration (physically adsorbed and interlayer water),
- dehydroxylation and decarbonation,
- collapse of the layered structure,
- formation of intermediate oxidic phases, and
- characteristics of the final mixed oxide.

Since the vibrations of carbonate in a low symmetry are apparently Raman inactive, Raman spectroscopy cannot be used to determine the stability of carbonates. However, the thermal stability of the hydroxyls in the hydrotalcites and the various oxidic phases can be analyzed very well. The ability to perform in situ measurements using infrared and Raman spectroscopy is an important aspect of the analyses, since ex situ analysis of samples decomposed at different temperatures may lead to rehydroxylation and retrotopotactic crystallization to the originally layered material, which is well-known for the Mg-Al hydrotalcite.13,16

The relatively high stability of the hydroxyls and carbonates in Ni-Al-HTlc compared to Co-Al-HTlc was previously observed by Infrared Emission Spectroscopy (IES) and thermal analysis.23 The transition temperatures observed by IES were in the same order to those observed in our study, although the measurements were performed at a higher heating rate. IES spectroscopy requires high temperatures to achieve good signals and thus the low temperature range (especially the collapse of the layered structure and the change of symmetry of the carbonates) can not be followed, limiting its application.26

**Table 3.** Summary of the transition temperatures (in °C) during the decomposition of Co-Al-HTlc and Ni-Al-HTlc in air determined by in situ infrared and in situ laser Raman spectroscopies.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Co-Al-HTlc</th>
<th>Ni-Al-HTlc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Infrared</td>
<td>Raman</td>
</tr>
<tr>
<td>Complete dehydration</td>
<td>200</td>
<td>n.i.</td>
</tr>
<tr>
<td>Carbonate rearrangement A</td>
<td>200</td>
<td>n.i.</td>
</tr>
<tr>
<td>Carbonate rearrangement B</td>
<td>&gt; 250</td>
<td>n.i.</td>
</tr>
<tr>
<td>Collapse of the HTlc</td>
<td>200-250</td>
<td>200-250</td>
</tr>
<tr>
<td>Complete dehydroxylation</td>
<td>300</td>
<td>250</td>
</tr>
<tr>
<td>Complete decarbonation</td>
<td>450-500</td>
<td>350</td>
</tr>
</tbody>
</table>

n.i. not identified.

A: from symmetric carbonate, interacting (mostly) to interlayer water, to low-symmetry carbonate interacting to hydroxyls of the brucite-like layers.
B: from low-symmetry carbonate interacting to hydroxyls of the brucite-like layers to low-symmetry carbonates coordinated to metal ions in the oxidic layers.
3.6. Low stability of Co-Al-HTlc: Oxidation of Co$^{2+}$ to Co$^{3+}$

The reason for the low thermal stability of the Co-Al hydrotalcite structure, as well as the single groups (interlayer water, hydroxyls, and carbonates) appears to be related to the oxidation of Co$^{2+}$ to Co$^{3+}$. Different authors have reported the oxidation process during drying or ageing of the co-precipitated Co-layered materials at relatively low temperature.\textsuperscript{13,44} Xu and Zheng\textsuperscript{55} have observed oxidation of Co$^{2+}$ already during the preparation of Mg$^{II}$Co$^{II}$Co$^{III}$HT. The weak exothermic signal around 350°C, indicated in the DSC profile of Co-Al-HTlc as IV (Fig. 7a), is attributed to further oxidation of Co$^{2+}$ to Co$^{3+}$ in the mixed oxide phase. This transition was observed in air, while it was absent during decomposition in inert.\textsuperscript{13} Some authors did not observe this signal during thermal decomposition of Co-Al-HTlc in air.\textsuperscript{23,56} This is due to the simultaneous occurrence of the oxidation process with the thermolysis of the solid, as reported by Uzunova et al.\textsuperscript{57}

![HT-XRD patterns for the thermal decomposition of Co-Al-HTlc](image)

**Fig. 11.** HT-XRD patterns for the thermal decomposition of Co-Al-HTlc: (a) in air at room temperature, in air at (b) 150°C, (c) 200°C, and (c) 500°C, and (d) in inert at 500°C. Reference XRD patterns: Co-spinel (JCPDS 43-1003, 44-160, and 38-814) and CoO (JCPDS 9-402).

The oxidation process can be confirmed by the change in color from pink to blackish brown upon thermal treatment, similar to the reported oxidation of Co(OH)$_2$ when exposed to air in an aqueous solution.\textsuperscript{58} Fig. 11 shows the HT-XRD patterns during thermal decomposition of Co-Al-HTlc. Upon heating of the as-synthesized material at 110°C and further to 150°C in air, the basal spacing $d$(003) shifts to higher diffraction angles, as a result of the removal of interlayer water. The intensity of the second harmonic reflections, planes (006) and (009) decreases, as well as the doublet close to 60° 2θ. The sample at 150°C partially retains a layered structure, but the disappearance of the reflection of the (006) and (009) planes indicates disorder in the stacking of the layers. At this temperature, new broad reflections at $2\theta$ values around 36 and 65° can be also identified, which suggests the presence of a mixture of the emerging mixed oxide phase and the dehydrated HTlc.\textsuperscript{25} This metastable phase recovers to the original layered material after exposure to the ambient for 12 h. At 200°C, the hydrotalcite structure collapses completely, leading to a poorly crystallized spinel-like mixed
oxide, in agreement with the decomposition of monometallic Co(II)-Co(III) hydrotalcite.\textsuperscript{59}
These reflections were absent in the sample decomposed in inert. In this case, thermal stability was significantly higher and CoO was the only crystalline phase identified (see Fig. 11f). This indicates that the crystalline phase observed in air at 200°C is Co$_5$O$_4$, formed as a consequence of the oxidation of Co$^{2+}$. Upon increasing the temperature, the diffraction lines of the oxide phase (solid solution of cobalt spinels Co(Co$_{0.5}$Al$_{0.5}$)$_2$O$_4$), sharpen as a consequence of enhanced crystallinity. The formation of a stable mixed oxide (solid solution) at this low temperature prevents the retrotopotactic transformation to the hydrotalcite phase in wet feed gas or carbonated aqueous solution of 0.5 M Na$_2$CO$_3$.\textsuperscript{60}

![Graph](image)

**Fig. 12.** UV-Vis spectra of (a) Co-Al-HTlc, (b) after treatment at 150°C for 1 h, (c) after treatment at 200°C for 1 h, and (d) Co$_5$O$_4$.

UV-Vis spectra provide relevant information concerning the oxidation of Co$^{2+}$ to Co$^{3+}$ upon thermal decomposition (Fig. 12). The spectrum of the sample decomposed at 150°C produced a broad absorption band at 600-800 nm, probably due to a Co$^{3+}$ state, which is absent in the spectrum of the as-synthesized material. This suggests that the thermal treatment at 150°C partially oxidizes Co$^{2+}$ species, which is in agreement with the relatively broad lines ascribed to the solid solution Co(Co$_{0.5}$Al$_{0.5}$)$_2$O$_4$ in the HT-XRD. The spectrum of the sample treated at 200°C shows an almost continuous absorption above 500 nm, very similar to that shown for Co$_5$O$_4$. The shoulder recorded around 550 nm in the as-synthesized material arises from Co$^{2+}$ in an octahedral environment [CoO$_6$] in the brucite-like layers.\textsuperscript{61} This shoulder is also present in the sample treated at 150°C, in agreement with the identification of the dehydrated hydrotalcite phase in the diffraction pattern. This shoulder disappears after treatment at 200°C. These results are in excellent agreement with previous work, where the oxidation of Co$^{2+}$ was monitored in the range 150-180°C by temperature-programmed oxidation.\textsuperscript{59}

### 4. Conclusions

*In situ* FT-IR and *in situ* laser Raman spectroscopies are shown to be powerful techniques to evaluate physico-chemical changes during the thermal decomposition of hydrotalcite-like compounds. These spectroscopic methods can be used to investigate transitions of the single groups (interlayer water, hydroxyls, carbonates) and the interactions between them, as well
as phase transitions of the hydrotalcite-layered structure upon thermal decomposition. The spectroscopic changes observed during the decomposition process correlate very well with X-ray diffraction, and thermogravimetric, and mass spectrometric analyses.

The following characteristics of the structure and decomposition mechanism of Co-Al and Ni-Al hydrotalcites have been identified. The infrared spectra of the Co-Al hydrotalcite at room temperature reveal the presence of carbonate in a low symmetry, which was not observed for Ni-Al hydrotalcite. Furthermore, a relatively higher amount of carbonate compared to hydroxyls in the as-synthesized Co-Al hydrotalcite is present, as revealed by the Raman spectra and MS decomposition profiles, and the relatively large c parameter deduced from the XRD pattern. Removal of interlayer water is complete at 200°C and 300-350°C for Co-Al-HTlc and Ni-Al-HTlc, respectively, and induces a rearrangement of the carbonate ions in the interlayer from high to low symmetry. The collapse of the layered structure occurs at lower temperatures for Co-Al-HTlc (250°C) than for Ni-Al-HTlc (350°C) and is accompanied by extensive dehydration, dehydroxylation and decarbonation. For Co-Al-HTlc, in the temperature range of 200-250°C an intermediate CoO phase was observed. Thermal decomposition of Co-Al-HTlc finally leads to a solid solution of Co-spinels, while a highly dispersed NiO phase strongly interacting with the Al₂O₃ support (forming a surface NiAl₂O₄ spinel) was identified after decomposition of Ni-Al-HTlc.

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Characterization of Isomorphously Substituted FeZSM-5 during Activation

Physico-chemical characteristics of isomorphously substituted FeZSM-5 both after preparation and activation have been determined by ICP-OES, XRD, TGA-DSC-MS, gas (Ar and N₂) physisorption, SEM, ²⁷Al and ²⁹Si MAS-NMR, NH₃-TPD, TEM, UV-Vis, FT-IR, H₂-TPR, EPR, ⁵⁷Fe Mössbauer, and voltammetric response techniques. The activation of as-synthesized FeZSM-5 comprises calcination at 823 K and a subsequent steam treatment (300 mbar H₂O in N₂) at 873 K. Calcination leads to complete removal of the template. During this process a significant fraction of iron is dislodged to extra-framework positions (ca. 50%), while Al is hardly affected. Steam treatment leads to significant dealumination of the zeolite structure, the complete extraction of isomorphously substituted iron, and the clustering of extra-framework iron into highly dispersed oxide nanoparticles of 1-2 nm, containing Fe and probably Al. Various Fe-species were identified in the final catalyst. A large fraction of iron in the ex-framework FeZSM-5 catalyst is in the form of these iron oxide nano-particles. No larger particles were identified. Apart from these nano-particles, framework iron, extra-framework isolated iron ions, as well as small oligonuclear iron oxo-complexes in the zeolite channels were identified by Mössbauer spectroscopy and voltammetry. Steam treatment of FeZSM-5 decreases the density and strength of acid sites and leads to mesopore formation (around 11 nm), while the apparent crystalline structure and morphology is not altered. In the steamed sample, at room temperature, iron is mainly present as Fe(III), with a fraction of Fe(II) (at least 10%). H₂-TPR indicates that the fraction of Fe(II) in the material increases up to 50% by pretreatment in H₂ at 623 K, inducing autoreduction of Fe(III) species. The fraction of Fe(III) reduced to Fe(II) depends on the duration of this pretreatment and appears to involve different species in the catalyst.
1. Introduction

Fe-based zeolites with MFI structure, including ZSM-5 and silicalite, receive increasing attention in the literature. Reactions catalyzed by these materials include among others isomerization, and oxidative dehydrogenation of alkanes,\textsuperscript{1,2} and selective oxidation of benzene to phenol, using N\textsubscript{2}O as the oxidant.\textsuperscript{3,4} FeMFI also plays an important role in environmental catalysis for the reduction of NO\textsubscript{x} and N\textsubscript{2}O with hydrocarbons (HC-SCR) or ammonia (NH\textsubscript{3}-SCR),\textsuperscript{5-12} direct N\textsubscript{2}O decomposition,\textsuperscript{13,14} and selective oxidation of NH\textsubscript{3} to N\textsubscript{2} with O\textsubscript{2}.\textsuperscript{15}

Various techniques have been described in the literature to characterize Fe-zeolites, including TEM, FT-IR, TPR, ESR, and recently EXAFS.\textsuperscript{14,16-24} Different forms of iron have been identified in FeZSM-5 (Fig. 1). These include: isolated ions either (a) in framework positions (isomorphously substituted), or (b) in extra-framework cationic positions, (c) binuclear and, in general, oligonuclear iron complexes in the zeolite channels, (d) iron oxide FeO\textsubscript{n}, nano-particles of size \( \leq 2 \) nm, and (e) large iron oxide particles (Fe\textsubscript{2}O\textsubscript{3}) in a wide distribution (up to 25 nm in size) located at the surface of the zeolite crystal.

![Schematic representation of the different Fe species identified in FeZSM-5.](image)

FeZSM-5 catalysts are often prepared by solid- and liquid-ion exchange, or sublimation methods, using commercial zeolites. Calcination of these materials usually leads to the formation of a significant fraction of large iron oxide particles (see Fig. 1e), which are known to be inactive in the different reactions catalyzed by FeZSM-5.\textsuperscript{3,16,17} Also, ion-exchange methods often lack reproducibility,\textsuperscript{16,25} which makes them unattractive from a catalytic point of view. Chemical vapor deposition (CVD) of FeCl\textsubscript{3} in the channels of H-ZSM-5 is undoubtedly a superior method for preparing FeZSM-5.\textsuperscript{6,16,19} The water-free conditions under which the exchange takes place allow full exchange of the ZSM-5 zeolite, where iron was found to be mainly present in the form of binuclear hydroxide clusters at ion exchange positions. However, in this case, the treatments after the CVD exchange strongly affect the state of the iron species. Calcination of the exchanged sample before a hydrolysis step mainly leads to the formation of large iron oxide (hematite) particles.\textsuperscript{18} The heating rate during calcination was also found crucial in the development of these particles.\textsuperscript{26,27}

Preparation of FeZSM-5 by isomorphous substitution of Fe in the MFI-framework and activation by heat treatment in vacuum at 1073 K was previously used by Panov \textit{et al.}\textsuperscript{3} to
synthesize active catalysts for the selective oxidation of benzene to phenol with N₂O. We have recently reported a modified route to prepare FeZSM-5,²⁰,²⁴ which consisted in the activation of the isomorphously substituted material by calcination and steam treatment (denoted as ex-framework method). This method leads to a superior activity (per Fe basis) for direct N₂O decomposition compared to other methods to prepare FeZSM-5, such as liquid (aqueous) and solid-ion exchange or sublimation. Furthermore, an improved stability for direct N₂O decomposition in the presence of O₂, NO, SO₂, and H₂O, typically present in tail-gases from nitric acid plants and combustion processes, has been observed.²⁷,²⁸ The ex-framework catalyst has also shown a high activity for selective oxidation of benzene to phenol with N₂O, with a phenol productivity of 0.1 g phenol kg cat⁻¹ h⁻¹.²⁰ The positive effect of steaming in the latter reaction compared to heat treatment in vacuum was also reported by Kharitanov et al.²⁹ and Notté³⁰, but a detailed characterization of the activation of the FeZSM-5 and nature of the species formed by the steaming procedure has not been reported. Previous investigations on the extraction of iron from isomorphously substituted Fe-silicate upon thermal treatment in the range of 773-1073 K in air has been reported by Bordiga et al.³¹ and Fejes et al.³²

In this chapter, the preparation and characterization of the activation of isomorphously substituted FeZSM-5 by calcination and steaming is presented, based on ICP-OES, XRD, SEM, gas (Ar, N₂) physisorption, ²⁷Al and ²⁹Si MAS-NMR, TEM, NH₃-TPD, UV-Vis, FT-IR, H₂-TPR, EPR, ⁵⁷Fe Mössbauer spectroscopy, and voltammetric response techniques. The results lead to a detailed description of the physico-chemical changes induced by the post-synthesis treatments, as well as of the nature of the different species in the catalysts.

2. Experimental

2.1. Material preparation

Isomorphously substituted FeZSM-5 was synthesized hydrothermally using tetrapropylammonium hydroxide as the template. A solution of the silica source (tetraethylorthosilicate, TEOS, Acros, 98%), the template (tetrapropylammonium hydroxide, TPAOH, Fluka, 20% in water), and NaOH was added to a mixture of aluminum(III) nitrate (Al(NO₃)₃·9H₂O, Merck, 99%) and iron(III) nitrate (Fe(NO₃)₃·9H₂O, Merck, 98.5%). The molar ratios between components were H₂O/Si = 45; TPAOH/Si = 0.1; NaOH/Si = 0.2; Si/Al = 36, and Si/Fe = 152. The solution was transferred to a stainless steel autoclave lined with Teflon and kept in a static air oven at 448 K for 5 days. The crystalline material was filtered and washed with deionized water until the sample was free of nitrates. The as-synthesized sample (FeZSM-5as), in which Fe(III) is isomorphously substituted in the zeolite framework, was calcined in air at 823 K for 10 h and then converted into the H-form by three consecutive exchanges with an ammonium nitrate solution (0.1 M) overnight and subsequent calcination at 823 K for 5 h (FeZSM-5c). Finally, the catalyst was steamed at ambient pressure (water partial pressure of 300 mbar and 30 ml min⁻¹ of N₂ flow) at 873 K during 5 h, yielding ex-FeZSM-5. The sample was stored at room temperature in dry atmosphere.

In order to perform ⁵⁷Fe Mössbauer measurements with the different samples, ⁵⁷Fe-enriched FeZSM-5as was prepared. For this purpose, a small piece of ⁵⁷Fe foil was dissolved in concentrated nitric acid (1 M). Subsequently, ammonium hydroxide was added to neutralize the solution, followed by the addition of the aluminum source. The synthesis and post-synthesis treatments were as described above.
2.2. Material characterization

**ICP-OES.** The chemical composition of the catalysts was determined by ICP-OES (Perkin-Elmer Plasma 40 (Si) and Optima 3000DV (axial)) and AAS (Perkin-Elmer 1100).

**XRD.** Powder X-ray diffraction patterns were measured in a Bruker AXS diffractometer with Bragg-Brentano geometry, and Cu Kα radiation (λ = 0.1541 nm). Data were collected in the 2θ range of 5 to 50° at a scan rate of 0.5° min⁻¹.

**TGA-DSC-MS.** Thermal analysis was carried out in a Thermal Sciences STA 1500H apparatus. The solid (10 mg sample with SiC dilution until 50 mg, particle size 75-100 μm) was placed in alumina sample crucibles (70 μl) using α-Al₂O₃ as reference. Tests were performed using dry airflow of 100 ml (STP) min⁻¹ at atmospheric pressure. The temperature was increased from 273 to 1273 K at 10 K min⁻¹. The evolution of the gases during the decomposition of FeZSM-5 was analyzed on-line by a quadrupole mass spectrometer (Balzers Quadstar 421). The thermobalance was coupled to the spectrometer through a heated capillary sampling tube. Masses analyzed were m/e 18 (H₂O), m/e 28 (CO), and m/e 44 (CO₂).

**Gas (Ar and N₂) adsorption.** Ar adsorption isotherms at 87 K were obtained in a Micromeritics ASAP 2010 apparatus. The pore size distribution was calculated from the adsorption branch of the isotherm using the Saito-Foley (SF) model. N₂ adsorption at 77 K was carried out in a QuantaChrome Autosorb-6B apparatus. The pore size distribution was calculated from the desorption branch of the isotherm using the Barret-Joyner-Halenda (BJH) model. Samples were previously evacuated at 623 K for 16 h. The BET method was used to calculate the surface area (S_BET) of the samples, while the micropore volume (V_micr) and external surface area (ESA) was determined with the t-plot method according to Lippens and de Boer.

**SEM.** Scanning Electron Microscopy images were recorded at 10 kV in a Philips XL 20 microscope. Samples were coated with gold to create contrast.

**MAS-NMR.** ²⁷Al and ²⁹Si Magic Angle Spinning-Nuclear Magnetic Resonance were recorded at 79.46 and 104.26 MHz respectively with a Varian VX-400S spectrometer. The narrow bore magnet (50 mm) was fitted with a high-speed magic angle spinning (MAS) Doty probe. The samples were spun in 5 mm-diameter rotors made of zirconia. The length of the r.f. pulses was 3.1 μs for Si and 0.5 μs for Al. The spinning frequency was in the range 4-4.5 kHz for Si and 7.0 kHz for Al. Acquisition time 0.05 s for Si and 0.2 s for Al. A time interval of 5 s for Si and 1 s for Al between successive accumulations was selected in order to avoid saturation effects. The number of accumulations (688 for Si and 10000 for Al) allowed a signal-to-noise ratio higher than 20. The ²⁷Al and ²⁹Si chemical shifts were referenced to Al(H₂O)₅⁺ and Si(CH₃)₄, respectively.

**NH₃-TPD.** Temperature-programmed desorption of ammonia measurements were carried out on a Micromeritics TPR/TPD 2900 equipped with a Thermal Conductivity Detector (TCD). The sample (40 mg) was pretreated at 723 K in He (50 ml min⁻¹) for 1 h. Afterwards, NH₃ (40 ml min⁻¹) was adsorbed at 473 K. After 15 min adsorbing NH₃ a flow of He (50 ml min⁻¹) was passed through the reactor during 30 minutes to remove weakly adsorbed NH₃ on the catalyst surface. This procedure was repeated three times. Desorption of NH₃ was monitored in the range of 473 to 873 K at 10 K min⁻¹.

**TEM.** Transmission Electron Microscopy was carried out on a Philips CM 30 T electron microscope with a LaB₆ filament as the source of electrons operated at 300 kV. Samples were mounted on a copper-supported carbon polymer grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient
conditions. In order to enhance the visibility of the small particles, the zeolites were amorphized by the electron beam. This process did not induce sintering of iron oxide particles in the specimen.

**UV-Vis.** The zeolites were investigated by diffuse Reflectance UV-Vis spectroscopy. Spectra were collected at ambient temperature on a Varian Cary 3 Bio spectrometer equipped with a 76 nm integration sphere and BaSO₄ was used a reference.

**FT-IR.** Fourier Transform Infrared spectra were recorded on a Nicolet Magna 550 Fourier transform spectrometer using a Spectratech diffuse reflectance (DRIFT) accessory, equipped with a high-temperature cell. The as-synthesized, calcined, and steamed samples were recorded in N₂ flow (30 ml min⁻¹) at 373 K. The samples were previously dried in situ in N₂ at 473 K for 1 h. The spectra were acquired by coaddition of 256 scans with a nominal resolution of 4 cm⁻¹. KBr (Alfa, FTIR grade) was used to record the background.

**H₂-TPR.** Temperature-programmed reduction with H₂ was performed in a home-made fixed-bed reactor (4 mm id) set-up, using a high purity mixture of 7.7 vol.% H₂ in Ar to reduce samples in the temperature range of 298-1273 K. Copper(II) oxide was used for calibration. The sample mass was diluted with SiC (volumetric ratio 1:1) in order to improve heat transfer in the catalyst bed. The following procedure was applied: (i) heating in He (or 10 vol.% N₂O in He) at 623 K for 2 h or 15 h, (ii) cooling down to room temperature in the same gas, (iii) flush with He during 1 h at room temperature (in the case of N₂O pretreatment), and (iv) switch to the reductive H₂ in Ar mixture and start the temperature program (heating rate 10 K min⁻¹). A fresh sample was used for each H₂-TPR experiment. The gas, at the reactor exit, was passed through a membrane drier to remove vapors and condensable gases before entering the TCD.

**EPR.** Electron paramagnetic resonance were studied in dry air or in situ by means of a Varian E9 spectrometer at room temperature and at 77 K. Samples were pretreated at 673 K in He. To fill the EPR tubes, a glove box was used contact with the atmosphere. In situ N₂O treatment was carried out by flowing pure N₂O through the reactor containing the catalyst at 623 K. After the temperature was decreased to 298 K, the N₂O flow was stopped. The reactor was closed to avoid contact with the atmosphere and placed into the EPR spectrometer.

**Mössbauer.** ⁵⁷Fe Mössbauer spectra were measured on a constant acceleration spectrometer in a triangular mode with a ⁵⁷Co:Rh source. Spectra for the different FeZSM-5 samples were obtained at 300 K, 77 K, and 4.2 K. The overall spectra were deconvoluted with calculated Mössbauer spectra that consisted of Lorentzian-shape lines. In the case of quadrupole doublets the line widths and the absorption areas of the constituent lines were constrained equal. Positional parameters were not constrained in the fitting procedure. Isomer shift values are reported relative to sodium nitroprusside. The accuracy of positional parameters is ± 0.03 mm s⁻¹.

**Voltammetry.** The voltammetric response of graphite-polyester composite electrodes (GPEs) modified by FeZSM-5 was measured in a standard three-electrode arrangement with a platinum auxiliary electrode and a saturated calomel reference electrode (SCE). Preparation of the composite electrode and modification by the zeolites has been described elsewhere. Linear scan voltammograms (LSVs) and differential pulse voltammograms (DPVs) were recorded at a potential scan rate (ν) of 20 mV s⁻¹ and pulse amplitude (ΔU) of 80 mV using a Metrohm E506 Polarimetry. Experiments were performed at 298 K in aqueous solutions of 0.1-1.0 M HCl (supporting electrolyte) under argon atmosphere. Hematite (Fe₂O₃, Fluka, 98%), goethite (FeO(OH), Fluka, 98%), and FeCl₃·6H₂O (Aldrich, >99%) were used as reference materials.
3. Results and Discussion

3.1. Chemical composition and X-ray diffraction

The elemental analysis of the as-synthesized, calcined, and steamed FeZSM-5 samples prepared in this study is summarized in Table 1. Comparison of the composition of the gels and the crystalline samples suggests that all the iron and aluminum is present in the solid, while a small part of the silicon is not incorporated. Only minor differences between the as-synthesized sample and the post-treated samples can be observed. The concentration of Na in the calcined and steamed FeZSM-5 is below detection limits.

The long-range structural order of FeZSM-5 upon calcination and steam treatment is maintained (Fig. 2). No evidence of any other phase besides ZSM-5 was found in the different samples.

Fig. 2. X-ray diffraction patterns of (a) FeZSM-5as, (b) FeZSM-5c, and (c) ex-FeZSM-5.

3.2. TGA-DSC/MS

Fig. 3 shows the TGA-DSC and MS profiles of the isomorphously substituted FeZSM-5as during heat treatment in air (simulating conditions during calcination). Three steps of weight loss can be distinguished, corresponding to (I) loss of physically adsorbed water (< 650 K), (II) burning of TPA (650-800 K), and (III) dehydroxylation processes (> 800 K). From the DSC profile it is concluded that the first process is endothermic whereas the other two are exothermic. Removal of the template accounts for 8 wt.% weight loss, in agreement with the fact that four TPA molecules per unit cell are included in the ZSM-5 structure. The assignments are corroborated by the MS analysis of the evolved gases. During the decomposition of the template only H₂O and CO₂ were observed (no CO), whereas at lower and higher temperatures water was the unique product identified. The presence of different peaks in the MS signal for CO₂ indicates that the template is occluded in different positions of the zeolite structure, affecting the decomposition temperature. The collapse of the zeolite lattice, typically identified by two exothermal transitions in the range 900-1500 K, was not observed in our profiles.
Table 1. Chemical composition and other characterization data of the crystalline zeolites.

<table>
<thead>
<tr>
<th></th>
<th>FeZSM-58as</th>
<th>FeZSM-5c</th>
<th>ex-FeZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Al ( \text{mol} )</td>
<td>31.1</td>
<td>31.6</td>
<td>31.3</td>
</tr>
<tr>
<td>Si/Fe ( \text{mol} )</td>
<td>126.2</td>
<td>124.9</td>
<td>121.7</td>
</tr>
<tr>
<td>Na ( \text{wt.%} )</td>
<td>0.44</td>
<td>&lt;0.01&lt;sup&gt;d&lt;/sup&gt;</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Fe ( \text{wt.%} )</td>
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<td>0.64</td>
<td>0.67</td>
</tr>
<tr>
<td>( S_{\text{BET}} ) ( \text{m}^2 \text{g}^{-1} )</td>
<td>-</td>
<td>425</td>
<td>372</td>
</tr>
<tr>
<td>( E_{\text{SA}} ) ( \text{m}^2 \text{g}^{-1} )</td>
<td>-</td>
<td>23</td>
<td>33</td>
</tr>
<tr>
<td>( V_{\text{total}} ) ( \text{cm}^3 \text{g}^{-1} )</td>
<td>-</td>
<td>0.24</td>
<td>0.23</td>
</tr>
<tr>
<td>( V_{\text{micro}} ) ( \text{cm}^3 \text{g}^{-1} )</td>
<td>-</td>
<td>0.16</td>
<td>0.14</td>
</tr>
</tbody>
</table>

<sup>a</sup> metal molar ratio in the synthesis gel: Si/Al = 36 and Si/Fe = 152.
<sup>b</sup> BET method; <sup>c</sup> t-plot method; <sup>d</sup> detection limit of ICP-OES.

3.3. Gas adsorption and SEM

Ar adsorption at 87 K was carried out to investigate changes in the microporosity of FeZSM-5 before and after steam treatment. The micropore size distribution of FeZSM-5c shows a well-defined peak at 0.56 nm \( (p/p_0 = 10^{-3}) \) (Fig. 4a), characteristic of the channels in the MFI structure. By steaming, a bimodal distribution is apparently obtained (at 0.56 and 0.8 nm). The intensity of the peak at 0.56 nm diminishes in ex-FeZSM-5 compared to FeZSM-5c and the peak at 0.8 nm develops. This suggests disappearance of micropores, which is confirmed by the cumulative curve. This is in agreement with the slightly lower specific surface area \( S_{\text{BET}} \) of the steamed sample (Table 1). Llewellyn et al.<sup>37</sup> explained by isothermal volumetry, micro-calorimetry, and neutron diffraction techniques on silicalite-1 that the relatively sharp peak centered at 0.8 nm \( (p/p_0 = 10^{-3}) \) is an artefact, caused by the transition of Ar molecules from a disordered phase (presumably a fluid) to a crystalline-like solid phase at the corresponding relative pressure. The appearance of this transition depends on the Si/Al ratio in the sample.<sup>38</sup> It is proposed that a high framework Si/Al ratio (Si/Al > 23) leads to a more homogeneous energetic state of the zeolite surface towards Ar adsorption.<sup>37,38</sup> The presence of the artefact is therefore an indication that dealumination of the zeolite framework has occurred.

The mesopore size distribution derived from the desorption branch of the \( N_2 \) isotherm of FeZSM-5c and ex-FeZSM-5 (Fig. 4b) shows different contributions. A broad peak centered at around 11 nm is identified in ex-FeZSM-5, which suggests the formation of mesopores, leading to a significant increase of the external surface area (ESA, Table 1) by creation of intercrystalline voids. SEM micrographs of the as-synthesized, calcined, and steamed FeZSM-5 samples showed no change in crystal morphology during the post-synthesis treatments. Fig. 5 shows a SEM micrograph of ex-FeZSM-5. The crystal
size distribution in the sample was quite uniform (2.5 μm in size) and no amorphous matter was detected at the external surface. It was possible to distinguish the crystal intergrowth phenomenon, typical in zeolites.

![Graphs showing pore size distribution](image)

Fig. 4. Pore size distribution of (●) FeZSM-5c and (♦) ex-FeZSM-5, calculated from (a) Ar at 87 K and (b) N₂ adsorption at 77 K isotherms, using SF (Saito-Foley) model and BJH (Barret-Joyner-Halenda) model, respectively.

As a consequence of mesopore formation, the micropore volume and the total pore volume in the steamed sample are slightly lower than in the calcined sample. This should be related to the presence of the generated extra-framework species (mainly Al) in the channels of the zeolite, inducing pore blockage. The mesopores are likely to be formed as a consequence of the extraction of Al and Fe in the steaming procedure from framework positions. This leads to lattice defects, which can be restored with Si atoms coming from external parts of the zeolite crystal. As a result, the framework becomes more siliceous and adjacent cages become interconnected through removal of Si from the least stable parts of the lattice. A local character of this process is inferred by XRD results (Fig. 2), showing no change in the crystal structure of the calcined and steamed samples. The peak at 3.9 nm (p/p₀ = 0.45) is also an artefact, attributed to the tensile strength effect of the liquid N₂ adsorbate at 77 K during desorption. The pore size distribution in the range of pore sizes from 2 to 3.9 nm differs in the calcined and steamed materials. The sharp peak at 2 nm in the steamed sample, which is less pronounced in the calcined sample, is considered to be the equivalent artefact observed in the Ar adsorption measurements at 0.8 nm (p/p₀ = 10⁻³).

![SEM micrograph of ex-FeZSM-5](image)

Fig. 5. SEM micrograph of ex-FeZSM-5.
3.4. $^{27}\text{Al}$ and $^{29}\text{Si}$ MAS-NMR

$^{27}\text{Al}$ and $^{29}\text{Si}$ MAS-NMR spectroscopy were carried out to investigate changes of the coordination of the atoms in the zeolite framework on calcination and steaming. The $^{27}\text{Al}$ MAS-NMR spectra of FeZSM-5as and FeZSM-5c (Figs. 6a-b) exhibit a sharp resonance at 55 ppm, assigned to tetrahedrally coordinated Al atoms in lattice positions. In general, the intensities of the signals in the NMR spectra are lower than typically observed for ZSM-5 containing only Al and Si, as a direct consequence of the paramagnetism of the Fe ions, whose unpaired electrons generate a local magnetic field that strongly perturbs the resonance of the $^{27}\text{Al}$ nuclei. The two peaks at -5 and 105 ppm are spinning side bands due to quadrupole interactions of $^{27}\text{Al}$ nuclei. The intensity of the peak at -5 ppm is larger than the spinning band at 105 ppm, suggesting the presence of another signal caused by small amounts of Al in extra-framework positions.

![Fig. 6. MAS-NMR spectra at 300 K of (a) FeZSM-5as, (b) FeZSM-5c, (c) ex-FeZSM-5.](image)

Calcination of FeZSM-5as hardly affects the $^{27}\text{Al}$ MAS-NMR spectrum, in agreement with previous dealumination studies on ZSM-5 zeolites. Steam treatment leads to dealumination of the zeolite framework by migration of Al(III) to extra-framework positions. In the $^{27}\text{Al}$ MAS-NMR spectrum of ex-FeZSM-5 (Fig. 6c), the resonance around 55 ppm significantly decreases and a broad band centered around -3 ppm appears, with a shoulder at approximately 30 ppm. The peak at -3 ppm is attributed to hexacoordinated Al species in octahedral positions, while the shoulder at 30 ppm indicates pentacoordinated or highly distorted tetrahedral Al species in extra-framework positions. The broadening of this signal is probably due to the presence of extra-framework Al with different coordination and positions in ex-FeZSM-5. In view of the spectra acquired, the degree of dealumination is hard to quantify. From the relative ratio of intensities of the signals at 55 and -3 ppm in the $^{27}\text{Al}$ NMR spectra ($I_{55}/I_{-3}$), it was roughly estimated that ~30-40% of framework aluminum is dislodged to extra-framework positions by the steam treatment. Different extra-framework Al species have been considered in the literature to be present in zeolite catalysts. Which of these species is actually formed upon dealumination cannot be assessed from these NMR spectra. The formation of the defects and/or extra-framework Al species in this zeolite
structure upon thermal treatment and/or steaming is worth a further investigation, since their role in the N₂O-related conversions is currently subject of controversy in the catalysis community. This point is further discussed in Chapter 9 of this thesis.

The ²⁹Si MAS-NMR spectra of the as-synthesized and calcined samples (Figs. 6a-b) show a broad signal with a maximum at -117 ppm and a shoulder around -120 ppm, corresponding to Si(2Al) and a weak signal at -109 ppm attributed to Si(1Al). The shoulder at -100 ppm, normally attributed to Si(2Al), was not observed in our spectra, indicating a highly dispersed state of Al in the zeolite framework. Dealumination of the calcined sample upon steaming is indirectly confirmed by the decrease of the signal at -109 ppm in the ²⁹Si MAS-NMR spectrum (Fig. 6c), indicating the absence of Si nuclei coordinated to aluminum after the dislodgment of Al to extra-framework positions.

3.5. NH₃-TPD

Steam treatment of FeZSM-5c also induces changes in the acidity of the catalyst, as shown by NH₃-TPD (Fig. 7). The two NH₃ desorption peaks identified in FeZSM-5c (at 540 K and 725 K, Fig. 7a) are indicative of the presence of acidic centers of different strength. According to literature, the low-temperature peak corresponds to weakly acidic sites and the high-temperature peak (> 673 K) to strong sites. The strength and number of the acidic sites decrease after the steam treatment, indicating that most of the acidic centers in the calcined sample may be Brønsted acids and arise from the presence of Al and Fe in framework. The acidic centers in the steamed sample show a broad distribution (at 675 K, Fig. 7b).

3.6. TEM

TEM was used to analyze the extraction of the Fe ions from the zeolite lattice upon calcination and steam treatment. The TEM micrograph of FeZSM-5as does not show any iron-related phase (Fig. 8a), suggesting that all the Fe is present in a highly dispersed state at isolated positions in the zeolite framework of the as-synthesized material. Calcination of FeZSM-5as to yield FeZSM-5c extracts some isomorphously substituted Fe to extra-framework positions, as concluded from the presence of small iron oxide particles in the TEM micrograph of FeZSM-5c (Fig. 8b). Steam treatment massively dislodges iron to extra-framework positions, inducing the formation of homogeneously dispersed iron oxide nano-particles of 1-2 nm (Fig. 8c). The extra-framework Al species generated during steam treatment might play a role in the formation of the iron oxide. Marturano et al. proposed that since Fe and Al oxide compounds have similar structural properties, it can be envisaged that the presence of extra-framework Al species might induce the epitaxial growth of the Fe oxides. Following this reasoning, it is likely that the observed particles also contain extra-framework Al species. In principle, due to the size of the nano-particles, they should be present at the external surface of the zeolite crystal. However, the local formation of mesopores of 11 nm identified by N₂ adsorption makes the presence of this species in the porous network of the zeolitic structure feasible.
3.7. UV-Vis

The colour change caused by the post-synthesis treatments (especially steaming) can be nicely followed by the naked eye. The as-synthesized and calcined samples were white. The accumulation of iron oxide/hydroxide in the zeolitic voids upon steaming changed the nearly white color to light brownish. UV-Vis spectra (Fig. 9) are dominated by a strong absorption in the range of 200-350 nm, due to the metal-oxygen charge transfer. The bands at 212 and 234 nm in the as-synthesized and calcined samples, attributed to $t_1 \rightarrow t_2$ and $t_1 \rightarrow e$ transitions, indicate the presence of iron in tetrahedral coordination in framework positions.

The calcination step to remove the template and the steaming treatment resulted in clear modifications of the spectra by (i) broadening of the charge transfer bands, (ii) a shift towards higher wavelengths, (iii) an increase in absorbance in the high-wavelength tail, and (iv) a decrease in the intensity of bands centered at 212 and 234 nm. These treatments basically produce the migration of iron towards extra-framework positions by cleavage of Si-O-Fe bonds and dealumination of the zeolite framework. The disappearance of the peak at 212 nm was accompanied by adsorption around 280 nm, which can be identified as a weak
shoulder in FeZSM-5c and as a broad band in ex-FeZSM-5. This band corresponds to the absorption of Fe(III) ions in octahedral complexes in extra-framework positions, and may indicate that iron might be present as isolated and/or clustered iron species. No bands were identified at 500 nm, which is the typical absorption of Fe(III) ions in an aggregate form, e.g. iron hydroxide clusters. Apparently, the low iron content in the material and the presence of iron oxide nano-particles (1-2 nm) leads to no measurable absorption in the visible region of the spectrum.

3.8. FT-IR

The effect of calcination and steam treatment of the infrared spectrum of FeZSM-5 in the region 4000-2500 cm\(^{-1}\) is shown in Fig. 10. The band at 3740 cm\(^{-1}\) in the as-synthesized material with a shoulder at lower frequency is assigned to isolated silanol groups on the external surface of zeolitic microparticles. A broad peak extending from 3600 to 2500 cm\(^{-1}\) (on which the narrow CH\(_2\) and CH\(_3\) template stretching modes at 3100-2850 cm\(^{-1}\) are clearly superimposed) is assigned to the OH stretching of the template (TPAOH). The lowered frequency and the large half-width, reveals that the hydroxyl groups are strongly interacting through hydrogen bonding. The band at 1433 cm\(^{-1}\), also characteristic of the template (C-N vibrations) was identified in the as-synthesized material (not shown).

Template removal at 823 K induces the disappearance of the bands characteristic of the template, while a band at 3610 cm\(^{-1}\) due to bridged hydroxyls with Brønsted acid character grows in a parallel way. The formation of a broad absorption band centred at 3480 cm\(^{-1}\) due to hydrogen-bonded silanolic species suggests that the template removal by thermal activation is accompanied by some extraction of M(III) (M = Al, Fe) with formation of hydroxyl nests. Since \(^{27}\)Al MAS-NMR shows no extraction of Al during calcination, it is inferred that Fe is significantly extracted during the calcination stage.

Steam treatment causes a considerable reduction of the peak associated with the Brønsted acid sites (3610 cm\(^{-1}\)), which indicates the massive dislodgment of Al atoms to extra-framework positions. In the steamed sample a band at 3670 cm\(^{-1}\) appears, which is usually assigned to extra-framework Al species. Besides the decrease of the 3610 cm\(^{-1}\) peak, the

**Fig. 10.** FT-IR spectra at 473 K of (a) FeZSM-5as, (b) FeZSM-5c and (c) ex-FeZSM-5 in the OH stretching region.
elimination of the broad absorption centred at 3480 cm⁻¹, associated with hydroxylated nests, is noticed. This observation was also reported by Bordiga et al. after calcination of Fe-silicalite at 973 K and was explained by a rearrangement of the zeolitic structure. In our infrared spectra, the OH stretching of the Si(OH)Fe groups could not be identified. This band is observed at 3630 cm⁻¹ for iron silicates.

Evolution of the framework stretching modes (1300-750 cm⁻¹) can also give indications for structural properties of the zeolites (Fig. 11). The assignments of the framework vibrations in MFI zeolites have been discussed in detail elsewhere. The shoulder at 1006 cm⁻¹ identified in the calcined material (Fig. 11a) has been associated with the vibrational modes of the [OxSiO]⁻ surrounding a framework Fe(III) atom. This assignment was supported by Raman spectroscopy, with an equivalent band at 1025 cm⁻¹. Steam treatment at 873 K causes the disappearance of the infrared shoulder at 1006 cm⁻¹ (Fig. 11b), which is further evidence that the thermal treatment in the presence of water vapor induces a decrease of the concentration of framework Fe(III) species.

Fig. 11. FT-IR spectra at 473 K of (a) FeZSM-5c and (b) ex-FeZSM-5 in the framework stretching region.

3.9. H₂-TPR

Fig. 12 shows the H₂-TPR profiles of the calcined and steamed samples after He and N₂O pretreatment at 623 K. The molar H₂/Fe ratios in these experiments are collected in Table 2. The TPR profile of FeZSM-5c pretreated in He (Fig. 12a) shows two maxima centered at 680 K (with a shoulder at 710 K) and 1000 K. The first peak (including the shoulder) is ascribed to the reduction of extra-framework Fe(III) species to Fe(II). The second peak is attributed to a residual fraction of framework Fe(III), which is hard to reduce. It is well-known that framework iron is more difficult to reduce than iron in extra-framework positions. The temperature difference observed for the two peaks is indicative of a great shielding effect of the zeolite framework, which protects framework Fe(III) from the reaction with hydrogen. The H₂/Fe ratio in the He-pretreated sample was 0.38. When the sample was pretreated in N₂O at 623 K the H₂/Fe ratio increased to 0.52 (Fig. 12b), which corresponds to the theoretical value (0.5) to reduce all Fe(III) to Fe(II) in the sample:

\[ 2\text{Fe}^{III}O_x + H_2 \rightarrow 2\text{Fe}^{II}O_{x-1} + H_2O \]
Comparing both pretreatments, only the area of the first reduction peak increases after the \( \text{N}_2\text{O} \)-pretreatment, while the second reduction peak hardly changes compared to the sample pretreated in He. This indicates that a significant amount (~25%) of exclusively the Fe species in extra-framework positions is in the Fe(II) oxidation state after calcination at 823 K and pretreatment in He at 623 K.

Table 2. Molar \( \text{H}_2/\text{Fe} \) consumption ratios derived from TPR experiments after pretreatment in He or \( \text{N}_2\text{O} \) at 623 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar ( \text{H}_2/\text{Fe} ) ratio</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
</tr>
<tr>
<td>( \text{FeZSM-5c} )</td>
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</tr>
<tr>
<td>( \text{ex-FeZSM-5} )</td>
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</tbody>
</table>

Lobree et al.\(^{59}\) have shown that the oxidation state and the nature of the iron species in a sublimed \( \text{FeZSM-5} \) catalyst depends on the iron content of the zeolite and the pretreatment. Iron was found as Fe(III) in cationic positions as Fe\(^{3+}\)(OH)\(^2\) for molar ratios of \( \text{Fe/Al} < 0.19 \), whereas above this level the reduction of a fraction Fe(III) to Fe(II) occurred. Additionally at \( \text{Fe/Al} > 0.56 \), iron is also present as particles of FeO. The formation of Fe(II) is explained by autoreduction of the Fe\(^{3+}\)(OH)\(^2\) species, which are located in highly reducible \( \alpha \) sites in ZSM-5 (in the 10-membered ring channel). The autoreduction of FeMFI, \( \text{i.e.} \) the facile interconversion between Fe(III) and Fe(II) in the zeolite upon thermal treatment (> 523 K) in inert or vacuum has been reported by several authors.\(^{16,55-57}\) The autoreduction process involves release of molecular oxygen and dehydration of initially present \([\text{Fe}^{3+}(\text{OH})_2]^+ Z\), leading to \([\text{Fe}^{2+}(\text{OH})]^+ Z\), where \( Z \) is the zeolite. It is likely that the autoreduction process has also occurred in our calcined sample. From the ratio of the areas of the \( \text{H}_2 \) consumption peaks (in the \( \text{N}_2\text{O} \) pretreated catalyst) it is estimated that ~50-60% of the framework iron in the as-synthesized material is already extracted by the calcination procedure. This value is higher than previously reported for Fe-silicalite,\(^{31}\) where 20-25% of framework iron was extracted upon thermal treatment of the as-synthesized sample in air at 773 K. This difference can be explained by the milder thermal treatment carried out in ref. 31 (773 vs. 823 K) and by the fact that isomorphously substituted Fe in silicalite is more stable than in

![Fig. 12. \( \text{H}_2 \)-TPR profiles of (a) \( \text{FeZSM-5c} \) (He), (b) \( \text{FeZSM-5c} \) (\( \text{N}_2\text{O} \)), (c) \( \text{ex-FeZSM-5} \) (He), and (d) \( \text{ex-FeZSM-5} \) (\( \text{N}_2\text{O} \)). Pretreatment of the sample between brackets. Heating rate: 10 K min\(^{-1}\).](image-url)
ZSM-5. Analogously, isomorphously substituted Fe in the ZSM-5 framework is less stable than Al and thus substantial extraction of iron takes already place upon calcination, while all Al remains in framework positions.68

In the steamed FeZSM-5 the peak at high temperatures is not present, indicating the absence of framework Fe species in this material. The total H₂/Fe ratio in ex-FeZSM-5 pretreated in He at 623 K for 2 h was 0.23 (Fig. 12c), which indicates the presence of ~ 50% of the iron as Fe(II). Pretreatment of the sample in N₂O leads to a similar pattern (Fig. 9d), with a molar H₂/Fe ratio = 0.47, close to the theoretical value for reduction of Fe(III) to Fe(II). To explain the low H₂/Fe ratio observed in the TPR profiles of ex-FeZSM-5 after He pretreatment, it can again be assumed that a significant fraction of iron in the sample is already present as Fe(II), suggesting autoreduction in the He pretreatment. The pretreatment of the steamed sample in He for 15 h leads to a lower H₂ consumption (H₂/Fe ~ 0.15), which indicates a clear dependence of the amount of reduced Fe(II) species with the time of the treatment. From the TPR experiments it can not be assessed accurately whether all Fe(II) in the pretreated samples is caused by autoreduction or if some already exists in the fresh steamed sample (generated upon the steam treatment). This point will be further addressed by Mössbauer spectroscopy. The reduction peak appears at higher temperatures in ex-FeZSM-5 (~815 K) than in FeZSM-5c (~680 K), which indicates that the iron species formed after steaming are somehow harder to reduce. The peak in the steamed sample appears at ~150 K higher temperatures than the first reduction peak in the calcined samples. This may be due to the stabilization of the 3+ oxidation state of iron in the nano-particles upon H₂ reduction by diffusion of extra-framework Al species into the iron oxide lattice.

An important feature of the samples investigated in this study is their stability against reduction to Fe⁰. This reduction behaviour has been observed in highly-dispersed Fe-zeolites, containing iron ions at cationic positions (isolated) or small metal complexes.5,6,7,10 Partial or total reduction to metallic iron was observed when preparation routes lead to large iron oxide particles.6,10 This was not the case in our steamed sample, where the small size of the iron species including the iron oxide nano-particles visible in TEM stabilizes the Fe(II) state against reduction to metallic iron with H₂.

3.10. EPR

Fig. 13 shows the X-band EPR spectra for the different zeolites. Signals appeared at g = 2.0 and g = 4.3 for all the samples. For the as-synthesized sample, the spectrum displayed a weak signal at g = 2.2. These signals are typical for Fe in zeolites, and are in accordance with the literature.59 The g = 2.2 signal was commonly assigned to Fe³⁺ ions in interstitial oxide and hydroxide phases.22-27 The appearance of a signal at g = 4.3 was often regarded as evidence of framework substitution in zeolites and AlPOs, while the signal at g = 2.0 has been always attributed to extra-framework Fe(III) at cationic positions.60,65 However, different authors pointed out that the signal at g = 4.3 may be due, at least in part, to the extra-framework Fe(III) species at cationic sites.59,66,67 Védrine et al.68 were the first to report that not only a signal at g = 4.3, but also at g = 2.0 might be indicative of framework Fe. It is thus concluded that the assignment of the structure of iron species by EPR is markedly ambiguous.

Signals at g = 2.0 and g = 4.3, with a shoulder at g = 9.6 can be identified in FeZSM-5c. The intensity of the g = 2.0 signal decreases when the signal at g = 4.3 grows in parallel. This can be explained if the g = 2.0 signal is attributed to framework Fe ions being extracted to extra-framework positions upon calcination (g = 4.3). The signal at g = 9.6 is due to transitions in the lower and upper doublets of rhombic (E > D) high-spin Fe³⁺ species, in which E is the rhombic and D the axial zero-field splitting parameter. The same species yielded the (almost) isotropic signal at g = 4.3, originating from the transition in the middle doublet. After steam treatment of the catalyst at 873 K, yielding ex-FeZSM-5, a new signal appeared at g = 6.4/5.7 and the
intensity of the signal at $g = 4.3$ significantly decreases. The latter signal is ascribed to a high-spin penta or hexa-coordinated Fe$^{3+}$ in axial distorted symmetry.\textsuperscript{22,67,69} \textit{In situ} treatment of ex-FeZSM-5 with pure Na$_2$O at 623 K slightly affects the EPR spectra. The most remarkable observation is that the position and intensity of the band at $g = 5.7/6.3$ changes: it is now more intense and at $g = 6.0$.

Fig. 14 shows the spectra of ex-FeZSM-5 recorded at 77 K before and after treatment of the sample with β-mercaptoethanol. After addition of this reducing agent, the signal at $g = 6.4/5.7$ disappears, suggesting that this species shows redox activity. New signals appeared around $g = 5.0$ and $g = 5.5$, which might correspond to a modified form of the tetrahedral framework iron ($g = 4.3$). Several authors have reported the remarkable reactivity of the $g = 6$ signal. El-Malki \textit{et al.}\textsuperscript{22} showed the disappearance of this band upon treatment of a sublimed FeZSM-5 with ammonia or steam, while Kucherov \textit{et al.}\textsuperscript{67} reported the same disappearance in NO and NO$_2$.

Volodin \textit{et al.}\textsuperscript{69} also noticed the sensitivity of this band to vacuum treatment and to the presence of water or NO. It is thus likely that the high-spin rhombic Fe$^{3+}$ plays a role in the catalysis by FeZSM-5.

3.11. $^{57}Fe$ Mössbauer spectroscopy

$^{57}Fe$ Mössbauer spectra of as-synthesized, calcined, and steamed FeZSM-5 samples recorded at 300 K in air are shown in Fig. 15. The spectrum of FeZSM-5as (Fig. 15a) shows a broad singlet with an average isomer shift, IS = 0.52 mm s$^{-1}$, which has been assigned to tetrahedrally coordinated Fe(III) ions.\textsuperscript{70} Such a broad singlet is typical for paramagnetic iron ions with slow electron spin relaxation, implying large Fe-Fe distances, and thus a homogeneous distribution of Fe(III) ions. This is in perfect agreement with framework incorporation of the iron atoms.

After calcination of the sample a considerable narrowing of the Mössbauer signal is observed together with the onset
of a paramagnetic doublet (Fig. 15b). This is the result of shortened electron spin relaxation times, indicating a shortening of the Fe-Fe distances. A likely explanation for these shortened distances is that calcination leads to removal of Fe(III) ions from the ZSM-5 framework. The extra-framework species may reside in cationic positions, form small iron oxo-complexes, and in minor extent, cluster in small nano-particles, as shown in the TEM micrograph of FeZSM-5c (Fig. 8b).

Steam treatment leading to ex-FeZSM-5 subsequently gives rise to a well-resolved paramagnetic doublet with an IS = 0.59 mm s\(^{-1}\) and quadrupole splitting, QS = 0.90 mm s\(^{-1}\) (Fig. 15c). The observation of a well-resolved doublet indicates a further increase in electron spin relaxation rates and is interpreted by a continued clustering of Fe(III) ions and small iron-oxo complexes into larger particles. In addition, a small shoulder on the high-energy line of this doublet is fitted with a second doublet with IS = 1.30 mm s\(^{-1}\) and QS = 1.59 mm s\(^{-1}\). The IS of this doublet suggests that a small part of the iron is present as Fe(II) in the steamed ex-FeZSM-5 (10% according to the spectral fitting in Table 3). This Fe(II), which is formed during the steaming procedure, partially explains the relatively low H\(_2\) consumption observed in TPR after He-pretreatment at 623 K. The remaining fraction of Fe(II) according to H\(_2\)-TPR (40% of the iron in the sample) should therefore due to autoreduction of Fe(III) to Fe(II) species during He pretreatment in the H\(_2\)-TPR experiments.

![Fig. 15. \(^{57}\)Fe Mössbauer spectra at 300 K in air of (a) FeZSM-5as, (b) FeZSM-5c, and (c) ex-FeZSM-5.](image)

In order to obtain additional information about the particle size distribution of the iron oxide nano-particles formed upon steam treatment, as well as the oxidation state of the iron atoms in ex-FeZSM-5, additional \(^{57}\)Fe Mössbauer spectra were recorded at 300 K, 77 K, and 4.2 K applying high vacuum (Fig. 16). Spectral parameters derived from these measurements are presented in Table 3. Two differences can be observed in the \(^{57}\)Fe Mössbauer spectra recorded at 300 K at ambient pressure in air and under high vacuum, respectively (Figs. 15c and 16a): in high vacuum an increased quadrupole splitting of the Fe(II) doublet can be observed, as well as a new broad spectral component with a contribution of 19%. The increased QS = 2.99 mm s\(^{-1}\) of the same Fe(II) species (QS = 1.59 mm s\(^{-1}\) in air and with the same spectral contribution, see Table 3) can be explained by the removal of physisorbed
water molecules upon evacuation. A justification for this explanation is that re-exposure of the evacuated ex-FeZSM-5 to ambient air results in a similar Mössbauer spectrum as presented in Fig. 15c. However, this similarity is observed only after prolonged exposure times (24 h). We explain this slow change rather by the uptake of water by a slow diffusional process than due to a chemical oxidation with molecular oxygen. The latter process should take place at a much faster pace.

![Mössbauer spectra](image)

Fig. 16. $^{57}$Fe Mössbauer spectra of ex-FeZSM-5 measured at (a) 300 K at 1·10$^{-6}$ mbar, (b) 77 K (liquid N$_2$) at 1·10$^{-6}$ mbar, and (c) 4.2 K (liquid He) at 1·10$^{-6}$ mbar.

The broad singlet with an estimated $I_S = 1.15$ mm s$^{-1}$ can be assigned as follows. Since a fully developed sextuplet is not observed in the spectrum at 77 K (Fig. 16b), it is not conceivable that the observed broad component at 300 K is caused by superparamagnetic iron oxide particles, which are close to the superparamagnetic transition temperature. More likely, is that this spectral component is due to isolated Fe$^{3+}$ ions with slow electron spin relaxation times. Because of the absence of such a component in the spectrum recorded under ambient conditions in air, we believe that these isolated iron atoms reside in extraframework positions. In these positions, the iron atoms are much more affected by the removal of water as a result of the vacuum treatment than when they would be isomorphously substituted. The presence of water in the pores of the zeolite will lead to a mobility of the extra-framework iron ions, which makes them invisible for the Mössbauer technique. Water removal by evacuation leads to increased interactions between these cationic iron species and the zeolite framework.

Several observations have been made which favour this argumentation. Firstly, a strong increase in total resonant absorption area is observed after exposure of the ex-FeZSM-5 material to high vacuum. From this, it is deduced that the iron species responsible for this broad component does not absorb resonantly when the material is in contact with air, implying that this iron species is invisible under these conditions. Secondly, similar to the disappearance of the Fe(II) component, this broad spectral component slowly fades away
upon re-exposure of this evacuated material to air, thereby illustrating the role of water on this reversible process.

Table 3. Mössbauer hyperfine parameters and relative intensities of the Fe species in ex-FeZSM-5.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>IS / mm s⁻¹</th>
<th>QS / mm s⁻¹</th>
<th>HF / T</th>
<th>RI / %</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K, air</td>
<td>0.59</td>
<td>0.90</td>
<td>-</td>
<td>90</td>
<td>Fe(III)</td>
</tr>
<tr>
<td></td>
<td>1.30</td>
<td>1.59</td>
<td>-</td>
<td>10</td>
<td>Fe(II)</td>
</tr>
<tr>
<td>300 K, 1·10⁶ mbar</td>
<td>0.61</td>
<td>1.02</td>
<td>-</td>
<td>71</td>
<td>Fe(III)</td>
</tr>
<tr>
<td></td>
<td>1.15</td>
<td>-</td>
<td>-</td>
<td>19</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>1.45</td>
<td>2.99</td>
<td>-</td>
<td>10</td>
<td>Fe(II)</td>
</tr>
<tr>
<td>77 K, 1·10⁶ mbar</td>
<td>0.77</td>
<td>1.14</td>
<td>-</td>
<td>55</td>
<td>Fe(III)</td>
</tr>
<tr>
<td></td>
<td>0.67</td>
<td>-</td>
<td>-</td>
<td>29</td>
<td>Fe(II)</td>
</tr>
<tr>
<td></td>
<td>1.54</td>
<td>3.48</td>
<td>-</td>
<td>13</td>
<td>Fe(II)</td>
</tr>
<tr>
<td></td>
<td>1.62</td>
<td>4.11</td>
<td>-</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4.2 K, 1·10⁶ mbar</td>
<td>0.76</td>
<td>-</td>
<td>48.8</td>
<td>60</td>
<td>Fe(III)</td>
</tr>
<tr>
<td></td>
<td>0.68</td>
<td>1.62</td>
<td>-</td>
<td>22</td>
<td>Fe(II)</td>
</tr>
<tr>
<td></td>
<td>1.65</td>
<td>3.99</td>
<td>-</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.77</td>
<td>3.08</td>
<td>-</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

* Isomer shift; b Quadrupole splitting; c Average hyperfine field; d Relative intensity.

The Mössbauer spectrum at 77 K shows the presence of the broad component more prominently, which now also contains the onset of a six-line pattern: a high-spin Fe(III) doublet and two Fe(II) components (Fig. 16b). Although the onset of a six-line pattern clearly indicates slow electron spin relaxation (thus that this component has magnetic character), the assignment of this spectral component is ambiguous. Under the assumption that the broad spectral component observed in the Mössbauer spectrum at 300 K and high vacuum is caused by isolated paramagnetic Fe(III) ions in extra-framework positions it is obvious to conclude that this magnetic component is also produced by these iron species. However, since TEM revealed the presence of iron oxide nano-particles (1-2 nm), this component could be the result of superparamagnetic behavior. This is in agreement with the fact that the spectral contribution of this magnetic component in the Mössbauer spectrum recorded at 77 K has grown partly at the expense of the Fe(III) doublet (see Table 3). At 4.2 K, the magnetic component has developed into a full-grown sextuplet (see Fig. 16c). The spectral contribution of this component has grown to ca. 60% of the total spectral area, again mainly at the expense of the Fe(III) doublet (see Table 3). This is now a clear indication that the iron oxide nano-particles show superparamagnetic behavior. Broad lines of the sextuplet may suggest an amorphous character of the nano-particles, with a lower hyperfine field (48.8 T) than in α-Fe₂O₃ (typically 50.2 T). If it is assumed that the broad spectral component in the Mössbauer spectrum recorded at 77 K and with a spectral contribution of 29% is predominantly caused by isolated paramagnetic iron atoms, a particle size close to 2 nm can be estimated for these superparamagnetic iron oxide particles. Additionally, it would mean that the magnetic contribution in the Mössbauer spectrum recorded at 4.2 K is composed of two components, i.e. isolated extra-framework iron atoms and iron oxide particles of ca. 2 nm in size, the so-called nano-particles. It is mentioned in Mössbauer studies by Calis et al.⁷² on calcined FeZSM-5 samples and, more recently, by Ovanesyan et al.⁷³ on a comparable FeZSM-5 zeolite as described here, that magnetic contributions from isolated paramagnetic iron atoms and superparamagnetic iron oxide particles with slow electron spin relaxation have similar magnetic hyperfine splitting, and therefore could largely overlap. Indeed, this result is in excellent agreement with the EPR signal at g = 6.0 in the steamed sample, belonging to isolated Fe³⁺ ions in cationic positions. Similar to the observation in the
Mössbauer spectrum recorded at 77 K, two Fe(II) components can be discriminated in the spectrum recorded at 4.2 K, although the nature of these Fe(II) sites is at present not clear.

3.12. Voltammetric response

Comparison of electrochemical response of the zeolites during different preparation stages provides valuable information about the disappearance and appearance of distinctive electroactive iron species in the samples. The characterization of electroactive Fe-species in zeolites is carried out among others based on different electrode preparations, supporting electrolytes, the shape of the voltammetric curves, and the dependence of the peak potentials with the pH of the electrolyte and the potential scan rate. A detailed description of the electrochemical methods and interpretation of the voltammetric responses is described in Chapter 6 of this thesis. Although the electron transfer to electroactive species in zeolite is subject of controversy, we have found strong evidence that the electrochemical observation corresponds to species associated to a 'boundary region' of the zeolite, situated close to the external surface, in agreement with other authors. Therefore, the electrochemistry measured not only corresponds to iron oxide particles at the external surface of the crystal, but also to framework iron ions and other small intrazeolitic species strongly attached to the zeolite (i.e. in the channels). However, since the electron transport from the electrode to the zeolite (or vice versa) occurs by tunneling, only a fraction of the zeolite crystal is effectively probed. Chapter 6 elaborates more on this aspect.

In this chapter, graphite-polyester composite electrodes (GPCES) were used, which show similar voltammetric responses compared to the polymer film electrodes used elsewhere. Fig. 17 shows a series of cathodic differential pulse voltammograms (DPVs) GPCES modified by (a) FeZSM-5as (b) FeZSM-5c, (c) ex-FeZSM-5, (d) FeO(FeO) (goethite) in 1.0 M HCl (supporting electrolyte). For FeZSM-5as, only peaks at +0.05 V (C1) and -0.15 V (C2) are well defined. For ex-FeZSM-5, a relatively complicated pattern can be observed, with reduction peaks at +0.65 (C1), +0.35 (C2), +0.28 (C3), -0.55 (C4) and -0.75 (C7) V vs. SCE. FeZSM-5c shows a voltammogram in between those of FeZSM-5as and ex-FeZSM-5. During calcination and steam treatment, peaks C1, C2, C3, C4 and C5 develop while peaks C4 and C5 virtually disappear. Comparison of the voltammetric response of ex-FeZSM-5, with that of goethite (FeO(FeO)) and hematite (FeO(FeO)) clearly indicates a different electrochemical behaviour of iron species in the steamed zeolite and the iron oxides.

A more detailed characterization of the electrochemical response of FeZSM-5-modified electrodes is presented in Fig. 18, in which cathodic (C) and anodic (A) linear scan voltammograms (LSVs) for GPCES modified by ex-FeZSM-5 (a and b) and FeZSM-5as (c and d) immersed into 0.1 M HCl are shown. In anodic scans initiated at -0.5 V vs. SCE over ex-FeZSM-5, peaks at -0.18 (A0), +0.36 (A3), +0.42 (A2) and +0.73 (A1) appear. Peaks A0 and A3 overlap the anodic counterparts of peaks C4 and C5, i.e., A4 and A5, respectively.

The electrochemical processes involved with the corresponding assignment are summarized in Table 4, based on explanations elaborated on Chapter 6. The C4/A4 and C5/A5 couples, which are mainly visible in the isomorphously substituted FeZSM-5as sample, can be assigned to electron-transfer processes involving framework iron atoms. In this case, the peak potentials are independent of the potential scan rate and pH of the supporting electrolyte. The existence of two couples has been attributed to two different framework redox isomers having quite similar coordination environments. A similar situation has been recently reported by Venkatathri et al. for vanadium-containing zeolites. The electroactive iron species can be described here in terms of O₃Fe(OH) centers, similar to O₃Ti(OH) redox isomers identified in TS-1.27,80
The electrode process \( C_6 \), which is characteristic of \textit{ex}-FeZSM-5, exhibits electrochemical parameters close to those described for the reductive dissolution of iron oxides and hydrous oxides,\(^{81}\) which is also suggested by similarity with the electrochemical response of the reference iron oxides (especially that of \( \text{Fe}_2\text{O}_3 \)). The peak potential of the process \( C_6 \) shows a linear dependency with the pH of the supporting electrolyte and the potential scan, exhibiting the same behaviour observed in hematite and goethite.\(^{36}\) The anodic process \( A_4 \) in \textit{ex}-FeZSM-5 has been assigned to the oxidative dissolution of iron(II) nano-particles.\(^{74}\) This process involves the presence of Fe(II) in the steamed sample, which is in agreement with the Fe(II) contribution identified in the Mössbauer spectrum of the fresh \textit{ex}-FeZSM-5 sample at 300 K in air (see Fig. 15c and Table 3). The peak \( C_7 \) in \textit{ex}-FeZSM-5 (Fig. 17c), which is also present in \( \text{Fe}_2\text{O}_3 \) and FeO(OH), is attributed to the reduction of iron oxide and electrochemically generated Fe\(^{2+} \) ions to metallic iron (metal deposition in Table 4). The couple \( C_5/A_5 \) corresponds to an electron-transfer step involving Fe\(^{3+} \) ions in solution as suggested by the presence of this couple in LSVs recorded of unmodified electrodes immersed into a diluted solution of 0.5 mM \( \text{FeCl}_3 \cdot 6\text{H}_2\text{O} \) in 0.1 M HCl (Fig. 18e). This peak is therefore attributed to a redox process involving iron-chloride complexes in solution, resulting from leaching of iron species in the zeolite boundary and reductive/oxidative dissolution processes. This is likely related to the presence of the small oxide particles.

![Graph](image-url)

**Fig. 17.** Cathodic DPVs for (a) FeZSM-5as, (b) FeZSM-5c, (c) \textit{ex}-FeZSM-5, (d) \( \text{Fe}_2\text{O}_3 \), (e), and FeO(OH) attached to PGCEs immersed into 1 M HCl; \( v = 20 \text{ mV s}^{-1} \); \( \Delta U = 80 \text{ mV} \).

The peak potential of the couple \( C_1/A_1 \) follows a linear dependency with the pH and the potential scan rate (not shown). In addition, the voltammetric curves exhibit a symmetric shape, which is characteristic of species strongly attached to the electrode surface. We have tentatively assigned the response to small oligonuclear oxo-iron complexes in the zeolite channels that remain attached to the zeolite boundary. These species undergo a rate-determining protonation process couple with the electron-transfer step, as suggested by the slope of the \( E_p \) vs. pH
dependency (65 mV). The peak potential of the couple C₂/A₂ also varies linearly with the potential scan rate but it is independent on the pH. This couple is attributed to a redox process involving isolated iron ions in cationic positions of the zeolite. This behaviour has been previously reported for Mn(salen) complexes encapsulated in the channels of zeolite Y.

Table 4. Summary of the electrochemical processes involving iron species in the FeZSM-5 system. Peak potentials (E_p) in mV vs. SCE from LSVs in 0.1 M HCl electrolyte; ν = 20 mV s⁻¹.

<table>
<thead>
<tr>
<th>Peak</th>
<th>E_p / mV</th>
<th>Iron species involved</th>
<th>Assignment¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁/A₁</td>
<td>+650</td>
<td>Oligonuclear oxo-Fe species</td>
<td>YE</td>
</tr>
<tr>
<td>C₂/A₂</td>
<td>+300</td>
<td>Isolated Fe-ions</td>
<td>YE</td>
</tr>
<tr>
<td>C₃/A₃</td>
<td>+280/+360</td>
<td>Fe ions in solution</td>
<td>D</td>
</tr>
<tr>
<td>C₄/A₄, C₅/A₅</td>
<td>+50,-150</td>
<td>Framework Fe-ions</td>
<td>YE</td>
</tr>
<tr>
<td>C₆/A₆</td>
<td>-550/-180</td>
<td>FeOₓ nano-particles</td>
<td>RD/OD</td>
</tr>
<tr>
<td>C₇</td>
<td>-750</td>
<td>Fe ions in solution</td>
<td>MD</td>
</tr>
</tbody>
</table>

¹ YE: electron-transfer process on intrazeolitic iron species attached to the zeolite boundary. RD/OD: reductive dissolution/oxidative dissolution or iron oxide nano-particles. D: electron-transfer process involving species in solution, MD: metal deposition.

Fig. 18. Cathodic (a, c) and anodic (b, d) LSVs for PGCEs modified by (a, b) ex-FeZSM-5 and (c, d) FeZSM-5as, immersed into 0.1 M HCl. Curve (e) corresponds to the cathodic response of a 0.5 mM FeCl₃·6H₂O and 0.1 M HCl solution at an unmodified PGCE; ν = 20 mV s⁻¹.

It can be concluded that electrochemical characterization during the different stages of the preparation of ex-FeZSM-5 provides unique information with respect to different iron species in the material, since various species coexisting in the catalyst can be identified simultaneously, based on their different electrochemical activity. In the steamed catalyst, iron oxide nano-particles, iron ions in cationic positions, and oligonuclear oxo-iron complexes in the zeolite channels can be distinguished. Voltammetric response techniques provide a fingerprint of the heterogeneous nature of the iron species in the catalyst. Analysis of our
samples by average techniques, like EXAFS, should be taken into special consideration in order to interpret the spectra properly.

4. Conclusions

The following physico-chemical changes have been observed in the two activation steps (calcination and steam treatment) of the isomorphously substituted FeZSM-5. In the as-synthesized material complete substitution of Fe(III) ions in the zeolite framework is concluded from $^{57}$Fe Mössbauer and TEM analyses. Calcination of the as-synthesized sample at 823 K leads to a complete removal of the template, but hardly affects the Al coordination. On the other hand, a considerable fraction of Fe (~50%) is already extracted to extra-framework positions. The created extra-framework species are highly dispersed in the zeolite channels, mostly present as isolated or oligonuclear iron-oxo complexes. The presence of both Fe(III) and Fe(II) oxidation states (25% Fe(II)) after treatment in He at 623 K in FeZSM-5c was observed, indicating significant autoreduction of Fe(III) species. During steam treatment, hydrolysis of the Al-OH and Fe-OH bonds takes place. As a consequence, the density and strength of acid sites diminish. The extraction of Al and Fe in the steaming procedure from framework positions also leads to the formation of a broad distribution of mesopores around 11 nm. The crystal structure and morphology are not affected by the activation by calcination and steaming. Dealumination of the zeolite framework leads to extra-framework Al species with different coordination and positions in ex-FeZSM-5, although the nature of the Al species cannot be assessed in detail. The dislodgement of iron can be described by a clustering process, where the framework and extra-framework species formed upon calcination partially approach each other and accumulate as small iron oxide nano-particles. A very homogeneous and highly dispersed distribution of these nanoparticles is obtained, with an average size of 1-2 nm. The presence of extra-framework Al species plays a role in the formation of these nano-particles and might be located in them. A considerable fraction of small iron oxide particles may be located inside the created mesopores, and not at the external surface of the zeolite. Other forms of iron included in the steamed catalysts consist of smaller iron species in the channels, as isolated charge compensating cations or oligonuclear oxo-iron species. The oxidation state of iron in the fresh steamed catalyst was assessed to be mainly Fe(III) with at least 10% Fe(II), suggesting that the steam treatment provokes the reduction of a fraction of Fe(III) species. Pretreatment of this sample in He at 623 K leads to formation of 50% Fe(II), the difference being attributed to autoreduction of Fe(III) to Fe(II) species. The amount of the Fe(III) reduced in ex-FeZSM-5 depends on the extent of the He pretreatment. H$_2$-TPR after pretreatment of the samples with N$_2$O at 623 K confirm that the reduction in steamed FeZSM-5 is limited to the Fe(II) state. No reduction to metallic iron takes place.

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References

Electrochemical Characterization of Catalysts.  
Iron Species in FeZSM-5

Solid state electrochemistry is presented as a unique method to characterize heterogeneous catalysts. This novel technique has been applied to determine the nature of iron species in the different stages of the activation of isomorphously substituted FeZSM-5 by calcination and steam treatment (ex-framework route). The electrochemical response of the zeolites in Paraloid B72 polymer film modified electrodes immersed in aqueous solutions of H$_2$SO$_4$, HCl, Na$_2$EDTA and NaCl electrolytes, provides information on the structural environment and oxidation state of the electroactive iron species in different FeZSM-5 catalysts. The electrochemistry of the various species identified, including tetrahedral iron ions in framework positions, isolated iron ions in cationic positions, dinuclear or oligonuclear oxo-iron species in the zeolite channels, and iron oxide nanoparticles, is elucidated.
1. Introduction

Preparation of FeZSM-5 via an ex-framework route encompasses the hydrothermal synthesis of isomorphously substituted FeZSM-5 followed by calcination at 823 K for 5 h and steam treatment (300 mbar H₂O in N₂ flow) at 873 K for 5 h. The physico-chemical changes during this preparation have been detailedly described in Chapter 5. From this study it was concluded that the heterogeneous nature of the iron species in FeZSM-5 makes the characterization of this catalytic system very difficult, and the application of multiple techniques was required to identify the various iron species co-existing in the material. This includes isomorphously substituted iron in the zeolite framework, isolated iron ions in cationic positions, oligonuclear oxo-iron species in the zeolite channels, and iron oxide particles in a wide range of sizes.

Electrochemical methods, also referred to as voltammetric techniques, can contribute to the characterization of various iron species in FeZSM-5. Although electrochemical techniques have been traditionally focused on studies in solution, the development of a variety of chemically modified electrodes has prompted systematic studies dealing with the characterization of solid samples. This approach has been labelled as solid state electrochemistry or chemistry of solid microparticles.1-4 This methodology has been previously applied to investigate the electrochemistry of single metal ions (Ag⁺, Cu²⁺)5-10 or metal complexes (Mn and Fe-salen, Co-phthalocyanine)11-16 encapsulated into the channels and cages of zeolite Y. However, there are no studies concerning the electrochemistry of tetrahedral framework iron, octahedral extra-framework iron species, and or iron oxide nano-particles in zeolite catalysts.

In this chapter we discuss the electrochemical characterization of the different iron species existing in isomorphously substituted FeZSM-5, as well as in the materials obtained by calcination and steam treatment. The electrochemical response of the zeolites were recorded in polymer (Paraloid B72) film-modified electrodes. To this end, the dependence of peak potentials on the pH and potential scan rate, as well as the shape of voltammetric responses in different electrolytes and their variation upon different electrode preparation were used.

2. On the electrochemistry of zeolite-attached species

For non-conducting solid microparticles, the electron-transfer processes occur at the three-phase boundary between the electrolyte solution (I), the solid particle (II), and the inert electrode (III) (Fig. 1). Charge conservation requires in general an exchange of ions (M⁺) between the solid and the solution phase. The electron transport from the electrode to the zeolite particle (reduction) or vice versa (oxidation) normally occurs via a tunneling mechanism. In the specific case of zeolite-modified electrodes, the interpretation of electrochemical responses has been subject of controversy regarding the mechanism of electron transfer to redox electroactive species in the material.6 Accordingly, different mechanisms has been proposed:

- **Extrazeolitic**, where the electron transfer process takes place outside of the zeolite after ion exchange of electroactive species of the zeolite with electrolyte cations.6,8
- **Intrazeolitic**, which involves electron transfer processes affecting electroactive species located in the channels of the outer cavities or subsurface zones of the zeolite.9,15
- **Surface-mediated electron-transfer**, which is a compromise between the intrazeolitic and extrazeolitic mechanisms. In this case, the process is confined in the more external sites of the zeolite, associated to a 'boundary' region of the zeolite grains. This mechanism was proposed for zeolite-encapsulated redox-active transition metal (Co, Fe) complexes in NaY.17 The results shown in this chapter provide additional evidence that the observed electrochemistry in zeolites corresponds to species associated present in this 'boundary' region.

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Fig. 1. Simplified scheme of the electron transfer processes during the electrochemical characterization of zeolites, exemplified for a reduction process.

In general, the analysis of electrochemical response is also complicated by the fact that different electroactive zeolite-associated species can be responsible for the observed electrochemistry. This especially applies to the FeZSM-5 system, where different iron species may co-exist (see Fig. 1 in Chapter 5). Secondly, various topological redox isomers at different locations of the zeolite may exist. In general, electroactive extra-framework iron ions can be:

- outside the zeolite, with no bonding or sorptive association,
- bound to the boundary (or external surface) of the zeolite,
- adsorbed into the voids of the zeolite, but able to sample the global pore lattice topology,
- size-included in the interior of a cage or a channel intersection of the zeolite.

The observed shape of the voltammetric peaks can be described by different theoretical models that predict significant differences in the shape of current-potential curves. Fig. 2 shows the theoretical Linear Scan Voltammograms (LSVs) for:

- reversible electron-transfer process involving species in solution,
- reversible electron-transfer process between species attached to the electrode surface,
- reductive dissolution of a solid.

Baker et al. explained that electroactive species are electrochemically reduced or oxidized in a thin layer of electrolyte solution existing between the zeolite particles and the electrode. Since electron-transfer steps must be coupled with the release of charge-balancing electrolyte cations, $M^+$, the overall electrochemical reaction rate may be controlled by the diffusion of such electrolyte cation, and/or by its interchange with zeolite-associated ions, and/or the diffusion of such zeolite-associated species through the channel system. Neglecting electroactive species in the bulk solution, and assuming that diffusion in this layer is fast in comparison to intrazeolite counter-diffusion and intracrystalline ion exchange, the system can be considered as a diffusion-controlled process yielding a voltammetric profile similar to that of diffusion-controlled processes in solution. This is characterized by a slow current decrease 100-150 mV past the voltammetric peak, in the so-called diffusive region of the voltammogram (Fig. 2a). The peak potential of this process varies with the potential scan rate.
For an electron-transfer process in which both the oxidized and reduced forms remain strongly attached to the electrode surface, a typical symmetric peak is obtained (Fig. 2b), whose profile is equivalent to that of a classical thin layer cell with the peak potential independent on the potential scan rate.\textsuperscript{22} Exceptionally, in ruthenates, one can have (b)-like peaks while dissolution takes place.\textsuperscript{23}

Among other possibilities, the reductive or oxidative dissolution of a set of solid microparticles, recently described in detail by Grygar for Fe(III) and Cr(III) oxides and ferrites,\textsuperscript{24} exhibits current-potential curves whose profile depends on the shape and size distribution of the particles. Although the exact voltammetric profile depends on the polydispersity of the particle set, typical current-potential curves can be distinguished to those previously described (Fig. 2c). In this case, the peak potential also varies with the potential scan rate.

![Current-potential curves](image)

**Fig. 2.** Characteristic profiles obtained in cathodic LSVs for (a) reversible electron-transfer process involving species in solution, (b) reversible electron-transfer process between species strongly attached to the electrode surface, and (c) reductive dissolution of a solid.

3. Experimental

3.1. Preparation of modified electrodes

The preparation method and physico-chemical characterization of as-synthesized, calcined, and steamed FeZSM-5 zeolites used in this study was described in detail in Chapter 5. Fig. 3 shows a representation of the electrodes prepared in this study. A freshly polished glassy carbon electrode (GCE) was used as working electrode (Fig. 3a). Paraloid-modified film electrodes (PFEs, Fig. 3b) were prepared by mixing 0.1 mg of the zeolite samples, previously powdered in an agate mortar, with 0.1 ml of 1 vol.\% acetone solution of Paraloid B72 (an acrylic copolymer of 70 vol.\% ethyl methacrylate and 30 vol.\% methyl acrylate) in a small glass vial. This copolymer provides porous coatings, and due to its adhesive properties it facilitates the attachment of the solid microparticles to the electrode surface.\textsuperscript{25,26} The resulting dispersion was placed in an ultrasonic bath for 5 min. The modified electrode was prepared by transferring a
few microlitres of such a dispersion onto the surface of a freshly polished GCE and allowing the solvent to evaporate in air. The coatings examined contained 0.5-1.5 mg cm\(^{-2}\) of the dry zeolite. This procedure involves a lightly-ground conditioning of the zeolite samples. A series of electrodes were also prepared by abrasive conditioning. In this case, a spot of finely distributed zeolite was placed on a glazed porcelain tail. Subsequently the lower end of the GCE electrode was vigorously rubbed over that spot of sample. Finally this spot was covered by the polymer coating (Fig. 3c). Blank experiments were performed on self-supported zeolite modified electrodes, i.e. in the absence of polymer, prepared by abrasive conditioning (Fig. 3d). In this case the zeolite layer was easily detached from the electrode surface and only a maximum of two or three scans could be recorded.

![Diagram showing different electrodes preparations](image)

**Fig. 3.** Different electrodes preparations: (a) bare glassy carbon electrode, (b) polymer-modified electrode (lightly-ground conditioning), (c) polymer-modified electrode (abrasive conditioning), and (d) self-supported zeolite-modified electrode (abrasive conditioning).

### 3.2. Instrumentation and procedures

The electrochemical experiments were carried out in a BAS C3-cell stand (Fig. 4). This cell firmly holds all the components of the electrochemical cell (vial, electrodes, cap) and provides a convenient means of stirring and purging the analyte solution. A standard three-electrode arrangement was used: working electrode, a platinum auxiliary electrode, and a saturated calomel reference electrode (SCE). All electrochemical experiments were performed at 298 K after the immersion of the electrodes in aqueous solutions under Ar atmosphere. \(\text{H}_2\text{SO}_4\) (Probus, > 98.5%), \(\text{NaCl}\) (Probus, > 98.5%), \(\text{Na}_2\text{EDTA}\) (Merck, > 98.5%), and \(\text{HCl}\) (Probus, > 98.5%) were used as supporting electrolytes, in concentrations ranging from 0.01 to 1 M. Control experiments were carried out with 0.2 mM \(\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}\) (Merck, > 99.0%) or 0.5 mM \(\text{FeCl}_3 \cdot 6\text{H}_2\text{O}\) (Panreac, > 98.5%) aqueous solutions.

The different electrochemical methods used in this study are shown in Fig. 5. Linear scan voltammograms (LSVs) and differential pulse voltammograms (DPVs) were recorded at potential scan rates ranging from 1 to 60 mV s\(^{-1}\) using a Metrohm E506 Polarecord. Cyclic voltammograms (CVs) were recorded using a BAS CV 50 W potentiostat. Single and multiple (from 2 to 10 cycles) voltammograms were recorded.
Fig. 4. Photograph of the electrochemical cell and the different components.

Fig. 5. Typical potential-time diagrams in (a) linear scan voltammetry (LSV), (b) cyclic voltammetry (CV), and (c) differential scan voltammetry (DPV).
4. Results and discussion

4.1. General voltammetric patterns

4.1.1. Cathodic linear scan voltammetry

Fig. 6 shows a series of cathodic differential pulse voltammograms (DPVs) for PFEs modified by (a) FeZSM-5as, (b) FeZSM-5c, (c) ex-FeZSM-5, (d) Fe$_2$O$_3$ (hematite) and (e) FeO(OH) (goethite) in 0.01 M HCl + 0.1 M NaCl aqueous solutions. For FeZSM-5as, only the peaks C$_3$ (+0.02 V vs. SCE) and C$_4$ (-0.16 V vs. SCE) are well defined. Ex-FeZSM-5 exhibits a relatively complicated electrochemical pattern. In this sample, the peaks C$_3$ and C$_4$ are practically invisible and new reduction peaks at +0.65 (C$_1$), +0.30 (C$_2$), +0.45 (C$_3$), -0.65 (C$_3$) and -0.74 (C$_2$) V vs. SCE appear. FeZSM-5c shows a voltammogram in between that of FeZSM-5as and ex-FeZSM-5. In the latter sample, the signals of both the as-synthesized and steamed samples are present, but with a relatively low current. This indicates a progressive transition of the electroactive iron species from the as-synthesized to the calcined zeolites, and further to the final steamed catalyst.

The results in Fig. 6 indicate that the electrochemistry of iron species in FeZSM-5 zeolites shows significant differences compared to that of iron oxides and hydrous oxides. PFEs modified with hematite and goethite show prominent cathodic peaks in the range from -0.25 to -0.80 V vs. SCE, and they are shifted to more positive potentials compared to the peaks of ex-FeZSM-5 in that region (C$_5$-C$_7$). All these electrochemical responses strongly differ from that of Fe$^{3+}$ ions, where only one well-defined reduction peak appears at +0.25 V (C$_3$), with a weak shoulder around -0.80 V. Peaks C$_5$ and C$_7$ can unambiguously be assigned to the reduction of Fe$^{3+}$ to Fe$^{2+}$ ions in solution and their subsequent reduction to metallic iron, respectively. Peaks C$_5$ and C$_6$ in ex-FeZSM-5 are attributed the reductive dissolution of iron oxide nano-particles, by similarity with the electrochemical response of the reference iron oxides (especially that of hematite). Accordingly, the peak C$_6$ can be represented by the following equation:

$$\text{Fe}^{3+} \text{O}_x + 2x \text{H}^+ + (2x+n-3) \text{e}^- \rightarrow (1-n) \text{Fe}^{3+} (aq.) + n \text{Fe}^{2+} (aq.) + x \text{H}_2\text{O}$$  (1)

where $n$ represents the fraction of Fe(III) effectively reduced to Fe(II). Under sufficiently acidic conditions (pH ~ 1), $n = 1$. According to Mancey et al.,$^{27}$ at potentials below -0.5 V, iron oxide and electrochemically generated Fe$^{2+}$ ions in aqueous solutions are reduced to metallic iron (peaks C$_5$-C$_7$ in Fig. 6). These results are in agreement with the electrochemistry of iron oxides and hydrous oxides, which was recently described by Grygar et al.$^{24,28-30}$ using paraffin impregnated graphite electrodes. The current of these peaks increases significantly upon steaming of the sample, which nicely agree with the clustering of iron species during this treatment and formation of iron oxide nano-particles described in Chapter 5. Cathodic LSVs involve dissolution of iron oxide nano-particles, as denoted by the fast decrease of the corresponding peak current in the second and subsequent scans (not shown). Peaks C$_3$ and C$_4$, which are mainly present in FeZSM-5as can in principle be attributed to the reduction of framework iron (III) species. Following a similar reasoning the peaks C$_1$ and C$_2$, characteristic of FeZSM-5c and ex-FeZSM-5, are assigned to the reduction of extra-framework iron species associated to the zeolite 'boundary', which have been generated during calcination and steam treatment.

4.1.2. Anodic linear scan voltammetry

Anodic LSVs (Fig. 6B) support foregoing assignments. Peaks A$_7$ and A$_5$ show the characteristic shape of stripping peaks, suggesting that they correspond to the oxidation of metallic iron generated at potentials near to -0.8 V to Fe$^{3+}$ (at -0.65 V) and Fe$^{4+}$ (at -0.25 V) ions in solution, respectively. This is in good agreement with the standard electrode potentials of the
Fig. 6. (A) Cathodic and (B) anodic LSVs of PFEs modified by (a) FeZSM-5as, (b) FeZSM-5c and (c) ex-FeZSM-5, (d) Fe₃O₄, and (e) FeO(OH) in 0.01 M HCl + 0.1 M NaCl aqueous solution. Profile (f) represents the LSV of a 0.5 mM FeCl₃·6H₂O aqueous solution at a bare GCE in the same electrolyte; v = 10 mV s⁻¹.
Fe$^{3+}$/Fe$^{0}$ and Fe$^{2+}$/Fe$^{0}$ couples (-0.74 and -0.28 V, respectively). This is experimentally confirmed from the electrochemical response of Fe$_{2}$O$_{3}$, FeO(OH), and solutions of FeCl$_{3}$·6H$_{2}$O. The electrode process $A_{5}$ is similar to that recently reported for zerovalent iron nano-particles synthesized on a non-porous hydrophobic polymer resin.$^{31}$ Peaks $A_{1}$-$A_{4}$ are the anodic counterparts of peaks $C_{1}$-$C_{4}$. Analogously to the case of the cathodic LSVs, peaks $A_{1}$ and $A_{2}$ were identified only in ex-FeZSM-5, while peaks $A_{3}$ and $A_{4}$ are well-defined only in FeZSM-5as.

The peak $A_{5}$ has been attributed to the oxidative dissolution of iron oxide nano-particles, according to:

$$\ce{Fe^{n}O_{y} + 2y H^{+} \rightarrow (1-n) Fe^{2+}(aq.) + n Fe^{3+}(aq.) + y H_{2}O + (n+2-2y)e^-}$$  \hspace{1cm} (2)

This indicates that both Fe(III) and Fe(II) species are present in the oxide nano-particles of the fresh steamed zeolite, which is in agreement with the contribution of both oxidation states in the $^{57}$Fe Mössbauer spectrum of this sample (see Chapter 5). The couple $C_{5}$/$A_{5}$ shows a typical diffusive behaviour (Fig. 2a) and can be attributed to a redox process involving iron-chloride complexes in solution resulting from leaching and reductive/oxidative dissolution processes. The peak potential of this electrode process is independent of the pH.

From this preliminary analysis a relatively complicated picture emerges: electroactive iron in FeZSM-5 zeolites can be divided into iron oxide nano-particles, with a similar electrochemical behaviour to that of iron oxides, and different iron species associated to boundary sites in the zeolite, in the framework or extra-framework positions. Table 1 summarizes the electrochemical processes involved and the corresponding assignments, which will be discussed in the next sections.

4.2. Experimental aspects of the voltammetric method

Different experimental aspects were investigated in order to validate the application of voltammetric techniques in the characterization of iron species in FeZSM-5.

4.2.1. Supporting electrolyte

The use of aqueous solutions of H$_{2}$SO$_{4}$ and HCl + NaCl as supporting electrolyte leads to a very similar electrochemical response of the zeolites. It is also crucial to evaluate the stability of the zeolite samples in the electrolytes during the measurements, as well as the reproducibility of the technique. Experiments performed with previous contact of the zeolite-modified electrode with the electrolyte for 1, 5, 10, and 15 minutes lead to same voltammetric responses, which suggests that the electrolytic media does not change the Fe-species in the time-scale of the experiments. No alteration of the crystal structure of the zeolites was detected during 15 min (the maximum exposure time used), as confirmed by the XRD patterns before and after contact with the supporting electrolyte.

4.2.2. Electrode

The reproducibility of the technique was also proven by performing the measurement with the same zeolite using different electrode preparations, and comparing the evolution of the voltammetric response. The response of zeolite-modified PFEs was identical to that recorded with self-supported zeolite-modified electrodes, which excludes any influence of the acrylic polymer binder on the electroactive iron species. Different electrodes also give similar results. This was concluded by comparison of the voltammetric patterns of FeZSM-5 using Paraloid B72-modified electrodes and graphite polyester composite (GPC) electrodes.$^{32}$ Preparation of electrodes by abrasive conditioning of zeolite-modified electrodes leads to more intense electrochemical responses than lightly-ground conditioning. These observations are consistent
with the attribution of the observed electrochemistry to iron species in the ‘boundary’ region of the zeolite. Since abrasive preparation involves further crushing of zeolite particles, the relative number of electrochemically accessible iron species is enhanced, and thus the peak current of the voltammetric processes.

4.2.3. What fraction of the zeolite is being probed?

A net change of 2-5 μC was passed during the LSV of ex-FeZSM-5, depending on the preparation method. Using the Faraday’s law, the number of utilized electroactive iron species can be estimated. It is concluded that ~0.5 mol.% of iron in the sample is electroactive, which makes the electron transfer via an intrazeolitic mechanism very unlikely (see §2). This amount is significantly lower in FeZSM-5as and FeZSM-5c (0.1-0.2 mol.%), which is consistent with the more favourable accessibility of iron oxide nano-particles in ex-FeZSM-5 via reductive or oxidative dissolution. Only a small fraction of electroactive species in the samples is being probed (probably in the region of the zeolite grain in contact with the electrode surface), due to the limited distance of electron tunnelling, contrary to the principle of the intrazeolitic mechanism. Therefore the surface-mediated electron-transfer mechanism is the most plausible description of this process, where the observed electrochemistry corresponds essentially to iron species in the ‘boundary’ region of the zeolite.

4.3. Electrochemistry of iron oxide nano-particles

4.3.1. Determination of the heterogeneity coefficient

The reductive dissolution of Fe(III) oxides and hydrous oxides in the absence of strongly complexing agents can be described by the following equation:

$$i = k_o q_o \left( \frac{q}{q_o} \right)^g \exp \left( -\frac{\alpha n F}{RT} (E-E_o) \right)$$

(3)

This expression assumes that the proton-assisted dissolution rate is much lower than the reduction rate of Fe(III) and that all dissolved iron is in the form of Fe²⁺. The dimensionless g coefficient, also known as heterogeneity coefficient, represents a geometric factor characteristic of a certain heterogeneity in the shape and size distribution of particles in relation to their electrochemical reactivity. The more diverse the set of particles is (from the electrochemical reactivity point of view), the higher the g value. This case can be treated as a surface reaction of monodisperse isotropic spheres, and thus it is established that the electrochemical rate constant depends on the particle size and the heterogeneity of its distribution. For monodisperse isotropic spherical particles \( g = 2/3 \) and for single-phase particle sets possessing a homogeneous size distribution \( g \sim 1 \). Higher g values (\( > 1 \)) indicate a broad distribution of particle size and shape.

Integration of eq. (3) yields current-potential (i-E) curves for chronoamperometry and linear scan voltammetry. In the last case, an equation similar to that derived by Brainina et al. for the case of irreversible reduction of solid particles in a carbon-paste electrode, applies for a voltammetric peak:

$$E_p = E_o - \frac{RT}{\alpha n F} \left[ \ln \left( \frac{\alpha n F \nu}{RT} \right) + \ln k_o \right]$$

(4)
Table 1. Summary of the electrochemical processes involving iron species in FeZSM-5. Peak potentials in mV vs. SCE from DPVs in 0.1 M HCl (except processes C₉ and A₉, in 0.1 M Na₂EDTA); \( \nu = 20 \text{ mV s}^{-1}; \Delta U = 80 \text{ mV} \).

<table>
<thead>
<tr>
<th>Peak(s)</th>
<th>( E_p/ \text{mV} )</th>
<th>Species involved</th>
<th>Assignment (^a)</th>
<th>Electrochemical process</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁/A₂</td>
<td>+20/+60</td>
<td>Framework</td>
<td>YE</td>
<td>( \text{Z<a href="b">O}_3\text{Fe}^{2+}(\text{OH})</a> + M^+ (aq.) + e^- \Rightarrow \text{Z<a href="b">O}_3\text{Fe}^{2+}(\text{OH})</a> + M^+ - Z(b) )</td>
</tr>
<tr>
<td>C₄/A₄</td>
<td>-180/-120</td>
<td>Fe-ions</td>
<td>YE</td>
<td>( \text{Z-Fe}_2^{3+}\text{O}_y(b) + x \text{H}^+(aq.) + x e^- \Rightarrow \text{Z-Fe}_2^{3+}\text{O}_y(b) )</td>
</tr>
<tr>
<td>C₁/A₁</td>
<td>+650</td>
<td>Oligonuclear oxo-Fe species</td>
<td>YE</td>
<td>( \text{Fe}^{3+}(b) + M^+ (aq.) + e^- \Rightarrow \text{Fe}^{3+} - Z + M^+ - Z(b) )</td>
</tr>
<tr>
<td>C₅</td>
<td>-450</td>
<td>Isolated Fe-ions</td>
<td>YE</td>
<td>( \text{Fe}^{3+} + 2x \text{H}^+(aq.) + (2x-2) e^- \rightarrow \text{Fe}^{2+} (aq.) + x \text{H}_2\text{O} )</td>
</tr>
<tr>
<td>C₆</td>
<td>-650</td>
<td>RD/MD</td>
<td>( \text{Fe}^{3+} + 2x \text{H}^+(aq.) + 2x e^- \rightarrow \text{Fe}^0 + x \text{H}_2\text{O} )</td>
<td></td>
</tr>
<tr>
<td>C₀</td>
<td>-360</td>
<td>RD/MD</td>
<td>( \text{Fe}^{3+} + x \text{H}_2\text{EDTA}^2- (aq.) + (2x-2) e^- \rightarrow \text{Fe(EDTA)}^{3+} (aq.) + x \text{H}_2\text{O} + (x-1) \text{EDTA}^4- )</td>
<td></td>
</tr>
<tr>
<td>A₆</td>
<td>-350</td>
<td>OD</td>
<td>( \text{Fe}^{3+} + 2y \text{H}^+(aq.) \rightarrow \text{Fe}^{3+} (aq.) + y \text{H}_2\text{O} + (3-2y) e^- )</td>
<td></td>
</tr>
<tr>
<td>A₉</td>
<td>-120</td>
<td>OD</td>
<td>( \text{Fe}^{3+} + y \text{H}_2\text{EDTA}^2- (aq.) \rightarrow \text{FeEDTA}^- (aq.) + y \text{H}_2\text{O} + (y-1) \text{EDTA}^4- + (3-2y) e^- )</td>
<td></td>
</tr>
<tr>
<td>A₅</td>
<td>-250</td>
<td>AS</td>
<td>( \text{Fe}^0 \rightarrow \text{Fe}^{3+} (aq.) + 3 e^- )</td>
<td></td>
</tr>
<tr>
<td>C₈/A₈</td>
<td>-280/-360</td>
<td>Fe-ions in solution</td>
<td>D</td>
<td>( \text{Fe}^{3+} + e^- \Rightarrow \text{Fe}^{3+} (aq.) + (x - y) \text{Cl}^- )</td>
</tr>
<tr>
<td>C₅/A₇</td>
<td>-750/-650</td>
<td>MD</td>
<td>( \text{Fe}^{3+} (aq.) + 2 e^- \Rightarrow \text{Fe}^0 )</td>
<td></td>
</tr>
</tbody>
</table>

\( b \) boundary, \( Z \) zeolite.

\(^a\) YE: electron-transfer process on iron species attached to the zeolite boundary; RD: reductive dissolution; OD: oxidative dissolution; AS: anodic stripping of metallic layers; D: electron-transfer process involving species in solution; MD: metal deposition.
Experimental data for the cathodic peak $C_5$ in Fig. 6 is in agreement with this model. From the linear dependencies of the peak potential with the pH and the logarithm of the scan rate:

\[
E_p = -370 - 60 \text{ pH} \quad \text{at} \quad \nu = 10 \text{ mV s}^{-1}
\]
\[
E_p = -465 - 115 \log \nu \quad \text{at} \quad \text{pH} = 1
\]

the kinetic parameters in eq. (4) can be estimated, resulting in $\alpha n = 0.51$ and $k_v = 0.024 \text{ s}^{-1}$. These values are in excellent agreement with those calculated from the Tafel plots (log $i$ vs. $E$) for the rising part of voltammetric responses in Fig. 6 and were used to obtain theoretical $i$-$E$ curves, using different values of the coefficient $g$. A set of these representations is compared in Fig. 7, which includes the experimental curve of the ex-FeZSM-5 modified PFE in 0.1 M HCl aqueous solutions using the estimated values of $\alpha n$ and $k_v$. The best fit was obtained for $g$ values ranging from 2.25 to 2.75, suggesting that iron oxide nano-particles in ex-FeZSM-5 consist of particle sets with a broad rate constant distribution. The relative heterogeneity of iron oxide nano-particles indicated by such high $g$ values and the homogeneous particle size indicated by TEM (1-2 nm) should not lead to confusion. TEM indicates the morphological characteristic of these particles, while the $g$ factor suggests a large heterogeneity of the iron oxide nano-particles in size or shape leading to a different electrochemical reactivity. The diverse location of nano-particles in the electrochemically accessible sites of the zeolite must also be reflected in a large $g$ value.

![Graph](image)

Fig. 7. Comparison of experimental voltammetric curve (solid line) corresponding to the peak $C_5$ of ex-FeZSM-5 modified PFE in 0.1 M HCl aqueous solution and theoretical $i$-$E$ curves (dashed lines) with different $g$ coefficients: (a) 1.5, (b) 2.0, and (c) 2.5, using $\alpha n = 0.51$ and $k_v = 0.024 \text{ s}^{-1}$; $\nu = 10 \text{ mV s}^{-1}$.

4.3.2. Experiments with complexing agents

Cyclic voltammetry

To further investigate the electron transfer mechanism in FeZSM-5, cyclic voltammograms of a 0.2 mM Fe(NO$_3$)$_3$·9H$_2$O aqueous solution at a bare GCE and of ex-FeZSM-5 modified PFE, in 0.10 M Na$_2$EDTA aqueous solutions were recorded (Fig. 8). In reductive dissolution processes, protonation or addition of a complexing agent precedes the charge transfer process, which is followed by removal of the generated ions from the electrode surface and
their diffusion to the bulk of the electrolyte solution.\textsuperscript{24,30} In the presence of a strong
complexing agent like EDTA\textsuperscript{2-}, reductive dissolution of iron oxide nano-particles (and in
general iron oxide particles) must proceed more or less rapidly depending on the
accessibility of iron species to the complexing agent.

The cathodic-to-anodic peak potential separation observed in Fig. 8a is attributed to a
chemical reaction succeeding the electron transfer step (EC mechanism).\textsuperscript{40} For the zeolite-
modified electrode, peaks at \(-0.36\) V (C\textsubscript{9}) and \(-0.20\) V (A\textsubscript{9}) were identified. The cathodic-to-
anodic peak potential is significantly lower than that of a 0.2 mM Fe(NO\textsubscript{3})\textsubscript{3} aqueous solution
(0.16 vs. 0.5 V, respectively), which suggests that a pure extrazeolitic electron transfer
mechanism is not taking place. Peak C\textsubscript{9} can be assigned to EDTA-assisted reductive
dissolution of iron oxide nano-particles and/or the reduction of extra-framework Fe(III)
species promoted by a relatively fast complexation step. Peak A\textsubscript{9} should correspond to an
oxidative dissolution process involving Fe(II) oxide nano-particles eventually overlapped
with the oxidation of Fe(II)-EDTA complexes in solution. After the measurement with the
zeolite-modified electrode, the resulting solution provided very weak voltammetric peaks at
potentials corresponding to ions in solution, indicating that these processes involve
essentially electrode-confined species. This is confirmed by the CV at a bare GCE immersed
into the resulting solution after 10 cycles performed on a ex-FeZSM-5 modified electrode
(Fig. 8c). The iron concentration in the solution resulting from the dissolution of iron nano-
particles was below \(10^{-6}\) M, in agreement with the foregoing considerations.

![Graph](image)

**Fig. 8.** CVs of (a) a 0.2 mM Fe(NO\textsubscript{3})\textsubscript{3} solution in 0.1 M Na\textsubscript{2}EDTA aqueous solution of the bare GCE, (b) ex-
FeZSM-5-modified PFE in the same electrolyte, and (c) the resulting solution after 10 cycles performed on
a ex-FeZSM-5 modified PFE at a bare GCE; \(v = 50\) mV s\textsuperscript{-1}. 

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**Differential pulse voltammetry**

To increase the sensitivity with respect to CV, differential pulse voltammetry (DPV) was used. Fig. 9 shows cathodic and anodic DPVs of PFEs modified by the different zeolites in 0.1 M aqueous solutions of Na₂EDTA. For FeZSM-5c and ex-FeZSM-5 the couple C₉/A₉ was identified. Peak potentials of peaks C₉ and A₉ in CVs are separated with respect to those recorded in DPVs (0.16 V and 0.05 V, respectively). This can be rationalized on considering that reductive/oxidative dissolution processes must be quite sensitive to the capacitive contribution of the DPV signal. Peaks at +0.18 (C₃) and 0.01 (C₄) V were identified in FeZSM-5as, as well as their anodic counterparts A₃ and A₄. This couple can be ascribed to electrode processes involving iron framework centers in the zeolite matrix. The electrode processes C₁/A₁ and C₂/A₂ however, cannot be identified.

The peak currents of ex-FeZSM-5 in Na₂EDTA electrolytes are consistently higher than those in HCl + NaCl and H₂SO₄ electrolytes. This is due to the increase in the dissolution rate of iron oxide nano-particles promoted by the EDTA complexation. Since this complexation must be restricted to iron ions in solution and eventually located in the more external sites of the zeolite, these results give an additional indication that only iron species located at the more external zeolite 'boundary' are electroactive under our experimental conditions.

![Graph showing DPVs](image)

**Fig. 9.** Cathodic (a, b, c) and anodic (d, e, f) DPVs in 0.1 M Na₂EDTA aqueous solution for PFEs modified with (a and d) FeZSM-5as, (b and e) FeZSM-5c, and (c and f) ex-FeZSM-5; v = 20 mV s⁻¹; ΔU = 80 mV.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Eₚ / mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₉</td>
<td>-360</td>
</tr>
<tr>
<td>A₉</td>
<td>-200</td>
</tr>
</tbody>
</table>

4.4. Electrochemistry of zeolite-associated iron species

As previously noted, the electrochemical processes C₁-C₄ and A₁-A₄ have been attributed to different iron species associated with the zeolite, *i.e.* in the framework or channels. The assignment is complicated due to the different zeolite-associated species that may be responsible for the observed electrochemistry. In order to elucidate the nature of the
electrochemical processes involving zeolite-associated species the experimental current-potential curves can be compared with those expected for two representative limiting cases: (i) a diffusion-controlled electron-transfer process involving dissolved species and (ii) a electron-transfer step involving oxidized and reduced species strongly attached to the electrode surface (see §2).

Due the uncompensated ohmic drop associated with the modified electrode configuration, the voltammetric response can be seriously distorted, and then the use of the region of voltammograms passing a peak can be considered as the most convenient approach for differentiating between both limiting cases, as it has been discussed for Mn(salen) complexes in Y zeolite.\textsuperscript{41} For a diffusion-controlled process, the Cottrell equation applies in the voltammetric curve at 100-150 mV after a voltammetric peak:

\[ i = n F A c \frac{D}{\pi t} \]  

(5)

This equation can be rewritten for a linear scan voltammetric experiment as:\textsuperscript{42,43}

\[ \frac{1}{i^2} = \frac{\pi}{D \nu (n F A c)^2} (E_{\text{diff}} - E) \]  

(6)

In contrast, for electron-transfer processes involving electroactive species strongly attached to the electrode surface, sharp voltammetric peaks are obtained (see Fig. 2b), with a fast decay of the current passing the voltammetric peak. Assuming a reversible process, the voltammetric curves must verify the following equation:\textsuperscript{22}

\[ i = \frac{n^2 F^2 \nu A \Gamma \alpha_b c_i}{b_{\text{eq}} b_{\text{d}} R T \left[ 1 + \frac{b_{\text{eq}}}{b_{\text{d}}} \exp \left( \frac{n F (E - E_0)}{RT} \right) \right]} \]  

(7)

For strongly adsorbed reactants and products, this model predicts symmetrical voltammetric curves with:

\[ E_{\text{ca}} = E_{\text{ca}} = E_0 + \frac{R T}{n F} \ln \left( \frac{b_{\text{eq}}}{b_{\text{d}}} \right) \]  

(8)

On comparing theoretical \( i-E \) plots for processes (i) and (ii) defined above, normalized to have identical peak potential and peak current, one can observe that the rising part of both voltammetric peaks is almost indistinguishable, whereas the diffusive region is remarkably different (Fig. 10A, curves a and b). In Fig. 10B theoretical log \( (i/i_p) \) vs. \( E-E_p \) plots for such electrode processes are compared with experimental data of the peak C\textsubscript{1}. Although experimental data diverges from theoretical curves for both (i) and (ii) models, the fast decay at potentials passing the voltammetric peak refers to an electron transfer process, similar to that of strongly electrode-attached species distorted by uncompensated ohmic drops.

\subsection{Framework iron species}

As it was previously discussed, couples C\textsubscript{3}/A\textsubscript{3} and C\textsubscript{4}/A\textsubscript{4} in Fig. 6 can be described in terms of one-electron transfer processes involving iron species in framework positions. Electrochemically accessible framework Fe(III) species attached to the zeolite matrix by
oxygen bridges, should be located at the zeolite boundary. These species can be labeled as topological redox isomers, as described for zeolite-encapsulated electroactive complexes by Bessel and Rolison.\textsuperscript{17} The reduction of such framework redox isomers requires an electron-transfer step coupled with interchange of a charge-balancing positive ion from the solution. The peak potentials of the couples C\textsubscript{3}/A\textsubscript{3} and C\textsubscript{4}/A\textsubscript{4} couples are essentially pH-independent. The electrochemical mechanism can be tentatively represented as:

\[
Z[O_\text{3}Fe^{II}(\text{OH})]\ (b) + \text{M}^+ (aq.) + e^- \rightleftharpoons Z[O_\text{3}Fe^{II}(\text{OH})]\ (b) + \text{M}^+ - Z (b) \tag{9}
\]

where Z denotes the zeolite and b the iron sites at the ‘boundary’ region of the zeolite. This process involves the incorporation of a charge-compensating cation from the electrolyte in the zeolite. The redox isomers of the zeolite framework consist presumably of O\textsubscript{3}FeOH units similar to O\textsubscript{3}TiOH, whose generation from hydrolysis of Si-O-Ti bridges has been reported.\textsuperscript{44–46} This redox process is similar to the reduction of framework titanium centers described for titanium silicate.\textsuperscript{47} The appearance of two responses in the voltammogram suggests the presence of framework iron ions of different nature (in electrochemical terms), which might be induced by the position in the zeolite or the atomic environment.

The peak potentials of the C\textsubscript{3}/A\textsubscript{3} and C\textsubscript{4}/A\textsubscript{4} couples also remain essentially independent on the potential scan rate, as expected for a thin-layer behaviour. As shown in Fig. 11, the relative peak current of the processes C\textsubscript{3}/A\textsubscript{3} and C\textsubscript{4}/A\textsubscript{4} varies on modifying the potential scan rate, the second couple being enhanced with regard to the first on increasing the potential scan rate. The different electrochemical response of both redox isomers can be explained by the different amount and accessibility of these boundary-associated framework iron species. This can be rationalized on considering that in the system under investigation, electroactive iron centers are probably confined to a narrow region of the zeolite grains. Roughly, this means that the electrochemically accessible centers are exhausted at a certain moment. It is conceivable that the most strongly attached redox isomer may be more reluctant to be depleted from the boundary region to the electrolyte solution. Accordingly, the observation of this species is favoured in long experiments; \textit{i.e.}, at low scan rates. The observation of the less strongly zeolite-attached isomer will be enhanced at short experiment durations (high scan rates). Concluding, the
obtained results suggest that the couple $C_3/A_3$ is attributable to framework iron centers more strongly attached to the zeolite 'boundary' than those responsible for the $C_4/A_4$ couple.

4.4.2. Extra-framework iron species

The couples $C_1/A_1$ and $C_2/A_2$, which appear at potentials ranging from +0.75 to +0.30 V were mainly observed in ex-FeZSM-5. As it is shown in Fig. 6, both cathodic and anodic peaks are weaker than the reductive dissolution of iron oxide nano-particles ($C_3$), suggesting that zeolite-attached iron species generated during steam treatment are involved in such electrochemical processes. Peak potentials of both couples vary slowly with the potential scan rate, $\nu$ (at $pH = 1$):

$$E_p (C_1) = 635 - 65 \log \nu$$
$$E_p (A_1) = 750 - 60 \log \nu$$
$$E_p (C_2) = 280 - 58 \log \nu$$
$$E_p (A_2) = 330 - 55 \log \nu$$

The peak potential of the $C_2/A_2$ couple is pH-independent, while the peak potential of the $C_1/A_1$ couple varies with the pH. For $C_1$ at $\nu = 10$ mV s$^{-1}$:

$$E_p (C_1) = -520 - 65 pH$$

The theoretical LSV curves for electroactive species strongly attached to the electrode surface are depicted in Fig. 12. The pH-independent peak $C_2$ is described as a one-electron process involving octahedrally coordinated extra-framework Fe ions located in the zeolite boundary, which may lead to either Fe$^{2+}$ ions in solution, according to:
$\text{Fe}^{\text{III}}\text{-Z (b)} + \text{M}^+(\text{aq.}) + e^- \rightarrow \text{Fe}^{\text{II}}\text{(aq.)} + \text{M}^+\text{-Z (b)}$ \hspace{1cm} (10)

or to Fe(II) species attached to the zeolite matrix:

$\text{Fe}^{\text{III}}\text{-Z (b)} + \text{M}^+(\text{aq.}) + e^- \rightarrow \text{Fe}^{\text{II}}\text{-Z} + \text{M}^+\text{-Z (b)}$ \hspace{1cm} (11)

It should be noted that the anodic counterpart of the process described by eq. (10) must merely correspond to a solution-phase oxidation:

$\text{Fe}^{\text{II}}\text{(aq.)} \rightarrow \text{Fe}^{\text{III}}\text{(aq.)} + e^-$ \hspace{1cm} (12)

whereas the anodic process coupled with eq. (11) involves presumably a charge-compensating cation from the zeolite boundary to the solution:

$\text{Fe}^{\text{II}}\text{-Z (b)} + \text{M}^+\text{-Z (b)} \rightarrow \text{Fe}^{\text{III}}\text{-Z} + \text{M}^+(\text{aq.}) + e^-$ \hspace{1cm} (13)

The small potential separation between the cathodic and anodic peaks in the voltammetric profile, close to that of electroactive species strongly attached to the electrode surface, strongly suggest that the reaction network formed by eqs. (11) and (13) applies.

The slope of the $E_p$ vs. pH dependency of $C_1$ (65 mV) suggests that the electron transfer step is accompanied by transfer of one proton per electron. The electrochemical process can be expressed as:

$\text{Z-Fe}^{\text{III}}\text{O}_y\text{(b)} + x\text{H}^+(\text{aq.}) + x e^- \rightarrow \text{Z-Fe}^{\text{II}}\text{O}_{y-x}(\text{OH})_x\text{(b)}$ \hspace{1cm} (14)

The model is consistent with the idea that the $C_1/A_1$ couple is due to electroactive iron centers, presumably representing dinuclear or oligonuclear oxo-iron species attached to the zeolite boundary. These species might be of similar nature to those previously proposed on the basis of EXAFS measurements over FeZSM-5 prepared by a sublimation method.\textsuperscript{48,49}

---

**Fig. 12.** Comparison of the theoretical (dashed lines) and experimental (solid lines) LSVs of ex-FeZSM-5 modified electrodes in 0.1 M H$_2$SO$_4$ aqueous solutions; $\nu = 10$ mV s$^{-1}$.  

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4.5. Evaluation of the voltammetric response technique

Comparison of electrochemical response of the Fe-zeolites provides valuable information about the disappearance and appearance of distinctive electroactive species during different preparation stages of ex-framework FeZSM-5. This technique provides a powerful fingerprint of the catalyst constitution, since it enables simultaneous identification and differentiation of the various species co-existing in the material based on their different electroactivity. This uniqueness of the voltammetric technique strongly contrasts with other specific techniques to characterize iron, which are limited by the size of the species (TEM) and the oxidation state (Fe$^{2+}$ in FT-IR after NO adsorption or Fe$^{3+}$ in EPR), or cases where iron-species of different nature overlap in the signal in question (e.g. $^{57}$Fe Mössbauer, H$_2$-TPR, UV-Vis). The distinction of different species proves the heterogeneous nature of the iron species in the material and provides essential information for the interpretation of average techniques. The information provided by the electrochemical method has implications for the correct interpretation of average techniques applied to these systems, e.g. for the determination of the average Fe coordination in the catalyst by EXAFS.

The electrochemical method is reproducible, flexible, fast, relatively cheap, and very small amount of sample is required. The procedure for electrode preparation and recording voltammetric information is also relatively simple. Since the electroactive species constitute only a small fraction of the iron in the sample, i.e. the electron transfer occurs in the boundary of the zeolite grains, no quantification of species or determination of relative amounts is possible. Indeed, the electron transfer mechanism should be investigated in more detail in order to understand the process in microscopic terms. This will provide essential information to improve interpretation of the electrochemical profiles. Obviously, interpretation and final assignment of voltammetric responses via the procedures described along the chapter is facilitated by extensive information from the various techniques presented in Chapter 5. However, at this moment, a “quick” visualization of the constitution of the catalyst with respect to iron is the main utility. This method is not limited to a certain structure or metal, and is thus considered as a very promising technique to characterize “multi-species” heterogeneous catalysts.

5. Conclusions

From the analysis of the electrochemical data of samples during the preparation of ex-framework FeZSM-5, the following conclusions can be drawn:

- Electrochemical methods constitute unique techniques to characterize electroactive iron species in isomorphously substituted FeZSM-5, as well as the corresponding materials obtained after calcination and steam treatment. Different iron species have been identified, including tetrahedral framework iron, octahedral extra-framework iron ions, dinuclear or oligonuclear oxo-iron species, and iron oxide nano-particles. The simultaneous identification of various electroactive iron species integrates the information achieved by other techniques. The technique is cheap (accessible), flexible, reproducible, and the experimental procedures are relatively simple.

- A systematic procedure is given to sequentially assign the different transitions observed in the voltammograms to certain electroactive species (oxidation state, structure) in the zeolites. The interpretation of the profiles is mainly based on the shape of voltammetric curves in different electrolytes (NaCl, HCl, H$_2$SO$_4$, Na$_2$EDTA), the electrode preparation procedure, and the dependence of peak potentials with pH and scan rate.
• The electrochemical measurements support the surface-mediated electron-transfer mechanism in the 'boundary' region of the zeolite. Pure extrazeolitic and/or intrazeolitic mechanisms can be excluded.

• The electrochemistry of iron oxide nano-particles existing in ex-FeZSM-5 is based on a proton-assisted reductive dissolution process at -0.45 V vs. SCE similar to that of iron oxides and hydrous oxides. The voltammetric pattern of these iron nano-particles suggests that there is a large heterogeneity (shape and size) in the electrochemical reactivity. The identification of iron (II) oxide nano-particles at potentials near to -0.2 V in ex-FeZSM-5 suggests the simultaneous co-existence of Fe(III) and Fe(II) in the steamed material, in good agreement with other techniques presented in Chapter 5.

• Isomorphously substituted Fe(III) ions attached to the zeolite lattice by oxygen bridges display quasi-reversible one-electron transfer processes at +0.02 and -0.18 V vs. SCE. These processes presumably involve two framework species with different electroactivity. This might be related with a different position (or atomic environment) of the iron atoms in the zeolite.

• Extra-framework iron (III) ions in isolated positions exhibit a quasi-reversible pH-independent reduction at +0.30 V vs. SCE whereas dinuclear and/or oligonuclear oxo-iron species attached to the zeolite boundary exhibit a pH-dependent redox process at +0.65 V. In both cases, the voltammetric curves are close to that of electron transfer steps for strongly electrode-attached species.

Acknowledgements. J.P.R. thanks Dr. A. Doménech and Dr. A. Ribera (University of Valencia, Spain) for the intensive and enjoyable cooperation in the development of electrochemical methods to characterize metal-zeolites. Prof. dr. J.A.R. van Veen is gratefully acknowledged for valuable comments on this chapter.

Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>surface area of the electrode</td>
<td>m²</td>
</tr>
<tr>
<td>bᵢ</td>
<td>specific activity coefficients of oxidized or reduced i species attached to the electrode (= exp(-ΔGᵢ° / RT))</td>
<td>-</td>
</tr>
<tr>
<td>c*</td>
<td>concentration of electroactive species</td>
<td>mol m⁻³</td>
</tr>
<tr>
<td>i</td>
<td>current</td>
<td>A</td>
</tr>
<tr>
<td>F</td>
<td>Faraday (1 F = 96500 C)</td>
<td>-</td>
</tr>
<tr>
<td>g</td>
<td>geometric factor in the surface reaction kinetic equation for a set of particles</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>diffusion coefficient</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>E</td>
<td>working electrode potential</td>
<td>V</td>
</tr>
<tr>
<td>Eₐₙ</td>
<td>potential at which the diffusive behaviour starts</td>
<td>V</td>
</tr>
<tr>
<td>E₀</td>
<td>standard electrode potential of the couple</td>
<td>V</td>
</tr>
<tr>
<td>kₒ</td>
<td>rate constant of the electrode at the standard potential of the electrode</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>n</td>
<td>number of electrons involved in the electrochemical process</td>
<td>-</td>
</tr>
<tr>
<td>q</td>
<td>charge</td>
<td>C</td>
</tr>
<tr>
<td>qₜ</td>
<td>total charge passed during the reaction</td>
<td>C</td>
</tr>
<tr>
<td>R</td>
<td>universal gas constant</td>
<td>J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>ΔGᵢ°</td>
<td>standard free energy of surface attachment of oxidized or reduced</td>
<td>J mol⁻¹</td>
</tr>
<tr>
<td>ΔU</td>
<td>pulse amplitude</td>
<td>V</td>
</tr>
<tr>
<td>α</td>
<td>electron transfer coefficient (= 1 for ideally reversible processes)</td>
<td>-</td>
</tr>
</tbody>
</table>
\( \nu = \) potential scan rate  \( V \, s^{-1} \)

\( \Gamma_i = \) surface concentration of oxidized or reduced \( i \) species  \( \text{mol m}^{-2} \)

**Subscripts and superscripts**

- \( \text{cat} \) = cathodic process
- \( \text{an} \) = anodic process
- \( \text{ox} \) = oxidized form
- \( \text{p} \) = peak (potential or current)
- \( \text{red} \) = reduced form
- \( x, y \) = stoichiometric fractions

**Acronyms and abbreviations**

- \( b \) = boundary region of the zeolite crystal
- \( \text{CV} \) = cyclic voltammetry
- \( \text{DPV} \) = differential pulse voltammetry
- \( \text{GCE} \) = glassy carbon electrode
- \( \text{GPCE} \) = graphite polyester composite electrode
- \( \text{LSV} \) = linear scan voltammetry
- \( \text{PFE} \) = polymer film electrode
- \( Z \) = zeolite

**References**

Ex-framework FeZSM-5 for Control of N₂O in Simulated Tail-Gases

In this chapter, the performance of a novel ex-framework FeZSM-5 catalyst for direct N₂O decomposition in simulated tail-gas from nitric acid plants (containing O₂, NOₓ, and H₂O) and combustion processes (containing O₂, CO₂, H₂O, and SO₂) is presented. The specific activity per mol of Fe of the ex-framework catalyst in N₂O/He was 4-10 times higher than observed for FeZSM-5 catalysts prepared by conventional solid and liquid-ion exchange and sublimation methods. The presence of NOₓ and SO₂ has a positive effect on the N₂O conversion over ex-FeZSM-5, decreasing the inhibition effect of H₂O, while O₂ and CO₂ do not influence catalytic performance. The operation temperature of ex-FeZSM-5 is decreased ~100 K by addition of propene to the feed mixture (selective catalytic reduction). The stability of ex-framework FeZSM-5 for direct N₂O decomposition, in the absence of any reductant, was remarkable, showing no significant deactivation (at N₂O conversion levels ranging from 20 to 65%) after 600 h time on stream. Sublimed and especially ion-exchanged FeZSM-5 catalysts showed a strong irreversible deactivation in feed mixtures containing H₂O and SO₂. The performance of the ex-framework catalyst has also been compared with that of different Rh-based catalysts. Co-Rh,Al mixed oxide, derived from a hydrotalcite precursor containing these metals, shows a remarkably high N₂O decomposition activity in N₂O/He. The initial activity of this catalyst in a simulated tail-gas mixture is higher compared to ex-FeZSM-5, but is severely suppressed by NO and the catalyst deactivated in the presence of H₂O and SO₂. This also applies to other Rh-based catalysts. Ex-framework FeZSM-5 appears to allow a flexible and cost-effective catalytic technology in tail-gases from chemical production and combustion processes. Different abatement options have been considered, depending on the source and the operating conditions of the process. Aspects of (monolithic) reactor design for an optimal catalyst implementation are discussed.
1. Introduction

Nitrous oxide (N₂O) has been identified as a greenhouse gas and a significant contributor to the destruction of ozone in the stratosphere.¹⁴ N₂O is produced by both natural and anthropogenic sources (Table 1). Agriculture is a major anthropogenic source, but control of these emissions is difficult due to the very diffuse nature of N₂O emissions. The major industrial source of N₂O is the production of nitric acid, which is a key bulk chemical in the fertiliser industry. N₂O is also produced during manufacture of adipic acid, glyoxal, caprolactam, acrylonitrile, and in general organic synthesis using HNO₃ as the oxidant or reactions involving ammonia oxidation. The emission of the chemical process industry is concentrated in a limited number of large N₂O sources, which holds the promise for an economic and efficient reduction strategy to fulfil the commitment in Kyoto (1997).⁶ Stationary combustion of fossil fuels, biomass, and municipal and industrial waste also involves a significant N₂O emission. An increasing contributor of N₂O releases from the catalytic converters in motor vehicles, N₂O being formed during NOₓ control.

<table>
<thead>
<tr>
<th>Table 1. Estimated amounts of N₂O emitted by various human activities.³⁷</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type of source</strong></td>
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<tr>
<td>Natural</td>
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<td>Soils</td>
</tr>
<tr>
<td>Oceans</td>
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<tr>
<td>Atmospheric chemistry</td>
</tr>
<tr>
<td><strong>Anthropogenic</strong></td>
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<td>Agriculture (including fertilizers)</td>
</tr>
<tr>
<td>Nitric acid production</td>
</tr>
<tr>
<td>Adipic acid production</td>
</tr>
<tr>
<td>Fossil-fuel combustion (stationary)</td>
</tr>
<tr>
<td>Fossil-fuel combustion (mobile)</td>
</tr>
<tr>
<td>Biomass combustion</td>
</tr>
<tr>
<td>Sewage treatment</td>
</tr>
<tr>
<td><strong>Total of all sources</strong></td>
</tr>
</tbody>
</table>

* Emissions of other chemical production processes are not quantified. b Emission is uncertain.

Table 2 gives typical concentration values of various sources. Emissions associated with nitric acid plants and combustion processes are characterized by concentrations of N₂O in the tail-gas below 1 vol.% and typically in the 0.05-0.5 vol.% range.⁴⁵ Different abatement technologies have been successfully developed for the other major industrial source, i.e. adipic acid plants, but these are not applicable to nitric acid plants or combustion processes.⁴⁵,⁷ In adipic acid plants, due the high N₂O concentration and the exothermicity of the decomposition reaction, a large increase in the temperature occurs within the catalyst bed. For instance, the decomposition of N₂O contained in a gas at 35 vol.% of N₂O leads to an adiabatic temperature rise of the gas of 923 K. In this temperature window, a large number of catalysts exhibit considerable activity. So, in this case, the activity of the catalyst is not a critical factor for the effectiveness of the technology.

| Table 2. Typical concentrations of components (ppm) in N₂O containing off-gases.³⁷ |
|---------------------------------|------|------|------|------|------|------|------|
| **Source** | **T / K** | **N₂O** | **NOₓ** | **O₂** | **H₂O** | **CO** | **SO₂** |
| Adipic acid | 475-575 | 25-40% | 0.5-1% | 4% | 2-3% | 300 | - |
| Nitric acid | 450-725 | 300-3000 | 300-3000 | 2-4% | 2-3% | - | - |
| FBC* | 975-1175 | 50-500 | 50-500 | 2-10% | ca. 10% | 10-1000 | < 2000 |
| TWC* | 300-1075 | 0-1000 | 0-2000 | 0-1000 | ca. 10% | 0-4000 | 20-100 |

* Fluid-bed combustor; b Aged three-way catalysts, values fluctuate due to air/fuel ratio.
In general, direct catalytic decomposition of N\textsubscript{2}O into N\textsubscript{2} and O\textsubscript{2} is an attractive option to reduce N\textsubscript{2}O emissions, but none of the catalysts proposed in the literature show a good activity and stability in N\textsubscript{2}O conversion under realistic conditions of feed composition and space velocities.\textsuperscript{7,8} Transition (Cu, Co, Ni) and noble-metal based catalysts (Rh, Ru, Pd) on different supports (ZnO, CeO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, ZrO\textsubscript{2}, or calcined hydrotricalites) are very active for N\textsubscript{2}O decomposition in N\textsubscript{2}O/He feeds, but the presence of other gases in the feed (NO\textsubscript{x}, H\textsubscript{2}O, SO\textsubscript{2}, CO) leads to strong inhibition and/or deactivation.\textsuperscript{9-17}

FeZSM-5 is an interesting catalyst because N\textsubscript{2}O conversion shows anomalous behaviour in the presence of tail-gas components compared to other catalytic systems.\textsuperscript{9,18-20} Different preparation methods have been reported to optimize the catalytic performance of FeZSM-5, not only in N\textsubscript{2}O decomposition,\textsuperscript{21-23} but also in de-NO\textsubscript{x} HC-SCR and selective oxidations.\textsuperscript{24-26} The methods normally applied include solid- and liquid ion exchange, or sublimation. From the different results in the literature it is concluded that development and optimization of preparation routes to prepare FeZSM-5 may lead to improved catalyst performance in the different processes catalyzed by this material.\textsuperscript{21,22,23,26} Several authors have claimed a good stability of FeMFI catalysts prepared by sublimation and (aqueous) ion-exchanged for N\textsubscript{2}O reduction in the presence of H\textsubscript{2}O and/or SO\textsubscript{2},\textsuperscript{8,14,22,23,29,30} This behaviour is induced by the co-addition of light hydrocarbons (methane, propane, propene, or LPG) as a reductant in the feed mixture, which also lowers the light-off temperature for N\textsubscript{2}O decomposition. Other authors also claimed that the use of reductant (hydrocarbon or ammonia) over Fe-zeolites reduces N\textsubscript{2}O and NO emissions simultaneously,\textsuperscript{24,25} but the catalysts do not exhibit sufficient activity due to different operation temperatures of both processes. The addition of reductant is not attractive in tail-gas abatement units due to the high operation costs associated. Data on stability of FeZSM-5 catalysts for direct N\textsubscript{2}O decomposition (without addition of reductant) in simulated tail-gases is hardly available.\textsuperscript{19,20}

In this paper we present a high activity and stability of a FeZSM-5 catalyst prepared via a novel ex-framework route in direct N\textsubscript{2}O decomposition in simulated tail-gases (containing O\textsubscript{2}, CO\textsubscript{2}, NO\textsubscript{x}, SO\textsubscript{2}, and H\textsubscript{2}O) at high space velocities (36000-120000 h\textsuperscript{-1}). The catalytic behaviour of ex-framework FeZSM-5 is compared with FeZSM-5 catalysts prepared by (solid and liquid) ion-exchange and sublimation methods and with Rh-based catalysts on different supports, including Al\textsubscript{2}O\textsubscript{3}, ZSM-5, USY, and calcined hydrotricalites. The implementation of ex-framework FeZSM-5 for N\textsubscript{2}O control (abatement and reutilization) in different sources is presented, including the analysis of various process options and aspects of reactor design.

2. Experimental

2.1. Catalyst preparation

FeZSM-5 catalysts

Isomorphously substituted FeZSM-5 was synthesized hydrothermally using TPAOH as the template.\textsuperscript{28} The as-synthesized samples were calcined in air atmosphere at 823 K for 10 h and converted into the H-form by three consecutive exchanges with a NH\textsubscript{4}NO\textsubscript{3} solution (0.1 M) (denoted as FeZSM-5c). Finally, the catalysts were activated in flowing steam at ambient pressure (water partial pressure of 300 mbar and 30 ml STP min\textsuperscript{-1} of N\textsubscript{2} flow) at 873 K during 5 h (denoted as ex-FeZSM-5). Other FeZSM-5 catalysts were prepared by solid-ion exchange with FeCl\textsubscript{3}-4H\textsubscript{2}O (sie-FeZSM-5) and liquid (aqueous) ion-exchange with Fe(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O (lie-FeZSM-5), following conventional procedures described in the literature.\textsuperscript{24,25} NH\textsubscript{4}-ZSM-5 (CBV 8020; Zeolyst) was used as the parent zeolite. Sub-FeZSM-5 was prepared by sublimation of FeCl\textsubscript{3} on H-ZSM-5 (Degussa), according to the method described elsewhere.\textsuperscript{26}
**Rh-based catalysts**

Rh/Al₂O₃, Ru/ZSM-5, and Rh/USY were prepared by incipient wetness method, using appropriate solutions of Rh(NO₃)₃, Al₂O₃ (CK300, Ketjen), NH₄-ZSM-5 (CBV 8020; Zeolyst), H-USY (CBV 720; Zeolyst) were used as supports. After the impregnation procedure, the samples were dried at 373 K for 5 h and calcined in static air at 825 K. Ex-Co-Rh,Al-HTlc was prepared by coprecipitation at constant pH and temperature at low saturation conditions and thermal decomposition in static air at 723 K for 18 h.¹⁶

2.2. Catalyst characterization

The chemical composition of the samples was determined by ICP-OES in a Perkin-Elmer Plasma 40 (Si) and Optimax 3000DV (axial). The total pore volume of the samples was determined by N₂ adsorption at 77 K (Autosorb 6B). Prior to the measurements the samples were evacuated at 623 K for 16 h. The surface area was determined using the BET method. TEM analysis was carried out on a Philips CM 30 T electron microscope. Rh dispersion in the catalysts (Dₚ) was determined by CO chemisorption using a volumetric apparatus (QuantaChrome Autosorb 1-C), assuming an adsorption stoichiometry Rh:CO = 1:1. Prior to chemisorption, the sample was reduced in H₂ (773 K, 1 h), followed by evacuation (773 K, 2 h) and cooling to room temperature in vacuum.

2.3. Activity tests

Activity and stability tests were carried out in a six-flow reactor system.³² Tests were made using 50 mg of catalyst shaped in particles with diameters of 125-250 µm and space-velocities ranging from 36000 to 120000 h⁻¹. Total pressure (P) was 3 bar. The partial feed pressure of the different gases depends on the tail-gas simulated:

- **Nitric acid production:** 4.5 mbar N₂O, 20 mbar O₂, 1 mbar NO, 15 mbar H₂O, balance He. C₃H₈ (4.5 mbar) was eventually added to the complete feed mixture. Experiments varying the partial feed pressure of NO (0-4.5 mbar) were also carried out.

- **Combustion processes:** 1.5 mbar N₂O, 120 mbar O₂, 150 mbar CO₂, 90 mbar H₂O, 0.75 mbar SO₂, balance He.

Individual and combined effects of these gas mixtures on the catalytic activity were investigated. For the assessment of the effect of individual gases on the N₂O conversion, fresh catalysts were used in every test. Before reaction, the catalysts were pretreated in 4.5 mbar N₂O (tail-gas from nitric acid production) or 1.5 mbar N₂O (tail-gas from combustion processes) in He at 723 K for 1 h and cooled down in the same gas to the starting reaction temperature. Generally, 1 h after a change of conditions the conversion levels for the different gases were constant and considered in steady state. Preliminary checks were made to ensure the absence of diffusion limitations on the reaction rate.³² At least two analyses were averaged for a data point. The product gases were continuously analyzed with a chemiluminescence NO-NO₂ analyzer (Ecophysics CLD 700 EL), and discontinuously analyzed for the other gases by GC (Chrompack CP 9001). The chromatograph was equipped with a thermal conductivity detector and a flame ionization detector, using a Poraplot Q column (for N₂O and CO₂ separation) and a Molsieve 5A column (for N₂, O₂, and CO separation). The mass balance for N, O, and C in these experiments closed within less than 1, 2, and 5%, respectively.
Table 3. Data of the catalysts used in this study.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al</th>
<th>Fe (^{\text{a}}) / wt.%</th>
<th>(V_{\text{pore}}) (^{\text{b}}) / cm(^3) g(^{-1})</th>
<th>(S_{\text{BET}}) (^{\text{c}}) / m(^2) g(^{-1})</th>
<th>(\Delta d) / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>ex-FeZSM-5</td>
<td>31.5</td>
<td>0.58</td>
<td>0.22</td>
<td>395</td>
<td>1-2</td>
</tr>
<tr>
<td>sie-FeZSM-5</td>
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<td>1.46</td>
<td>0.27</td>
<td>370</td>
<td>5-15</td>
</tr>
<tr>
<td>lie-FeZSM-5</td>
<td>37.5</td>
<td>1.50</td>
<td>0.28</td>
<td>375</td>
<td>7-25</td>
</tr>
<tr>
<td>sub-FeZSM-5</td>
<td>14.0</td>
<td>5.0</td>
<td>0.30</td>
<td>–</td>
<td>3-12</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rh-based catalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
</tr>
<tr>
<td>Rh/Al(_2)O(_3)</td>
</tr>
<tr>
<td>Rh/ZSM-5</td>
</tr>
<tr>
<td>Rh/USY</td>
</tr>
<tr>
<td>ex-CoRh(_2)Al-HTlc</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\) ICP-OES; \(^{\text{b}}\) \(N_2\) adsorption at 77 K; \(^{\text{c}}\) (size) distribution of iron oxide particles, as determined from TEM; \(^{\text{d}}\) Metal molar ratio: Si/Al in zeolites, and Co/Al in the mixed oxide; \(^{\text{e}}\) dispersion, from CO chemisorption.

3. Results and discussion

3.1. Activity in \(N_2O/He\)

Table 3 shows the characterization results of the FeZSM-5 catalysts used in this study. The Fe content in ex-FeZSM-5 is about three and eight times higher in the ion-exchanged catalysts (\(\approx 1.5\) wt.\%) and sublimed catalyst (5 wt.\%), respectively. Fig. 1 shows that sub-FeZSM-5 and ex-FeZSM-5 induce similar absolute \(N_2O\) conversion levels in a \(N_2O/He\) feed and significantly higher conversion levels than the ion-exchanged catalysts. Sie-FeZSM-5 is more active than lie-FeZSM-5. Calculation of the turnover frequency (TOF), i.e. the specific activity for \(N_2O\) decomposition per mol of (total) iron at different reaction temperatures gives a clear indication of the iron utilization in the catalysts (Fig. 2). At e.g. 700 K, this value is more than 4, 7, and 10 times higher for ex-FeMFI than for sie-FeZSM-5, sub-FeZSM-5, and lie-FeZSM-5, respectively. Activation of the calcined FeZSM-5c sample with steam at 873 K is crucial to create active species in the ex-framework catalyst, as can be concluded by comparison of the activity curves of both calcined and steamed samples in Fig. 1.

![Fig. 1. \(N_2O\) conversion vs. \(T\) over (♦) ex-FeZSM-5, (▲) FeZSM-5c (before steaming) (●) sie-FeZSM-5, (◊) lie-FeZSM-5, and (△) sub-FeZSM-5. Conditions: 4.5 mbar \(N_2O\) in He; \(P = 3\) bar; \(GHSV = 36000\) h\(^{-1}\).](image-url)
Fig. 2. TOF values (mol of N₂O converted per mol of Fe s⁻¹) for the different FeZSM-5, determined after 1 h time on stream. Conditions: 4.5 mbar N₂O in He; P = 3 bar; GHSV = 60000 h⁻¹.

Fig. 3 shows the N₂O conversion vs. temperature curve of different Rh-catalysts in a N₂O/He feed at 60000 h⁻¹. The activity curve of ex-FeZSM-5 at the same experimental conditions is also displayed for comparative purposes. The temperature for a certain N₂O conversion differs ~300 K between ex-Co-Rh,Al-HTlc (the most active catalyst in our experiments) and ex-FeZSM-5. The activity of the Rh-catalysts is influenced by the support, following the sequence: $ex$-Co-Rh,Al-HTlc ≳ Rh/Al₂O₃ > Rh/USY > Rh/ZSM-5. The activity data suggest a correlation between the Rh dispersion in the catalyst and the N₂O conversion: the higher the Rh dispersion, the higher the N₂O decomposition activity. These results are in agreement with previous studies over Rh-catalysts,³₃ where the influence of both support and Rh precursor in the N₂O decomposition activity was investigated. The metal dispersion of $ex$-Co-Rh,Al-HTlc was not determined by CO-chemisorption, because during the pretreatment in H₂ a significant fraction of cobalt is reduced, leading to overestimation of the
amount of Co adsorbed (apparent dispersion > 100%). No Rh-related particles were observed in the TEM analysis of this sample, which suggests a particle size of < 1 nm, leading to dispersions of > 80%, as expressed in Table 3. The high dispersion of Rh in the mixed oxide is a consequence of the preparation method via a hydrotalcite precursor and an optimized decomposition temperature, based on previous investigations with in situ infrared and Raman spectroscopies.34,35

3.2. Performance in simulated tail-gases

3.2.1. Nitric acid plants

The performance of ex-FeZSM-5 in simulated tail-gas from nitric acid plants (containing \( \text{N}_2\text{O} \) and \( \text{O}_2 \), NO, and \( \text{H}_2\text{O} \)) is shown in Fig. 4. \( \text{N}_2\text{O} \) conversion was measured after 1 h time on stream in a specific feed composition. Ex-FeZSM-5 shows a substantial \( \text{N}_2\text{O} \) conversion above 700 K in a \( \text{N}_2\text{O}/\text{He} \) feed. Addition of \( \text{O}_2 \) to the feed hardly affects the activity, while NO enhances the reaction rate considerably. Apparently, molecular oxygen does not dissociate over FeZSM-5 and does not compete with \( \text{N}_2\text{O} \) for active sites. NO promotes \( \text{N}_2\text{O} \) conversion by accelerating the desorption rate of adsorbed \( \text{O}^* \) species (deposited by \( \text{N}_2\text{O} \) decomposition). The mechanism of this catalytic reaction is described in detailed elsewhere.36 Water severely inhibits the reaction, probably by hydroxylation of the active sites and adsorption in the zeolite channels. Nevertheless, in the complete gas mixture (\( \text{N}_2\text{O}+\text{O}_2+\text{NO}+\text{H}_2\text{O} \)), ex-FeZSM-5 still shows a significantly higher activity than in \( \text{N}_2\text{O} \) alone (100% conversion at 750 K). The promoting effect of NO is thus stronger than the inhibition by \( \text{H}_2\text{O} \).

![Fig. 4 N2O conversion vs. T over ex-FeZSM-5 in simulated tail-gases from nitric acid plants. Conditions: (■) 4.5 mbar \( \text{N}_2\text{O} \), (○) 4.5 mbar \( \text{N}_2\text{O}+\text{70 mbar O}_2 \), (●) 4.5 mbar \( \text{N}_2\text{O}+\text{1 mbar NO} \), (○) 4.5 mbar \( \text{N}_2\text{O}+\text{15 mbar H}_2\text{O} \), (●) 4.5 mbar \( \text{N}_2\text{O}+\text{70 mbar O}_2+\text{1 mbar NO}+\text{15 mbar H}_2\text{O} \), (●) 4.5 mbar \( \text{N}_2\text{O}+\text{70 mbar O}_2+\text{1 mbar NO}+\text{15 mbar H}_2\text{O}+\text{4.5 mbar C}_3\text{H}_8 \), balance \( \text{He} \); \( P = 3 \text{ bar} \); \( \text{GHSV} = 60000 \text{ h}^{-1} \).](#)

This extraordinary behaviour distinguishes ex-framework FeZSM-5 from other \( \text{N}_2\text{O} \) decomposition catalysts. Fig. 5 shows the individual and combined effect of the different gases on the \( \text{N}_2\text{O} \) conversion over ex-Co-Rh\( \text{Al-HTlc}. \) In this case, the \( \text{N}_2\text{O} \) conversion was not affected by oxygen, but the presence of NO severely inhibits the reaction, via surface nitrite/nitrate formation, shifting the reaction to 200 K higher temperatures. The inhibition

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effect of water is even more severe than that of NO. A similar trend was observed for the other Rh-catalysts. As a result of these inhibition effects, the operation temperature of the Rh-based catalysts is similar to that of ex-framework FeZSM-5 (Fig. 6) in simulated tail-gas conditions. It should be mentioned that the activity of ex-Co-Rh,Al-HTlc in terms of absolute conversion at a certain temperature is significantly higher than observed for the other catalysts: e.g. N₂O conversion in the complete feed mixture over ex-Co-Rh,Al-HTlc and ex-FeZSM-5 at 700 K is 70 and 40%, respectively.

Fig. 5. N₂O conversion vs. T over ex-Co-Rh,Al-HTlc in simulated tail-gases from nitric acid plants. Conditions: (นะครับ) 4.5 mbar N₂O, (◊) 4.5 mbar N₂O + 70 mbar O₂, (●) 4.5 mbar N₂O + 1 mbar NO, (○) 4.5 mbar N₂O + 15 mbar H₂O, (▲) 4.5 mbar N₂O + 70 mbar O₂ + 1 mbar NO + 15 mbar H₂O; balance He; P = 3 bar; GHSV = 60000 h⁻¹.

Fig. 6. N₂O conversion vs. T over (▲) ex-FeZSM-5, (●) ex-Co-Rh,Al-HTlc, (▲) Rh/Al₂O₃, (■) Rh/USY, and (◊) Rh/ZSM-5. Conditions: 4.5 mbar N₂O + 70 mbar O₂ + 1 mbar NO + 15 mbar H₂O; balance He; P = 3 bar, GHSV = 60000 h⁻¹.
The temperature of N₂O decomposition over ex-FeZSM-5 can be further decreased by addition of hydrocarbons to the feed (selective catalytic reduction). Addition of 4.5 mbar of propene (molar N₂O/C₃H₆ feed ratio of 1) leads to a reduction in temperature of 100 K in the simulated tail-gas, achieving 100% N₂O conversion at 675 K (Fig. 4). Addition of propene does not influence the N₂O conversion over Rh-catalysts, since Rh shows a high activity for oxygen activation. This facilitates the combustion of propene at lower temperatures than those needed for activation of N₂O.

![Graph showing N₂O conversion vs. molar NO/N₂O feed ratio at 625 K and 700 K](image)

**Fig. 7.** N₂O conversion vs. molar NO/N₂O feed ratio over (◯) ex-FeZSM-5 and (●) ex-Co-Rh,Al-HTl at the temperatures indicated in the figure. Conditions: 4.5 mbar N₂O and 0-4.5 mbar NO; balance He; P = 3 bar; GHSV = 60000 h⁻¹.

![Graph showing N₂O conversion as a function of space velocity (GHSV) and time-on-stream over ex-FeZSM-5, sie-FeZSM-5, lie-FeZSM-5, and sub-FeZSM-5](image)

**Fig. 8.** N₂O conversion as a function of (a) the space velocity (GHSV) over ex-FeZSM-5 and (b) time-on-stream over (◯) ex-FeZSM-5 (60000 h⁻¹, 700 K), (●) ex-FeZSM-5 (120000 h⁻¹, 700 K), (●) sie-FeZSM-5 (36000 h⁻¹, 725 K) (◯) lie-FeZSM-5 (36000 h⁻¹, 775 K), and (△) sub-FeZSM-5 (36000 h⁻¹, 700 K). Feed composition: 4.5 mbar N₂O + 70 mbar O₂ + 1 mbar NO + 15 mbar H₂O; balance He; P = 3 bar.
Chapter 7

The activity measurements shown in Figs. 4 and 5 indicate a remarkable opposite effect of NO in ex-FeZSM-5 (promoting) and ex-Co-Rh,Al-HTlc (and in general other Rh-based catalysts, inhibiting). Fig. 7 shows the N₂O conversion at different molar NO/N₂O feed ratios in both catalytic systems. Ex-FeZSM-5 shows a dramatic improvement in N₂O conversion upon addition of NO, while the conversion over ex-Co-Rh,Al-HTlc is strongly inhibited. Both promotion and inhibition effects are especially significant after addition of small amounts of NO to the feed, i.e. at molar NO/N₂O feed ratios < 0.2. NO inhibition over ex-Co-Rh,Al-HTlc was completely reversible, since the original conversion was obtained in less than 1 h after removing NO from the feed mixture.

The remarkable behaviour of ex-FeZSM-5 in simulated tail-gas mixtures is not limited to its activity, but also includes stability. N₂O conversion over ex-FeZSM-5 exhibits a remarkable stability during 50 h in the complete feed mixture (excluding the hydrocarbon) at different space velocities, ranging from 36000 h⁻¹ to 120000 h⁻¹ (Fig. 8). Sub-FeZSM-5 shows slight deactivation at 36000 h⁻¹. Significant deactivation was observed for the sie-FeZSM-5 and lie-FeZSM-5 catalysts.

![Graph showing N₂O conversion](image)

**Fig. 9.** N₂O conversion vs. time on stream over (a) ex-FeZSM-5 and (b) ex-Co-Rh,Al-HTlc in (○, ◊) 4.5 mbar N₂O and (○, ◦) 4.5 mbar N₂O + 70 mbar O₂ + 1 mbar NO + 15 mbar H₂O; balance He; P = 3 bar; GHSV = 60000 h⁻¹. Temperatures as indicated in the figure.

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In a more severe stability test during 600 h, the stability of ex-FeZSM-5 and ex-Co-Rh,Al-HTlc have been compared (Fig. 9). The ex-framework catalyst shows a remarkable stability along the experiment at 675 and 725 K. As it was already shown in Fig. 4, the N₂O conversion in the tail-gas mixture (excluding the hydrocarbon) is higher than in a N₂O/He feed over this catalyst. N₂O conversion over ex-Co-Rh,Al-HTlc at 675 K is stable during the first 25 h, but afterwards the activity decreases significantly. After 300 h, the catalyst has lost ~60% of the original activity. After switching the tail-gas mixture to a mixture of N₂O in He, the conversion measured was 80%, which indicates certain deactivation, since in the activity test shown in Fig. 5 the N₂O conversion was 100% under these experimental conditions. Since NO inhibition over the Rh-catalysts is reversible, it can be suggested that water is responsible for deactivation of these formulations. After exposing the catalyst to the complete tail-gas mixture (> 400 h) the conversion rapidly decreases up to the level at 300 h and slowly decreases further with time. This deactivation behaviour, being characteristic in the different Rh-catalysts tested in this study, limits their practical application in catalytic N₂O abatement in tail-gases from nitric acid plants.

The catalysts presented in this chapter were the most promising ones from an extensive screening program (not shown here). Catalysts based on other metals like Ru, Pd, Co, and Ni on different supports also exhibit high activities in N₂O-He feeds, but all of them present a poor performance in simulated tail-gas conditions. In all these cases, even the presence of oxygen inhibits the reaction significantly.

3.2.2. Stationary combustion processes

The performance of ex-FeZSM-5 in simulated tail-gases from combustion facilities (containing N₂O and O₂, CO₂, H₂O, and SO₂) at 75000 h⁻¹ is shown in Fig. 10. A substantial conversion above 700 K in a N₂O/He feed is obtained. Analogously to the former activity tests, addition of O₂ does not affect the activity, while water causes severe inhibition. CO₂, a common constituent of tail-gas in combustion processes, did not influence the performance of the catalyst. The catalytic activity is enhanced considerably by the presence of SO₂ in the feed. In the complete gas mixture (N₂O+O₂+CO₂+H₂O+SO₂), ex-FeZSM-5 shows N₂O conversions of 90% at 800 K, which is somewhat lower than in the N₂O/He mixture. In this case, the promoting effect of SO₂ does not compensate the strong inhibition of H₂O. Small amounts of SO₂ in the feed (~50 ppm) completely suppress the activity in N₂O decomposition of Rh-catalysts, and the effect is completely irreversible. The original activity was not recovered even after regeneration of the catalyst in air at 773 K. Again, this makes the application of noble-metal based catalysts from a practical point of view very unattractive.

The resistance of ex-FeZSM-5 to deactivation by SO₂ and H₂O is remarkable. Stability is a crucial requirement for application of catalytic after-treatment in combustion facilities, even when catalysts maintain mild activity. N₂O conversion over ex-FeZSM-5 exhibits a significant stability in the complete feed mixture at 75000 h⁻¹ (Fig. 11). After switching from N₂O/He to the complete tail-gas mixture at 740 K, the N₂O conversion gradually decreases during the first 75 h, obtaining stable behaviour afterwards. After ~200 h on stream, the feed gas was switched back to N₂O-He. N₂O conversion rapidly increases (black diamonds, Fig. 11), and the original N₂O conversion was practically recovered after 5 h. At 760 and 780 K, a very stable behaviour is observed in simulated tail-gas for both catalysts, with no sign of deactivation. Additionally, the inhibition by the feed mixture is completely reversible. This result is particularly remarkable if one realizes that the SO₂ pressure used in this study corresponds to 750 ppm SO₂ under atmospheric flue-gas conditions, which typically contains only 10-50 ppm SO₂. The total amount of SO₂ passed over the catalysts during the 600 h
experiments (Fig. 11) corresponds to an amount of SO$_2$ emitted by a conventional combustion facility over more than a year, at 50 ppm levels.

**Fig. 10.** N$_2$O conversion vs. $T$ over ex-FeZSM-5 in simulated tail-gases from combustion processes. Conditions: (♦) 1.5 mbar N$_2$O, (○) 1.5 mbar N$_2$O + 120 mbar O$_2$, (△) 1.5 mbar N$_2$O + 150 mbar CO$_2$, (◊) 1.5 mbar N$_2$O + 90 mbar H$_2$O, (●) 1.5 mbar N$_2$O + 0.75 mbar SO$_2$, (▲) 1.5 mbar N$_2$O + 120 mbar O$_2$ + 150 mbar CO$_2$ + 90 mbar H$_2$O + 0.75 mbar SO$_2$; balance He; $P = 3$ bar; GHSV = 75000 h$^{-1}$.

**Fig. 11.** N$_2$O conversion vs. $T$ over ex-FeZSM-5 in (♦) 1.5 mbar N$_2$O and (○) 1.5 mbar N$_2$O + 120 mbar O$_2$ + 150 mbar CO$_2$ + 15 mbar H$_2$O + 0.75 mbar SO$_2$; balance He; $P = 3$ bar; GHSV = 75000 h$^{-1}$. Temperatures as indicated in the figure.
The catalysts prepared by the ion-exchange and sublimation methods were further investigated at three different temperatures and exposure times in N₂O/He (bars A and E in Fig. 12) and in the simulated feed mixture (bars B, C, and D in Fig. 12). This figure shows the following: (i) there is a significant reduction of N₂O conversion by changing the gas composition from N₂O/He to the tail-gas mixture (compare bars A and B at different temperatures), (ii) activity progressively decreases with exposure time (1, 5, and 20 h) to the simulated feed mixture (compare bars B, C, and D), (iii) sub-FeZSM-5 is much less affected by changing the feed composition than the ion-exchanged catalysts, while lie-FeZSM-5 is the most sensitive to the feed composition, (iv) the catalysts show irreversible deactivation, i.e. N₂O conversion does not reach the original level after removal of the additional gas components in the feed mixture (compared bars A and E at different temperatures). The irreversible deactivation is especially remarkable in lie-FeZSM-5, while sie-FeZSM-5 and especially sub-FeZSM-5 recover a significant fraction of their original activity after removing H₂O and SO₂ from the feed mixture. The poor activity and stability of the ion-exchanged samples is not related only to the formation of stable sulfates in the catalyst surface. Also H₂O was found to depress the activity over these catalytic systems.

**Fig. 12.** N₂O conversion over (a) sie-Fe[Al]MFI, (b) lie-Fe[Al]MFI, and (c) sub-Fe[Al]MFI in (A) 1.5 mbar N₂O in He (in the legend of Fig. 11), and after exposure to the complete gas mixture (in the legend of Fig. 11) during (B) 1 h, (C) 5 h, and (D) 20 h, (E) as (A), 5 h after switching from the tail-gas mixture back to N₂O in He; P = 3 bar; GHSV = 75000 h⁻¹. Temperatures as indicated in the figure.
When \( \text{SO}_2 \) is present in the feed, most of the catalysts for \( \text{N}_2\text{O} \) decomposition rapidly deactivate \(^{4,7,8,13,14,16} \). It is proposed that the \( \text{SO}_3 \) reacts with most of these catalysts to form stable sulfates, which destroy the catalyst activity. Several authors have considered the addition of reductants (methane, propane, propene, or LPG) in the feed composition, not only to promote catalytic activity of the FeMFI catalyst substantially but also to prevent the formation of sulfate species and/or increase the stability towards \( \text{H}_2\text{O} \).\(^{7,23,29,30} \) However, catalytic reduction of \( \text{N}_2\text{O} \) by addition of hydrocarbons implies an increase of the operating costs in the after-treatment, which is in principle not attractive. In addition, selective reduction of \( \text{N}_2\text{O} \) often leads to incomplete hydrocarbon combustion and high CO yields.\(^{24} \) Hydrocarbon slip and CO emission can be simultaneously remedied e.g. by incipient wetness impregnation of Pd on the FeMFI catalyst, enhancing its oxidation performance.\(^{22} \)

The positive effect of \( \text{SO}_2 \) on \( \text{N}_2\text{O} \) decomposition over FeZSM-5 was previously reported by some of us.\(^{9} \) We have proposed that \( \text{SO}_2 \) scavenges adsorbed \( \text{O}^* \) (deposited by \( \text{N}_2\text{O} \) decomposition, reaction (1)) and thus regenerates the active site (reaction (2)).

\[
\begin{align*}
\text{N}_2\text{O} + \text{SO}_2 & \rightarrow \text{N}_2 + \text{SO}_3 + \text{O}^* \\
\text{SO}_2 + \text{O}^* & \rightarrow \text{SO}_3 + \text{O}^* 
\end{align*}
\]

In this study, the product gases were not analyzed for \( \text{SO}_3 \). Centi et al.\(^{23} \) have recently attributed the stability of FeZSM-5 prepared by chemical vapor deposition of FeCl\(_3\) on H-ZSM-5 towards \( \text{SO}_2 \) (using C\(_3\)H\(_8\) as the reductant) to the inability of the catalyst to oxidize \( \text{SO}_2 \) to \( \text{SO}_3 \). This was concluded from the absence of \( \text{SO}_3 \) in the product gases, as determined by absorption in NaOH mixtures and analysis by ionic chromatography of the presence of sulfate ions in the solution. The remarkable stability of our ex-framework catalyst indeed suggests that \( \text{SO}_2 \) hardly chemically interacts with the catalyst surface. So \( \text{SO}_2 \) scavenges adsorbed \( \text{O}^* \) species, without formation of stable sulfates on the catalyst surface. Still, \( \text{SO}_2 \) (reaction (2)) should be a better reductant than \( \text{N}_2\text{O} \) (reaction (3)), since both reactions compete to reduce an oxidized site, regenerating it. It can tentatively be proposed that the improved \( \text{N}_2\text{O} \) conversion is caused by a favourable oxygen desorption, due to the presence of adsorbed \( \text{SO}_2 \) on the catalyst surface, as analyzed for the NO-promoted \( \text{N}_2\text{O} \) decomposition in Chapter 8 of this thesis.

\[
\text{N}_2\text{O} + \text{O}^* \rightarrow \text{N}_2 + \text{O}_2 + \text{O}^* 
\]

In FeZSM-5 catalysts prepared by sublimation or (solid and liquid) ion-exchange, it seems that interaction of \( \text{SO}_2 \) with the Fe sites is strong and stable sulfate formation dramatically reduces \( \text{N}_2\text{O} \) decomposition.

### 3.2.3. Ex-framework FeZSM-5 vs. other catalysts

The data show that a critical factor in designing catalysts for \( \text{N}_2\text{O} \) decomposition in tail-gases is to reduce the inhibition effect by oxygen, \( \text{NO}_x \), \( \text{H}_2\text{O} \), and \( \text{SO}_2 \). FeZSM-5 catalysts show an extraordinary behaviour, since they are not inhibited by \( \text{O}_2 \) and show an improved activity in the presence of \( \text{NO} \).\(^{9,18,19} \) A novel ex-framework route to prepare FeZSM-5 also leads to a high stability in the presence of \( \text{H}_2\text{O} \) and \( \text{SO}_2 \), while catalysts prepared by other preparation methods are severely inhibited and deactivated. The difference in performance of the different FeZSM-5 catalyst can be related to the preparation method, which leads to different constitutions of the catalysts with respect to dispersion, morphology, and structure of the active sites. A remarkable homogeneous distribution of highly dispersed \( \text{FeO}_x \) nanoparticles of 1-2 nm in FeZSM-5 is obtained by the ex-framework method. The other preparation methods fail to obtain a homogeneous distribution of the iron oxide particles in
the catalyst, as is revealed by the broad FeO₃ cluster size distribution indicated as $\Delta d$ in Table 3. When assuming that the particles observed by TEM are responsible for N₂O decomposition activity, the lower activity of the ion-exchange and sublimation methods compared to ex-framework catalysts in N₂O decomposition could be explained. However, large FeO₃ particles at the external surface of the zeolite are widely accepted to be inactive in reactions catalyzed by FeZSM-5.²¹,²³,²⁷ As shown in Chapters 5 and 6, the ex-framework catalyst is very heterogeneous material with respect to iron. Apart from iron oxide nanoparticles, oligonuclear oxo-iron species and isolated iron ions in the zeolite channels have been identified. This complicates the elucidation of the nature of the active species for the observed extraordinary catalytic behaviour. An attempt to determine the nature of the active sites of this catalyst for N₂O activation and decomposition is given in Chapter 9, where small oligonuclear oxo-iron species in the zeolite channels are proposed to be the active sites.

Rh-catalysts (especially ex-Co-Rh,Al-HTIc) show very high initial N₂O decomposition activities, even in the presence of O₂, NO, and H₂O. However, stability tests (600 h) show that the catalysts progressively deactivate by H₂O, and the more stable ex-FeZSM-5 system clearly overcomes their activities. Deactivation by SO₂ in Rh-based catalysts is more severe, suppressing their activity after 1 h time on stream. Regeneration of these catalysts by thermal treatment in inert does not lead to the recovery of the original activity. These factors limit the practical application of Rh-catalysts, and of many other formulations based on noble or transition metals.

3.3. Options for N₂O control in different sources

3.3.1. Nitric acid plants

During nitric acid manufacture, N₂O is produced as an unwanted by-product in the catalytic oxidation of ammonia over the Pt-Rh catalyst. The N₂O passes through the plant and is emitted in the tail-gas. The current technology for de-NOₓ applications in nitric acid plants, i.e. the selective catalytic reduction using ammonia as a reductant and V₂O₅-type catalysts, does not reduce N₂O emissions. Several options for N₂O destruction in nitric acid plants are currently developed.⁵ R&D efforts focus on two locations in the plant (Fig. 13): (a) and (b) in the ammonia burner, i.e. in process options, and ((c), (d), and (e)) in the tail-gas.

**In process options.** Different in process options (in positions (a) and (b) in Fig. 13) have been considered.⁵ Efforts in position (a) focus on (i) the optimization of the geometry of the Pt-Rh gauzes or (ii) the replacement of the Pt-Rh catalyst by Co₃O₄. Options to mitigate N₂O in the ammonia converter behind the Pt-Rh catalyst (position b) are (iii) the homogeneous gas-phase decomposition of N₂O by increasing the residence time in the ammonia converter, and (iv) the catalytic N₂O decomposition. Options (i) and (ii) concern the optimization of the NO yields during ammonia oxidation, which indirectly leads to a lower N₂O production. All the possibilities for improvement in option (i) are not yet exhausted and currently the potential reduction of N₂O emissions is uncertain. The second option, replacement of the current catalyst by Co₃O₄ presents two major drawbacks: the ammonia conversion efficiency is substantially lower (88-92%) compared to the Pt-Rh catalyst (95-97%) and also Co₃O₄ suffers from deactivation due to reduction to CoO in the upper parts of the bed.⁶⁰ Abatement of the N₂O formed in the ammonia converter is considered in options (iii) and (iv). Option (iii) implies a new reactor design,⁶¹ requiring a substantial investment in existing plants, and thus high retrofit costs. Option (iv) is the most promising in this position of the plant. It involves catalytic N₂O decomposition at high temperature and for many plants would offer a simple and cost-effective way to remove N₂O. The catalyst could be easily installed in place of the Raschig rings that support the Pt-Rh gauzes and the Pd-catchment. Possible
drawbacks are that catalyst lifetime may be short due to harsh conditions (temperature of 1075-1175 K and pressure up to 13 bar) and that also the selectivity to NO decreases, since NO decomposition may be catalyzed. This would cause production losses and consequently influence the cost efficiency of the overall process dramatically. BASF adapted a Cu-Zn-Al spinel for this purpose, but more tests are required to determine the long-term chemical and mechanical stability, activity, and selectivity of this system. Other nitric acid producers are currently investigating this option.41-43

Fig. 13. Options to control N₂O emissions in nitric acid plants, with typical conditions in different locations.

**Tail-gas options.** Destruction of N₂O at a point between the outlet of the absorber and the outlet of the tail-gas expansion turbine (positions (c), (d), or (e) in Fig. 13) may be a more robust option, since the conditions are less severe and these options do not interfere with the process of HNO₃ production. Application of tail-gas abatement in nitric acid plants requires high low-temperature activity and stability in the presence of O₂, NOₓ, and H₂O. Thermal decomposition of N₂O in the tail-gas is economically unfeasible. Although a recuperative heat exchanger can be installed, it is likely that heat must be continuously supplied from an external source to compensate heat losses in the system, since the diluted N₂O concentration in the tail-gas causes only a small temperature rise.5

A more realistic solution is the installation of a catalytic abatement unit. Essentially, no physical limit exists (except pressure drop) for the size of the reactor. This allows the design of a reactor for very high levels of N₂O removal. A producer might also decide to install a
more generously sized reactor than that immediately required, allowing for the addition of extra-catalyst later to cope with prospective N₂O emission regulations, or to optimize the catalyst requirement against the level of a greenhouse gas tax. Either direct N₂O decomposition or selective catalytic reduction of N₂O with hydrocarbons has been considered in different locations. From the point of view of catalytic activity, the best location of the after treatment would be at the inlet of the expansion turbine (position (c) in Fig. 13). In this location, the temperature and pressure of the tail-gas ranges from 525 to 775 K and from 4 to 10 bar, respectively, depending on the process variant.

The use of ex-framework FeZSM-5 for direct N₂O decomposition, which shows stable N₂O conversion (> 90%) at 725 K and 60000 h⁻¹, appears viable in large modern dual-pressure plants (with high-temperature tail-gases, ranging from 725 to 775 K). This technology can contribute to greenhouse gas abatement in a cost-attractive way, since ex-FeZSM-5 does not contain any expensive noble metal and keeps a remarkable stability. The high space velocity used in this study (60000 h⁻¹) compared to a more realistic situation (~30000 h⁻¹) and the relatively low pressure (3 bar vs. 4-10 bar in real conditions) guarantee a lower operation temperature for the same N₂O conversion.

For low-temperature tail-gases (500-525 K), typical in low-(single or dual) pressure plants, ex-FeZSM-5 would additionally require extra-heat exchange to preheat the feed mixture, or the addition of hydrocarbon as reducing agent. The use of hydrocarbons leads to a dramatic increase of the operation costs (4 times higher than direct N₂O decomposition), due to the hight cost associated with the reductant (30-70% of the total annual cost). Reduction of N₂O with ammonia is also possible, but it generally requires higher temperatures than N₂O reduction with hydrocarbons. Although ammonia is readily available in a nitric acid plant, it is probable that reduction with ammonia will be not competitive.

Temperature and pressure of the tail-gas downstream of the expander are milder (position (d) in Fig. 13), i.e. 375-475 K and 1 bar, which would require preheating of the off-gases to about 723 K by a natural-gas-fired in-line burner, as well as the addition of reducing agents to the feed mixture. Another process option that can be considered is the installation of the after-treatment upstream of the de-NOₓ SCR unit (position (e) in Fig. 13). This may be favourable to improve N₂O conversion at lower temperatures, since NO promotes N₂O decomposition over ex-FeZSM-5. The operation temperature of a de-NOₓ SCR using ammonia ranges from 575 to 725 K, depending on various parameters (type of de-NOₓ catalyst, residence time, amount of ammonia injected, etc.). In this process option, care should be taken to avoid N₂O formation during NOₓ reduction.

As it can be concluded from the above description, the temperature of the tail-gas is the most important parameter that would influence the location of the catalyst unit and the abatement options. This strongly depends on the plant and should be analyzed individually in each case. Anyway, the large variety of options facilitates the search of a suitable treatment.

3.3.2. Stationary combustion processes

Fluidized-bed combustors (FBCs) of fossil fuels, biomass, and nitrogen-containing industrial or municipal waste have been developed as environmental friendly alternative for traditional forms of combustion. The low combustion temperature at which FBCs operate results in low emission levels of NOₓ, which coincides with the optimal conditions for sulfur-capture. Unfortunately these merits are offset by a strongly increased emission of N₂O.

In fluid-bed combustion, several locations can be identified where ex-FeZSM-5 can be applied (Fig. 14): (a) in the bed or (b) in the freeboard, (c) after the cyclone, and (d) after the preheater. Each location requires different characteristics for a catalyst. In the combustor (position (a) and (b)), calcined limestone and other Ca-containing materials are preferred,
since they are highly thermostable and very resistant to attrition.\(^7\) Position (c) seems to be viable for ex-framework FeZSM-5, because of high N\(_2\)O decomposition activities at the temperature of the dust-free gas. In location (d), a high low-temperature activity is demanded, and ex-FeZSM-5 would require additional heat exchange to preheat the feed mixture, or addition of a hydrocarbon as reducing agent. In combustion processes the major requirement for a working catalyst is the tolerance of the catalyst against deactivation by SO\(_2\). Ex-framework FeZSM-5 can be used for direct N\(_2\)O decomposition, due to the promotion effect of SO\(_2\) on the reaction rate, and the stability in wet conditions (in the absence of hydrocarbons).

![Diagram of fluid-bed combustor](image)

**Fig. 14.** Options to control N\(_2\)O emissions in fluid-bed combustors.

### 3.3.3. Chemical production

**Adipic acid plants**

In the manufacture of adipic acid, an intermediate for nylon 6,6, N\(_2\)O is produced in large amounts (300 g N\(_2\)O per kg adipic acid produced) during oxidation of a mixture of cyclohexanone and cyclohexanol by HNO\(_3\) (Fig. 15). Due to the high concentration of N\(_2\)O in the tail-gas (in the range of 25-40 vol.%), different thermal and catalytic technologies have been successfully developed. Decomposition of N\(_2\)O in these concentrated streams lead to adiabatic temperature rises of 500-700 K, which enables autothermal operation by installation of recuperative heat exchangers. The majority of the large adipic acid producers (Asahi, BASF, Bayer, DuPont, Rhône-Poulenc, and Solutia) have implemented N\(_2\)O abatement units, leading to a emission reduction of this source from 0.6 Mton N\(_2\)O y\(^{-1}\) in 1991 to < 0.1 Mton N\(_2\)O y\(^{-1}\) nowadays (see Table 1).

A novel approach for control of N\(_2\)O emissions from this source is the reutilization of N\(_2\)O as selective oxidant in the environmental benign and sustainable industrial manufacture of chemicals. The AlphOx\(_{TM}\) process, which has been developed jointly by Solutia and the Boreskov Institute of Catalysis, consists of the use of the waste N\(_2\)O for the selective oxidation of benzene to phenol, incorporating this reaction as a key stage in a new modified adipic acid production.\(^47\) This scheme also starts with benzene, which in this case is first oxidized to phenol, and only then goes to hydrogenation (Fig. 15). N\(_2\)O, produced at the last stage, returns to the front end of the overall process closing the cycle. This process offers an
attractive alternative to the three-step “cumene” process for phenol production, suppressing by-product formation and hazardous wastes, as well as considerable energy savings. Panov and coworkers did pioneering work in the one-step hydroxylation of benzene to phenol with N₂O, which is catalyzed by FeZSM-5.⁴⁷,⁴⁸

![Diagram of the reaction](image)

**Fig. 15.** Production of adipic acid with the recycling of nitrous oxide.

In view of the promising future of the N₂O reuse concept in green chemistry (from waste to chemical), we have tested ex-framework FeZSM-5 in the selective oxidation of benzene to phenol. Table 4 shows typical parameters describing the catalyst performance in a fixed-bed laboratory reactor.⁴⁷,⁴⁹ The high phenol selectivity is a remarkable feature of the catalyst. Its productivity is 100 g phenol per 1 kg of catalyst per hour, which is at the top end of the best industrial catalysts for selective oxidation reactions, reported elsewhere.⁴⁷

**Table 4.** Reaction parameters during selective oxidation of benzene to phenol with N₂O over ex-FeZSM-5.⁴⁷,⁴⁹

<table>
<thead>
<tr>
<th>Reaction parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact time / s</td>
<td>2</td>
</tr>
<tr>
<td>Benzene : N₂O : N₂ molar ratio</td>
<td>5 / 20 / 75</td>
</tr>
<tr>
<td>Benzene conversion / mol.%</td>
<td>27</td>
</tr>
<tr>
<td>N₂O conversion / mol.%</td>
<td>85</td>
</tr>
<tr>
<td>Phenol selectivity⁴ / mol.%</td>
<td>100</td>
</tr>
<tr>
<td>Productivity / kg phenol kg cat⁻¹ h⁻¹</td>
<td>0.1</td>
</tr>
</tbody>
</table>

⁴ Other products (CO₂, diols) were not identified in the GC analysis.

In other sources such as nitric acid plants or combustion processes, where diluted N₂O streams are present, the selective adsorption of N₂O on metal ion-exchanged ZSM-5 has been proposed to produce a concentrated stream of N₂O (> 5 vol.%).⁵⁰ However, the interference of other components in the tail-gas in the adsorption process and the periodic operation (adsorption-desorption cycles) make the practical application of this process option unlikely. In these cases, tail-gas abatement options are preferred.

**Other organic syntheses**

Other “newly identified” sources of N₂O from chemical production plants where a catalytic abatement can be effectively used are the production of acrylonitrile, caprolactam,
glyoxal, and in general organic syntheses using HNO₃ as an oxidant or processes involving ammonia oxidation. Acrylonitrile, precursor of nylon 6,6 and copolymers like SAN (styrene acrylonitrile) or ABS (acrylonitrile-butadiene-styrene), is produced by ammoxidation of propylene with ammonia and oxygen in a fluidized-bed catalytic reactor. This process generates N₂O during ammonia combustion, in a similar way to the case described for nitric acid plants. However, no data on concentrations, temperatures, and emissions have been reported. Substantial amounts of N₂O are also formed during the production of hydroxylamine, an intermediate in the manufacture of caprolactam (monomer for nylon 6 fibers and plastics). This tail-gas contains N₂O (usually in high concentrations), NOₓ, H₂O, SO₂, HCN, and NH₃. N₂O concentration in the tail-gas can largely vary (from 500 ppm to 60 vol.% in Dutch caprolactam plants), depending on the process variant. Concentrated N₂O off-gas is produced during the manufacture of glyoxal (intermediate in the production of copolymers, pharmaceuticals, resins, pesticides, etc.) by reaction between acetaldehyde and nitric acid. In this case, N₂O is accompanied by NO, O₂, and H₂O.

![Diagram](image_url)

**Fig. 16.** Tail-gas treatment in a glyoxal production unit (adapted from ref. 50).

The high N₂O concentration in these tail-gases (even up to 60 vol.%), resembling the situation described above for adipic acid plants, should in principle make extrapolation of developed technologies from this source straightforward. The recovery of the large amount of concentrated N₂O as a selective oxidant is an option, but the utility of the product (e.g. phenol) in the plant or its surroundings may be limited. In these cases different end-of-pipe technologies have been developed. As previously mentioned, control of the exotherm of N₂O decomposition is a notable design parameter in catalytic/thermal units to abate this gas. Diluting the tail-gas is an efficient way to deal with this issue. Clariant SA in cooperation with IRMA have recently installed a N₂O decomposition unit at a glyoxal production site using an ion-exchanged Fe-ferrierite catalyst. In this after-treatment, shown in Fig. 16, the N₂O in the tail-gas is diluted from 85 to 10 vol.% by air at the inlet of the process, in order to control properly the exothermicity of the reaction and to suit the catalyst stability. The adiabatic temperature rise in the reactor is ~200 K, which is used to preheat the incoming tail-gas up to 673 K. The same concept can be applied using ex-FeZSM-5 in these sources, in view of the excellent activity and stability.
3.3.4. Mobile combustion processes

Large N₂O emissions are a consequence of measures to control the emission of environmentally harmful NOₓ in vehicles.³⁷ Road traffic constitutes the most important mobile source of NOₓ (one-half of the anthropogenic emissions). Two sources of N₂O can be distinguished: (a) de-NOₓ catalysts in Diesel and lean-burn gasoline engines, and (b) three-way catalysts (TWCs) in conventional gasoline engines.⁷

**De-NOₓ, SCR**

Selective catalytic reduction (SCR) of NOₓ to N₂ under excess oxygen using hydrocarbons has been studied extensively, in order to establish a lean de-NOₓ technology, applicable to diesel and lean-burn gasoline-engine exhaust gas.⁵⁴,⁵⁵ Among the vast amount catalytic formulations investigated, low-temperature Pt-catalysts appear to be the most attractive in terms of de-NOₓ activity and stability against poisons and thermostability, but a serious drawback is the high N₂O yield (up to 70% of the NOₓ converted, Fig. 17).⁵⁶,⁵⁷ Thermodynamically, the transformation of NO into N₂O is less favoured than the transformation into N₂, and thus the high N₂O selectivity of this HC-SCR reaction over platinum catalysts has kinetic reasons. At low temperatures (473-523 K), where NOₓ is effectively reduced by the hydrocarbon, the N-O cleavage may become slower than N-N coupling step, leading to N₂O formation.⁵⁸ However, the reaction pathway is still a matter of debate.⁵⁹

![Fig. 17. SCR of NOₓ with hydrocarbons: Active de-NOₓ catalysts based on Pt have very low N₂ selectivities, yielding large amounts of N₂O. Optimization of the N₂ selectivity can be achieved with a dual-bed system, i.e. implementing a consecutive de-N₂O function (macroscopic bifunctionality).](image)

Several attempts to optimize the N₂ selectivity over platinum catalysts have been reported in the literature,⁶⁰-⁶³ but none of them resulted to be successful. We have focussed on the influence of the nature of the support, platinum dispersion and loading, and the influence of sodium promotion on the activity and selectivity over Pt-catalysts. These variables affect the de-NOₓ activity, but no clear trend was found with respect to the intrinsic N₂/N₂O selectivity.⁵⁶-⁵⁸ Another strategy is to combine periodic modification of engine operation with adaptation of the catalyst formulation (Pt/BaO/Al₂O₃) resulting in a “Nitrate Storage Reduction" system, exploiting a high selectivity of the Pt-phase under oxygen poor conditions.⁵⁴ Unfortunately, the nitrate storage function suffers from sulfur poisoning.

An alternative tactic for optimizing the N-O cleavage rates and increase the N₂ selectivity of the system is to insert a catalytic function for N₂O decomposition (Fig. 17), leading to the development of a macroscopic functionality. The simplest way to realize this strategy is to connect a lean de-NOₓ converter and a de-N₂O converter in series, which is the backbone idea of the dual-bed catalytic system developed by us.³⁷,⁵⁸,⁶⁴ A photograph of the dual-bed system is shown in Fig. 18, where two fixed-bed reactors are connected in series with
individual temperature control. Pt-based catalysts (on zeolites (USY, ZSM-5), activated carbon, Al₂O₃, and SiO₂) were considered as the de-NOₓ bed. Various catalytic formulations has been tested for N₂O decomposition and selective catalytic reduction of N₂O with C₃H₆, including mixed oxides derived from hydrotalcites (ex-Co-Rh,Al-HTIc and ex-Co,Pd-La,Al-HTIc), and metal zeolites (FeZSM-5 and PdZSM-5).³⁷

On a laboratory-scale reactor, we have shown the preliminary development of a dual-bed catalytic system for the consecutive removal of NO and N₂O, presenting a highly active, selective, and stable operation under lean-burn engine exhaust conditions. For the de-NOₓ, HC-SCR with propene using a dual-bed system with Pt-USY and ex-framework FeZSM-5 as de-NOₓ and de-N₂O catalysts, respectively, NOₓ conversions > 90% to N₂ were obtained, i.e. with no emission of N₂O, even in the presence of H₂O and SO₂ (Fig. 19).³⁸ Ex-framework FeZSM-5 was the optimal de-N₂O catalyst, showing promotion by NO (unconverted in the first bed) and SO₂, and stable behaviour in the presence of water. Secondary hydrocarbon addition over ex-FeZSM-5 (see Fig. 19) shifts the N₂O decomposition activity to lower

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**Fig. 18.** Photograph of the dual-bed system for simultaneous NOₐ and N₂O reduction.

**Fig. 19.** Overview of operation parameters of the dual-bed system for HC-SCR of NOₓ to N₂.
temperature. Current challenges to overcome for the application of this promising system in vehicles is the independent control regulation of the temperature in the de-NO$_x$ and de-N$_2$O catalysts, and experiments with more realistic space velocities.

The dual-bed approach can be also realized in the SCR of NO$_x$ with NH$_3$ in the presence of oxygen. At the optimal SCR conditions (temperature window) N$_2$O is formed as a non-selective product of the reaction between NO and NH$_3$, while at higher temperatures N$_2$O formation is due to NH$_3$ oxidation.$^{65}$

**Aged TWCs**

Another increasing source of N$_2$O in mobile combustion, where the dual-bed system can be effectively applied, results from the aging of three-way catalysts (TWC) in conventional gasoline engines.$^7$ Fresh commercial three-way catalysts (TWC) have the maximum N$_2$O production at low temperatures, but upon aging (deactivation) this shifts to higher temperatures into the window where the catalyst frequently operates (500-700 K), inducing a continuous production of N$_2$O. At these temperatures, the components of the TWC (La$_2$O$_3$, CeO$_2$, Pt, and Rh) are not able to decompose N$_2$O.$^7$ At higher temperature, N$_2$O is either not formed or directly converted over the TWC-catalyst. The major challenges for the N$_2$O decomposition catalysts are high activity at low N$_2$O concentration with SO$_2$ resistance and thermostability, which are fulfilled by ex-FeZSM-5.

### 3.3.5. Catalyst implementation: “from powder to reactor”

Laboratory screening is carried out with a catalyst powder or pellets. Small particles normally do not apply in conventional industrial fixed-bed reactor because of the high-pressure drop. The implementation of any catalytic abatement unit in stationary sources (chemical production or combustion processes) requires a close look to the reactor type, in order to achieve maximum yields under efficient and safe operation. The practical form and shape of the catalyst is a crucial aspect to obtain reliable design data for full-scale implementation. In this section, a numerical comparison between a fixed-bed reactor with shaped particles and monolithic reactor with structured catalysts is presented (Figs. 20a and b, respectively). This is exemplified for the catalytic decomposition of N$_2$O in front of the tailgas expander in nitric acid plants (position (c) in Fig. 13). For the calculation, the activity data of ex-FeZSM-5 in the simulated tail-gas mixture in Fig. 4 were used.

![Fig. 20. Schematic representation of (a) a fixed-bed reactor and (b) a monolithic reactor.](image)

**Basis of design.** The calculations were carried out for a nitric acid plant of a capacity of 1500 ton HNO$_3$ per day and a volumetric flow of the tail-gas of $2 \times 10^8$ Nm$^3$ h$^{-1}$. An allowable pressure drop of 200 mbar was fixed, with a reactor diameter of 2 m. N$_2$O conversion of 80%
(X = 0.8) was targeted at reaction temperature of 750 K. The expressions used in the calculations can be found in the appendix of this chapter.

**Fixed-bed reactor.** Fig. 21 shows the dependency of reactor volume, effectiveness factor, and pressure drop with different design parameters (total pressure \( P \) upstream of the expander and size of the extrudates) in a fixed-bed reactor. Due to the high intrinsic reaction rates, the reaction in common particles (extrudates) will exhibit severe diffusion limitations. Only the outer part of the particle is used for the reaction, which in turn would call for small catalyst particles. However, these lead to a severe pressure drop. At \( P = 4 \) bar, none of the particle sizes used satisfies the criterion of pressure drop allowance (grey area), even for particles of 10 mm. This is due to the corresponding increased space time in the reactor at a lower total pressure. Low effectiveness factors (<40%) are obtained for acceptable situations (\( d_p > 4 \) mm at 10 bar). In these cases, reactor volumes ranging from 3 to 8 m³ are required. Setting higher N₂O conversion targets or operation at lower temperatures is impractical using this design. Obviously, the requirements are more difficult to meet if a lower maximum pressure drop is required.

**Monolithic reactor.** For gas phase applications, typically using high space velocities, structured catalysts are very convenient. Decoupling of the hydrodynamics, kinetics, and transport phenomena can be achieved by structured catalysts. In the current case monolithic structures allow the combination of high intrinsic activity, high catalyst effectiveness, and a low-pressure drop. Cell density, expressed as cells per squared inch (cpsi) and wall thickness (\( \delta \) in Fig. 20) are design parameters of monolithic reactors.

There is a wide range of commercially available monolithic structures, which makes the reactor monolith selection quite flexible. We have considered here extruded monoliths with the ex-FeZSM-5 catalyst. Fig. 22 shows the effectiveness factor at different wall thickness and total pressure of the tail-gas. The high effectiveness obtained, e.g. \( \eta \sim 90\% \) for \( \delta = 0.4 \) mm contrasts with the low values in the packed-bed reactor, <40% for a proper particle/extrudate size. The reactor volume required depends on the cell density and wall
thickness, being even smaller in magnitude as required for a fixed bed (Fig. 23). This clearly indicates that the high catalyst effectiveness in a monolith compensates for the lower amount of catalyst as compared to a fixed-bed reactor.

Fig. 22. Effectiveness factor as a function of the wall thickness of the extruded monolith. Tail-gas conditions: Nitric acid plant, position (c) in Fig. 13, P = 4 or 10 bar, T = 750 K and X = 0.8.

Fig. 23. Monolith reactor volume at different cell density and wall thickness of the extruded monolith (δ). Tail-gas conditions: Nitric acid plant, position (c) in Fig. 13, P = 4 or 10 bar, T = 750 K and X = 0.8.

Fig. 24. Pressure drop at different cell density and wall thickness of the extruded monolith (δ). Tail-gas conditions: Nitric acid plant, position (c) in Fig. 13, P = 4 or 10 bar, T = 750 K and X = 0.8.
Another major advantage is the low-pressure drop of the monolith structure, due to the relative open frontal area in the channels (Fig. 24). Many different options (cell density combined with wall thickness) can be applied. Based on these figures, an optimal design can be proposed. Using a high cell density and a large wall thickness leads to low reactor volumes, increased pressure drop and decreased catalyst effectiveness. A monolith of 200 cpsl and $\delta = 0.4$ mm (a quite standard geometric design, shown in Fig. 25) leads to high effectiveness (~90%), small reactor volumes (1.0 and 2.5 m$^3$), at 10 and 4 bar, respectively), and low pressure drop (< 100 mbar). From the reactor volume, bed heights of 0.3 and 0.7 m are derived (the reactor diameter is fixed at 2 m). Another valuable advantage of the monolithic reactor compared to the fixed-bed reactor is the flexibility for operation under different requirements of pressure and conversion, without violating operational constraints. E.g. by doubling the reactor height 99% conversion is achieved at a pressure drop of 40 mbar.

The structured reactor concept is optimal for catalytic N$_2$O removal in nitric acid plants, not only for direct N$_2$O decomposition or N$_2$O reduction with hydrocarbons or other fuels in the tail-gas, but also in the in process gas catalytic N$_2$O decomposition (position b) in Fig. 13). In the latter case, much higher reaction rates are expected due to the temperature and pressure. Therefore, external mass transfer controls the process. From our calculations assuming gas phase and laminar flow in the channels, it is concluded that a monolithic geometry provides sufficiently high activities (Chapter 1).

The monolithic catalyst for N$_2$O abatement in stationary sources can be implemented as shown in Fig. 26. The monolith catalyst, typically in square units of ca. 150x150 mm$^2$, can be packed in catalyst baskets, which are inserted in catalyst layers. A typical practice in the

---

**Fig. 25.** Selected extruded monolith. Cell density = 200 cpsl, wall thickness = 0.4 mm, and cell pitch = 1.8 mm.

**Fig. 26.** Reactor and catalyst design for N$_2$O abatement options in tail-gases from stationary sources.
reactor design to allow flexible operation (prospective or more stringent regulations or operation changes in the plant) consists of leaving spare space for an extra layer of catalyst. The possible addition of reductant is also considered in the figure. The vast commercial experience gained in de-NOₓ NH₃-SCR,⁶⁹,⁷⁰ can be extrapolated to the design and implementation of this system.

Structured reactors can be effectively applied in the other sources discussed previously. This specially applies to combustion processes (see Fig. 14), where a high dust and erosion tolerance are essential requirements in the reactor design. In chemical processes with concentrated N₂O streams, the thermostability is a key aspect for the successful application of monoliths.

**Other reactor configurations.** As an alternative reactor configuration with low-pressure drop, “lateral flow” type modules based on the fixed-bed concept can also be considered. This reactor concept has been developed by CRI Catalysts and Shell Research for e.g. de-NOₓ SCR with ammonia in nitric acid plants using Ti-V based catalysts (Fig. 27).⁷¹ The modules, filled with catalyst particles of 1-2 mm, are hoisted into the reactor housing and placed on top of a support grid. This grid holds the weight of the modules, but it also provides a gas tight sealing between the modules and the grid. The gas passes the module only once, and the gas flow may be in an upward, downward, or horizontal direction. In this reactor the total cross sectional bed area is larger than the reactor diameter, and thus pressure drop is minimized. The effectiveness of the small catalyst particles, is largely improved compared to a conventional fixed-bed reactor. The disadvantage of this system is the increased reactor volume compared to the monolithic reactor (by a factor of 2-3). In addition, dust and erosion resistance are much less favourable than in monoliths, where a large open frontal area is present.

4. Conclusions

An ex-framework preparation route leads to an active and stable FeZSM-5 catalyst for direct N₂O decomposition in simulated tail-gases (containing O₂, NO, CO₂, H₂O and SO₂). This result indicates a great potential of this catalytic system for commercial applications, in tail-gases from nitric acid plants and combustion processes in fluid-bed reactors. Other applications include adipic acid, caprolactam, glyoxal, and acrylonitrile production plants, where both N₂O abatement and utilization (as selective oxidant) can be applied. A dual-bed converter is proposed for mobile sources. The superior performance (activity and stability) of the ex-framework catalysts compared to the FeMFI catalysts prepared by conventional (solid and liquid)-ion exchanged and sublimation methods indicates a crucial role of the preparation method on the formation of the active sites in N₂O decomposition. Noble-metal based catalysts, although showing very high activities in a N₂O/He feed (especially ex-Co-Rh,Al-HT1c), are severely inhibited by NO, H₂O, and SO₂, and suffer from deactivation during time on stream. This limits their application in tail-gas situations. Monolithic reactors are optimal for implementation of the catalyst in the tail-gas unit, since allow the combination of high intrinsic activity, high catalyst effectiveness, and low-pressure drop.
Acknowledgements. J.P.R. gratefully acknowledges J. García-Cortés and Prof. dr. C. Salinas-Martínez de Lecea (Química Inorgánica, Universidad de Alicante) for the intensive cooperation in the development of the dual-bed system for consecutive NO\textsubscript{2}-N\textsubscript{2}O removal.

References

5. Chapter 1 of this thesis.
36. Chapter 8 of this thesis.
40. V. Schumacher, G. Bürgler, T. Fetzer, M. Baier, M. Hesse, DE 19819882A1, 1999, to BASF.
Appendix. General equations used in the reactor design (see Fig. 20).

<table>
<thead>
<tr>
<th></th>
<th>Fixed-bed reactor</th>
<th>Monolithic reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cylindrical extrudates)</td>
<td>(extruded monolith, square channels)</td>
</tr>
<tr>
<td><strong>Partial pressure and concentration</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$p(N_2O) = P \ y(N_2O)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C(N_2O) = \frac{p(N_2O)}{R \ T}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Rate constants (plug-flow model, 1st order irreversible reaction)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_w = \frac{F(N_2O)<em>0}{W</em>{col} \ C(N_2O)_0} \ \frac{1}{(1-X(N_2O))}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_v = k_w \ \rho_{col}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Catalyst effectiveness</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Particle</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_p$</td>
<td>$d_h = D - \delta = \frac{4 \ A_{th}}{O_{th}}$</td>
<td></td>
</tr>
<tr>
<td>$D = \sqrt{\frac{25.4^2}{c \ psi}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L = \frac{d_p}{4}$</td>
<td>$L = \frac{\delta}{2}$</td>
<td></td>
</tr>
<tr>
<td>$\phi = L \ \sqrt{\frac{k_v \ (1-\epsilon_r)}{D_{eff}}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta = \frac{\tanh(\phi)}{\phi}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_{v,obs} = k_v \ (1-\epsilon_r) \ \eta$</td>
<td>$k_{v,obs} = k_v \ (1-\epsilon_{mu}) \ \eta$</td>
<td></td>
</tr>
<tr>
<td>- Reactor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\tau_r = \frac{V_{col}}{\varphi_{v,g}} = \ln \left( \frac{1}{1-X(N_2O)} \right) \frac{1}{k_{v,obs}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\epsilon_s$</td>
<td>$\epsilon_m = \frac{(D-\delta)^2}{D^2}$</td>
<td></td>
</tr>
<tr>
<td>$V_s = \frac{V_{col}}{1-\epsilon_s}$</td>
<td>$V_m = \frac{V_{col}}{1-\epsilon_m}$</td>
<td></td>
</tr>
<tr>
<td>$h_s = \frac{V_s}{\pi \ \frac{d_s^2}{4}}$</td>
<td>$h_m = \frac{V_m}{\pi \ \frac{d_m^2}{4}}$</td>
<td></td>
</tr>
<tr>
<td><strong>Hydrodynamics</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$u_s = \frac{\varphi_{v,g} \ A_s}{A_s}$</td>
<td>$u_{ch} = \frac{\varphi_s}{A_{th}}$</td>
<td></td>
</tr>
<tr>
<td>$A_s = \frac{\pi \ d_s^2}{4}$</td>
<td>$A_{th} = \frac{\pi \ d_m^2 \ \epsilon_m}{4}$</td>
<td></td>
</tr>
<tr>
<td>$R_e = \frac{\rho_s \ \ d_s \ u_{ch}}{\mu_s}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
\[ \Delta P_s = h_s \left( \frac{150 \mu_s u_s (1-\varepsilon_s)^2}{d_p^2} + 1.75 \frac{\mu_s u_s^2 (1-\varepsilon_s)}{d_p} \right) \]

\[ \Delta P_m = \frac{56.92}{Re} \frac{\rho_s u_{in}^2}{d_p} \]

**Physical properties of the gas mixture:**

\[ \frac{1}{D} = \frac{1}{D(N_2O-N_2)} + \frac{1}{D_k(N_2O)} \]

\[ D(N_2O-N_2) = 18.583 \cdot 10^{-4} \sqrt{\frac{T^4}{P \sigma(N_2O-N_2) \Omega_r(N_2O-N_2)}} \]

\[ D_k(N_2O) = 97 r_c \sqrt{\frac{T}{M_w(N_2O)}} \]

\[ D_{eff} = \frac{D}{D_k} \frac{\varepsilon_p}{r_p} \]

\[ \rho_s = \frac{P M_w}{R T} \]

\[ \mu_s = (30.43 + 0.4989 T - 0.0001093 T^2) \cdot 10^{-7} \]

**Notation**

- \( A_b \): cross sectional area of the fixed bed
- \( A_{ao} \): cross sectional area of monolith channel (open)
- \( C(N_2O) \): concentration of \( N_2O \)
- \( \rho_s \): cell density (cell per square inch)
- \( d \): diameter
- \( D \): monolith cell pitch (square channel)
- \( D(N_2O-N_2) \): binary diffusivity of \( N_2O \) in \( N_2 \)
- \( D_k(N_2O) \): Knudsen diffusivity of \( N_2O \) in a cylindrical pore
- \( D^* \): average diffusivity
- \( D_{eff} \): effective diffusivity
- \( F(N_2O) \): molar flow of \( N_2O \)
- \( h \): height
- \( k_0 \): rate constant per unit catalyst volume
- \( k_r \): rate constant per unit catalyst mass
- \( L \): characteristic catalyst dimension
- \( M_{w(i)} \): molar mass of species \( i \)
- \( O_{ai} \): periphery of the monolith's channel cross section
- \( P(N_2O) \): partial \( N_2O \) pressure
- \( P \): total pressure
- \( r_c \): average pore radius
- \( R \): universal gas constant
- \( Re \): Reynolds number
- \( T \): temperature
- \( u \): average superficial velocity
- \( V \): volume
- \( W_{cat} \): catalyst mass
- \( X(N_2O) \): fractional conversion of \( N_2O \)
- \( y(N_2O) \): molar fraction of \( N_2O \)
Greek

δ = monolith wall thickness
ε = porosity
φ = generalized Thiele modulus (1st order irreversible reaction)
φ_{gs} = volumetric gas flow
η = catalyst effectiveness factor
μ = dynamic viscosity
ρ = density
σ(N_{2}O-N_{2}) = collision diameter for pair N_{2}O-N_{2}
τ = average residence time in the reactor
τ_{p} = particle tortuosity factor
ΔP = pressure drop in the reactor
Ω_{0}(N_{2}O-N_{2}) = collision integral for the pair N_{2}O-N_{2}

Subscripts and superscripts

b = bed or fixed-bed reactor
cat = catalyst
ch = monolith channel (open area)
eff = effective
g = gas
h = hydrodynamic (monolith channel)
m = monolithic reactor
mw = monolith wall
o = at reactor feed
obs = observed
p = particle
r = reactor (fixed bed or monolith)
s = superficial

References

NO-Assisted N₂O Decomposition over Fe-Based Catalysts

The decomposition of N₂O is strongly promoted by NO over Fe-catalysts supported on zeolites (ex-framework FeMFI catalysts, sublimed Fe/ZSM-5, ion-exchanged Fe-ZSM-5, Fe-Beta, and Fe-USY) and conventional supports (Fe/Al₂O₃ and Fe/SiO₂) in a wide temperature range (550-900 K). Mixtures of NO and O₂ in the N₂O-containing feed lead to the same promoting effect as NO only. The promoting effect of NO is catalytic, and besides NO₂, O₂ is formed much more extensively at lower temperatures than in the absence of NO. The promotion effect only requires low NO concentrations in the feed, with no significant improvements at molar NO/N₂O feed ratios higher than 0.25. No inhibition by NO was identified even at a molar NO/N₂O feed ratio of 10, suggesting different sites for NO adsorption and oxygen deposition by N₂O. The latter sites seem to be remote from each other. Transient experiments over ex-framework FeZSM-5 further elucidate the mechanism of NO promotion. In situ FT-IR/MS experiments indicate that NO is strongly adsorbed on the catalyst surface up to at least 650 K. A change in gas phase composition from NO to N₂O results in the formation of adsorbed NO₂. Switching back to the original NO gas phase induces a rapid desorption of NO₂, restoring the original NO absorption frequencies. During the infrared measurements, bands typical of nitro- or nitrate groups were not observed. Multitrack experiments on ex-framework FeZSM-5 show that release of oxygen from the catalyst surface during direct N₂O decomposition is a rate determining step, due to the slow oxygen recombination, which is favoured by high reaction temperatures. NO addition promotes this oxygen desorption. Adsorbed NO accommodates oxygen from N₂O and the formed adsorbed NO₂ can react with a second oxygen from the neighboring site, thus accelerating the recombination of oxygen from N₂O. Less than 0.9% of the Fe seems to participate in this promotion. Adsorbed NO may even facilitate the migration of atomic oxygen to enhance their recombination. A model is proposed to explain the phenomena observed in the NO-assisted N₂O decomposition, including NO₂ decomposition.
1. Introduction

Fe-based zeolite catalysts are currently extensively studied, because of high activity in i) selective catalytic reduction of NO and N₂O with hydrocarbons or ammonia,¹⁴ ii) N₂O-mediated selective oxidation of benzene to phenol,⁹,¹¹ iii) direct catalytic N₂O decomposition,¹²-¹⁴ and selective oxidation of NH₃ to N₂.¹⁵ We have recently reported an extraordinary performance of a specific FeZSM-5 catalyst prepared via an ex-framework method in the N₂O decomposition reaction.¹⁶ The ex-framework catalyst (on a per Fe basis) shows a significantly higher activity than catalysts prepared via other procedures, such as liquid (aqueous)- or solid-ion exchange, or sublimation. Also the stability of this particular catalyst in simulated tail-gas mixtures from nitric acid plants and fluidized-bed combustors is excellent.¹⁶,¹⁷

An intriguing general feature of FeZSM-5 catalysts in N₂O decomposition is that NO significantly enhances the activity, while the opposite effect is usually observed for other catalytic systems, e.g. based on noble metals (Ru or Rh).¹⁸,¹⁹ This peculiar behaviour of FeZSM-5 makes it very attractive to use in applications where both N₂O and NO are present, such as in tail-gas of nitric acid plants. The positive effect of NO on the N₂O conversion was first reported by some of us in 1996, using a FeZSM-5 prepared by liquid (aqueous) ion exchange with Fe(II) sulfate.²⁰ At that time it was proposed that NO and also SO₂ in the gas phase scavenged adsorbed oxygen (deposited by N₂O during the oxidation of active sites, eq. (1)), leading to the formation of NO₂ and regeneration of the active site (eq. (2)).

\[
N₂O + * \rightarrow N₂ + O* \quad (1)
\]

\[
NO + O* \rightarrow NO₂ + * \quad (2)
\]

Reduction of an oxidized site by NO as represented in eq. (2) should lead to a stoichiometric process in which NO and N₂O react to form N₂ and NO₂:

\[
N₂O + NO \rightarrow N₂ + NO₂ \quad (3)
\]

Recently Sang and Lund¹⁴ further discussed the mechanism of NO-assisted N₂O decomposition over a sublimed FeZSM-5 catalyst. These authors proposed a nitrite/nitrate redox cycle (eqs. (4) and (5)) by reaction with N₂O, yielding O₂ and N₂.

\[
N₂O + NO₃* \rightarrow N₂ + O₂ + NO₂* \quad (4)
\]

\[
N₂O + NO₂* \rightarrow N₂ + NO₃* \quad (5)
\]

It was also proposed that nitrites and nitrates play a role in N₂O decomposition in the absence of NO, based on spectroscopic results of Sachtler et al.¹³,²¹ and O₂ exchange experiments performed in the early eighties by Leglise et al.²² Further experimental evidence was not provided by Sang and Lund.¹⁴

In this chapter the NO-assisted N₂O decomposition over ex-framework FeZSM-5 is further discussed. It will be shown that the NO-assisted N₂O decomposition is not a special feature of FeZSM-5 catalysts, but a general phenomenon occurring over many Fe-containing zeolitic (Beta, USY) and non-zeolitic (Al₂O₃, SiO₂) catalysts. Activity data on the effect of the molar NO/N₂O feed ratio and reaction temperature on the performance of these catalysts will be presented. Based on flow and pulse experiments, in combination with in situ FT-IR/MS, steady-state and transient phenomena regarding the chemistry of N₂O, NO, and NO₂ over Fe-catalysts are investigated, and, possible catalytic cycles in the NO-assisted N₂O decomposition are proposed.
2. Experimental

2.1. Catalyst preparation

The chemical composition of the different catalysts used in this study is summarized in Table 1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method</th>
<th>Si/Al or Si/Gax</th>
<th>Fe' / wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ex-[Fe,Al]MFI(a)</td>
<td>Ex-framework</td>
<td>32.6</td>
<td>0.66</td>
</tr>
<tr>
<td>ex-[Fe,Al]MFI(b)</td>
<td>Ex-framework</td>
<td>32.6</td>
<td>0.64</td>
</tr>
<tr>
<td>ex-[Fe,Ga]MFI</td>
<td>Ex-framework</td>
<td>32.6</td>
<td>0.58</td>
</tr>
<tr>
<td>ex-[Fe]MFI</td>
<td>Ex-framework</td>
<td>-</td>
<td>0.68</td>
</tr>
<tr>
<td>Fe/ZSM-5</td>
<td>Sublimation</td>
<td>14.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Fe-ZSM-5</td>
<td>Ion-exchange</td>
<td>37.5</td>
<td>1.44</td>
</tr>
<tr>
<td>Fe-Beta</td>
<td>Ion-exchange</td>
<td>11.0</td>
<td>1.50</td>
</tr>
<tr>
<td>Fe-USY</td>
<td>Ion-exchange</td>
<td>15.5</td>
<td>1.28</td>
</tr>
<tr>
<td>Fe/Al₂O₃</td>
<td>Incipient wetness</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe/SiO₂</td>
<td>Incipient wetness</td>
<td>-</td>
<td>2.0</td>
</tr>
</tbody>
</table>

x determined by ICP-OES.

2.1.1. Ex-framework Fe-catalysts

Isomorphously substituted FeMFI was synthesized hydrothermally using tetrapropylammonium hydroxide as the template. The molar ratios between the components was H₂O/Si = 45, TPAOH/Si = 0.3, Si/Al = 36, and Si/Fe = 152. The as-synthesized sample, in which Fe(III) is isomorphously substituted in the zeolite framework, was calcined in air at 823 K for 10 h and was then converted into the H-form by three consecutive exchanges with an ammonium nitrate solution (0.1 M) overnight and subsequent calcination at 823 K for 5 h. Finally, the catalyst was treated in flowing steam at ambient pressure (water partial pressure of 300 mbar and 30 ml min⁻¹ of N₂ flow) at 873 K during 5 h, yielding a sample denoted as ex-[Fe,Al]MFI(a).

In a modified synthesis route, ex-[Fe,Al]MFI was prepared using the same molar metal ratios but a lower molar TPAOH/Si ratio (0.1 instead of 0.3). This was done by adding NaOH to the synthesis gel in a molar NaOH/Si ratio of 0.2 (denoted as ex-[Fe,Al]MFI(b)). Following this route, ferrigallosilicate (denoted as ex-[Fe,Ga]MFI) and ferrisilicate (denoted as ex-[Fe]MFI) were also prepared. Addition of NaOH to the synthesis gel induces a lower template concentration and thus a larger crystal size of the final catalysts (0.4 µm in ex-[Fe,Al]MFI(a) vs. 2.0-2.5 µm in ex-[Fe,Al]MFI(b), ex-[Fe,Ga]MFI, and ex-[Fe]MFI catalysts). More details on the preparation methods and characterization of these materials can be found in Chapters 5 and 9 of this thesis.

2.1.2. Other Fe-catalysts

Fe/ZSM-5 was prepared by sublimation of FeCl₃ on HZSM-5 (Degussa, Si/Al = 14.0), according to the method described by Sachtler et al.² Fe-ZSM-5, Fe-Beta, and Fe-USY were prepared by liquid (aqueous)-ion exchanged with diluted solutions (0.30 mM) of Fe(NO₃)₃·9H₂O (Fe-ZSM-5 and Fe-USY) and FeSO₄·7H₂O (Fe-Beta). The parent zeolites were provided by Zeolyst (NH₄-ZSM-5: CBV8020, Si/Al = 37.5, NH₄-Beta: CP814E, Si/Al = 11, H-USY: CBV720; Si/Al = 15.5). The exchange was carried out under vigorous stirring during 15 h. The zeolites were then filtered, washed thoroughly, dried, and finally calcined in static air at 825 K for 5 h. Fe/Al₂O₃ and Fe/SiO₂ were prepared by incipient wetness impregnation, with appropriate aqueous solutions of iron(II) gluconate, Fe[OHCH₂(CHOH)₄CO₂]₂·2H₂O.
Al₂O₃ (CK300) and SiO₂ were purchased from Ketjen and Grace, respectively. After the impregnation the samples were dried at 363 K followed by calcination at 493 K for 1 h and at 773 K for 5 h.

2.2. Activity tests

Activity measurements were carried out in a six-flow reactor system,²⁴ using 50 mg of catalyst (125-200 µm) and a space velocity (GHSV) of 60000 h⁻¹ at atmospheric pressure. The feed conditions used were 1.5 mbar N₂O, 0-15 mbar NO, 0-0.2 mbar NO₂, and 0-20 mbar O₂, with He as balance gas. Before reaction, the catalysts were pretreated in N₂O (1.5 mbar N₂O in He) at 723 K for 1 h and cooled in that gas flow to the initial reaction temperature. In the temperature range of 550-925 K, deactivation of the catalysts was absent. N₂O, N₂, and O₂ were analyzed with a GC (Chrompack CP 9001) equipped with a thermal conductivity detector, using a Poraplot Q column (for N₂O separation) and a Molsieve 5A column (for N₂ and O₂ separation). NO, NO₂, and NO₃ concentrations were determined with a chemiluminescence NO₃ analyzer (Ecophysics CLD 700 EL).

2.3. FT-IR/MS experiments

The FT-IR (Fourier Transform Infrared) measurements were performed using an in situ infrared cell with CaF₂ windows.²⁵ The set-up is shown in Fig. 1. Gas flows were set by mass-flow controllers and composition programming was carried out using a 4-way valve, which was configured to select two separate gas feeds. Using a flow of 30 ml min⁻¹, the cell (volume 3.8 ml) was completely refreshed in about 10 s after switching the valve. For the infrared measurements, the catalyst was pressed in the form of a self-supporting wafer (~70 mg cm⁻²) at a pressure of 3 ton cm⁻². Pretreatment of the wafer consisted of drying at 573 K in He (30 ml min⁻¹) for 1 h. Spectra were recorded using a Nicolet Magna infrared 860 spectrometer equipped with a nitrogen cooled MCT detector and a rapid scan interferometer. Unless stated otherwise, spectra were recorded against a background of the sample at the reaction temperature under He at 4 cm⁻¹ resolution, using co-addition of 48 scans. Transient experiments were performed using a rapid scan collection mode. Again 48 scans were co-added for each spectrum using scan length minimization, leading to a complete spectrum collection time of 7.7 s. The infrared measurements were performed using a 3 vol.% N₂O in He mixture, and a 5 vol.% NO in He mixture. The purity of all the gases was > 99.985%. The

![Fig. 1. General view of the in situ FT-IR set-up; 1: gas supply, 2: pressure indicator, 3: mass-flow controllers; 4: Valco valve; 5: IR cell + oven; 6: temperature controller; 7: to MS analysis; 8: back-pressure controllers; 9: vent line.](image)
transients in gas phase composition were followed using a Quadrupole Mass Spectrometer (Pfeiffer Thermostar) connected on line to the outlet of the in situ infrared cell via a capillary.

2.4. Multitrack experiments

Experimental set-up. A detailed description of the Multitrack (Multiple Time Resolved Analysis of Catalytic Kinetics) system, shown schematically in Fig. 2, is presented elsewhere. Two different gases can be dosed to the reactor by means of high-speed pulse valves, yielding pulses of $10^{17}$ molecules within 100 μs. The reactor with the catalyst sample is located in a high vacuum system, and during pulsing the peak pressure remains below 3 Pa. The catalyst bed (100 mg, pellet size 125-200 μm) is packed between two layers of inert SiC-particles (particle size 230 μm), consisting of 200 mg and 125 mg before and after the bed, respectively. In the reactor, the shape and composition of the gas pulse change due to processes such as diffusion, adsorption, and reaction. At the reactor exit the reaction products are analyzed by four quadrupole mass spectrometers positioned in-line with the reactor axis. All mass spectrometers are able to analyze one of the components in the exit gas stream with a maximum sample frequency of 1 MHz. In this study most analyses were carried out with the mass spectrometer located closest to the exit of the catalytic reactor (MS4 in Fig. 2). As the signal-to-noise ratio in this system is excellent, single pulses are sufficient to obtain good peak signals. This is an important aspect, as transient phenomena may remain unobserved when several pulse responses have to be averaged.

Procedure. Several types of Multitrack experiments were performed with ex-[Fe,Al]MFI(a). Before the measurements, the ex-[Fe,Al]MFI(a) catalyst was evacuated in the Multitrack reactor at 723 K for 3 h. The mechanistic studies of direct N₂O decomposition were carried out by continuously pulsing pure N₂O (~160 nmol per pulse) with intervals of 2 s ('cycle time') at different temperatures in the range of 623 to 973 K, and recording the masses m/e 28 (N₂), m/e 32 (O₂), and m/e 44 (N₂O). Isothermal O₂ desorption was followed as a function of time after stopping N₂O pulsing (usually after ~100 pulses) in the temperature range of 673-798 K. The effect of NO on the N₂O decomposition was studied in dual-pulse experiments, in which pulses of N₂O (pure, ~160 nmol per pulse) and NO (15 vol.% NO in Ar, ~24 nmol NO per pulse) are sequentially fed to the reactor with a time interval of 1 s between the pulses and a cycle time of 2 s. Isothermal transient desorption effects after stopping N₂O or NO pulsing were followed at different temperatures, ranging from 698 to 923 K. In these experiments, the masses m/e 30 (NO) and m/e 46 (NO₂) were additionally analyzed. The purity of the gases was > 99.985%.

![Fig. 2. Photograph and schematic representation of the Multitrack set-up.](image-url)
3. Results

3.1. Activity data

3.1.1. Ex-framework catalysts

The N₂O decomposition activity of ex-[Fe,Al]MFI(a) in different feed mixtures is presented in Fig. 3. In a N₂O/He feed, the catalyst shows a substantial N₂O conversion only above 700 K. Addition of NO (0.4 mbar; NO/N₂O = 0.27) enhances the reaction rate considerably. The N₂O conversion curve is shifted to about 100 K lower temperatures. The presence of oxygen (20 mbar O₂) in the feed (N₂O + NO + O₂ in He) hardly affects the catalyst activity. The same promotion effect was obtained over the other ex-framework catalysts (Fig. 4). For these catalysts, the trend in activity in the N₂O-He feed (ex-[Fe,Al]MFI(b) ≥ ex-[Fe,Ga]MFI > ex-[Fe]MFI) is maintained when NO is added to the feed mixture. For the different Fe-zeolites, the promotion effect by NO on the N₂O conversion also leads to a significant decrease in the apparent activation energy (Table 2), which has been estimated around the inflection (50% conversion) of the activity vs. temperature curves by assuming a plug-flow model and first-order reaction in N₂O.

![Graph showing N₂O conversion vs. temperature over ex-[Fe,Al]MFI(a) in different feed mixtures.](image)

**Fig. 3.** N₂O conversion vs. temperature over ex-[Fe,Al]MFI(a) in different feed mixtures: (○) 1.5 mbar N₂O in He, (●) 1.5 mbar N₂O + 0.4 mbar NO in He, (♦) 1.5 mbar N₂O + 0.4 mbar NO + 20 mbar O₂ in He; P = 1 bar; GHSV = 60000 h⁻¹.

Fig. 5 shows the influence of the molar NO/N₂O ratio in the feed on the N₂O conversion at reaction temperatures ranging from 623 to 723 K. N₂O conversion is dramatically improved at low NO partial pressures (NO/N₂O < 0.25). From this value up to NO/N₂O = 10, little effect on N₂O conversion is noticed.

**Table 2.** Apparent activation energy ($E_{a,app}$) of the ex-framework catalysts for direct N₂O decomposition in the absence or presence of NO in the feed gas.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E_{a,app}$, N₂O / kJ mol⁻¹</th>
<th>$E_{a,app}$, N₂O + NO / kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ex-[Fe,Al]MFI(a)</td>
<td>161</td>
<td>106</td>
</tr>
<tr>
<td>ex-[Fe,Al]MFI(b)</td>
<td>137</td>
<td>90</td>
</tr>
<tr>
<td>ex-[Fe,Ga]MFI</td>
<td>141</td>
<td>90</td>
</tr>
<tr>
<td>ex-[Fe]MFI</td>
<td>155</td>
<td>100</td>
</tr>
</tbody>
</table>

*a Feed: 1.5 mbar N₂O in He; P = 1 bar; GHSV = 60000 h⁻¹.

*b Feed: 1.5 mbar N₂O + 0.2 mbar NO in He; P = 1 bar; GHSV = 60000 h⁻¹.
Fig. 4. N\textsubscript{2}O conversion vs. temperature over \((\diamond, \bullet)\) ex-[Fe,Al]MFI(b), \((\triangle, \blacktriangle)\) ex-[Fe,Ga]MFI, \((\square, \blacksquare)\) ex-[Fe]MFI. Conditions: \((\diamond, \triangle, \square)\) 1.5 mbar N\textsubscript{2}O in He and \((\bullet, \blacktriangle, \blacksquare)\) 1.5 mbar N\textsubscript{2}O + 0.4 mbar NO in He; \(P = 1\) bar; GHSV = 60000 h\textsuperscript{-1}.

The NO, NO\textsubscript{2}, and NO\textsubscript{x} profiles provide further information on the effect of NO on the catalytic performance. In a N\textsubscript{2}O+NO/He feed, the formation of NO\textsubscript{2} over ex-[Fe,Al]MFI(a) increases as a function of reaction temperature (Fig. 6), reaching a maximum at 650-675 K, \textit{i.e.} around the inflection point of the N\textsubscript{2}O decomposition activity curve (Fig. 3). Above this temperature, NO\textsubscript{2} formation decreases before completely disappearing at 775 K. The total NO\textsubscript{x} level is constant in the temperature range investigated, indicating that NO\textsubscript{x} is not converted to N\textsubscript{2} or N\textsubscript{2}O. The amount of NO\textsubscript{2} formed is beyond the thermodynamic equilibrium of the NO and O\textsubscript{2} reaction (eq. (6)), suggesting that the rate of the N\textsubscript{2}O and NO reaction is higher than the decomposition rate of NO\textsubscript{2} over the catalyst. The equilibrium composition of NO\textsubscript{2} was calculated in two ways. If the oxygen present at a certain temperature (generated during N\textsubscript{2}O decomposition) is used, the short dashed line in Fig. 6 is calculated. Equilibrium composition of NO and NO\textsubscript{2} was also determined assuming an O\textsubscript{2} availability corresponding with the amount if N\textsubscript{2}O conversion would be 100%.

Fig. 5. N\textsubscript{2}O conversion \textit{vs.} the molar NO/N\textsubscript{2}O feed ratio over ex-[Fe,Al]MFI(a) at different temperatures: \((\blacktriangle)\) 623 K, \((\bullet)\) 648 K, \((\triangle)\) 673 K, \((\diamond)\) 698 K, and \((\times)\) 723 K. Partial N\textsubscript{2}O pressure was fixed at 1.5 mbar and partial NO pressure varied from 0 to 15 mbar; \(P = 1\) bar; GHSV = 60000 h\textsuperscript{-1}.  

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Fig. 6. Partial pressure of (●) NO, (○) NO₂, and (△) NO₃ vs. temperature over ex-[Fe,Al]MFI(a). Conditions: 1.5 mbar N₂O + ~0.4 mbar NO in He; P = 1 bar; GHSV = 60000 h⁻¹. Equilibrium composition of NO and NO₂ (eq. (6)) are represented by dashed lines (see text for details).

(p(O₂) = 0.75 mbar). These theoretical partial pressure profiles of NO and NO₂ are displayed in Fig. 6 by the long dashed lines. The occurrence of the N₂O and NO reaction should be attributed to the catalytic performance of ex-[Fe,Al]MFI(a), since no NO₂ formation was observed over an inert material (SiC) in the same feed composition (not shown).

\[ 2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2 \]  

(6)

The profiles for ex-[Fe,Al]MFI(a) in a mixture of N₂O+NO+O₂/He are shown in Fig. 7a. The obtained NO/NO₂ ratio at low temperatures (~575 K) is lower than in the absence of O₂. In the presence of oxygen a larger fraction of NO in the feed mixture is oxidized to NO₂ (compare profiles in Figs. 6 and 7a). Again, the amount of NO₂ produced is beyond the thermodynamic equilibrium in eq. (6) (taking 0.4 mbar NO and 20 mbar O₂ in He as input values in the calculation), while the presence of large amounts of oxygen shifts the

Fig. 7. Partial pressure of (●) NO, (○) NO₂, and (△) NO₃ vs. temperature over ex-[Fe,Al]MFI(a). Conditions (a): 1.5 mbar N₂O + 0.4 mbar NO + 20 mbar O₂ in He, and (b) 0.4 mbar NO + 20 mbar O₂ in He; P = 1 bar; GHSV = 60000 h⁻¹. Equilibrium composition of NO and NO₂ (eq. (6)) are represented by dashed lines.
theoretical equilibrium composition to higher NO₂ concentrations. However, comparing the profiles in Figs. 7a and 7b indicates that oxidation of NO to NO₂ occurs to a lesser extent in the absence of N₂O. In the NO oxidation with O₂ (Fig. 7b) the equilibrium composition of NO₂ was reached above 650 K and was not exceeded, which somehow indicates that the behaviour observed in Figs. 6 and 7a is caused by a reaction between NO and N₂O.

![Graph showing NO₂ or O₂ formed vs. N₂O converted to N₂](image)

**Fig. 8.** NO₂ (♦) and O₂ (◊) formed vs. N₂O converted at 700 K over ex-[Fe,Al]MFI(a) at different partial NO pressures (mbar) in the feed. Crosses (×) represent the NO₂ + O₂ measured experimentally and the diagonal dashed line the mass balance for oxygen. The numbers refer to the NO/N₂O ratio in the feed. Conditions: 1.5 mbar N₂O + (0-1 mbar NO) in He; P = 1 bar; GHSV = 60000 h⁻¹.

![Graph showing partial pressure vs. temperature](image)

**Fig. 9.** Partial pressure of (♦) NO, (◊) NO₂, and (⊙) NO₃ vs. temperature over ex-[Fe,Al]MFI(a). Feed composition: 0.2 mbar NO₂ in He; P = 1 bar; GHSV = 60000 h⁻¹. Equilibrium composition of NO and NO₂ (eq. (6)) are represented by dashed lines.

In Fig. 8 the amount of NO₂ produced (♦) and O₂ produced (◊) is plotted vs. the amount of N₂O reacted to N₂ at 700 K for different inlet partial NO pressures. These results clearly show that the stoichiometric reaction of N₂O with NO to NO₂ and N₂ (eq. (3)) cannot solely explain the promotion effect observed in Figs. 3 and 4. Besides inducing the formation of NO₂, the presence of NO in the N₂O containing feed also significantly enhances the
production of O₂, closing the oxygen mass balance (long dashed line in Fig. 8). Further information on the relatively low amount of NO₂ formed compared to the amount of N₂O decomposed, can be related to the decomposition reaction of NO₂ to NO and O₂. By feeding a mixture of NO₂ in He over ex-[Fe,Al]MFI(a), the NO₂ decomposition rate was analyzed. The result for p(NO₂)₀ = 0.2 mbar is shown in Fig. 9. NO₂ is converted into NO and O₂ over ex-[Fe,Al]MFI(a) in the temperature range where the promotion effect of NO occurs. Equilibrium is reached above 700 K, which indicates that NO₂ decomposition and NO oxidation by O₂ (eq. (6)) occur fairly fast. This result suggests that NO₂ decomposition might contribute to the formation of O₂. Production of NO is hardly observed over inert material (SiC, not shown).

Fig. 10. N₂O conversion vs. temperature over (a) low-temperature catalysts: (□, ■) Fe/ZSM-5, (△, ▲) Fe-ZSM-5, (○, ◆) Fe-Beta, (◇, ※) Fe-USY, and (●, ◆) Fe/Al₂O₃, and (▼, ▼) Fe/SiO₂. Conditions: open symbols: 1.5 mbar N₂O in He; solid symbols: 1.5 mbar N₂O + 0.4 mbar NO in He; P = 1 bar; GHSV = 60000 h⁻¹.

Fig. 11. Partial pressure of (●, ◆) NO and (○, ◆) NO₂ vs. temperature over Fe-Beta (circles) and Fe/Al₂O₃ (diamonds). Feed composition: 1.5 mbar N₂O + 0.2 mbar NO in He; P = 1 bar; GHSV = 60000 h⁻¹. Equilibrium composition of NO and NO₂ (eq. (6)) are represented by dashed lines.
3.1.2. Other Fe-catalysts

Fig. 10 shows that the promotion effect of NO is not a unique feature of ex-framework Fe-zeolite catalysts. Sublimed Fe/ZSM-5, and Fe-ZSM-5 Fe-Beta, Fe-USY catalysts prepared by liquid (aqueous)-ion exchange (Fig. 10a), as well as Fe-supported on Al₂O₃ and SiO₂ (Fig. 10b) all show a significant enhancement of the N₂O conversion when NO is added to the feed. The observed beneficial effect of NO is larger for Fe-zeolites than for Fe/Al₂O₃ and Fe/SiO₂ manifested by a larger shift in operation temperature between the promoted and non-promoted systems or by an increased N₂O conversion at the same temperature. The temperature shift in Fe-zeolites and Fe-supported oxides for 50% N₂O conversion is ~100 K and ~50 K, respectively. In e.g. Fe/ZSM-5 or Fe-Beta, conversion increases from 10 to 100% at 698 K in the presence of NO, while the conversion over Fe/Al₂O₃ only increases from 10 to 30% at 823 K. The ion-exchanged catalysts operate in a similar temperature range as the ex-framework catalysts (compare Figs. 3 and 10a). Promotion of N₂O decomposition and formation of NO₂ over Fe/Al₂O₃ and Fe/SiO₂ take place at much higher temperatures. The last observation is derived from the NOx profiles over these catalysts, which are shown in Fig. 11 for Fe-Beta and Fe/Al₂O₃. Again, the value of the partial NO and NO₂ pressures indicates that these are not controlled by the NO/O₂ equilibrium.

3.2. In situ FT-IR/MS experiments

3.2.1. NO adsorption

To verify whether N₂O could be decomposed into (adsorbed) NO/NO₂ or nitrites and nitrates, a pellet of ex-[Fe,Al]MFI(a) was exposed to a flow (30 ml min⁻¹) of 3 vol.% N₂O in He for 2 h at 373 K and 573 K, respectively. Besides the features of gas phase N₂O, adsorbed species could not be observed, indicating a weak interaction of N₂O with the catalyst. Apparently the reactions leading to adsorbed NO or NO₂ species reported by others for ion-exchanged FeZSM-5 catalysts and catalysts prepared via sublimation of FeCl₅ in the zeolite pores are absent for the ex-framework catalyst. Spectra of NO adsorbed on ex-[Fe,Al]MFI(a) at 353 K and 373 K is presented in Fig. 12, showing absorption frequencies at 2133, 1886, and 1874 cm⁻¹. The origin of the 2133 cm⁻¹ band has recently been discussed extensively, and has been assigned to positively charged NO, occupying cationic positions in the zeolite structure. Bands in the range of 1750-1920 cm⁻¹ have often been observed in the spectra of

![Infrared spectrum of NO adsorbed on ex-[Fe,Al]MFI(a) at 373 K in flow (30 ml min⁻¹) of 5 vol.% NO in He against a background of the catalyst at the same temperatures in He.](image-url)
NO adsorbed on zeolite and oxide supported Fe catalysts, but the assignment is ambiguous. Hadjiivanov et al.,29 Lobree et al.,30,31 and Lezcano et al.32 recently discussed the origin of these bands. Both the 1874 cm\(^{-1}\) band and 1886 cm\(^{-1}\) bands are assigned to mono-nitrosylic species associated with Fe in the 2\(^+\) state (Fe\(^{II}\)-NO). The species causing the 1874 cm\(^{-1}\) absorption was assigned by Lobree et al.\(^{31}\) to Fe-sites in little accessible \(\beta\) exchange positions.\(^{26}\) The 1886 cm\(^{-1}\) band was observed by Lezcano et al.\(^{32}\) including bands at slightly lower wavenumbers (1873 and 1867 cm\(^{-1}\)), but unfortunately the origin of the multiplet was not discussed, and the major 1886 cm\(^{-1}\) band assigned to Fe\(^{II}\)-NO on the basis of the assignments of the 1874 cm\(^{-1}\) band by others. A more detailed infrared study to explain the origin of the doublet at 1874 and 1886 cm\(^{-1}\) is presented elsewhere.\(^{33}\)

3.2.2. Transient experiments

The transients occurring when NO adsorbed on ex-[Fe,Al]MFI(a) is exposed to N\(_2\)O were measured at 523 and 598 K.\(^{34}\) Due to similarities, only the result at 523 K is presented in this chapter (Figs. 13-15). The gas phase composition was changed from 5 vol.% NO in He to 3 vol.% N\(_2\)O in He and back to 5 vol.% NO in He. Upon the introduction of N\(_2\)O in the cell at 523 K, bands assigned to gas phase N\(_2\)O appear at around 2225 cm\(^{-1}\) in the infrared spectra presented in Fig. 13. A continuous decrease of the bands assigned to adsorbed NO can be observed. After an induction period, a new band develops around 1632 cm\(^{-1}\), which continuously grows in intensity and can be assigned to adsorbed NO\(_2\) on Fe\(^{II}\).\(^{28,30,31}\) The induction period of 30 s observed in this process was less pronounced in the spectra at 598 K (~10 s, not shown). The corresponding gas phase product evolution at 523 K is shown in Fig. 14 (region I). A time delay is observed between the time of switching the gas from NO to N\(_2\)O, and the formation of N\(_2\), in agreement with the infrared observations. The formation of NO\(_2\) was not detected at both temperatures. Upon switching the gas phase composition from N\(_2\)O back to NO, a rapid transition of the 1635 cm\(^{-1}\) to the original bands at around 1886 and 1874 cm\(^{-1}\) were observed in Fig. 15. At the same time the MS analysis shows that NO\(_2\) is formed immediately (region II in Fig. 14), as well as some N\(_2\). The N\(_2\) produced is related to the limited time that both NO and N\(_2\)O are present in the infrared cell.

![Fig. 13. Transient infrared spectra of NO adsorbed on ex-[Fe,Al]MFI(a) at 523 K upon switching a flow (30 ml min\(^{-1}\)) of 5 vol.% NO in He to a flow (30 ml min\(^{-1}\)) of 3 vol.% N\(_2\)O in He. Spectra were recorded against a background of the catalyst at 523 K in He.](image-url)
Fig. 14. Transient in gas composition upon switching a flow (30 ml min⁻¹) of 5 vol.% NO in He to a flow (30 ml min⁻¹) of 5 vol.% N₂O in He at t = 0 s (region I), and back to a flow (30 ml min⁻¹) of 5 vol.% NO in He at t = 250 s (region II).

Fig. 15. Transient infrared spectra of NO₂ adsorbed on ex-[Fe,Al]MFI(a) at 523 K upon switching a flow (30 ml min⁻¹) of 5 vol.% N₂O in He back to a flow (30 ml min⁻¹) of 5 vol.% NO in He. Spectra were recorded against a background of the catalyst at 523 K in He.
3.3. Multitrack experiments

3.3.1. N₂O decomposition

Multitrack was used to further investigate the formation of O₂ during N₂O decomposition and the influence of NO in the N₂O conversion (O₂ formation) over ex-[Fe,Al]MFI(a). A typical Multitrack profile during direct N₂O decomposition at 823 K over this catalyst after 100 pulses is presented in Fig. 16. The N₂O and N₂ signals are very similar in shape. The O₂ response signal of the N₂O pulse deviates from the N₂O and N₂ signal, being much broader. In order to discriminate if the shape of the oxygen is due to a mechanistic feature of N₂O decomposition or simply due to non-reactive adsorption-desorption phenomena of O₂ along the catalyst bed, molecular oxygen was pulsed. In this case the pulse is very similar in shape to that of N₂ and N₂O (Fig. 16), confirming the validity of the first hypothesis.

The delay of the oxygen signal was further investigated by pulsing N₂O at different reaction temperatures. These results are shown in Fig. 17. In the range 573-673 K, a very broad oxygen signal is observed. At 723 K the oxygen signal becomes more pronounced. Around 873 K the signal significantly sharpens, indicating that the rate of desorption of oxygen from the catalyst surface is significantly enhanced. Valuable information on the dynamic oxygen desorption process from the catalyst surface is also obtained from the desorption profiles of O₂ shown in Fig. 18. In these experiments, the O₂ signal is continuously monitored after stopping N₂O pulsing after 100 pulses at temperatures between 673 and 798 K. At 673 K, surface oxygen slowly desorbs from the catalyst surface at a constant rate during more than 25 s after stopping N₂O pulsing. Desorption is considerably faster at increasing temperatures. At e.g. 698 K desorption takes ~15 s, decreasing to ~7 s at 723 K and so on. At 798 K, oxygen desorption is relatively fast (~5 s after stopping N₂O pulsing). This trend indicates the relative stability of surface oxygen species with temperature.

![Graph](image.png)

**Fig. 16.** Typical Multitrack profiles of N₂O, N₂, and O₂ during pulsing of pure N₂O over ex-[Fe,Al]MFI(a) at 823 K. The upper profile results from separate experiments pulsing pure O₂ over the catalyst bed at the same temperature.
Fig. 17. O₂ profiles from Multitack during continuous pulsing of pure N₂O over αx-[Fe,Al]MFI(a) at different temperatures. Cycle time = 2 s.

Fig. 18. Oxygen desorption profiles measured by Multitack after stopping N₂O pulses (N₂O off) over αx-[Fe,Al]MFI(a) at different temperatures.
3.3.2. NO-assisted $\text{N}_2\text{O}$ decomposition

To study the effect of NO on $\text{O}_2$ formation in $\text{N}_2\text{O}$ decomposition, dual-pulse experiments were carried out at different temperatures, in which $\text{N}_2\text{O}$ and NO were pulsed at 0.1 and 1 s, respectively, repeated in cycles of 2 s. The $\text{O}_2$ response in different stages of the experiment at 698, 773, and 973 K is shown in Figs. 19-21. Pulsing $\text{N}_2\text{O}$ (at 0.1 s) over ex-[Fe,Al]MFI(a) at 698 K only leads to a slight increase of the base-line (Fig. 19, profile a), indicating very slow desorption of $\text{O}_2$. Alternate pulsing of $\text{N}_2\text{O}$ and NO for 10 cycles leads to a remarkable effect on the $\text{O}_2$ response at the time of the $\text{N}_2\text{O}$ pulse. The $\text{O}_2$ response sharpens (Fig. 19, profile b), indicating a significantly faster $\text{O}_2$ desorption in $\text{N}_2\text{O}$-NO cycles than in the experiment with only $\text{N}_2\text{O}$. Stopping NO pulsing results in a transition back to the original catalyst behaviour in 20 cycles (40 s), with a very broad $\text{O}_2$ response (Fig. 19, profiles c, d, and e). During the dual-pulse experiments at these temperatures, no NO or NO$_2$ signals were observed at the time of the $\text{N}_2\text{O}$ pulse, which indicates that NO does not block $\text{N}_2\text{O}$ decomposition sites. NO$_2$ formation was observed, but only at the time of the NO pulse (not shown). The MS technique did not allow quantification of the NO$_2$ desorption.

The same transient effect of oxygen desorption was observed at 773 K. In this case, the promotion effect disappears significantly faster, 6 cycles (12 s) after stopping NO pulsing (from profile a to profile d in Fig. 20). This indicates that adsorbed species formed at the time of the NO pulse are involved in the enhanced $\text{O}_2$ formation and their stability towards desorption determines the duration of the effect. The sharp oxygen signal is rapidly recovered after 4 pulses of NO (profiles e and f in Fig. 20). At high temperatures (973 K) the effect of NO on the oxygen desorption behaviour over ex-[Fe,Al]MFI(a) is negligible (Fig. 21). Here, the $\text{O}_2$ profiles obtained by pulsing $\text{N}_2\text{O}$ only, or alternating $\text{N}_2\text{O}$ and NO, are very similar. It should be noted that at such high temperature $\text{N}_2\text{O}$ conversion over ex-[Fe,Al]MFI(a) was 100% both in the absence and in the presence of NO under flow conditions.

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Fig. 19. $\text{O}_2$ profiles measured by Multittrak during catalytic decomposition of $\text{N}_2\text{O}$ over ex-[Fe,Al]MFI(a) at 698 K using cycle intervals of 2 s: (a) pulsing $\text{N}_2\text{O}$ (at 0.1 s) after 100 cycles, (b) subsequent pulsing $\text{N}_2\text{O}$ (at 0.1 s) and NO (at 1.1 s) after 10 cycles, (c), (d), and (e) pulsing $\text{N}_2\text{O}$ only (at 0.1 s), 5, 10, and 20 cycles after switching off the NO valve, respectively.
Fig. 20. $O_2$ profiles measured by Multitrack during catalytic decomposition of $N_2O$ over ex-[Fe,Al]MFI(a) at 773 K using a cycle time of 2 s: (a) pulsing $N_2O$ (at 0.1 s) and NO (at 1.1 s) after 10 cycles, (b), (c), and (d) pulsing $N_2O$ only (at 0.1 s), 2, 3, and 6 cycles after switching off the NO valve, (e) and (f) pulsing $N_2O$ (at 0.1 s) and NO (at 1.1 s), 2 and 4 cycles after switching on the NO valve, respectively.

Fig. 21. $O_2$ profiles measured by Multitrack during catalytic decomposition of $N_2O$ over ex-[Fe,Al]MFI(a) at 973 K; (a) pulsing $N_2O$ at 0.1 s and (b) pulsing $N_2O$ (at 0.1 s) and NO (at 1.1 s). Cycle time = 2 s.
4. Discussion

4.1. Role of the structure of the Fe-species in NO-assisted N₂O decomposition

The nature of the active sites in Fe-zeolites (especially in FeMFI) prepared by various methods, has already been discussed extensively in the literature. Isolated iron ions or oligonuclear oxo-iron species in the zeolite channels, as well as iron oxide particles (of different sizes and distributions) are generally identified in these heterogeneous systems. The nature and relative amounts of the various species depend on the preparation method, which determines the catalytic activity.

The different activities of the catalysts in Figs. 3, 4, and 10 should be related to the nature of the active site for N₂O activation. The strength of the Fe-O bond formed in the first step of the catalytic cycle (eq. (1)) strongly depends on the nature of the iron species in the material, and here the zeolite structure plays a crucial role in determining the specificity of these species. It is beyond the scope of the present chapter to discuss the exact nature of the active site in N₂O decomposition, although it is a highly challenging issue for catalysis (see Chapter 9).

In view of the heterogeneous nature of the catalyst formulations with respect to iron, it is not surprising that the promoting effect of NO on N₂O decomposition has been identified for zeolite catalysts of different constitutions (e.g. those prepared via an ex-framework route vs. the catalysts prepared by ion-exchange or sublimation methods). Even Fe-catalysts on conventional supports (Al₂O₃, SiO₂), prepared by incipient wetness impregnation, also show an improved activity. In the latter catalysts iron is basically present as iron oxide particles (in a wide distribution of sizes). Apparently, the NO promotion is not specific of a certain type of Fe-species. This is most likely the result of the high affinity of NO to reduced Fe-sites, irrespective of the local structure of these sites. The high affinity of NO for reduced Fe-sites has been demonstrated in various infrared studies, the absorption frequencies being assigned to different Fe configurations present in zeolites and located on conventional supports. The order in activity of the different catalysts is not changed after addition of NO, which indicates a certain uniformity of the active sites promoted by NO. So, alternatively the activity and promotion effect may be attributed to the same species, present in different amounts in the various catalysts.

4.2. Mechanism of NO-assisted N₂O decomposition

4.2.1. N₂O decomposition

As already indicated in the Introduction, the beneficial effect of NO on the activity of FeZSM-5 has been assigned by Kapteijn et al. to scavenging of adsorbed oxygen (O*), regenerating the active site (eq. (2)). The present experimental results show that scavenging of adsorbed O* by NO is not the only mechanism of promotion, and that NO also enhances O₂ formation. Multitack experiments here show that oxygen desorption from the catalyst surface is a relatively slow step in the reaction mechanism. Scheme 1 shows a typical reaction pathway for catalyzed N₂O decomposition, including the transition between the structures involved (I-III). First, a vacant site (□) is oxidized by reaction with N₂O (reaction [1.1]) leading to O□ species (denoted unambiguously as O*). The reaction of a second N₂O molecule with the oxidized site results in the regeneration of the sites, according to reaction [1.2]. Oxygen desorption can also take place by recombination of adsorbed oxygen atoms (reaction [1.3]). In view of the slow oxygen desorption (Figs. 16-18), the recombination of two oxygen atoms (located on two different sites) appears the most likely explanation for O₂ formation. These oxygen atoms can be originally separated, i.e. deposited at remote iron sites (Scheme 1, structure III). The dynamic nature of the adsorbed oxygen in the zeolite was
studied by Valyon et al.\textsuperscript{41} by step switching experiments from N\textsubscript{2}O to N\textsubscript{2}\textsuperscript{18}O over Fe-Mor. These studies showed that adsorbed \textsuperscript{18}O species (deposited by N\textsubscript{2}\textsuperscript{18}O) in Fe-Mor can exchange with the lattice oxygen of the zeolite in the vicinity of the Fe, so the oxygen must have a certain mobility to achieve this. The slow oxygen desorption in Fe-zeolites can then be understood by a slow migration of adsorbed oxygen atoms. This rate of desorption is higher at higher temperatures (Figs. 17 and 18), and is attributed to a higher oxygen mobility and recombination. Once adsorbed atomic O\textsuperscript{*} species meet each other, desorption takes place rapidly, since no O\textsubscript{2} adsorption was observed for FeZSM-5.\textsuperscript{12,42,43}

\includegraphics{scheme1.png}

\textbf{Scheme 1.} Schematic representation of a typical N\textsubscript{2}O decomposition mechanism.

\subsection*{4.2.2. NO-assisted N\textsubscript{2}O decomposition}

The rate of oxygen desorption from the catalyst surface is greatly enhanced by NO addition. Indeed, a significant increase was found in the amount of oxygen formed if NO was added to the N\textsubscript{2}O-containing feed (Figs. 19 and 20), and only a relatively small amount of NO is needed to dramatically increase the N\textsubscript{2}O decomposition rate (Fig. 5). Although during this process NO\textsubscript{2} is formed, even beyond the thermodynamic equilibrium between NO, O\textsubscript{2} and NO\textsubscript{2} according to eq. (6) (see e.g. Fig. 6), the enhanced oxygen production strongly suggests a catalytic effect of NO. If eq. (2) would be the only promotion route induced by the addition of NO, a progressive increase in conversion upon increasing the inlet NO partial pressure would be expected. This is not the case, the promotion occurs already at relatively low substoichiometric amounts of NO, indicating the catalytic nature, and reaches a limiting value at increasing molar NO/N\textsubscript{2}O feed ratios up to 10. This suggests the involvement of NO adsorption, and that the sites where NO is adsorbed are not in competition with N\textsubscript{2}O decomposition sites. Competitive adsorption would have resulted in inhibition, especially at high partial NO pressures. From the observation that at 698 K only 4 NO pulses are needed to restore the promotion effect, the pulse size and the amount the catalyst used, and assuming that all NO adsorbed at Fe sites, it can be calculated that less than 0.9\% of the Fe present is involved in the promotion. This also suggests that a very low fraction of the Fe is active in the reaction.
Promotion by NO induces a significant decrease of ~45-55 kJ mol\(^{-1}\) in the activation energy of the catalyst for N\(_2\)O decomposition, which has been also observed in the reaction of N\(_2\)O and CO (with respect to direct N\(_2\)O decomposition) over ion-exchanged transition metal (Fe, Co, Cu) ZSM-5 catalysts,\(^9\) suggesting a similar effect on the reaction mechanism, i.e. the removal of oxygen from the active site.

The relative contribution of enhanced oxygen desorption vs. the formation of NO\(_2\) over the catalysts needs some further discussion. At relatively low temperatures the first phenomenon is stronger than at high temperatures, as indicated by the Multitrack analyses. Above 900 K the oxygen response in the case of ex-[Fe,Al]MFI(a) at the N\(_2\)O pulse is no longer affected by alternating N\(_2\)O-NO pulsing (Fig. 21). To explain the enhancement of the O\(_2\) desorption rate at the time of the N\(_2\)O pulse, an adsorbed species formed at the time of the NO pulse needs to be involved. The amount of adsorbed NO will be reduced at high temperatures, while oxygen desorption at high temperatures already proceeds fast. This adsorption involvement is supported by the slower decay of the NO promotion at lower temperatures in the dual-pulse Multitrack experiments after stopping NO pulsing. The absence of the enhanced O\(_2\) desorption effect at high temperatures, is in agreement with the relatively smaller promoting effect of NO on the performance of metal oxide (Al\(_2\)O\(_3\), SiO\(_2\)) supported Fe-catalysts vs. zeolitic Fe catalysts. In the former catalytic systems, it is likely that removal of O\(^+\) by NO, as stated in eq. (2), plays a more important role in the promotion than enhanced O\(_2\) desorption. Sang and Lund\(^{14}\) use the interconversion of nitrates and nitrites to explain the enhancement of N\(_2\)O conversion by NO. However, for Al\(_2\)O\(_3\) and SiO\(_2\)-supported Fe catalysts this explanation does not appear very likely, since nitrites and nitrates are not stable at the conditions where the promoting effect is observed. Furthermore, in the infrared analysis of the Fe-catalysts, nitrate bands have never been observed,\(^{13,21}\) but only adsorbed NO and NO\(_2\) species.

Although NO\(_2\) is decomposed over Fe-based catalysts into NO and O\(_2\), the contribution of NO\(_2\) decomposition to the formation of O\(_2\) in the NO-assisted N\(_2\)O decomposition is likely to be limited. The Multitrack experiments clearly show that oxygen desorption is triggered at the time of the N\(_2\)O pulse, and not at the time of the NO pulse. NO\(_2\) formation is observed at the time of the NO pulse, indicating displacement of adsorbed NO\(_2\) by NO as confirmed by transient in situ FT-IR/MS studies over ex-[Fe,Al]MFI(a). In the Multitrack formation of O\(_2\) and NO\(_2\) is decoupled: NO\(_2\) is mainly released due to displacement by NO and probably by thermal desorption, while O\(_2\) is formed during the N\(_2\)O pulses.

The first observation is confirmed by transient in situ FT-IR/MS studies over ex-[Fe,Al]MFI(a). Infrared results suggest that NO\(_2\) adsorption on the catalyst surface is weaker than that of NO. It should be mentioned that this is apparently a specific feature of the ex-framework catalyst, since other authors have suggested the opposite, i.e. NO\(_2\) is more strongly adsorbed on FeZSM-5 catalysts than NO.\(^{30,38}\) If NO\(_2\) decomposition, like presented in Fig. 9, would contribute significantly to O\(_2\) formation, an O\(_2\) response would have been expected at the time of the NO pulse, rather than at the time of the N\(_2\)O pulse only. This excludes eq. (3) to be the only reason for the promotion effect.

4.2.3. Reaction pathways and proposed mechanism

In view of the results presented in this chapter, various pathway(s) are needed to explain the catalytic effect of NO on the N\(_2\)O decomposition.\(^{40}\) The different experimental observations are depicted in Scheme 2. The transitions of the different structures considered (I-IV) are also considered in the reaction mechanism. Initially, N\(_2\)O reacts on a vacant site, yielding N\(_2\) and leaving an oxidized site (reaction [2.1]). On the catalyst, a substantial amount of adsorbed NO is present, as observed by in situ FT-IR. Due to the absence of inhibition by NO in the activity tests and the fact that no NO signal appears at the time of the
N₂O pulse in the Multitrack experiments, it is concluded that the NO adsorption and N₂O decomposition do not compete for the same site, so both processes occur at different Fe-species (light and dark solid grey areas in Scheme 2). Adsorption of N₂O (as O⁺) and NO in two open coordinations at the same iron site seems hardly probable, since dinitrosyls were not identified by infrared studies in this system. The production of NO₂ is shown in reaction [2.2], which is likely the major mode of promotion for high-temperature catalysts, i.e. Fe/Al₂O₃ and Fe/SiO₂. For low-temperature Fe-zeolite catalysts, N₂O activation occurs next to an adsorbed NO molecule (*NO). At these lower temperatures (550-700 K) the oxidized site (O□) subsequently oxidizes adsorbed NO to adsorbed NO₂ (reaction [2.3]), yielding structure III in Scheme 2. Subsequently, NO₂ desorption is induced by adsorption of NO (reaction [2.4]), as was observed from the Multitrack experiments by the presence of a NO₂ signal at the time of the NO pulse. This closes the catalytic cycle in the conversion of N₂O and NO to N₂ and NO₂ at lower temperatures. This is in excellent agreement with the transient FT-IR/MS experiments, where NO₂ formation is observed upon switching from N₂O to NO.

![Scheme 2](image)

<table>
<thead>
<tr>
<th>Name</th>
<th>Elementary step</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>[2.1]</td>
<td>N₂O + □ → N₂ + O□</td>
<td>I → II</td>
</tr>
<tr>
<td>[2.2]</td>
<td>NO + O□ → NO₂ + □</td>
<td>II → I</td>
</tr>
<tr>
<td>[2.3]</td>
<td>*NO + O□ → *NO₂ + □</td>
<td>II → III</td>
</tr>
<tr>
<td>[2.4]</td>
<td>NO + *NO → NO₂ + *NO</td>
<td>III → I</td>
</tr>
<tr>
<td>[2.5]</td>
<td>N₂O + O□ → N₂ + O₂ + □</td>
<td>II → I</td>
</tr>
<tr>
<td>[2.6]</td>
<td>*NO₂ + O□ → *NO + O₂ + □</td>
<td>IV → I</td>
</tr>
<tr>
<td>[2.7]</td>
<td>*NO₂ + □ → *NO + O□</td>
<td>III → II</td>
</tr>
</tbody>
</table>

**Scheme 2.** Possible pathways in the NO-assisted N₂O decomposition over ex-[Fe,Al]MFI(a).

Different options can be proposed to explain the enhanced oxygen formation. Again N₂O activation occurs next to an adsorbed NO molecule, yielding structure II in Scheme 2. Subsequently a second N₂O molecule reacts with the site, yielding N₂ and O₂ (reaction [2.5]), and structure I is regenerated. The enhanced oxygen desorption from the active center has been ascribed to a reduced stability of adsorbed oxygen, induced by either electronic or steric effects of the NO adsorbed on neighbouring oxidized sites. A more plausible explanation for
the enhanced oxygen desorption is reaction [2.6]. The increased N₂O decomposition is simply explained by the recombination of oxygen present in adsorbed NO₂ and oxygen species deposited by N₂O on a neighbouring site.

Thus the adsorbed NO serves to accommodate temporarily the deposited oxygen from the N₂O, freeing the neighbouring site for deposition of a second oxygen. This would imply the presence of remote sites for the N₂O decomposition. Consequently, the migration of oxygen atoms to recombine to molecular oxygen constitutes the rate determining process in N₂O decomposition. Taking this further, it could be speculated that the presence of NO on the catalyst surface enhances the mobility of adsorbed oxygen via intermediate NO₂ species. This mechanism, schematically depicted in Scheme 3, leads to a faster oxygen recombination, and thus an accelerated O₂ desorption. The transfer of the oxygen atom from one NO to the other is well possible, as previously observed for NO and ¹⁵N[¹⁸O] step changes over Cu-ZSM-5 and Cu-Y.⁴¹,⁴⁴ Of course, the O₂ formation by two adjacent adsorbed NO₂ groups can not be ruled out.

Finally the observed NO₂ decomposition over ex-[Fe,Al]MFI(a) and in general Fe-zeolites (reaction [2.7] in Scheme 2) in flow experiments deserves some further discussion. It has been proposed that N₂O decomposition over Fe-zeolites yields the so-called α-oxygen,⁹ that has the ability, to selectively oxidize benzene to phenol. Since the Fe-zeolites are able to convert NO₂ into NO and O₂ at relative high rates, i.e. equilibrium is attained at 700 K, it could be hypothesized on the basis of the proposed schemes, that NO₂ is also able to produce adsorbed (atomic) oxygen species (from structure (III) to (II) in Scheme 2). So in principle it could be used as selective oxidant. A drawback however, will be that the catalyst also effectively helps the O₂ formation, thus rendering NO₂ into a less efficient reactant than N₂O. Alternatively, mixtures of O₂ and NO could be used.

![Scheme 3. Proposed NO-assisted oxygen desorption mechanism during N₂O decomposition.](image)

The results in this paper have implications for the application of N₂O in selective oxidations. In the AlphOx™ process,⁴⁵ the N₂O originates as a co-product of the oxidation of cyclohexaneone/cyclohexanol mixtures by nitric acid. This N₂O contains also NO. It is clear that this NO has to be removed to large extent otherwise it will lower considerably the utilization of N₂O in the benzene oxidation, by providing an escape route for the so-called α-oxygen from N₂O. This can translated in an accelerated oxygen desorption and/or the sequestration of reactive O* as adsorbed *NO₃ species, impeding the effective transfer of atomic oxygen to the benzene molecule.

The isolated nature of the active sites prohibits the dissociation of O₂ explaining the absence of O₂ inhibition. The formation of NO₂ beyond thermodynamic equilibrium of eq. (6) indicates that eq. (3) proceeds faster that eq. (6) under competitive conditions, where NO, N₂O, O₂, and NO₂ are simultaneously present. The NO₂ formation is in fact due to the
displacement by NO, which adsorbs stronger. Hence, O₂ formation by adjacently adsorbed NO₂ will be suppressed under these circumstances, but could explain the results of Fig. 9 in the absence of N₂O. Alternatively, O₂ formation from NO₂, via reaction [2.6], requires the competition between N₂O and NO₂ to oxidize a vacant \( \square \)-site. If N₂O is a more efficient oxidizer of these sites, NO₂ levels beyond thermodynamic equilibrium of eq. (6) are well feasible.

At this point it is worth noting two other catalyzed reactions where NO serves as an \textquoteleft atomic\textquoteright oxygen transport facilitator. The first is the old lead chamber process for SO₂ oxidation, in which NO acts as a gaseous carrier.\textsuperscript{46} The second is the role of NO in the bifunctional catalysis to oxidize soot.\textsuperscript{47,48} There a catalyst, \textit{e.g.} metal oxide (Cr₂O₃, Co₃O₄, CuO) or Pt-based, oxidizes NO with O₂ to NO₂ and the latter oxidizes the soot at temperatures where O₂ is not active. Although in these examples the oxygen is transported through the gas phase, in the current study this occurs via an adsorbed mode. As mentioned before this property of NO may be utilized in other (selective) oxidation reactions.

5. Conclusions

NO strongly promotes N₂O decomposition over Fe-based catalysts. The promoting effect is observed for many different formulations and appears independent on the nature of the bulk of the Fe-species in the catalyst. The temperature at which N₂O decomposition occurs, is strongly dependent on the catalyst. Small amounts of NO in the feed (NO/N₂O < 0.25) are sufficient to produce a substantial increase in N₂O conversion for all the catalysts. Higher partial NO pressures (NO/N₂O > 0.25) lead to a saturation behaviour of the N₂O conversion, although no inhibition by NO is observed, even at NO/N₂O = 10. Apparently, different sites are involved in the NO adsorption and the deposition of oxygen by N₂O. The latter site seem to be located remote from each other, rendering the oxygen atom recombination the rate determining process. High temperatures stimulate this process but also in the presence of adsorbed NO at lower temperatures. Adsorbed NO may temporary accommodate oxygen deposited by N₂O on a neighbouring site allowing the deposition of a second oxygen and their recombination. Less than 0.9% of the Fe seems to participate in this promotion, indicating the low density of active sites. Additionally, adsorbed NO may facilitate the migration of oxygen through NO₂ intermediates enhancing the change of recombination to O₂.

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References

On the Nature of Active Species in Ex-Framework FeMFI Catalysts for N₂O Conversion

In this chapter the role of the different metal species in ex-framework FeMFI catalysts for direct N₂O decomposition is evaluated. From the preparation, characterization, and testing of MFI zeolites with different framework compositions (Fe-Al-Si, Fe-Ga-Si, and Fe-Si) and without iron in the synthesis gel (< 0.002 wt.%), it is concluded that extra-framework iron species are essential for direct N₂O decomposition, while Lewis and Brønsted acidic sites play a minor role for a maximum N₂O decomposition activity. Based on an extensive characterization, different iron species are identified in the catalysts depending on the composition of the zeolite framework and the conditions of the steam treatment. The optimum temperature during steam activation is in the region where extraction of framework iron is complete without extensive clustering of extra-framework iron species into oxide particles. This optimum temperature is much lower in the iron zeolites containing Al and Ga (873-923 K) than in the purely siliceous zeolite catalyst (1123 K), due to the higher stability of iron in the silicalite framework. High partial steam pressures (> 100 mbar H₂O in N₂) favour the extraction of framework iron by hydrolysis of Si-O-Fe bonds, enabling the application of lower activation temperatures. Our observations suggest that small intrazeolitic iron species in extra-framework positions are crucial in direct N₂O decomposition. This result is supported by the decrease in activity upon increasing the crystal size of the zeolite, indicating the presence of intracrystalline transport limitations, and by the increased activity after the application of an alkaline post-treatment of the catalyst to improve the catalyst accessibility by creation of mesopores. Based on the results presented here and in Chapter 8, it is concluded that oligonuclear iron species play a more important role than isolated ions in direct N₂O decomposition, while in reactions including hydrocarbons isolated species may be more involved.
1. Introduction

The origin of the catalytic activity in the selective oxidation of benzene to phenol with N₂O over iron-containing ZSM-5 zeolites has been intensively debated over the last decade, but the nature of the active site is not agreed upon. Different sites in the catalyst could be involved in the formation of the so-called α-oxygen derived from activation of N₂O, which is believed to determine the catalyst activity. This includes Brønsted (H) and Lewis (Al, Ga) acid sites, as well as transition metals (Fe) in extra-framework positions. In other reactions catalyzed by FeZSM-5, where iron is accepted to control the catalytic performance, the controversy lies on the nature of the iron species responsible for the activity. Panov et al. have suggested that active iron in FeZSM-5 prepared by isomorphous substitution of Fe in the zeolite framework and heat treatment in vacuum at 1173 K consists of species with binuclear structure, based on quantum-chemical calculations and Mössbauer studies. Binuclear iron species in FeZSM-5 resemble the binuclear sites in methylenoxygenase (MGO), an enzyme capable to hydroxylate methane to methanol at room temperature. Sachtl er et al. also proposed binuclear species in FeZSM-5 prepared by sublimation of FeCl₃ into the H-ZSM-5 channels to be the active species for direct N₂O decomposition and selective catalytic reduction (SCR) of NOₓ with i-butane. Several authors support the presence of binuclear species in such a catalyst based on EXAFS results. Small oligonuclear iron complexes of composition Fe₆O₄ (referred to as ultra-stable nanoclusters) have also been identified as active redox centers in SCR of NOₓ with propene over liquid ion-exchanged FeZSM-5 catalysts. Contrarily, Heinrich et al. have claimed that isolated iron ions are the active sites for SCR of NOₓ with i-butane in FeZSM-5 prepared via a novel mechanochemical route.

In spite of the considerable efforts to characterize these materials, no definite evidence supporting these statements has been given and available data are not yet sufficient to conclude exclusively on the structure of the active iron. What is widely accepted is that large iron oxide particles at the external surface of the zeolite crystal are inactive in the different reactions catalyzed by FeZSM-5. The unification/generalization of the various interpretations with respect to the active sites is extremely complicated due to:

- The intrinsic heterogeneous nature of iron in the catalyst, which makes the identification and quantification of the different species difficult.
- Application of widely different preparation approaches and amounts of iron in the catalyst, which strongly affects the catalyst constitution and ultimately the catalytic performance.
- Various catalytic reactions following a different mechanism (N₂O decomposition, selective reduction of NOₓ or N₂O with NH₃ or hydrocarbons, selective oxidation), which may determine the required structure of the active site.

We have previously shown the excellent performance of ex-framework FeZSM-5 compared to FeZSM-5 catalysts prepared by other methods in direct N₂O decomposition in simulated tail-gas from nitric acid plants and combustion processes. This catalyst was prepared by isomorphous substitution of Fe in the zeolite framework, followed by calcination and steaming. Steam treatment leads to massive dislodgement of framework iron (analyzed by UV-Vis, FT-IR, Fe Mossbauer, H₂-TPR), as well as to significant extraction of Al to extra-framework positions (²⁷Al MAS-NMR). Due to the hydrolysis of Si-O-M bonds, this process causes a decrease of the density and strength of acid sites (NH₃-TPD).

In this chapter, we have investigated the role of various species in the zeolite described above for direct N₂O decomposition. To this end, the ex-framework route has been applied to synthesize zeolite catalysts with different framework composition (combinations of Fe, Al, and Si). These catalysts have been characterized by ICP-OES, neutron activation analysis,
$^{27}$Al and $^{71}$Ga MAS-NMR, N$_2$ adsorption, TEM, and voltammetric response techniques. Optimization of the steam activation treatment (temperature and water content) for tuning the catalyst constitution; preparation of zeolites with different crystal size, and by ion-exchange methods; and alkaline post-treatment of the catalysts enable to draw conclusions regarding the nature of the active species in N$_2$O decomposition and provides clues to improve the performance of these catalysts.

2. Experimental

2.1. Catalyst preparation

2.1.1. Ex-framework catalysts

**Hydrothermal synthesis.** Isomorphously substituted ferrialuminosilicate [Fe,Al]MFI, ferrigarlosilicate [Fe,Ga]MFI, and ferrisilicate [Fe]MFI and the same zeolites excluding iron in the synthesis gels, i.e. [Al]MFI, [Ga]MFI, and [-]MFI (silicalite-1) were synthesized hydrothermally using TPAOH as the template. High purity chemicals were used in the preparations (> 99.95 %). The molar ratio between the components was H$_2$O/Si = 45, TPAOH/Si = 0.1, NaOH/Si = 0.2, Si/Al or Si/Ga = 36, and Si/Fe = 152. During the synthesis, a solution of the silica source (TEOS), and NaOH was added to a mixture of the metal nitrates. The solution was transferred to a stainless steel autoclave lined with Teflon and kept in a static air oven at 448 K for 5 days. The crystalline material was filtered and washed with deionized water until the sample was free of nitrates.

In a modified synthesis, [Fe,Al]MFI was prepared by excluding NaOH in the synthesis gel, and thus increasing the concentration of TPAOH. In this case, NaOH/Si and TPAOH/Si was 0 and 0.3, respectively. The other molar ratios were kept constant. This sample is denoted as [Fe,Al]MFI(sc), where sc stands for small crystal (see §3.1.2).

**Calcination and steam treatment.** The as-synthesized samples, containing the different metals in the zeolite framework, were calcined in air at 823 K for 10 h and converted into the H-form by three consecutive exchanges with a NH$_4$NO$_3$ solution (0.1 M) for 12 h and subsequent air calcination at 823 K for 5 h. Finally the catalysts were activated in a flow of nitrogen and steam at ambient pressure, using a water partial pressure of 20-500 mbar H$_2$O and 30 ml (STP) min$^{-1}$ of N$_2$ flow at different temperatures in the range of 673-1273 K during 5 h. Along the chapter, the calcined and steamed zeolites are denoted by prefix c- and ex-, respectively.

**Alkaline post-treatment.** The steamed ferrialuminosilicate was treated in alkaline solution according to the method described elsewhere. Briefly, ex-[Fe,Al]MFI was stirred in a 0.2 M NaOH aqueous solution (pH = 13.3) at 353 K for 1 h. The slurry was then cooled down immediately using an ice bath, filtered, rinsed at 353 K with distilled water, and finally dried at 383 K. This sample is denoted as ex-[Fe,Al]MFI(at).

2.1.2. Ion-exchanged catalysts

Other Fe-catalysts were prepared by conventional aqueous-ion exchange with Fe(NO$_3$)$_3$·9H$_2$O, using conventional methods described in the literature. The parent zeolites were NH$_4$-ZSM-5 (CBV 8020, PQ) and calcined aluminosilicate (c-[Al]MFI). The exchange was carried out under vigorous stirring during 15 h at room temperature. After filtration, washing, and drying, the ion-exchanged catalysts were calcined and steamed according to the procedure described above. The final catalysts are denoted as ex-Fe-ZSM-5 and ex-Fe-[Al]MFI.
2.2. Catalyst characterization

**Chemical composition.** Chemical composition of the samples was determined by ICP-OES (Perkin-Elmer Plasma 40 (Si) and Optima 3000DV (axial)). For some samples, traces of iron were determined by instrumental neutron activation analysis.

**XRD.** Powder X-ray diffraction patterns were measured in a Bruker AXS diffractometer with Bragg-Brentano geometry, and Cu Kα radiation (λ = 0.1541 nm). Data were collected in the 2θ range of 5 to 50° at a scan rate of 0.5° min⁻¹.

**SEM.** Scanning Electron Microscopy images were recorded at 10 kV in a Philips XL 20 microscope. Samples were coated with gold to create contrast.

**MAS-NMR.** ²⁷Al and ⁷¹Ga Magic Angle Spinning-Nuclear Magnetic Resonance was recorded at 79.5 and 183.0 MHz respectively with a Varian VXR-400S spectrometer. The narrow bore magnet (50 mm) was fitted with a high-speed magic angle spinning (MAS) Doty probe. The samples were spun in 5 mm-diameter rotors made of zirconia. The length of the r.f. pulses was 0.5 μs for Al and 0.4 μs for Ga. The spinning frequency was 7.0 kHz for Al and 8.0 kHz for Ga. Acquisition time was 0.2 s for Al and 0.4 s for Ga. A time interval of 1 s for Al and 3 s for Ga between successive accumulations was selected in order to avoid saturation effects. The number of accumulations (10000 for Al and 5000 for Ga) allowed a signal-to-noise ratio higher than 20. The ²⁷Al and ⁷¹Ga chemical shifts were referenced to Al(H₂O)₆³⁺ and Ga(H₂O)₆³⁺, respectively.

**N₂ adsorption.** N₂ adsorption at 77 K was carried out in a QuantaChrome Autosorb-6B apparatus. Samples were previously evacuated at 623 K for 16 h. The BET method was used to calculate the surface area (Sₐ) of the samples, while the micropore volume (Vₘ) was determined with the t-plot method according to Lippens and de Boer. The BJH model was applied to calculate the pore size distribution from the adsorption isotherms.

**TEM.** Transmission Electron Microscopy was carried out on a Philips CM 30 T electron microscope with a LaB₆ filament as the source of electrons operated at 300 kV. In some cases, the zeolites were amorphized by the electron beam in order to enhance the visibility of the small iron oxide particles.

**Voltammetry.** The voltammetric response of graphite-polyester composite electrodes modified by FeMFI samples was measured in a standard three-electrode arrangement with a platinum auxiliary electrode and a saturated calomel reference electrode (SCE). Preparation of the composite electrode and modification by the zeolite samples has been described elsewhere. Cathodic linear scan voltammograms (LSVs) were recorded at a potential scan rate of 20 mV s⁻¹ using a Metrohm E506 Polarrecord. Experiments were performed at 298 K in aqueous solutions of 1.0 M HCl under argon atmosphere.

2.3. Activity tests

Activity measurements were carried out in a six-flow reactor system, using 50 mg of catalyst (125-200 μm) and a space velocity (GHSV) of 60000 h⁻¹ at atmospheric pressure. The feed composition was 1.5 mbar N₂O in He. Before reaction, the catalysts were pretreated in the feed mixture at 723 K for 1 h and cooled in that gas flow to the initial reaction temperature. N₂O, N₂, and O₂ were analyzed with a GC (Chrompack CP 9001) equipped with a thermal conductivity detector, using a Poraplot Q column (for N₂O separation) and a Molsieve 5A column (for N₂ and O₂ separation). The effect of the feed composition on the N₂O decomposition activity over ex-[Fe-Al]MFI was studied in gas mixtures containing N₂O (1.5 mbar), O₂ (50 mbar), NO (0-1.5 mbar), and C₃H₆ (0-1.5 mbar) in He at GHSV = 75000 h⁻¹ and atmospheric pressure.

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3. Results

3.1. Catalyst characterization

3.1.1. Chemical composition

Table 1 shows the chemical composition of the different materials prepared in this study. The catalysts have a comparable molar Si/(Al or Ga) ratio and iron content. The ex-framework catalysts prepared without iron show Fe levels < 0.002 wt.% (detection limit of the neutron activation analysis). In the ion-exchanged catalysts, Fe contents ranging from 0.25 to 0.70 wt.% were achieved, with a similar Si/Al ratio. The commercial steamed support contained 170 ppmw of iron. The chemical composition of the steamed Fe-Al zeolite and the product obtained after NaOH-treatment, ex-[Fe,Al]MFI(at), is very similar, suggesting that no leaching of metal takes place. This was confirmed by leaching tests, revealing a negligible amount of the metals (Si, Fe, Al) in the filtrate, corresponding to ± 2% of the amount in the solid.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Preparation method</th>
<th>Si/(Al or Ga)</th>
<th>Fe / wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ex-[Al]MFI</td>
<td>Ex-framework</td>
<td>32.5</td>
<td>&lt; 0.002 a</td>
</tr>
<tr>
<td>ex-[Ga]MFI</td>
<td>Ex-framework</td>
<td>31.1</td>
<td>&lt; 0.002 a</td>
</tr>
<tr>
<td>ex-[Fe,Al]MFI b</td>
<td>Ex-framework</td>
<td>31.6</td>
<td>0.67</td>
</tr>
<tr>
<td>ex-[Fe,Al]MFI(sc)</td>
<td>Ex-framework</td>
<td>35.5</td>
<td>0.61</td>
</tr>
<tr>
<td>ex-[Fe,Ga]MFI</td>
<td>Ex-framework</td>
<td>32.6</td>
<td>0.58</td>
</tr>
<tr>
<td>ex-[Fe]MFI</td>
<td>Ex-framework</td>
<td>∞</td>
<td>0.68</td>
</tr>
<tr>
<td>ex-[Fe,Al]MFI(at)</td>
<td>Ex-framework</td>
<td>32.9</td>
<td>0.70</td>
</tr>
<tr>
<td>ex-[Fe,Al]MFI(a)</td>
<td>Ion exchange + steaming</td>
<td>32.4</td>
<td>0.51</td>
</tr>
<tr>
<td>ex-[Fe,Al]MFI(b)</td>
<td>Ion exchange + steaming</td>
<td>32.5</td>
<td>0.25</td>
</tr>
<tr>
<td>ex-H-ZSM-5</td>
<td>Commercial sample</td>
<td>37.5</td>
<td>0.017 a</td>
</tr>
<tr>
<td>ex-Fe-ZSM-5</td>
<td>Ion-exchange + steaming</td>
<td>37.5</td>
<td>0.64</td>
</tr>
</tbody>
</table>

*instrumental neutron activation analysis; b silicalite-1; c samples (a) or (b) differ in the iron content.

3.1.2. XRD and SEM

The X-ray diffraction patterns of the as-synthesized zeolites showed typical reflections of MFI structure and no additional crystalline phase. The long-range crystalline order and the crystal size of the as-synthesized zeolites was not altered by the different post-synthesis treatments (calcination, steaming, and alkaline treatment), as concluded from XRD and SEM analyses (not shown). The zeolites prepared using TPAOH/Si = 0.2 and NaOH/Si = 0.1 show a uniform crystal size distribution (ranging from 2.0 to 2.5 μm in size). This is shown for ex-[Fe,Al]MFI in Fig. 1a. The zeolite prepared with a higher template concentration (TPAOH/Si = 0.3 and no NaOH), yielding ex-[Fe,Al]MFI(sc), show a significantly (~5-6 times) smaller crystal size (~0.4 μm, Fig. 1b). The hydrophobic character of the alkyl chains of tetraalkylammonium cations (TPA+) favors the nucleation of zeolite crystals (among Na+ ions or pH of the synthesis gel) due to its superior templating or structure-directing properties, promoting the formation of many smaller crystals.\(^{33,34}\)

3.1.3. MAS-NMR

The \(^{27}\text{Al}\) MAS-NMR spectrum of c-[Fe,Al]MFI shows a relatively sharp resonance at 55 ppm, which has been assigned to tetrahedrally coordinated Al in lattice positions (Fig. 2).\(^{29}\) The two peaks at -5 and +105 ppm are spinning side bands due to quadrupole
interactions of the $^{27}$Al nuclei. The intensity of the band at -5 ppm is higher than that at +105 ppm, suggesting the presence of a small fraction of extra-framework Al species in this sample. Steam treatment leads to dealumination of the zeolite framework by migration of Al(III) to non-framework positions. In the spectrum of the steamed sample, the resonance around 55 ppm significantly decreases and a broad band centered at -3 ppm appears, with a shoulder at 30 ppm. The peak at -3 ppm is attributed to hexacoordinated Al species in octahedral positions,\textsuperscript{29} while the shoulder at 30 ppm indicates pentacoordinated Al species in non-framework positions.\textsuperscript{5,30} The broadening of this signal suggests the presence of extra-framework Al species with different coordination.

Similar results were obtained for the zeolite sample containing Ga (Fig. 3). The calcined zeolite shows one $^{71}$Ga NMR response at 160 ppm, which has been identified as originating from tetrahedrally coordinated framework gallium.\textsuperscript{31} The broad signal is due to the high quadrupolar interactions of the gallium nuclei. Steam treatment (300 mbar H$_2$O at 873 K for 5 h) leads to the decrease of the signal at 160 ppm and the appearance of a band at 0 ppm, typical of octahedrally coordinated gallium species.\textsuperscript{32}

![Fig. 1. SEM micrographs of (a) ex-[Fe,Al]MFI and (b) ex-[Fe,Al]MFI(sc).](image)

![Fig. 2. $^{27}$Al MAS-NMR spectra of (a) c-[Fe,Al]MFI and (b) ex-[Fe,Al]MFI.](image)

![Fig. 3. $^{71}$Ga MAS-NMR spectra of (a) c-[Fe,Ga]MFI and (b) ex-[Fe,Ga]MFI.](image)
3.1.4. N\textsubscript{2} adsorption

*Activation by steam.* Table 2 shows the adsorption parameters of the calcined and steamed zeolites, as obtained from the N\textsubscript{2} adsorption isotherms in Fig. 4. The total pore volume of the samples is similar. A slight decrease in the micropore volume, coupled to a decrease of the BET surface area, is identified upon steam treatment of the Al and Ga-containing zeolites. This suggests that a small fraction of micropores are converted in mesopores due to the extraction of Al and Ga to extra-framework positions upon steam treatment. This can also be concluded from the hysteresis in the adsorption-desorption isotherms at $p/p_\infty > 0.45$ (Figs. 4b-c), which is absent in the calcined-only material (Fig. 4a). The isotherm of *ex-[Fe]MFI* resembles that of the calcined precursor (compare Figs. 4a and 4d), indicating a similar texture before and after steam treatment. This result suggests a higher stability of ferrisilicalite against steam treatment and that the textural changes in the other zeolites are mainly caused by the presence of extractable Al and Ga framework species. The same trend was observed in the zeolite samples containing no iron. The textural properties of the *ex-[Fe,Al]MFI* zeolites with large and small crystals are also very similar.

![Fig. 4. N\textsubscript{2} adsorption-desorption isotherms at 77 K of (a) c-[Fe,Al]MFI, (b) ex-[Fe,Al]MFI, (c) ex-[Fe,Ga]MFI, and (d) ex-[Fe]MFI. Conditions of steam treatment: 300 mbar H\textsubscript{2}O in N\textsubscript{2} at 873 K for 5 h.](image-url)
Table 2. Textural properties of the calcined and steamed FeMFI catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$V_{\text{micro}}^a$ / cm$^3$ g$^{-1}$</th>
<th>$V_{\text{total}}$ / cm$^3$ g$^{-1}$</th>
<th>$S_{\text{BET}}^b$ / m$^2$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c$-[Fe,Al]MFI</td>
<td>0.16</td>
<td>0.24</td>
<td>425</td>
</tr>
<tr>
<td>$ex$-[Fe,Al]MFI</td>
<td>0.14</td>
<td>0.23</td>
<td>372</td>
</tr>
<tr>
<td>$ex$-[Fe,Al]MFI(sc)</td>
<td>0.14</td>
<td>0.23</td>
<td>380</td>
</tr>
<tr>
<td>$ex$-[Fe,Al]MFI(at)</td>
<td>0.11</td>
<td>0.57</td>
<td>415</td>
</tr>
<tr>
<td>$c$-[Fe,Ga]MFI</td>
<td>0.16</td>
<td>0.25</td>
<td>423</td>
</tr>
<tr>
<td>$ex$-[Fe,Ga]MFI</td>
<td>0.15</td>
<td>0.24</td>
<td>385</td>
</tr>
<tr>
<td>$c$-[Fe]MFI</td>
<td>0.18</td>
<td>0.23</td>
<td>427</td>
</tr>
<tr>
<td>$ex$-[Fe]MFI</td>
<td>0.18</td>
<td>0.23</td>
<td>431</td>
</tr>
</tbody>
</table>

$^a$ t-plot method; $^b$ BET method.

Alkaline post-treatment. Alkaline treatment of $ex$-[Fe,Al]MFI leads to substantial changes in the N$_2$ adsorption isotherms. The type I isotherm in $ex$-[Fe,Al]MFI, with a plateau at high $p/p_0$ (Fig. 5a), which is characteristic of microporous materials without a significant meso- or macroporosity, constrains with the behaviour of the alkaline-treated sample (Fig. 5b). $ex$-FeZSM-5(at) shows a much higher adsorption capacity at $p/p_0 > 0.4$ as a result of newly created mesoporosity at $\sim 10$ nm (inset in Fig. 5). The apparent difference between the isotherms of $ex$-[Fe,Al]MFI in Figs. 4b and 5a is due to the different scale. The progressive increase at $p/p_0 \sim 1$ in the alkaline-treated sample is probably a result of the enhanced surface roughness of the crystals as a result of the alkaline treatment, as was identified by SEM analysis.\textsuperscript{35,36} Table 2 shows that destruction of micropores only can not fully account for the mesopore formation in $ex$-[Fe,Al]MFI(at) with respect to $ex$-[Fe,Al]MFI, since the increase in mesopore volume ($\sim 0.4$ cm$^3$ g$^{-1}$) is much larger than the decrease in microporosity ($\sim 0.05$ cm$^3$ g$^{-1}$), not even taking into account substantial removal of framework material. This suggests the formation of a new mesoporosity.

![Fig. 5. N\textsubscript{2} adsorption-desorption isotherms at 77 K of (a) $ex$-[Fe,Al]MFI and (b) $ex$-[Fe,Al]MFI(at). Inset figure: pore size distribution determined from the adsorption branch of the isotherm of $ex$-[Fe,Al]MFI(at), using the BJH model.\textsuperscript{26}](image-url)
3.1.5. TEM

Activation by steam. The TEM micrographs of the steamed [Fe,Al]MFI and [Fe,Ga]MFI samples activated in 300 mbar H₂O in N₂ at 873 K for 5 h show the formation of homogeneously dispersed nano-particles of 1-2 nm in size (Figs. 6a-b), which are likely situated at the external surface of the zeolite crystal (extrazeolitic species). These nano-particles were not observed in TEM micrographs of analogous steamed sample without iron, ex-[Al]MFI or ex-[Ga]MFI, i.e. containing extra-framework Al and Ga species, suggesting that they mainly contain iron oxide. However, due to the massive extraction of Al and Ga upon steam treatment as indicated by MAS-NMR, the presence of Al or Ga in these particles can not be excluded. These nano-particles were not observed in ex-[Fe]MFI (Fig. 6c), suggesting that (i) the dislodged iron species are highly dispersed in the zeolite channels and/or (ii) at 873 K, a large fraction of iron in the sample is still in framework positions. Nano-particles of similar size to those in ex-[Fe,Al]MFI and ex-[Fe,Ga]MFI (Fig. 6a-b) were observed in ex-[Fe]MFI at a steam activation temperature of 1123 K. The particle size distribution of iron oxide in the samples containing Al and Ga steamed at 1123 K is slightly broader (1-4 nm), indicating an extended clustering of iron.

The ion-exchanged catalysts exhibit large particles of iron oxide, with a distribution of 5-15 nm (see Fig. 6d for ex-Fe-[Al]MFI). This is a typical feature of ion-exchanged catalysts and contrasts with the more homogeneously dispersed state of iron in the ex-framework zeolites.

Alkaline post-treatment. Fig. 7 shows the TEM micrographs of ex-[Fe,Al]MFI before and after the alkaline treatment. The steamed sample shows the lattice planes of the zeolite. Iron oxide particles can be observed, being more clearly visible in the high-magnification micrograph (Fig. 6a). Upon alkaline treatment, the lattice planes of the zeolite can be still observed, in agreement with XRD, but an extensive amount of mesopores are formed. The size of the “holes” observed in the zeolite crystal can be estimated to be around 10 nm, in good agreement with the pore size distribution of this sample (see inset in Fig. 5). A second change occurring upon alkaline treatment of the zeolite is the invisibility of the iron oxide nano-particles observed in the steamed material. This has been ensured by taking high-magnification pictures of this sample, which only showed the zeolite crystal.

3.1.6. Voltammetry

Activation by steam. The voltammetric response of graphite-polyester electrodes modified with the zeolite samples provides useful information on the nature of the iron species in the different catalysts used in this study. The voltammetric responses C₁-C₇ shown in Fig.8 have been assigned in detail elsewhere. The cathodic process C₅ (+) in ex-[Fe,Al]MFI and ex-[Fe,Ga]MFI (Figs. 8a-b), which were activated in 300 mbar H₂O in N₂ at 873 K for 5 h, is attributed to the reductive dissolution of iron oxide nano-particles (observed by TEM) to Fe²⁺ in solution. This response is not present in ex-[Fe]MFI under these activation conditions (Fig.8c), which is in excellent agreement with TEM analysis (see Fig. 6c). Processes C₁ (>) and C₂ (<), assigned to oligonuclear oxo-iron species and isolated iron ions in extra-framework positions, respectively, are present in the three samples. Ex-[Fe]MFI shows two well defined peaks C₄ and C₅ (>) in Fig.8c), which indicate the presence of a substantial amount of iron in framework positions. These peaks are virtually absent in ex-[Fe,Al]MFI and ex-[Fe,Ga]MFI. This result confirms a more difficult dislodgment of framework iron ions (by hydrolysis of Si-O-Fe) in Fe-silicalite compared to those containing additionally Al or Ga. Peaks C₃ (>) and C₇ (>) are assigned to the reduction of electrochemically generated Fe³⁺ (to Fe²⁺) and Fe²⁺ (to Fe⁰) in solution.
Fig. 6. High-resolution TEM micrographs of (a) ex-[Fe,Al]MFI, (b) ex-[Fe,Ga]MFI, (c) ex-[Fe]MFI, and (d) ex-Fe-[Al]MFI(a). Steam treatment: 300 mbar H₂O in N₂ at 873 K for 5 h.

Fig. 7. TEM micrographs of (a) ex-[Fe,Al]MFI and (b) ex-[Fe,Al]MFI(at).
An effective extraction of isomorphously substituted iron ions in ex-[Fe]MFI can be achieved by performing the steam activation at a higher temperature (1123 K), as concluded by the decreased intensity of the C₄ and C₅ signals (◊). This severe treatment leads to clustering of extra-framework iron species into iron oxide nano-particles (peak C₆, + in Fig. 8d). This is in good agreement with TEM, since nano-particles were identified at this activation temperature. The [Fe,Al]MFI and [Fe,Ga]MFI zeolites steamed at 1123 K lead to the following result: the intensity of the signal corresponding to iron oxide increases (C₆, +), coupled with a decreased intensity of the peaks belonging to iron species in isolated positions (C₂, ▼) or in small oligonuclear intrazeolitic complexes (C₁, ▼). This result suggests the presence of a larger relative amount of iron oxide in the samples treated at higher temperatures, due to the clustering of small iron species during steam treatment at higher temperature. This was also suggested from TEM analysis. There is thus a strong dependency of the constitution of the catalyst, i.e. nature and relative amount of iron species, depending

![Image of E/V vs. SCE graph with symbol assignments](image)

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Assignment</th>
<th>Electrochemical process</th>
</tr>
</thead>
<tbody>
<tr>
<td>▼</td>
<td>C₁</td>
<td>Oligonuclear Fe-ions</td>
<td>Electron-transfer (species in the solid)</td>
</tr>
<tr>
<td>▼</td>
<td>C₂</td>
<td>Isolated Fe-ions</td>
<td>Electron-transfer (species in the solid)</td>
</tr>
<tr>
<td>◊</td>
<td>C₃</td>
<td>Fe³⁺ → Fe²⁺</td>
<td>Electron transfer (species in dissolution)</td>
</tr>
<tr>
<td>◊</td>
<td>C₄, C₅</td>
<td>Framework Fe-ions</td>
<td>Electron-transfer (species in the solid)</td>
</tr>
<tr>
<td>+</td>
<td>C₆</td>
<td>Fe-oxide</td>
<td>Reductive dissolution</td>
</tr>
<tr>
<td></td>
<td>C₇</td>
<td>Fe²⁺ → Fe⁰</td>
<td>Metal deposition</td>
</tr>
</tbody>
</table>

Fig. 8. LSVs of GCEs electrodes modified by (a) ex-[Fe,Al]MFI (873 K), (b) ex-[Fe,Ga]MFI (873 K), (c) ex-[Fe]MFI (873 K), (d) ex-[Fe]MFI (1123 K) in 1.0 M HCl aqueous solution; v = 20 mV s⁻¹. Steam activation temperature between brackets (see Chapters 5 and 6 for a detailed assignment).
on the framework composition and the conditions of steam activation. The voltogram of the ion-exchanged catalysts (not shown) exhibit a marked response between -0.4 and -0.8 V, which is a clear indication that in this catalyst iron is mainly present as iron oxide particles of a relatively large size at the external surface of the crystal, as concluded from TEM.

**Alkaline post-treatment.** The NaOH-treated ex-[Fe,Al]MFI(at) shows a similar response as the steamed catalyst in Fig. 8a (not shown), indicating that the nature of the iron species is not altered by this post-treatment. This result does not support the observation by TEM, where the iron oxide nano-particles disappear due to the alkaline treatment. This point is further discussed in §4.3.

3.2. Activity

3.2.1. Importance of the steam activation

Fig. 9 shows the N<sub>2</sub>O conversion vs. temperature curves of isomorphously substituted FeMFI after calcination (at 823 K for 5 h) and steam treatment (in 300 mbar H<sub>2</sub>O in N<sub>2</sub> at 873 K for 5 h). Activation of the zeolites with steam is crucial to create active species in the catalysts. The steamed catalysts show significant conversion at 700 K, while the calcined samples only exhibit a measurable conversion at 800 K. The steamed catalysts containing Al and Ga give almost identical conversions, higher than ex-[Fe]MFI. The calcined catalysts give very similar conversion independently of the framework composition. Apparently, iron ions of tetrahedral coordination in the zeolite framework, mainly present in the calcined zeolites, play no role in this reaction. Activation of N<sub>2</sub>O, the first step in these N<sub>2</sub>O-related conversions, requires coordination of atomic oxygen to the active site, impossible for framework iron being saturated by surrounding oxygen atoms of the lattice.

![Figure 9](image)

**Fig. 9.** N<sub>2</sub>O conversion vs. temperature over (▲) ex-[Fe,Al]MFI, (●) ex-[Fe,Ga]MFI, (▼) ex-[Fe]MFI, (△) c-[Fe,Al]MFI, (◇) c-[Fe,Ga]MFI, and (○) c-[Fe]MFI. Conditions: 1.5 mbar N<sub>2</sub>O in He, P = 1 bar, GHSV = 60000 h<sup>-1</sup>.

3.2.2. Optimization of the steam treatment

The similar (or different) catalyst constitution with respect to iron is the most plausible explanation for the identical (or different) activity curves of the steamed catalysts shown in Fig. 9. The characterization of the steamed ex-[Fe-Al]MFI and ex-[Fe-Ga]MFI catalysts leads to similar results, and strongly differs from ex-[Fe]MFI. A significant fraction of iron in
(inactive) framework positions was identified by voltammetry of ex-[Fe]MFI, which in principle accounts for the lower activity compared to the catalysts containing Al and Ga, where the extraction of framework iron was more extensive. This result suggests that there exists an optimal activation treatment for maximizing the N₂O decomposition activity, which depends on the catalyst composition. Therefore, the N₂O decomposition activity was measured for FeMFI catalysts activated at different conditions of partial steam pressures (20-500 mbar in N₂) and temperatures (473-1200 K) during 5 h.

**Water content.** Fig. 10 shows that the conversion of N₂O over the catalysts at 748 K increases with increasing H₂O pressure during steam treatment at 873 K. A significant improvement is observed in the range 0-300 mbar H₂O (Fig. 10). At high steam contents, hydrolysis of Si-O-Fe bonds and thus dislodgement of framework iron to more active extra-framework positions is facilitated. Above 300 mbar H₂O there is little improvement in N₂O conversion for the samples containing Al and Ga.

**Activation temperature.** The N₂O conversion over the steamed catalysts (at 300 mbar H₂O) measured at 748 K shows an optimal activation temperature (Fig. 11), which depends on the composition of the zeolite framework. Ex-[Fe,Al]MFI and ex-[Fe,Ga]MFI exhibit a similar behaviour, yielding the highest N₂O conversion at activation temperatures of 850-900 K. The position of this maximum is shifted to a significantly higher temperature in ex-[Fe]MFI, around 1125 K. The presence of an optimal temperature is explained as follows: below the optimum, a large fraction of iron is still in framework positions, i.e. unavailable for the N₂O decomposition reaction. The presence of Al or Ga destabilises the zeolite framework, inducing an easier escape of iron (at ~225 K lower activation temperature than in the siliceous catalyst). Above the optimal activation temperature, where the dislodgement of framework iron is complete, the activity drops as a consequence of the extensive clustering of intrazeolitic iron species, migrating to the outer surface of the zeolite crystal to form iron oxide nano-particles observed by TEM. The conversion over the three catalysts activated at the optimal temperature is fairly similar, proving that the activity differences in Fig. 9 are indeed a consequence of the suboptimal activation of ex-[Fe]MFI.

### 3.2.3. Role of extra-framework Al and Ga species

The role of the generated Al and Ga extra-framework species upon steam treatment was investigated by preparing the same zeolitic materials without Fe in the synthesis gel. The iron content in these samples was below the detection limit of 0.002 wt.% Fe (<20 ppmw, see Table 1). The activity of these catalysts is shown in Fig. 12. Results with commercial H-ZSM-5 samples (before and after steam treatment) are included for comparison. Iron-free extra-framework catalysts, containing a significant amount of extra-framework Al and Ga species, exhibit much lower N₂O decomposition activities than the Fe-containing catalysts (compare Figs. 9 and 12); N₂O conversion was complete in ex-[Fe,X]MFI at 850 K while no conversion was observed in ex-[X]MFI at this temperature. Furthermore, steam-treated purely siliceous zeolite (ex-[−]MFI) shows the same conversion as the steamed catalysts with Al or Ga (ex-[Al]MFI and ex-[Ga]MFI). Before and after steaming, the iron-free zeolites show nearly similar activities (see Fig. 12 for c- and ex-[Al]MFI). These results indicate that the activation by steam in Fe-free zeolites does not improve direct N₂O decomposition and suggests a minor role of extra-framework Al and Ga species in the reaction. Calcined commercial H-ZSM-5 shows a similar activity as ex-[X]MFI zeolites prepared without iron. Significant improvement is obtained after steaming of the commercial zeolite, yielding ex-H-ZSM-5. This catalyst shows substantial N₂O conversion (36%) at 850 K, which, however, is still significantly lower than the ex-[Fe]MFI catalysts. The increased N₂O decomposition activity is attributed to the presence of significant traces of iron (0.017 wt.%, 170 ppmw) in the parent
commercial zeolite. In the calcined commercial zeolite, iron is likely still present in framework positions, remaining inactive for N₂O decomposition. Only after steam treatment, the extra-framework iron is active for the reaction.

**Fig. 10.** N₂O conversion at 748 K vs. partial H₂O pressure during steam treatment at 873 K for 5 h over (●) ex-[Fe,Al]MFI, (○) ex-[Fe,Ga]MFI, and (▲) ex-[Fe]MFI. Reaction conditions: 1.5 mbar N₂O in He, $P = 1$ bar, GHSV = 60000 h⁻¹.

**Fig. 11.** N₂O conversion at 748 K vs. activation temperature during steam treatment in 30 vol.% H₂O for 5 h over (●) ex-[Fe,Al]MFI, (○) ex-[Fe,Ga]MFI, and (▲) ex-[Fe]MFI. Reaction conditions: 1.5 mbar N₂O in He, $P = 1$ bar, GHSV = 60000 h⁻¹.
Fig. 12. \( \text{N}_2\text{O} \) conversion vs. temperature over (▲) ex-[Al]MFI, (◇) c-[Al]MFI, (▽) ex-[Ga]MFI and (◇) ex-[V]MFI, (□) c-H-ZSM-5, and (■) ex-H-ZSM-5. Conditions: 1.5 mbar \( \text{N}_2\text{O} \) in He, \( P = 1 \) bar, \( \text{GHSV} = 60000 \) h\(^{-1}\).

### 3.2.4. Influence of the preparation method

Fig. 13 shows the \( \text{N}_2\text{O} \) conversion over ex-[Fe,Al]MFI, and other Fe-catalysts prepared by liquid (aqueous)-ion exchange, using both commercial NH\(_4\)-ZSM-5 and home-made c-[Al]MFI, followed by steam treatment in 300 mbar H\(_2\text{O} \) in N\(_2\) at 873 K for 5 h. The ion-exchanged catalysts using the commercial (ex-Fe-ZSM-5) or synthesized aluminosilicate (ex-Fe-[Al]MFI) have a very similar activity, while the catalyst prepared by incorporation of Fe in the zeolite framework and further activation by steam (ex-framework method) shows significantly higher \( \text{N}_2\text{O} \) conversions. These differences are attributed to the method to incorporate iron in the catalyst. In the ion-exchanged catalysts a major fraction of iron is in extra zeolitic positions, forming large iron oxide particles which are inactive for \( \text{N}_2\text{O} \) decomposition at temperatures where substantial conversion is obtained over ex-[Fe,Al]MFI. The \( \text{N}_2\text{O} \) decomposition activity of ion-exchange catalysts increases with the iron content in the catalysts (compare ex-Fe-[Al]MFI(a) and ex-Fe-[Al]MFI(b), Table 1). The steamed Fe-free ex-[Al]MFI and commercial ex-H-ZSM-5 are plotted for comparison.

Fig. 13. \( \text{N}_2\text{O} \) conversion vs. temperature over steamed samples of: (▲) ex-[Fe,Al]MFI, (▼) ex-Fe-[Al]MFI(a), (+) ex-Fe-[Al]MFI(b), (△) ex-[Al]MFI, (×) ex-Fe-ZSM-5, and (■) ex-H-ZSM-5. Conditions: 1.5 mbar \( \text{N}_2\text{O} \) in He, \( P = 1 \) bar, \( \text{GHSV} = 60000 \) h\(^{-1}\).
3.2.5. Influence of the crystal size and alkaline treatment

Fig. 14 shows the activity curves of steamed Fe-Al-Si zeolites with different crystal sizes, as well as the sample post-treated in alkaline medium. For the samples of different crystal size (see Fig. 1 and §3.1.2), the N₂O decomposition activity is initiated at the same temperature (~650 K), with similar conversion levels up to 715 K. Above this temperature the conversion over the zeolite with smaller crystal size (ex-[Fe,Al]MFI(sc)) increases faster. Determination of the apparent activation energies from the slope of the conversion-temperature curves (assuming first-order kinetics) leads to 137 and 161 kJ mol⁻¹ for the catalyst with large (2.5 μm) and small crystals (0.4 μm), respectively. An extensive characterization of both catalysts by EPR, TEM, FT-IR of adsorbed NO, H₂-TPR, UV-Vis, and voltammetric response according to the procedures described here and in Chapter 5, led to the conclusion that the iron species were of a similar nature. This in principle rules out a different catalyst constitution as an explanation for the different activities observed.

![Graph](image)

**Fig. 14.** N₂O conversion vs. temperature over: (●) ex-[Fe,Al]MFI, (△) ex-[Fe,Al]MFI(sc), and (◆) ex-[Fe,Al]MFI(at). Conditions: 1.5 mbar N₂O in He, P = 1 bar, GHSV = 60000 h⁻¹.

From the characteristic shape of the activity curves (very similar activities at low temperature and lower apparent activation energy for the catalyst with large crystals), the activity differences can be explained by intracrystalline diffusion limitations, meaning that the reaction is partially controlled by transport through the zeolite crystals. The absence of extra- and intraparticle diffusion limitation was experimentally checked, as explained in Chapter 2. This intracrystalline diffusion indicates that the active iron species are located in the zeolite channels, i.e. intrazeolite species. So, the extrazeolitic iron oxide nano-particles do not participate in the observed activity at low temperatures, since they are easily accessible.

Alkaline treatment of the catalyst with large crystals yielding ex-[Fe,Al]MFI(at), also leads to a significantly improved activity, going beyond that of ex-[Fe,Al]MFI(sc). The apparent activation energy of the catalyst increases up to 185 kJ mol⁻¹.

3.2.6. Influence of the feed composition

Addition of propane to the N₂O-feed mixture leads to a significant improvement of the activity of ex-[Fe,Al]MFI (by selective catalytic N₂O-reduction) compared to direct N₂O decomposition. Reaction temperature is reduced by ~100 K, as can be concluded by comparison of Figs. 9 and 15 for this catalyst. Addition of NO to this system inhibits the
reaction. The negative effect increases at increasing partial NO feed pressure, approaching the activity curve of the catalyst with no hydrocarbon. This behaviour is opposite to the effect of NO shown in Chapter 8 and elsewhere,\textsuperscript{38} where it promotes the N\textsubscript{2}O conversion.

![Graph showing N\textsubscript{2}O conversion vs. temperature over FeMFI catalysts](image)

**Fig. 15.** N\textsubscript{2}O conversion vs. temperature over ex-[FeAl]MFI in: (■) 1.5 mbar N\textsubscript{2}O + 1.5 mbar C\textsubscript{3}H\textsubscript{8} + 50 mbar O\textsubscript{2}, (∧) 1.5 mbar N\textsubscript{2}O + 1.5 mbar C\textsubscript{6}H\textsubscript{6} + 50 mbar O\textsubscript{2} + 0.2 mbar NO, (○) 1.5 mbar N\textsubscript{2}O + 1.5 mbar C\textsubscript{6}H\textsubscript{6} + 50 mbar O\textsubscript{2} + 0.6 mbar NO, (□) 1.5 mbar N\textsubscript{2}O + 1.5 mbar C\textsubscript{3}H\textsubscript{8} + 50 mbar O\textsubscript{2} + 1.5 mbar NO, and (×) 1.5 mbar N\textsubscript{2}O + 0.2 mbar NO; balance He, P = 1 bar, GHSV = 60000 h\textsuperscript{-1}.

4. Discussion

4.1. Relative activity of species in FeMFI

Steam treatment of isomorphously substituted FeMFI catalysts is a crucial step to generate active species for N\textsubscript{2}O decomposition. During the steam treatment, framework iron species are extracted to active extra-framework positions by hydrolysis of Si-O-Fe bonds. During steam treatment, partial dislodgement of Al and Ga is also produced, as concluded from MAS-NMR. Framework Fe species are saturated with oxygen of the zeolite lattice, being unable to coordinate atomic oxygen species (from N\textsubscript{2}O). This also explains the inability of isomorphously substituted iron in FeZSM-5 to activate N\textsubscript{2}O for the selective oxidation of benzene to phenol.\textsuperscript{39,40}

Our experiments show that the presence of extra-framework iron species is essential for the catalytic activity in direct N\textsubscript{2}O decomposition,\textsuperscript{41} and it is thus likely that they are essential in the activation of N\textsubscript{2}O in the benzene-to-phenol reaction. Louis \textit{et al.}\textsuperscript{42} have recently claimed that calcined H-ZSM-5 (with an iron content < 0.1 wt.%, 1000 ppmw) coated on stainless steel grids is able to selectively oxidize benzene to phenol. Although the iron traces were not specifically mentioned to determine the activity, it is discussed that the incorporation of iron species from the carrier material into the zeolite matrix during the synthesis of the coatings may lead to an improved catalytic performance (70% higher) with respect to the fixed bed with the same zeolite.

The role of Brønsted acidic sites does not seem to be crucial for N\textsubscript{2}O decomposition, since steam treatment diminishes the concentration of strong acid sites appreciably, while the activity increases. Sobolev \textit{et al.}\textsuperscript{43} also concluded based on infrared studies that Brønsted acidity is not required for the one-step oxidation of benzene with phenol over FeZSM-5. Vereshchagin \textit{et al.}\textsuperscript{44} showed that acidic properties of NaH-ZSM-5 have no effect on the reactivity of α-oxygen towards benzene. Contrarily Notté\textsuperscript{45} found an optimum between the
amount of α-sites (extra-framework iron ions able to activate N₂O) and the Brønsted acidity over steamed ZSM-5 with traces of iron (200-250 ppm). Pirutko et al. ⁴⁶ have recently speculated that the charge-compensating positions of MFI matrices with Brønsted acidity (Al-Si, Ga-Si) play an important role in the mechanism of the α-site formation on iron sites, being favourable compared with neutral MFI matrices (B-Si, Ti-Si).

Lewis acid sites are not relevant for N₂O decomposition either, since Fe-free MFI samples (< 0.002 wt.% Fe) hardly show an improved N₂O conversion after steaming, whereas substantial amounts of extra-framework Al and Ga species are formed. The sole presence of Al and Ga extra-framework species does only lead to activities above 850 K, much higher than the temperatures required for iron containing catalysts (< 700 K). Panov et al. ⁷ ⁴⁷ claimed that Lewis acidity is not sufficient to provide hydroxylation activity to the catalyst, since no correlation exists between acidity and activity, although other authors attribute the oxidation activity to coordinatively unsaturated Al or Ga atoms in extra-framework positions, ³ ⁵ based on circumstantial, so indirect, evidence.

4.2. Tuning the catalyst constitution and performance

4.2.1. Optimal steaming activation

What is clear so far is the inactive nature of iron in tetrahedral framework coordination and the requirement of iron extraction to achieve an active form. But what is/are the active iron form(s)? Based on the characterization results shown here and in Chapter 5, the extraction of framework iron in FeMFI can be considered as a clustering process, leading to a distribution of the iron species (Fig. 16). Dislodgement takes place of framework iron to extra-framework positions as isolated ions in exchangeable positions or further as oligonuclear species. Depending on the size of the oligonuclear cluster, this can be intrazeolitic, i.e. located in the zeolite channels, or extrazeolitic, i.e. located at the external surface of the zeolite crystal. A more severe treatment causes a more extensive degree of aggregation of iron entities into larger oligomers and ultimately results in the formation of iron oxide particles, like those visible in TEM (Figs. 6a-b).

![Diagram of iron species in FeMFI catalysts upon steam activation](image)

Fig. 16. Extraction and clustering of iron species in FeMFI catalysts upon steam activation.

The catalyst constitution, i.e. the nature and relative amount of iron species in the catalysts, is greatly affected by the conditions of the steam treatment (partial steam pressure and temperature), and ultimately determines the activity of the formulation. Both activation variables, steam pressure and temperature, are strongly linked: activation under steam-rich conditions (> 100 mbar H₂O in N₂) reduces the temperature for a certain iron extraction, which indeed induces a more tender clustering, i.e. a reduced formation of iron oxide in the
catalyst. The optimal preparation of catalysts via activation of isomorphously substituted FeMFI for N₂O decomposition involves a fine-tuning of the steam activation conditions for maximized conversions. The activation temperature should be adjusted to achieve the extraction of inactive framework iron but to avoid extensive clustering into inactive iron oxide particles. In agreement, the ion-exchanged catalysts, where a major part of the iron is present as large iron oxide particles, show a decreased activity compared to the ex-framework catalysts. This is further supported by the activity results in Fig. 9, where ex-[Fe]MFI, having no nano-particles and a large fraction of iron in framework position, shows a very similar activity as ex-[Fe-Al]MFI and ex-[Fe-Ga]MFI. The slight difference is due to the suboptimal utilization of iron remaining in the framework. From this, one can conclude that intrazeolitic iron species in extra-framework positions play a crucial role in the reaction. However, achieving a state where 100% of the iron is in extra-framework positions without any clustering into iron oxide appears to be very challenging, due to the heterogeneous distribution of iron species after the activation process.

Dislodgement of framework Fe is facilitated in the presence of Al or Ga, by destabilisation of the zeolite framework, leading to optimal activation temperatures of 873-923 K (in 300 mbar H₂O for 5 h). This contrasts with the higher temperature (1123 K) required for the optimum in Fe-silicalite. At the optimum activation treatment, the N₂O decomposition activity is the same in the catalysts, but the milder treatment of the Al- and Ga-containing FeMFI zeolites makes their practical application more conceivable. The influence of the framework composition on the state of iron at a certain activation conditions should be individually analyzed otherwise it may lead to erroneous interpretations. Panov et al. showed that the concentration of α-sites is 10-30 times lower in Fe-silicalite compared to FeZSM-5 for the same Fe content and activation conditions (1173 K in vacuum). In other words, 10-30 times more iron is needed in Fe-silicalite to have the same amount of α-oxygen, which determines the catalyst activity in the benzene-to-phenol process. In a more recent publication by the same group, Fe-containing (Al-Si) and (Ga-Si) zeolite matrices have been compared with (B-Si) and (Ti-Si) matrices, concluding that the neutral zeolites need 10-100 times more iron to achieve the same concentration of α-oxygen sites than in (Al-Si) and (Ga-Si) matrices. As discussed earlier, this behaviour has been attributed to the presence of charge-compensating cations in zeolites with Brønsted acidity, which favours the formation of active extra-framework iron species in the benzene-to-phenol reaction. A plausible explanation for this observation can also be provided from our experimental results. Due to the stability of framework iron in the siliceous matrix, a considerable amount of inactive framework iron is present under this treatment. The former statement can be reformulated by saying that in the ZSM-5 matrix iron is dislodged to extra-framework positions 10-30 times easier than in silicalite.

4.2.2. Benefits of steam treatment in the catalyst performance

Steam treatment shows advantages compared to the original thermal treatment in vacuum for the application of in the one-step selective oxidation of benzene to phenol with N₂O. In FeZSM-5 (Si/Al = 34 and 0.13 wt.% Fe), temperatures above 1023 K are required to create extra-framework iron species (optimal at 1173 K) in the catalyst. These demanding activation conditions may limit the practical application of these catalysts. In a patent, the Panov's group already showed that activation of isomorphously substituted FeZSM-5 with steam (50 vol.% H₂O) enabled a much lower activation temperature (reduced to 873-898 K) with a higher phenol productivity and stability (lower activity decay). Ribera et al. and Nott also reported on the benefits of steam treatment to improve the catalyst performance of iron-containing ZSM-5 zeolites in the selective oxidation of benzene to phenol with N₂O.
It is worth noting that in our study the optimal activation temperature of the Fe-Al-Si system (i.e. FeZSM-5) for N$_2$O decomposition was very similar (873-923 K) to that reported elsewhere for the benzene-to-phenol reaction, which evidences certain similarities (with respect to the nature of the active iron species) between both reactions. We also believe that steam treatment plays a crucial role in the remarkable hydrothermal stability of ex-FeZSM-5 for N$_2$O decomposition in wet tail-gases from nitric acid plants or combustion processes. The same performance also applies for the ex-framework FeMFI catalysts with Ga, or the purely siliceous. Activation of the zeolite catalyst in a steam-rich atmosphere (30 vol.% H$_2$O) is also considered as a suitable pretreatment to stabilise the structure of the zeolite and the active sites in simulated process gas (containing ca. 3 vol.% H$_2$O). This has been confirmed by characterization of the spent catalysts (after 600 h in a mixture of N$_2$O, O$_2$, NO$_x$, or SO$_2$, and H$_2$O) by $^{27}$Al MAS-NMR and other techniques specific for iron. The stability test did not cause further dealumination of the zeolite and the nature of the iron species was not modified either.

4.3. Intrazeolitic nature of the active Fe species

4.3.1. Effect of crystal size

Further indication regarding the intrazeolitic nature of active extra-framework iron species in FeMFI for N$_2$O decomposition is provided by the characterization and activity results of ex-[Fe,Al]MFI with different crystal size (0.4 and 2.5 μm). The shape of the activity curves and apparent activation energies has been assigned to the presence of diffusion transport limitations in the zeolite crystal. The high diffusivity of N$_2$O in pure silicalite-1 obtained from Multitrack experiments with large crystals (125 μm), however, does not predict this. The transport hindrance of reactants and products through the zeolite channels is therefore ascribed to the presence of active species in the pores of the zeolite. Intracrystalline diffusion limitations may also explain the higher activity of the zeolite with smaller crystals (ex-[Fe,Al]MFI(80)) in the selective oxidation of benzene to phenol with N$_2$O. The presence of intracrystalline transport limitations over Co- and Cu-exchanged zeolites (Mor, Beta, MFI) has also been reported for the selective reduction of NO, with light hydrocarbons, using zeolite crystal (0.2-1.3 mm) of similar size as those applied in this study.

4.3.2. Effect of alkaline post-treatment

Post-treatment of the large crystal ex-[Fe,Al]MFI catalyst in NaOH at 353 K also leads to a considerable improvement of the N$_2$O conversion, even higher than observed for the small crystals (Fig. 14). Associated to this improved activity, two remarkable observations concerning the post-treated material should be mentioned:

- Spectacular change in the textural properties of the catalyst by extensive creation of mesopores, inducing the destruction of 30% of the original micropores in the zeolite (see Fig. 5 and Table 2).
- "Apparent" disappearance of iron oxide nano-particles (compare Figs. 7a-b).

There is an extensive knowledge on the acid treatment of zeolites to change the Si/Al in the framework, and thus the properties connected with this ratio. Less information has been available about the base treatment of zeolite. In contrast to the acid treatment, which preferentially removes framework Al atoms, the base treatment by use of alkali solutions was found to preferentially remove framework siliceous species. Previous studies on the alkaline-treatment of zeolites such as ZSM-5, or silicalite by Na$_2$CO$_3$ or NaOH solutions, showed that selective removal of the siliceous species occurs without changes in
the crystallinity of the zeolite, in agreement with our XRD and TEM results. The mechanism of formation of the mesopores observed by TEM is not well understood, and further research is required in order to reveal this surprising phenomenon. Ogura et al. recently claimed erroneously the formation of uniform pores of 4 nm after NaOH treatment of commercial ZSM-5 due to the removal of amorphous silicon in twinned MFI crystals. We have proven the existence of a broader size distribution of the generated pores, centered at 10 nm. More harsh conditions (pH > 14) even result in macropore formation, visible by SEM.

Since the selective dissolution of silicon appears to be responsible for the pore formation, a reduced content of this metal in the post-treated solid would be expected. However, hardly any metal leaching is observed during the alkaline treatment, as concluded from the very similar chemical composition of both the original and the treated zeolites, and the analysis of the filtrate. This can be explained based on previous studies, where it has been reported that the dissolved siliceous species easily precipitate onto the surface of the zeolite crystals, forming a layer of amorphous silica. The amorphous phase may cover the iron oxide nanoparticles, which would explain their invisibility in TEM.

In a recent dissertation, Lu Gang has reported the improved activity of Cu-Y zeolite for ammonia oxidation to N₂ after a NaOH treatment, according to the procedure reported by Suzuki et al. This surprising behaviour was attributed to a change in constitution of the catalyst with respect to copper, going into the more active copper-oxygen aggregates, [Cu-O-Cu]²⁺ inside the zeolite supercage. Unfortunately, no analytical evidence to support this statement was provided. It is not clear whether this is the case in our system. The nature of the iron sites before and after the alkaline treatment is quite similar based on the voltammetric responses, but quantification is not feasible. A lower onset temperature for N₂O decomposition is also not expected if more active sites are created, since the oxygen desorption is the rate-determining step. A possible explanation for the improved activity of ex-[Fe,Al]MFI(at) is thus the improved accessibility as a consequence of mesopore creation, contributing to a facilitated transport of reactants and products to the intrazeolitic active sites. The catalyst with small crystals may also already suffer from diffusion limitations. Ogura et al. also assigned the improved performance of commercial MFI zeolite after NaOH treatment for cumene cracking, to the improved transport of the reactant through the zeolite channels. An improved diffusivity of benzene (by a factor of 2) through the channels of ZSM-5 was obtained in the same study.

4.3.3. What intrazeolitic form of Fe induces the activity?

The intrazeolitic nature of the active iron species seems to be clear, but in what form(s)? From the mechanistic studies of the N₂O decomposition over ex-FeZSM-5 investigated by the Multitrack technique it was concluded that the rate determining step in the reaction is the desorption of molecular oxygen by recombination of atomic oxygen species coordinated to extra-framework iron sites. This difficult recombination, which may involve migration of atomic oxygen through the zeolite, may be favoured over oligonuclear iron complexes compared to isolated iron ions (in exchangeable positions), due to the close proximity of the atomic oxygen species. This, of course, assumes that isolated ions do not possess more than one open coordination. The number of iron atoms in an active cluster cannot be assessed from our current results, but at least it should be able to fit in the zeolite channels or in the mesopores formed upon steam treatment (Fig. 4). In view of the heterogeneous nature of the FeMFI system, it would be of no surprise to have a distribution of active oligonuclear centers, which indicates the limitation of the application of the EXAFS technique for a hard determination of the iron coordination in the catalyst's active site.

A common approach followed in the literature consists of searching "the" iron centers responsible of the activity exhibited by FeZSM-5. Often, binuclear iron species are suggested
as "universal" active species in various reactions with an intrinsically different mechanism, e.g. selective catalytic reduction of NO, with hydrocarbons in the presence of excess oxygen or selective oxidations with N$_2$O (benzene to phenol, methane to methanol). However, no direct experimental evidence (only limited) of their presence in FeZSM-5 and the role in catalysis is available so far.\textsuperscript{7,12-16} The relative activity of the iron species should depend on the reaction mechanism. In direct N$_2$O decomposition, oligonuclear species are preferred in view of the close proximity of the Fe centers and the easier oxygen recombination. In other reactions mentioned above, isolated iron atoms may be actively participating in the reaction. The increased N$_2$O conversion with hydrocarbons (selective reduction) compared to direct N$_2$O decomposition (see Fig. 15) may apply here. The increased activity with propane should be related to the improved removal of atomic oxygen from the catalyst surface. In this case, the reductant regenerates the active site \textit{via} a clean-off mechanism. If so, isolated iron ions could also contribute to the observed activity. The same concept holds for the selective oxidation of hydrocarbons. Another indication of the strong relationship between the structure or nature of the active site and the mechanism of the reaction comes from the opposite role of NO in the N$_2$O decomposition. In direct N$_2$O decomposition, the effect is beneficial and adjacent iron sites are required (with adsorbed O* and NO*) to facilitate the recombination of atomic oxygen and thus O$_2$ desorption. In selective catalytic reduction, where single iron sites might be catalytically active, the presence of NO would lead to inhibition by competitive adsorption of NO* or NO$_2$* species. In these reactions, the activation of the hydrocarbon and the zeolite acidity may also play an important role.\textsuperscript{45,63} So bifunctionality and optimal iron oxide cluster size are the key parameters for the system. This shows parallels with copper oxide clusters in Cu/Y zeolites for NH$_3$ oxidation and the ensemble size effect in metal catalyzed reactions.\textsuperscript{60} A conclusive answer may be obtained from the synthesis of FeMFI zeolites with uniform iron species (of same nature).

5. Conclusions

The following conclusions can be derived from this study:

- The ex-framework route described in Chapter 5 for FeZSM-5 has been successfully applied to synthesize MFI zeolites with different framework compositions (combination of Si, Al or Ga, and Fe).
- Steam treatment is crucial to create active species in the catalyst for N$_2$O decomposition, by creation of extra-framework iron species. Framework iron is unable to activate N$_2$O. Extra-framework Al and Ga species, acting as Lewis acidic centers, and Bronsted sites play a minor role in N$_2$O decomposition.
- The catalytic activity for N$_2$O decomposition depends on the catalyst constitution with respect to iron. The nature of the iron species and the relative amount is strongly influenced by the conditions of the steam treatment. Higher partial steam pressures are favourable, and an optimum in temperature is found, as a compromise between the insufficient removal of framework iron at too low and the extensive clustering of iron species into iron oxide particles at too high temperatures. This suggests a crucial role of extra-framework iron species in the reaction.
- The optimal activation conditions depend on the composition of the zeolite framework. The presence of Al or Ga provides an easier escape route of iron to extra-framework positions and reduces the activation temperature for maximal N$_2$O conversion by 225 K compared to Fe-silicalite.
- The intrazeolitic nature of the iron species in direct N$_2$O decomposition over FeMFI zeolites is also supported by the presence of measurable intracrystalline diffusion limitations in catalysts with larger crystal size. Alkaline-treatment of the zeolite leads to
improved N₂O decomposition activities, as a consequence of the largely improved accessibility by mesopore formation.

- From the mechanistic aspects of the N₂O decomposition reaction discussed in Chapter 8, iron atoms in close proximity, i.e. as oligonuclear complexes in the zeolite channels, contribute more to N₂O decomposition than isolated iron ions, due to the more facile oxygen desorption (rate-determining step). In other N₂O-conversion reactions, like those involving hydrocarbons, isolated sites may contribute appreciably to the catalytic action. Every reaction mechanism requires its optimal cluster size.

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References

Summary and Evaluation

In this chapter, the results presented in this thesis are summarized. The main achievements are recapitulated and the impact of the work for catalysis is evaluated.
1. Background

Nitrous oxide (N\textsubscript{2}O) has been identified as a greenhouse gas and a contributor to the destruction of ozone in the stratosphere. Control measures to reduce anthropogenic N\textsubscript{2}O emissions would effectively contribute to reach the target agreed upon at the Third Conference of the Parties to the United Nations Framework on Climate Change in Kyoto (Japan) of the Parties in Kyoto in 1997 (e.g. 8% reduction of 1990 levels by 2010 in EU).\textsuperscript{1} N\textsubscript{2}O emissions that can be reduced on the short term are associated with chemical industry and combustion processes (Fig. 1), representing 40% of the total N\textsubscript{2}O emission in the EU.

Different options have been identified for N\textsubscript{2}O abatement. Direct catalytic decomposition of N\textsubscript{2}O into N\textsubscript{2} and O\textsubscript{2} is a cost-effective option to reduce N\textsubscript{2}O emissions, but none of the catalysts proposed in the literature show the combination of a good activity and stability in N\textsubscript{2}O conversion under realistic conditions of feed composition and space velocities. A less attractive option for N\textsubscript{2}O abatement comprises the use of fuels for the selective (SCR) and non-selective (NSCR) catalytic reduction. Thermal and catalytic technologies for N\textsubscript{2}O control have already been successfully developed for adipic acid plants. In this source, also reuse of N\textsubscript{2}O as selective oxidant to produce valuable chemicals is attractive. However, these options are not applicable to other sources, due to differences of the tail-gas in temperature, pressure, and composition. Since most of these processes are not commercially available, catalyst development is indispensable to realize efficient and economically viable control of this pollutant, complying with the more and more stringent regulations.

![Annual N\textsubscript{2}O emission in the EU (1990-1998):](image)

Fig. 1. Anthropogenic N\textsubscript{2}O emissions per sectors in the EU averaged for the period 1990-1998. The specific sources that can be effectively abated to meet the commitments in Kyoto (1997) are included.

2. Objective and approach

This thesis has focused on the development of novel catalysts for N\textsubscript{2}O control in simulated tail-gases of different sources. The requirements of a suitable catalytic formulation primarily depend on the characteristics of the source to be applied. Major attention is paid on searching active and stable formulations for direct N\textsubscript{2}O decomposition at low temperature and in the presence of O\textsubscript{2}, NO\textsubscript{x}, SO\textsubscript{2} and H\textsubscript{2}O, i.e in typical tail-gases from nitric acid plants and combustion processes. It is desirable to develop a versatile catalyst for application in other N\textsubscript{2}O-related reactions, including selective catalytic reduction and oxidation. The approach followed to reach the goals covers aspects of different levels distinguished in catalyst development (Fig. 2):
- **Macrolevel**, regarding the integration of the catalytic unit in the chemical plant. This requires a detailed technical knowledge of the process and evaluation in terms of cost efficiency of the different abatement options.

- **Mesolevel**, which mainly focuses on the reactor selection ("putting the catalyst in shape"). Different reactor types are evaluated for the final implementation of the catalyst, based on the different design parameters and operating conditions.

- **Microlevel**, aiming at the development of a suitable catalytic formulation. Fig. 3 applies well to the order of activities in this development level. These include an extensive catalyst preparation and characterization, primary screening, quantitative testing and reactor modeling, kinetic and mechanistic studies, and stability tests. Understanding of the reaction mechanism and identification of active sites in the catalyst is crucial at this level.

**Fig. 2.** Levels during development and implementation of a catalytic process ("M-m-μ" approach).

**Fig. 3.** Stages during a catalyst development program in the microlevel.
3. Summary and Evaluation

3.1. Macrolevel: Process selection

The macrolevel involves the study of the different options where the catalytic unit can be installed within a relatively complex process, being the source of N₂O. In principle, different potential locations can be selected with variable conditions (temperature, pressure, concentrations). The position of the N₂O decomposition unit strongly affects N₂O abatement options (thermal or catalytic decomposition, reduction, etc.), and ultimately the process requirement (activity, stability, selectivity). An exhaustive inspection, which is indispensable for an optimal selection is exemplified in Chapter 1, describing the different process options to reduce N₂O emissions during nitric acid production. The reason to dedicate a separate chapter to this source is twofold. Firstly, nitric acid manufacture is the largest source of untreated N₂O in the chemical industry. Secondly, it is probably the most complex source for process selection with a wide variety of possibilities, and thus most interesting from an academic point of view.

![Abatement option diagram](image)

**Fig. 4.** Cost efficiency of the different N₂O abatement options in existing nitric acid plants.²

Multiple abatement options were identified, according to the position of the N₂O decomposition unit in the plant. From the technical data and economic evaluation presented, two options are considered as cost-effective control measures in existing plants (Fig. 4): the in process-gas catalytic decomposition behind the Pt-Rh gauzes and Pd catchment in the ammonia burner, and the tail-gas catalytic decomposition upstream of the gas expander. Other options involving modifications or replacement of the Pt-Rh catalyst, redesign of the ammonia burner for homogeneous N₂O decomposition, and tail-gas options using reducing agents (NSCR or SCR) are not economically attractive. In process-gas N₂O decomposition (Fig. 5a) involves operation at high temperature (1075-1175 K) and pressure (1-13 bar), yielding high N₂O conversion levels (> 80%). The implementation of the catalyst is rather straight-forward and the investment cost is low. The risks and challenges for the development and application of catalysts under these conditions are relevant to activity, selectivity, stability, pressure drop, and product quality. The Achilles heel of this option concerns the selectivity of the ammonia oxidation process, i.e. the risk for decomposing some
NO\textsubscript{3}, thereby losing product (HNO\textsubscript{3}). This aspect determines the impact of the abatement unit on the economy of the plant. The mechanical and chemical stability of the catalyst is of special importance at these severe conditions and also plays a role in applying this technology.

![Diagram](image)

Fig. 5. Schematic representation of the (a) in process-gas catalytic N\textsubscript{2}O decomposition and (b) the tail-gas catalytic N\textsubscript{2}O decomposition upstream the expander in nitric acid plants, with the range of typical operating conditions.

Direct N\textsubscript{2}O decomposition in the tail-gas upstream the expander (Fig. 5b) offers the great advantage of not influencing the nitric acid production process, since changes to the heart of the plant (the burner and the absorption section) do not take place. Another advantage of this option is that there is essentially no physical limit to the amount of the catalyst that can be installed. This allows the reactor to be designed for very high levels of N\textsubscript{2}O removal (up to 100%). Possible problems with maximum allowable pressure drop can be overcome with a proper reactor design (see next section). The temperature of the tail-gas, ranging from 525 K (in old low-pressure plants) to 775 K (or even higher in dual-pressure plants), is the most important aspect for assessing the feasibility of this technology. Although many catalysts for N\textsubscript{2}O decomposition have been reported, none of them show a good activity and stability in N\textsubscript{2}O conversion under realistic conditions of feed composition and space velocities. Furthermore, industrial requirements of lifetime and insensitivity to deactivation have not been taken into consideration. The objective of this thesis has been to develop active and stable formulations for this application. Catalytic evaluation of promising catalysts under realistic conditions (especially FeZSM-5) show that high N\textsubscript{2}O conversion levels using direct decomposition is feasible above 725 K. This implies possible application in plants with high-temperature tail-gases. Only 1/3 of all plants falls into this category, but since these are normally of large capacity, they are responsible for more than 50% of the total emission. For low-temperature tail-gases, preheating of the tail-gas or addition of reductant can be used. This has a big impact in the cost-effectiveness of the abatement unit, with a 4-fold higher cost than direct N\textsubscript{2}O decomposition.

The same approach presented for nitric acid plants can be followed in other sources. Process options in (mobile and stationary) combustion sources, and other chemical production plants have been examined in Chapter 7. All the control options proposed are based on the extraordinary catalytic performance of ex-framework FeZSM-5 under simulated tail-gas conditions. For stationary combustion in fluid-bed combustors, end-of-pipe catalytic abatement after the cyclone is attractive. A dual-bed system has been developed for N\textsubscript{2}O abatement during control of NO\textsubscript{x} in car converters (de-NO\textsubscript{x}, SCR catalysts in Diesel and/or
lean-burn gasoline engines and aged three-way catalysts (TWCs) in conventional gasoline engines). Tail-gases of chemical production processes with a high N₂O concentration have also been examined. Two control options are considered to be effective: catalytic decomposition with dilution of the feed or reutilization of N₂O as oxidant for the synthesis of valuable chemicals, i.e. in the one-step selective oxidation of benzene to phenol. The last process is of great benefit in adipic acid manufacture, since phenol can be used in the same plant as a raw material, moving towards more sustainable processing.

3.2. Mesolevel: Reactor selection

Laboratory screening is carried out with a catalyst powder, granules, or particles. These normally can not be applied in conventional industrial fixed-bed reactors because of the high-pressure drop as a result of the typically high space velocities. The implementation of any catalytic abatement unit in the different processes described in §3.1 requires a close look to the reactor type, in order to achieve maximum yields under efficient and safe operation. The practical form and shape is a crucial aspect to obtain reliable design data for full-scale implementation. Because of the demand for increased conversion, selectivity, and energy efficiency, the chemical reactor of the 21st century will be characterized, at least for high space velocity applications, by the presence of “structure” on all length scales. In this way, ‘precision technology’ can be obtained.

Decoupling of the hydrodynamics, kinetics, and transport phenomena can be achieved by structured catalysts.3 In Chapter 7 a design has been presented based on two reactor alternatives for N₂O decomposition in tail-gases of nitric acid plants: conventional fixed-bed with extrudates and monolithic reactors. The basis of design and most relevant comparative results from the calculations are shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fixed-bed reactor</th>
<th>Monolithic reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Extrudates</td>
<td>Extruded monolith</td>
</tr>
<tr>
<td>Geometry</td>
<td>Diameter: 6 mm</td>
<td>Cell density: 200 cpsi, square channels</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wall thickness: 0.4 mm</td>
</tr>
<tr>
<td>Pressure / bar</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Reactor volume / m³</td>
<td>5</td>
<td>2.2</td>
</tr>
<tr>
<td>Bed height / m</td>
<td>0.8</td>
<td>0.7</td>
</tr>
<tr>
<td>Catalyst effectiveness η / -</td>
<td>0.33</td>
<td>0.95</td>
</tr>
<tr>
<td>Pressure drop / mbar</td>
<td>630</td>
<td>60</td>
</tr>
</tbody>
</table>

**Basis of design:** Nitric acid plant of 1500 ton HNO₃ per day, Tail-gas flow = 2.10⁶Nm³ h⁻¹, Temperature = 750 K, Pressure upstream the expander = 4 or 10 bar, N₂O conversion = 80%, Pressure drop = 200 mbar, Reactor diameter = 2 m.

This table shows the superior behaviour of the monolithic reactor in tail-gas after-treatment, typically at high space velocities. The reaction in shaped particles exhibits severe diffusion limitations, leading to low effectiveness factors. Only the outer part of the particle is used for the reaction, which in turn would call for small catalyst particles. However, these lead to a severe pressure drop, which would negatively affect the efficiency of the tail-gas expander. In the current case, monolithic structures allow the combination of high intrinsic activity, high catalyst effectiveness, and a low-pressure drop. The high catalyst effectiveness in a monolith often compensates for the lower amount of catalyst as compared to a fixed-bed.
reactor, leading to smaller reactor volumes. Another valuable pro of the monolithic reactor compared to a fixed bed is the flexibility for operation under different requirements of pressure and conversion, without violating operational constraints. The monolithic reactor also proved superior to other reactor configurations with low pressure-drop based on the fixed-bed concept, like the lateral flow reactor (LFR). There is a wide range of commercially available monolithic structures (Fig. 6), which makes monolith selection very flexible.

![Fig. 6. Typical cell densities of monoliths, in cells per square inch (cpsi).](image)

- **Optimal catalyst effectiveness**
- **Low pressure drop**
- **Good mechanical properties**
- **Dust and erosion resistance**
- **Freedom in reactor orientation**
- **Compact, rigid, easy to handle...**

**Fig. 7.** Key advantages of monolithic reactors in environmental applications.

Monoliths offer a number of advantages that have led to their widespread use in (gas-phase) environmental applications (Fig. 7). One example of successful implementation of monoliths can be found in the catalytic car converter (Fig. 8). Original pellets or granules catalysts have been widely substituted by structured catalysts, consisting of a ceramic honeycomb monolith with parallel, open channels. The smoothness of the monolithic structure offers less resistance to flow than that of a pellet-type catalyst.

The implementation of the monolithic reactor in stationary sources can be based on the vast knowledge and experience gained in NH₃-SCR units for NOₓ control. An artistic impression of the reactor unit for catalytic N₂O removal in the different stationary sources treated in this thesis is shown in Fig. 9. The monolithic catalyst, normally in unit elements of e.g. 150×150 mm, is usually housed in catalyst baskets, which are layered to cover the reactor diameter. Less restriction can be found to the height of the monolithic units. Extra space for an

![Fig. 8. Fixed-bed (a) and monolithic (b) reactors used for pollution control in car exhausts.](image)
additional catalyst layer is a normal precautionary measure for changing operation conditions in the plant or more stringent regulations. The potential use of fuels for catalytic \( \text{N}_2\text{O} \) reduction would additionally require the installation of a control system for the dosage of the reductant.

![Diagram of reactor design](image)

**Fig. 9.** General reactor design for \( \text{N}_2\text{O} \) abatement in chemical production and stationary combustion processes.

### 3.3. Microlevel - Catalyst selection

The microlevel, which is related to the development of the catalytic formulation (see Fig. 3), is crucial in the assessment and feasibility of the overall process and the main focus of this work. A summary of the achievements and conclusions from the results presented in this thesis is given below, including the significant impact on other topics in catalysis.

#### 3.3.1. Catalyst performance testing and reactor phenomena

**The six-flow reactor: an efficient testing unit**

In catalysis research, the testing unit is crucial to obtain catalytic data efficiently and quantitatively, as reviewed in Chapter 2. An automated *six-flow reactor* system for secondary catalyst screening was further developed (Fig. 10). This laboratory reactor, which is a valuable tool for catalyst development, was used for high-throughput screening, quantitative testing, stability tests, and kinetic investigations. The set-up targets an optimization of already-existing formulations, without excluding the discovery of new materials. This "parallel testing unit" is increasingly being applied and commercialized by several companies. Why six? Is it magic? you may wonder. Well,..., there is some reasoning behind. It turns out that six-reactors (five catalyst + reference) give a reasonable optimum
between catalyst preparation, testing, data mining, and results interpretation for a single Ph.D. student.

**Catalyst bed dilution: Friend or Foe?**

The versatility, accuracy, and reproducibility of the six-flow reactor was proven by its application in a detailed study on transport phenomena in diluted fixed-bed laboratory reactors (Chapter 3). Inert bed dilution is often applied by many researchers in fixed-bed reactors or trickle bed-reactors in view of various advantages (Fig. 11). The influence of **catalyst distribution** and the **amount of diluent** has been investigated based on experimental work and simulations using a Random Particle Distribution model.\(^{10,11}\) A general **criterion for maximum allowance of diluent** was derived. This criterion (equation in Fig. 11), based on observable quantities, notably refines former criteria. Improvements include the incorporation of the conversion level and the fact that it does not contain intrinsic kinetic parameters, which are unknown beforehand in kinetic investigations. This work significantly contributes to daily catalysis research activities.

![Fig. 10. The six-flow reactor.](image)

**ADVANTAGES**
- Improve heat conduction in the bed
- Spread of heat production (consumption) along a larger volume
- Minimize effect of axial dispersion
- Larger heat exchange area
- Decouple hydrodynamics and kinetics

**DRAWBACKS**
- Negative effect on the reactant conversion
  - **Bed distribution**
  - **Amount of diluent**:

\[
\Delta = \left( \frac{b}{1-b} \right) \frac{X_{deq} \cdot d_p}{2 \cdot h_{bed}}
\]

**Improving degree of mixing**

![Fig. 11. Pros and cons of catalyst bed dilution in fixed-bed laboratory reactors.](image)

3.3.2. Hydrotalcites and mixed oxide catalysts

**Thermal decomposition of HTIs: A novel spectroscopic approach**

The thermal decomposition of several Co- and Ni-based hydrotalcites to mixed oxide catalysts (Fig. 12) in different atmospheres has been analyzed in Chapter 4 by means of **in situ spectroscopic FT-IR and Raman techniques** (Fig. 13). Previous studies of these transitions were performed **ex situ**. For the first time, Raman spectroscopy during decomposition of these materials has been successfully applied. The spectroscopies complement each other and are in excellent agreement with other characterization
techniques. This methodology was primarily applied to optimize the activation conditions of hydrotalcites to mixed oxides catalysts. The spectroscopic work developed in this chapter significantly contributes to determine structure-activity relationships over activated hydrotalcites for solid base catalysis, e.g. aldol condensations. The application of infrared and Raman spectroscopies is not limited to the use of hydrotalcites as catalysts or catalyst precursors, but also as adsorbents or ion-exchangers. The same approach may contribute to the understanding of the decomposition mechanism of other clays (e.g. bentonite, smectite).

Fig. 12. Thermal decomposition of hydrotalcites to mixed oxide (spinel) catalysts.

Fig. 13. Infrared and Raman (R) assignments (in cm⁻¹) during thermal decomposition of Co-Al and Ni-Al hydrotalcites to mixed oxides.¹²,¹³
Ex-HTIcs: promising catalysts for N₂O decomposition

The application of hydrotalcites as catalyst precursor is based on the:

- ability to accommodate a large variety of bivalent and trivalent cations,
- homogeneous mixture of the cations on an atomic scale (high dispersions),
- formation of thermostable mixed oxides with a high surface area (ex-HTIcs).

Although not specifically included in this thesis, we have reported several studies dealing with the effect of multiple additions on the structural and catalytic properties of the resulting multimetallic mixed oxides.\textsuperscript{15,16} Ni- and especially Co-systems containing noble metals (Rh, or combinations of La and Pd) lead to very high N₂O decomposition activities. This is illustrated in Chapter 7 for a Co-Rh,Al mixed oxide. Addition of Mg to the formulation yields surprising properties of the catalyst, acting as a structural promoter and a stabilizing agent against SO₂ poisoning in catalytic N₂O decomposition.\textsuperscript{15}

A major drawback of these catalysts for N₂O decomposition in simulated tail-gases is the severe inhibition and/or deactivation caused by the presence of additional gases in the feed. This behaviour is extrapolable to many other formulations, e.g. supported oxides and zeolite catalysts containing noble metals (Rh, Ru, and Pd-based) and transition metals (Co- and Cu-based). Inhibition by oxygen and NO₂ is usually reversible, but addition of H₂O and/or SO₂ deactivates the catalysts rapidly. This strongly limits the practical application of these catalysts. Preparation of iron-containing mixed oxides via the hydrotalcite route did not lead to the excellent catalytic properties described below for FeMFI in tail-gas conditions, which evidences the importance of the iron "host", i.e. the zeolite.

3.3.3. FeMFI system

A novel ex-framework route to prepare FeMFI catalysts has been developed. Detailed characterization studies regarding the catalyst constitution during activation by steam (Chapters 5, 6, and 9), activity and stability tests dealing with N₂O control in simulated tail-gases from different sources (Chapter 7), and mechanistic investigations (Chapter 8) have been presented and discussed. Different key aspects of this part of the research are evaluated below.

![Diagram showing the formation of active iron species during activation of isomorphously substituted FeMFI by calcination and steam treatment: the ex-framework route.](image)

Fig. 14. Formation of active iron species during activation of isomorphously substituted FeMFI by calcination and steam treatment: the ex-framework route.\textsuperscript{17}
FeMFI: "simply" a heterogeneous catalytic system

The ex-framework route starts with the preparation of isomorphously substituted FeMFI, followed by calcination and activation in steam. A detailed description of the physico-chemical changes and nature of iron species in the isomorphously substituted FeZSM-5 (ferrialuminosilicate) and the products of activation is given in Chapter 5, based on an extensive characterization. The integration of numerous techniques leads to a picture of the heterogeneity of this system with respect to iron. Upon calcination and activation by steam, isomorphously substituted Fe is extracted from the framework, leading to isolated ions, oligomeric species, or oxide particles (Fig. 14). This complex process of formation of extra-framework species can be envisaged as a clustering process and calls for a multipletechnique approach to characterize these systems. Precautions should be taken during interpretation of analytical data based on an average of this system, e.g. EXAFS, techniques identifying species by oxidation state (e.g. FT-IR of adsorbed NO, EPR) or size (e.g. TEM), and those unable to discriminate different species (e.g. ^57Fe Mössbauer, H2-TPR, UV-Vis). The ex-framework catalyst does not contain large iron oxide particles. It strongly differs from other FeZSM-5 catalysts prepared by conventional (solid and liquid) ion-exchange or sublimation methods. In Chapter 9 the ex-framework route has been extended to other framework compositions (combinations of Fe, Ga or Al, and Si). These different compositions consist of heterogeneous systems, but the nature and relative amount of iron species can be tailored by optimization of the steam treatment, which ultimately determines the catalytic performance (discussed below).

Chapter 6 presents a novel voltammetric technique to characterize heterogeneous catalysts. In this particular solid-state electrochemical method, different metal species in the catalyst are investigated by their characteristic electrochemical response, which depends on the oxidation state and chemical structure. This method is quite valuable for analysis of complex catalyst systems. The voltammetric method is reproducible, relatively cheap, and experimentally simple. This technique has been successfully applied to characterize iron species during activation of isomorphously substituted FeZSM-5 (Chapters 5 and 6) and FeMFI zeolites with other framework composition (Chapter 9). This technique provides a quick fingerprint of the catalyst constitution with respect to the nature of the iron, since it

Fig. 15. Principle of the voltammetric method to characterize heterogeneous catalysts, with advantages and drawbacks.18,19
Lachgas (N₂O) is zowel een broeikasgas als een stof die de ozonlaag afbreekt. Binnen de chemische industrie vindt de grootste uitstoot van lachgas plaats bij fabrieken die salpeterzuur produceren. Onderzoekers van TU Delft hebben nieuwe vormen van de katalysator FeZSM-5 gemaakt, die het lachgas in de uitstoot van salpeterzuurfabrieken goed kunnen afbreken tot stikstof en zuurstof. Katalytische ontsluiting is een aantrekkelijke manier om de uitstoot te verminde- ren, maar het is lastig een goede katalysator te vinden die werkt in de aanwezig- heid van hoge concentraties zuurstof, NOₓ en water, gassen die tegelijk met lachgas vrijkomen.

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**Fig. 16.** Application of ex-FeZSM-5 in tail-gases of nitric acid plants (C2W, May, 2001).

**Ex-framework FeZSM-5: a breakthrough in catalytic N₂O control**

The ex-framework catalysts show a superior performance for direct N₂O decomposition compared to FeZSM-5 catalysts prepared by ion exchange and sublimation methods and noble metal-based systems (Chapter 7). The chemical stability of ex-FeZSM-5 is remarkable (during tests of 600 h) in simulated tail-gases of nitric acid plants and stationary combustion processes, i.e. in mixtures containing N₂O, O₂, NOₓ, H₂O, and SO₂ (Fig. 16). The performance of the ex-framework catalysts appears to enable a cost-effective and efficient technology in different N₂O sources. Application of direct N₂O decomposition over this catalyst in other chemical production sources is also described in Chapter 7.

A spectacular feature of ex-FeZSM-5 is the versatility to catalyze other reactions involving N₂O. Selective catalytic reduction of N₂O in the presence of hydrocarbons improves the performance of this catalyst, shifting temperature for N₂O removal to lower values. This feature gives noticeable flexibility for application in processes under extreme conditions, i.e. in low-temperature tail-gases of nitric acid plants, or in N₂O-sources containing reductants. A successful application of these properties is a dual-bed system (Fig. 18) to reduce N₂O emissions in low-temperature de-NOₓ HC-SCR catalysts from Diesel or gasoline lean-burn engines. With the on-going regulations and agreements, N₂O emissions from vehicles are expected to be controlled in the near future. This novel configuration, where NO and N₂O are consecutively removed, yields a highly active, selective, and stable operation. Extrapolation of this system to aged TWCs in conventional gasoline engines is put forward.
Oxidation catalysis is one of the most dynamic and fruitful areas of catalysis.\textsuperscript{24,25} There is an area where the achievements of oxidation catalysis are still modest regardless of many efforts, such as the oxidative hydroxylation of paraffins to alcohols and of aromatic hydrocarbons to phenols. Two reactions of this type are the oxidation of methane to methanol and benzene to phenol, which are often included into the top 10 most difficult challenges of modern chemistry. At present, benzene oxidation to phenol is carried out via the three-step cumene process leading to acetone as by-product. The last process produces 95\% of the 4.5 billion pounds of phenol required annually for manufacturing phenol-formaldehyde resins. Novel processes to convert benzene to phenol in one step would eliminate the need to neutralize acids, separate organic compounds as by-products, or to be concerned with potentially unstable intermediate products in the cumene process.

\begin{align*}
\text{C}_6\text{H}_6 + \text{H}_2\text{O}_2 & \rightarrowarrow{315-345 \text{ K}} \text{Metal complexes} \rightarrowarrow{\text{Ti-silicates}} \text{OH} + \text{H}_2\text{O} \quad \text{Low H}_2\text{O}_2 \text{ selectivity} \\
\text{C}_6\text{H}_6 + \text{HNO}_3 & \rightarrowarrow{575-675 \text{ K}} \text{V}_2\text{O}_5, \text{MoO}_3 \rightarrowarrow{\text{OH}} \text{OH} + \text{NO}_2 + \text{H}_2\text{O} \quad \chi \sim 52\%, \ S \sim 90\% \\
\text{C}_6\text{H}_6 + 2\text{CuSO}_4 + 2\text{H}_2\text{O} & \rightarrowarrow{573 \text{ K}} \text{CuSO}_4 + \text{H}_2\text{SO}_4 \quad \chi \sim 0.1\%, \ S \sim 90\% \\
\text{C}_6\text{H}_6 + \text{H}_2\text{O} & \rightarrowarrow{475-575 \text{ K}} \text{Fe-Cu-Mn oxide} \rightarrowarrow{\text{OH}} \text{OH} + \text{H}_2 \quad (?) \quad \chi \sim 15\%, \ S \sim 97\% \\
\text{C}_6\text{H}_6 + \text{N}_2\text{O} & \rightarrowarrow{575-675 \text{ K}} \text{FeZSM-5} \rightarrowarrow{\text{OH}} \text{OH} + \text{N}_2 \quad \chi \sim 85\%, \ S \sim 98\%
\end{align*}

Fig. 18. One-step oxidation of benzene to phenol by monooxygen donors.\textsuperscript{24}

Following the pioneering work of Panov \textit{et al.},\textsuperscript{24,26} in this field, we have successfully tested \textit{ex-FeZSM-5} in the direct hydroxylation of benzene to phenol with N\textsubscript{2}O, obtaining a high benzene conversion going selectively to phenol (Table 2).\textsuperscript{27} As shown previously, these results contrast with the low values using molecular O\textsubscript{2} as the oxidant (benzene conversion of 0.3\% and no selectivity to phenol),\textsuperscript{24} and is also superior compared to other promising monooxygen donors and catalysts in the direct oxidation (Fig. 18).

This approach opens a new concept for N\textsubscript{2}O control. In this respect, Solutia and the Boreskov Institute of Catalysis have developed a new phenol synthesis route, the so-called AlphOX\textsuperscript{TM} process,\textsuperscript{24} where benzene is selectively oxidized to phenol with N\textsubscript{2}O over FeZSM-5 (Fig. 20). The gaseous stream produced upon reaction of cyclohexanol and cyclohexanone mixtures with nitric acid during adipic acid manufacture is highly concentrated in N\textsubscript{2}O (25-40 vol.\%) and is recycled to the front end of the overall process, closing the cycle. Instead of
spending efforts and money on N₂O neutralization, the new phenol process uses N₂O as a valuable raw material, thus mimicking the wasteless strategy of nature.

Table 2. Parameters during N₂O-mediated oxidation of benzene to phenol over ex-FeZSM-5.²⁷

<table>
<thead>
<tr>
<th>Reaction parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene : N₂O : N₂ molar ratio</td>
<td>5 / 20 / 75</td>
</tr>
<tr>
<td>Benzene conversion / mol. %</td>
<td>27</td>
</tr>
<tr>
<td>N₂O conversion / mol. %</td>
<td>85</td>
</tr>
<tr>
<td>Phenol selectivity / mol. %</td>
<td>100</td>
</tr>
<tr>
<td>Productivity / kg phenol kg cat⁻¹ h⁻¹</td>
<td>0.1</td>
</tr>
</tbody>
</table>

* Other products (CO₂, diols) were not identified in the GC analysis.

Fig. 19. The AlphOx™ process: N₂O reutilization concept applied in the adipic acid manufacture.²⁴

**NO catalyzes N₂O decomposition over Fe-catalysts**

An intriguing feature of FeZSM-5 catalysts in N₂O decomposition is that NO and SO₂ significantly enhance the activity, while the opposite effect is usually observed for other catalytic systems based on noble metals or transition metal oxides. This peculiar behaviour of FeZSM-5 makes it very attractive in sources where both N₂O and NO or SO₂ go together. The positive effect of these gases on the N₂O conversion was first reported by Kapteijn et al. in 1996,²⁸ using a FeZSM-5 prepared by liquid-ion exchange with Fe(II) sulfate. The mechanistic aspects of these observations were not investigated. In Chapter 8, the NO-assisted N₂O decomposition mechanism over different Fe-catalysts has been elucidated by means of steady-state activity data and in situ transient Multitrack and FT-IR/MS studies.²⁹,³⁰ The findings provide valuable information, not only in a practical sense, but especially on the fundamental understanding of different catalytic processes involving N₂O. The following questions (and answers) can be put forward:

- **How does NO promote N₂O decomposition?**

Oxygen desorption from the catalyst surface by recombination of atomic oxygen atoms is the rate-determining step in N₂O decomposition over Fe-catalysts (Fig. 20 and Fig. 21a). This process is dramatically accelerated by the presence of small amounts of NO. The promotion effect is catalytic and was observed for different Fe-catalysts in the range of 550-900 K. The mechanism depends on the temperature. At low temperatures, in zeolitic systems, adsorbed
NO species on iron sites act as a carrier for oxygen in the zeolite. This improves the migration of atomic oxygen species and their recombination to molecular $O_2$, as was concluded from Multitrack studies (Figs. 21b and 22). In high-temperature Fe-catalysts, the predominant mechanism is the scavenging effect of atomic oxygen by NO, yielding mainly $NO_2$ (Fig. 21c).

- **Are certain iron species in the catalyst needed for the NO promotion?**

The promotion effect of NO does not require a specific type of iron sites. The NO-assisted $N_2O$ decomposition is exhibited by FeZSM-5 prepared by different methods (ex-framework, ion-exchange, sublimation) by other zeolites (Fe-Beta, Fe-USY) and even with conventional supports (Fe/$Al_2O_3$, Fe/$SiO_2$). The only difference between zeolitic and non-zeolitic systems is the temperature window, which essentially depends on the catalyst constitution, *i.e.* nature and relative amount of iron sites (discussed in Chapter 9). From our results it is also concluded that NO does not inhibit $N_2O$ decomposition, even at $N_2O/NO$ molar ratios of 0.1. This strongly indicates that NO and $N_2O$ are adsorbed on different iron sites. Based on transient Multitrack experiments and assuming that all NO adsorbed at Fe sites, it was calculated that less than 0.9% of the Fe present in ex-FeZSM-5 is involved in the promotion!!. This indicates that a very low fraction of the Fe is active in the reaction.

- **Could the promotion of $N_2O$ conversion by $SO_2$ over ex-framework FeMFI catalysts be explained in a similar way?**

$SO_2$ in the adsorbed phase can potentially transfer atomic oxygen *via* $SO_3$ formation, so in principle a similar mechanism can be tentatively proposed. The investigation of the $SO_2$ effect in ex-framework catalyst remains a challenge for future work. Development of suitable analysis of the product gas in steady-state measurements is primarily required. A similar transient approach used for NO, using *in situ* infrared and Multitrack, should give a definitive answer.
- Is NO promotion a general aspect in all N₂O-related reactions?

  **Unfortunately NO!** The effect of NO turns out to be negative in other reactions involving N₂O. In the AlphOx™ process for selective oxidation of benzene to phenol with N₂O (Fig. 19), the tail-gas recycled to the front-end contains apart from a large amount of N₂O also some NO (one order of magnitude lower) formed during the oxidation of cyclohexanol and cyclohexanone mixture with nitric acid. A high efficiency of the benzene-to-phenol process mediated by N₂O can only be guaranteed if NO is removed to a large extent e.g. by NH₃-SCR. Otherwise the utilization of N₂O in the benzene oxidation will drop considerably, since NO provides an escape route for the so-called ω-oxygen from N₂O. This can be translated in an accelerated oxygen desorption and/or the sequestration of reactive O* as adsorbed NO₂ species, hindering the transfer of atomic oxygen to the benzene molecule. A similar inhibition effect by NO was observed in the catalytic reduction of N₂O with hydrocarbons (Chapter 9).

- Does NO catalyze other processes following a similar mechanism?

  It is worth noting two other catalyzed reactions where NO serves as an atomic oxygen transport facilitator (Fig. 23): (a) the old lead chamber process for SO₂ oxidation, and (b) the promoted soot oxidation in the presence of NO over bifunctional catalysts. In these examples the oxygen is transported through the gas phase, while in our case it occurs through adsorbed species. This emphasizes the general role of NO as oxygen transfer agent.

**Optimization of the steam treatment in FeMFI catalysts**

In Chapter 9 the ex-framework method presented in Chapter 5 has been extended to other MFI zeolites, with combinations of Fe, Al or Ga, and Si. The framework composition and the steam activation (temperature and water content) determine the catalyst constitution (nature and relative amount of iron species in the catalyst) and ultimately the catalytic performance, as concluded from an extensive characterization and testing program. Steam treatment of FeMFI catalysts proves to be superior for activation of FeMFI catalysts compared to purely thermal treatments, because of a more effective extraction of isomorphously substituted iron to extra-framework positions at lower temperatures.
Fig. 23. Other processes catalyzed by NO: (a) lead-chamber process for $\text{H}_2\text{SO}_4$ production and (b) NO-activated soot oxidation over bifunctional metal oxide catalysts.$^{31,32}$

It was concluded that "steam-created" extra-framework iron species are essential for N$_2$O activation, while Lewis and Brønsted acidic sites play a minor role in the reaction.$^{33}$ The N$_2$O decomposition activity exhibits a maximum as a function of activation temperature, whose position depends on the composition of the zeolite framework (Fig. 24). Below the optimal temperature, dislodgement of framework iron is limited due to mild conditions, while above the maximum clustering of iron species in the channels leads to formation of inactive iron oxide at the external surface of the zeolite crystal (see schematic clustering mechanism in Fig. 14). The optimal activation temperature is significantly higher in the sample with no Al or Ga (1125 vs. 873-923 K), since these induce easier escape for tetrahedral iron to active extra-framework positions. Based on our experimental results, iron species of low nuclearity in the zeolite channels (intrazeolite species) are proposed to be the active species in the reaction.

Fig. 24. Structure-activity relationship during steam activation of ex-framework FeMFI catalysts with different framework compositions. Steam treatment at 748 K in 30 vol.% H$_2$O for 5 h.

Based on mechanistic studies on direct N$_2$O decomposition presented in Chapter 8, oligonuclear oxo-iron species are good candidates for the active site, since oxygen desorption (the rate determining step, see Figs. 20 and 21a) should be more facile if Fe ions are in close proximity, i.e. forming small clusters in the zeolite porous network. The dimension of the
iron oligomeric complexes can not be assessed at present, but based on the process of formation, there could be a distribution of clusters sizes (different \( y \) values in the oligonuclear oxo-Fe species in Fig. 14). In this sense, binuclear \((y = 2)\) or oligonuclear \((e.g. Fe_2O_4 \; y = 4)\) species have been proposed elsewhere as possible structures of the active sites for selective oxidations and de-NO, HC-SCR.\(^{24,34,35}\) It is pointed out here that techniques \((e.g. \text{EXAFS})\) to determine average Fe coordination require careful interpretation.

The nature of the active species in other \(N_2O\)-related processes, \(e.g.\) selective oxidation or reduction may change with respect to direct \(N_2O\) decomposition, due a different reaction mechanism. Here a role of isolated iron ions can not be excluded, since oxygen recombination is not an issue and the reductant can “clean-off” the oxidized isolated site. The inhibition effect by NO in these reactions, opposite to its promotion effect in direct \(N_2O\) decomposition, also suggests a modification of the structure of the active site in these reactions. Concluding, every process should be studied individually and a generalization of universal structure of “the” active species seems unlikely.

4. Concluding remarks

Many catalysts are able to decompose \(N_2O\) into \(N_2\) and \(O_2\), but under simulated process conditions most of them do not show sufficient activities. Furthermore, poor chemical stability is typically obtained, which limits the application in real situations. The catalyst development presented in this thesis mainly aimed at searching a “miraculous” formulation, capable of withstanding harsh tail-gas conditions. A novel FeMFI system puts at our disposal a great variety of efficient and cost-effective catalytic technologies for control of \(N_2O\) in various anthropogenic sources. Three key properties summarize the unusual behaviour of this catalyst in \(N_2O\)-related conversions:

- **High activity at low temperature and stability in the presence of inhibitors, crucial for direct \(N_2O\) decomposition.** NO and \(SO_2\) promote \(N_2O\) decomposition over this catalyst.
- **Improved performance in the presence of hydrocarbons, shifting operation to lower temperatures**, which makes this formulation attractive in selective catalytic reduction of \(N_2O\). NO inhibits this reaction.
- **Selective oxidation** of benzene to phenol highlights the ability of \(N_2O\) as monoxygen donor and the catalyst’s ability to coordinate a “special” atomic oxygen species. The specificity of \(N_2O\) as a selective oxidant and the nature of the Fe species capable of coordinating the so-called \(\alpha\)-oxygen species are believed to be key factors in this catalytic process.

Such a versatile and flexible catalyst is superior to other promising formulations tested during the course of this research, and is considered as a breakthrough for abatement and utilization of \(N_2O\).

Still challenges remain, however, for the future. The most important is to reveal the optimal active site constitution and the controlled synthesis of such catalysts combined with the optimal transport properties. Both will depend on the reaction under consideration. Computational methods are expected to play an essential role in optimizing the catalyst architecture.

References


(c) http://www.howstuffworks.com/catalytic-converter.htm.


"I am sure the air in heaven must be this wonder working gas of delight", so wrote poet Robert Southey of nitrous oxide, N₂O, a colourless and sweet-smelling gas, also known as nitrogen oxide, dinitrogen oxide, dinitrogen monoxide, hyponitrous acid anhydride, and factitious air. Different aspects regarding the history of N₂O are shown in Fig. 1. More details can be read elsewhere.¹ N₂O was discovered by Priestley in 1772.² In 1799, Davy of the Pneumatic Institute in Bristol, England, experimented with the physiological properties of N₂O, such as its effects upon respiration. He administered the gas to visitors to the institute, who experienced euphoria, mirth, and a certain degree of analgesia, coining the term “laughing gas”. The experiences were published in 1800.³ From that moment, the primary use of N₂O was for recreational enjoyment in public shows, carnivals, and exhibitions. Forty years later, in 1844, Dr. Wells, a British dentist, demonstrated the therapeutic applicability of N₂O,⁴ being considered much later as the father of modern anesthesia.

Fig. 1. (a) Joseph Priestley, the discoverer of N₂O; (b) Humphry Davy, who firstly recognizes the analgesic properties of N₂O; (c) Dr. Horace Wells, the discoverer of modern anesthesia, (d) illustration on the effects of N₂O in 18th century; (e) bills such as this advertised the use of N₂O as a form of entertainment in 1844; (f) On December 11, 1844, Dr. Wells had a tooth extracted after inhaling N₂O.
N₂O has been long considered as a relatively harmless species and has suffered from a lack of interest from scientists, engineers and politicians. Today’s applications of N₂O are summarized in Fig. 2. N₂O is mainly used as weak anaesthetic (90%) to help allay fear and anxiety for phobic patients in dentistry and cryosurgery. Another important application of N₂O is as propellant for aerosols (5-8%) such as food products, cosmetics, shaving cream, and some insect sprays. An increasing use is as an additive in rocket fuels and in racing cars for boosting horsepower. N₂O also finds application in analytical chemistry, as oxidizing agent with acetylene flames in atomic absorption spectroscopy.

![Fig. 2. Legitimate uses of N₂O, including the main advantages for its application.](image)

During the last decade a growing concern on N₂O can be noticed in two different aspects: as harmful gas in our atmosphere and a popular drug for teenagers. The present note warns on the danger and misuses of nitrous oxide in today’s society.

In our atmosphere N₂O has a double role, acting as a greenhouse gas in the troposphere and being the main source of nitrogen oxides (NOₓ) in the stratosphere depleting the ozone layer (Fig. 3). The long average lifetime of N₂O in the troposphere (~150 years) makes it 310 times more effective at trapping heat than CO₂. Like other greenhouse gases, N₂O is transparent to incoming solar radiation. However, these gases are efficient in trapping heat radiated from the Earth’s surface by absorbing or re-emitting it. The dramatic impact that the rising global temperature might have on our land, water, and air is well-known. As a consequence, N₂O was included in the Kyoto protocol (1997), which calls for the stabilization of emissions of a six-gas basket, viz. carbon dioxide (CO₂), methane (CH₄), hydrofluorocarbons and perfluorocarbons (HFCs and PFCs), sulfur hexafluoride (SF₆), and the mentioned nitrous oxide (N₂O). On top of this, the reaction that converts N₂O to NO₂ destroys the ozone layer. Stratospheric ozone, which forms a protective shield against...
biologically harmful ultraviolet sunlight, was long taken for granted. Research in the 1970s revealed that manmade chlorofluorocarbons, CFCs, were rapidly depleting the ozone layer.\textsuperscript{13,14} In 1987, the Montreal protocol called for the stabilization of ozone depletor gases (CFCs, halons, carbon tetrachloride, methyl chloroform), but N\textsubscript{2}O was unfortunately, or better mistakenly, not included there.\textsuperscript{15} At this time, there are no doubts on the negative effect of N\textsubscript{2}O on the ozone layer, but there is no consensus on a quantitative value for its ozone-depleting potential.\textsuperscript{16}

How much N\textsubscript{2}O gets into the atmosphere? Quite some, around \textasciitilde 20 Mton N\textsubscript{2}O per year. How? The main route is through microbial decomposition of nitrogen-containing compounds in the soil, especially upon agricultural practices using nitrogen-containing fertilizers. It is also a byproduct of fossil fuel combustion from mobile and stationary sources and chemical production processes. The worldwide production of N\textsubscript{2}O for the applications in Fig. 2 amounts \textasciitilde 50 kton y\textsuperscript{-1}, which is mostly emitted as such during/after its use (as anesthetic agent and propellant). This emission is significant, representing \textasciitilde 10\% of the global annual emission of N\textsubscript{2}O from the production of nitric acid (400 ton N\textsubscript{2}O y\textsuperscript{-1}, the major source in the chemical industry). However, these emissions are not quantified in national inventories.\textsuperscript{9,17}

![Diagram of the Greenhouse Effect and Ozone Layer Depletion](image)

**Fig. 3.** Dual environmental impact of N\textsubscript{2}O as a strong greenhouse gas and ozone layer depletor.

**N\textsubscript{2}O, a harmful gas disguised in whipped cream cans**

In spite of the "well-documented" environmental role of N\textsubscript{2}O, several aspects related to this gas lack stringent control by government and industries, leading to misinformation and potential danger to the customer. The aerosol industry began phasing out CFCs in the mid-1970s. Today, more than 99\% of the consumer aerosol products produced do not contain CFC propellants, except for a small fraction (less than 2\%) specifically approved by the government for essential medical and other unique uses, such as inhalers for asthma patients.\textsuperscript{17} However, the most popular replacements are other harmful products, like hydrocarbons (mixtures of propane, butane, and isobutane) and N\textsubscript{2}O.

The extensive use of N\textsubscript{2}O as propellant in food industries, namely in whipped cream cans, leaps to the eye as one of the clear examples of misinformation to the end-user. This product, usually presented in attractive cans with images of fancy desserts and fresh berries, camouflages paradoxical information concerning the environment: a medley of misleading logos and incorrect messages can be found at the back of the containers, tagging the "CFC-free" product "environment-friendly" or "ozone-friendly", "harmless for the ozone layer", and...
"does not attack the ozone layer", etc. (Fig. 4). Normally, the propellant is mentioned as: nitrous oxide, N₂O, or by the corresponding E-number: E-942. In some cases, it is neglected and even wrongly declared. A striking example is shown in Fig. 5, with a label stating the corrosive NO (oxido nitrico in Portuguese) as being the propellant used. Some other food products in pressurized cans, like the so-called "Easy Cheese" (commercialized in US), are suspected to use N₂O, but the propellant is not mentioned in the labels.

This "eco-friendly" product has an edge. "Go green" seems to be the new marketing buzzword. Many companies tried to win customers by capitalising on the concern for the environment, but by changing style rather than substance. A large number of products are being marketed with various claims about their low impact on the environment or about their superior environmental credentials. Many of the claims cannot be verified, are vague, woolly, or misleading. In the western countries, customers consider eco-products as an important parameter for purchasing. The emergency of the green customer helped to force companies to look into the impact on the environment of the operations and products. But it is almost impossible for customers to know what exactly is being claimed and whether the product really is "green". In this sense the crucial intermediate task of market inspectors or legislators is being done carelessly or without sufficient expertise.

Finding a suitable replacement for N₂O in aerosols for the food industry is challenging, due to the excellent properties of this gas summarized in Fig. 2. However, it is unacceptable that N₂O keeps on being considered as beneficial for our environment, while it is just the opposite and only beneficial for the wealth of manufacturers. At the least all claims regarding the environmental friendliness of products based on N₂O as propellant should be forbidden since they are misleading and incorrect.

Fig. 4. Examples of the misleading/erroneous labels in whipped cream cans.
N₂O, a popular drug of teenagers

The effect of N₂O in the human body during anesthesia has been well described elsewhere.¹⁹ Anesthetic gases like N₂O induce the loss of sensations and possibly loss of consciousness that is required for some dental and surgical procedures. The painkilling and numbing qualities of N₂O that is inhaled begin to take effect when the gas is at concentrations of 10 vol.%. At higher concentrations, approaching 100 vol.% a sense of well-being, or "high", is experienced.²⁰ N₂O induces a state of behavioral disinhibition, analgesia, and euphoria. A person under the influence of N₂O may have slurred speech, have difficulties in maintaining balance in walking, be slow to respond to questions, be immune to any stimulus such as pain, loud noises, and speech, lapse into unconsciousness.

Inhaling laughing gas has gained a new popularity and its related effects and consequences are anything but positive. Rising abuse first became an issue in the United States during the late 1970s. After declining in the 1980s, it began to spike again in the mid-1990s, and is growing fast (up 50 percent among people aged 18 to 25 since 1994). What are the reasons for this fashion? N₂O is easy to get and cheap. According to the best available data, N₂O and other inhalants figure into at least 100 deaths a year in the U.S. alone. An example is given in Fig. 7. Yet recent discoveries about the dangers of inhaling the gas are not widely disseminated and people assume it to be safe. Recently, more and more information about effects, action, etc. of N₂O, is being distributed on the Internet by governments and social institutions of different countries.²⁰-²⁶

Usually, the gas is inhaled from large balloons, filled from tall tanks or small canisters called *whippets* (Fig. 8), which can be legally (!) purchased in supermarkets, clubs, boutiques, kitchen-supply stores, and through mail-order magazine ads.²⁷-³¹ It is even possible to buy the "official" balloon to contain the laughing gas, and the conversion devices that release the gas into balloons (Fig. 9).³⁰ N₂O has become a popular money-maker. Vendors sell the balloons for between $2 and $5 at parties, concerts and sports arenas. Whippets can be bought for $6 to $10 per 10-count box. Big tanks are sold at kitchen-, medical- and auto-supply stores for $100 to $200. A 30 kg tank of the compressed gas would fill 15 m³. At $5 per 7 liters
balloon, one tank could gross more than $10000. N₂O is a “quick” drug because it dissolves extremely well in synaptic lipid membranes. So it is not a coincidence that nitrous oxide is a whipped cream propellant and an inhalation anesthetic: this gas dissolves in fatty cream and it also dissolves in fatty cell membranes.

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**The Washington Post**

**Saturday, October 21, 2000**

**Va. Student’s Death Leads to Drug Conviction**

*By Josh Wacht*
*Washington Post Staff Writer*

A federal jury in Roanoke has convicted an Arizona man of illegally selling nitrous oxide as a drug over the Internet almost one year after a Virginia Tech student from Fairlax died after inhaling the gas.

Prosecutors hailed Thursday’s verdict in U.S. District Court as the first of its kind, dealing what they hope is a heavy blow to Internet and mail-order companies that sell the gas to clients who want to inhale it for a short and intense high.

Because of nitrous oxide’s legitimate uses, prosecutors have had trouble proving that the sale of the legal but potentially deadly gas was aimed at selling any other drug across state lines. Nitrous oxide cartridges are commonly sold to make whipped cream, and nitrous gas is often mixed with oxygen for use as a sedative in dentists’ offices. The cartridges can be found all across the country in head shops, gourmet food stores and convenience stores.

Andrew McCoy, 21, died last November after inhaling the gas in his apartment in Blacksburg. Authorities found a number of used cartridges near his body, along with a box linking them to a Tampa, Ariz., company. Police traced the cartridges to the now-defunct Web site www.bongman.com, where McCoy had purchased them days before.

The operator of bongman.com, Lawrence Tresman, 26, was found guilty of five felony counts of violating the federal Food and Drug Act, specifically for selling a misbranded drug over state lines while trying to mislead law enforcement officials. According to prosecutors, Tresman said boxes of the three-ounce cartridges on his site, marketing the product as a drug, but covering his tracks by saying it was for food use only.

Tresman could face up to 15 years in prison and a fine of $1.25 million when he is sentenced in January.

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“The biggest concern for us is that nitrous oxide use certainly is a fast-growing problem,” said Assistant U.S. Attorney Craig “Jake” Jacobson, who prosecuted the case. “Everyone has considered it a free gas because people think that it’s harmless, and they have been selling it with impunity. Unfortunately, it took a death to bring it to our attention.”

Jacobson said much of the difficulty with bringing such a case is that it isn’t illegal to sell nitrous oxide. Instead, prosecutors have to prove that the sale is intended for misuse and that the seller knows clients will use the gas as a drug. Tresman’s attorneys argued that he simply sold a legal product and labeled it for its proper use.

McCoy, a computer sciences major and Eagle Scout who graduated from Thomas Jefferson High School in 1999, told friends that he researched nitrous oxide on the Internet and had decided it was a safe alternative to other drugs and alcohol, his mother said yesterday. McCoy, who had twice bought cartridges over the Internet, smuggled Nov. 14 after he died a plastic bag over his head to inhale the gas.

“Threaten consequences to pay for believing what he read on the Internet,” said McCoy’s mother, Susan, who also said the family plans to scatter his ashes on Skyline Drive today. “I am absolutely thrilled that the government took this so seriously because it would have been easy for the police to say that this was some dumb college kid who killed himself with drugs. People need to know it’s a dangerous drug.”

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Fig. 7. Dramatic consequences of N₂O abuse.

There is some evidence that excessive or prolonged use of nitrous oxide can damage the bone marrow and nervous system by interfering with the action of vitamin B-12. Excessive use causes nausea, vomiting, and disorientation, and since N₂O impairs both the motor control and coordination, it is wise to avoid inhaling it while standing. A main danger is the risk of suffocation. Users who sniff N₂O directly from a tank or a big enough balloon in a confined space, in a small room, inside an automobile or other vehicle cab, or by placing their head inside a plastic bag can pass-out permanently if nobody intervenes. Breathing it directly from pressurized tanks is dangerous for two reasons. First, gas flowing from such tanks is very cold due to expansion, causing frostbite of noses, lips and (most serious) vocal cords. Being anesthetized, a user may be unaware of such injuries until too late. Second, because N₂O should be mixed with oxygen (at least 20%) if it is to be breathed for more than a few minutes. A person who is rendered unconscious by N₂O is likely to stop breathing
within a few seconds as a result of a depressed central nervous system (brain, brain stem, and spinal cord). Depression is caused by a combination of the effects of nitrous oxide and the lowered oxygen content that occurs as pure N₂O displaces oxygen from the lungs with each succeeding inhalation of the gas, i.e., the person is asphyxiated. If a person remains conscious and stops breathing N₂O, recovery (full consciousness and alertness) can occur within minutes. A person who loses consciousness, however, and continues to inhale the pure gas (providing a supply is still available) is most likely to die.

Fig. 9. Example of web page where one can buy all kind of N₂O-related components (chargers, adapters, party balloons, ...).³⁰

Commercial sales total in the tens of millions of dollars each year, not including the uncounted underground trade in nitrous oxide. That's a lot of gas, and a lot of dizziness, headaches, and other side effects. So, one may conclude that N₂O is not a laughing matter and does not add up to tons of fun after all.

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Gekatalyseerde N₂O Activering

Veelbelovende (Nieuwe) Katalysatoren voor Bestrijding en Toepassing

1. *N₂O, het probleem*... Lachgas (N₂O) is lange tijd beschouwd als relatief onschuldig voor het milieu, en heeft daarom niet zo in de belangstelling gestaan van wetenschappers, ingenieurs en politici. De afgelopen tien jaar is men zich echter gaan realiseren dat N₂O een schadelijk gas is in onze atmosfeer. Het levert een bijdrage aan het broeikas-effect in de troposfeer (5%), en draagt bij aan de afbraak van de ozonlaag in de stratosfeer (5%). Hoewel N₂O emissies veel lager zijn dan die van CO₂, is het effect van N₂O ongeveer 310 keer sterker dan dat van CO₂. Er zijn dus maatregelen nodig om de door de mens veroorzaakte emissies van N₂O terug te dringen. Volgens de doelstellingen van de "Third Conference of the Parties to the United Nations Framework on Climate Change" in Kyoto (Japan), dient een reductie ter grootte van 8% van de N₂O emissie in 1990 gerealiseerd te zijn in het jaar 2010 binnen de EU. Het is teleurstellend dat N₂O indertijd niet is opgenomen in het verdrag ten aanzien van componenten die de ozonlaag aantasten, het "Montreal Protocol on Substances that deplete the Ozone Layer" (Canada, 1987), terwijl het meehelpen aan de afbraak. Er bestaat dus een dubbele reden N₂O emissies te reduceren.

2. *Welke N₂O emissies kunnen effectief worden aangepakt?*... Regulering van de emissies in de landbouw, het grootste deel van de totale N₂O emissie ten gevolge van menselijke activiteiten, is niet makkelijk te realiseren. Dit is het gevolg van onzekerheden ten aanzien van parameters die emissiefactoren beïnvloeden, en gebrek aan gegevens over de efficiëntie van mogelijke maatregelen om de reductie te beperken. N₂O emissies ten gevolge van *chemische produktieprocessen* en van *verbrandingsprocessen* (~35% in de EU) kunnen op korte termijn worden aangepakt. Deze emissies zijn geconcentreerd in een beperkt aantal stationaire bronnen wat een goede kans biedt voor een succesvolle bestrijding. De belangrijkste industriële bronnen zijn de adipinezuur- en salpeterzuurproduktie. Andere geïdentificeerde bronnen zijn de produktie van caprolactam, glyoxal, acrylonitril, en in het algemeen processen waarbij salpeterzuur als oxidator wordt toegepast, of processen waarbij ammoniak wordt geoxideerd. Het gebruik van fossiele brandstoffen, verbranding van (huis-, tuin- en keuken-) afval, en biomassa veroorzaken ook de vorming van aanzienlijke hoeveelheden N₂O. Een snel toenemende bron van N₂O is bovendien de transportsector, ten gevolge van de drieweg katalysator om o.a. NOₓ (NO en NO₂) emissies te beperken.

3. *Welke mogelijkheden zijn er om de N₂O emissie te beperken?*... Verschillende mogelijkheden zijn er om de emissie van N₂O te beperken. Directe ontdeling van N₂O in N₂ en O₂ is vanuit het oogpunt van kosten een aantrekkelijke methode. Thermische en katalytische technologieën zijn al succesvol ontwikkeld voor fabrieken voor de produktie van adipinezuur. In dit geval kan N₂O vanwege de hoge concentraties (25-40 vol.%) zelfs hergebruikt worden binnen het proces voor de selectieve oxidatie van benzene naar fenol. Deze optie is echter niet aanwezig voor de andere genoemde bronnen van N₂O door de lage concentraties van N₂O in het afgas (0.05-0.5 vol.%). Door de samenstelling van het afgas van met name salpeterzuurfabrieken en verbrandingsovens, is geen enkele van de in de literatuur voorgestelde katalysatoren geschikt voor de direkte ontdeling van N₂O. Een (economisch) minder aantrekkelijk alternatief is het gebruik van brandstof om selective katalytische reductie (SCR) of niet-selectieve katalytische reductie (NSCR) uit te voeren.
Katalysatorontwikkeling is dus noodzakelijk om efficiënte en economisch haalbare oplossingen te vinden om de emissie van N₂O te beperken. Dit wordt voor met name producenten van salpeterzuur steeds belangrijker, aangezien de wetgeving voor N₂O emissies al maar strenger wordt.

4. Wat is het hoofddoel van het onderzoek beschreven in dit proefschrift?... Gezien het voorgaande is het onderzoek met name gericht op de ontwikkeling van nieuwe katalysatoren voor de ontleding van N₂O, die werken onder de condities van verschillende typen afgas. De aandacht is vooral gericht op het afgas van salpeterzuurfabrieken en verbrandingsprocessen. Dit betekent dat de katalysator bij een relatieve lage temperatuur actief moet zijn, en dat de activiteit niet sterk (negatief) mag worden beïnvloed door O₂, NOₓ, SO₂ en H₂O, componenten die in deze typen afgas aanwezig zijn. Natuurlijk zou het prachtig zijn als deze katalysatoren kunnen worden ingezet bij andere N₂O-gerelateerde processen, zoals selectieve katalytische reductie, en selectieve oxidatie reacties.

5. Hoe is het probleem benaderd?... De toegepaste methodiek integreert de ontwikkelingsaspecten van katalysatoren op drie niveau’s: macro-, meso-, en micro-niveau. Dit wordt in de volgende paragrafen nader toegelicht.

   - **Macrolevel (processelectie).** Dit niveau heeft betrekking op de integratie van de katalytische N₂O ontleidings 'unit' in de chemische fabriek. In principe kan deze 'unit' op verschillende plaatsen in de fabriek geïntegreerd worden. Deze plaats bepaalt vervolgens de condities waaronder de actieve N₂O ontleidings katalysator moet opereren (temperatuur, druk, gas-samenstelling). Voordat katalysatoren ontwikkeld kunnen worden, moet dus allereerst de meest kosteneffectieve optie worden uitgezocht. Een uitgebreide beschrijving van een dergelijke exercitie, kunt u lezen in *Hoofdstuk 1* van dit proefschrift voor salpeterzuur fabrieken, en *Hoofdstuk 7* voor andere bronnen van N₂O.

   - **Mesolevel (reactorselectie).** Op basis van kinetische meetgegevens worden verschillende reactor-typen voor de implementatie van de katalysator in het proces geëvalueerd in *Hoofdstuk 7*. Deze implementatie is gebaseerd op verschillende ontwerpparameters en procescondities. Dit niveau heeft ook betrekking op de vormgeving van het katalytische materiaal, zodat een optimaal activiteitsgedrag wordt verkregen in de reactor die het best past in het proces.

   - **Microlevel (katalysatorselectie).** Dit is het meest belangrijke deel van dit proefschrift, beschreven in de *Hoofdstukken 2-9*, en omvat katalysatorbereiding, testmethodes in laboratoriumreactoren, identificatie van de meest veelbelovende katalytische materialen en katalysatoroptimalisatie. Dit laatste verwijst in het algemeen naar verbeterde of nieuwe methoden om katalytische materialen te synthetiseren en te karakteriseren. Ook spelen kwantitatieve activiteits- en stabiliteits-metingen, alsmede onderzoek naar het reactiemechanisme ('in-situ studies') een belangrijke rol.

6. Wat is er bereikt?... Vele katalysatoren zijn in staat om N₂O om te zetten in O₂ en N₂, maar vele vertonen onvoldoende activiteit onder vereiste procescondities. Meestal wordt de activiteit negatief beïnvloed door andere componenten, zoals NO (salpeterzuurfabriek) en SO₂ (verbrandingsprocessen). Bovendien laat ook de stabilitiet van de katalytische materialen dikwils te wensen over. Er is echter één uitzondering op de regel. Dit zijn katalysatoren gebaseerd op ijzer en zeolietmaterialen (ZSM-5). Met name als deze katalysatoren worden bereid volgens een nieuwe route, die uitgaat van materialen waarbij
ijzer in de structuur van de zeoliet wordt ingebouwd (ex-framework route), levert dit katalysatoren op die kunnen worden ingezet in efficiente en kosteneffectieve technologieën voor de bestrijding of het gebruik van N₂O in de chemische industrie of bij verbrandingsprocessen (Hoofdstuk 7). Drie essentiële eigenschappen van deze materialen kunnen als volgt worden samengevat:

- Zij bezitten een hoge activiteit bij lage temperaturen, en een goede stabiliteit onder procescondities voor de directe onttreding van N₂O. NO en SO₂ bevorderen zelfs de onttreding van N₂O over deze katalysator.
- Zij bezitten uitstekende activiteit in de aanwezigheid van koolwaterstoffen, waardoor de N₂O onttredingstemperatuur aanzienlijk verlaagd kan worden. Deze katalysatoren zijn dus zeer aantrekkelijk om toe te passen in de zogenaamde selectieve katalytische reductie (SCR) van N₂O.
- De materialen kunnen worden toegepast in de selectieve oxidatie van benzeen naar phenol, waarmee de toepasbaarheid van N₂O als een zuurstof donor in oxidatiereacties wordt aangetoond. De specifieke eigenschappen van N₂O in deze reactie, in combinatie met bepaalde, op Fe gebaseerde actieve plaatsen, wordt toegeschreven aan de vorming van zogenaamde ‘α-zuurstof’ species die in de selectieve oxidatie waarschijnlijk een cruciale rol spelen.

De vondst van een materiaal dat in zoveel verschillende reacties en onder uiteenlopende condities kan worden ingezet, wordt gezien als een doorbraak in de bestrijding en toepassing van N₂O. Voor een efficiënt en veilig proces is een goed reactorontwerp nodig. Binnen het salpeterzuurproces moet de ijzer-zeoliet katalysator toegepast worden in de vorm van monolieten. De monolieterreactor paart een lage drukval aan een hoge katalysator effectiviteit waardoor de hoge intrinsieke activiteit behouden blijft en er geen procesverstoring optreedt. Hierdoor zijn kleinere reactoren nodig dan bijvoorbeeld vast-bed reactoren.

7. Wat draagt dit onderzoek bij aan de heterogene katalyse?... Behalve dat dit onderzoek de ontdekking van een actieve en stabiele katalysator heeft opgeleverd, zijn in het algemeen nog een aantal belangrijke aspecten van onderzoek in de heterogene katalyse nader onderzocht.

7.1. Activiteitsbepaling en reproduceerbaarheid meetresultaten

Een goede test-eenheid is essentieel om efficiënt kwantitatieve data te verkrijgen ten aanzien van de activiteit van een katalytisch materiaal. Dit wordt nader toegelicht in Hoofdstuk 2. Een volledige geautomatiseerde ‘6-flow’ reactor is in dit project toegepast om zogenaamde 'high-throughput screening' mogelijk te maken. In de terminologie van combinatoriële chemie zou deze test-eenheid onder de noemer 'secondary screening' vallen: dat wil zeggen dat een voorselectie van mogelijke veelbelovende materialen al is gemaakt. De reproduceerbaarheid van de kwantitatieve resultaten die met deze veelzijdige testeenheid zijn verkregen, is in verschillende experimenten aangetoond, onder andere tijdens een gedetailleerde studie naar de transportverschijnselen in de toegepaste reactoren waar hoge eisen aan de kwaliteit van de meetgegevens gesteld werden. Het verdunnen van de actieve katalysator met inactief silicium carbide kan onjuiste resultaten opleveren. De invloed van de verdeling van de katalysator in de reactor is gemodelleerd aan de hand van het 'Random Particle Distribution' model, waarbij een algemeen criterium is afgeleid dat de maximaal toelaatbare verdunning van de katalysator in de reactor weergeeft (Hoofdstuk 3).
7.2. Hydrotalcieten en gemengde oxidische katalysatoren

De thermische ontleiding van hydrotalcieten wordt uitgebreid beschreven in *Hoofdstuk 4*. Met name *in situ* infraroodspectroscopie en Raman-spectroscopie zijn toegepast om de zogenaamde retrotopotactische omzettingen van deze materialen te bestuderen. In de literatuur beschreven studies werden veelal *ex-situ* uitgevoerd, in procedures waarin de materialen eerst aan de buitenlucht werden blootgesteld. Tevens zijn voor het eerst Raman spectra verkregen van hydrotalcieten tijdens het ontleidingsproces. De spectroskopische procedures die in het kader van dit onderzoek zijn ontwikkeld, dragen bij aan het begrip van de structuur-activiteits relatie van deze geactiveerde materialen. De spectroskopische resultaten zijn ook zeer bruikbaar voor de ontwikkeling van structuur-activiteitsrelaties van hydrotalcieten in diverse andere katalytische toepassingen, zoals in vast-zaau catalyse en metaal katalyse. Tenslotte kan de methodologie worden toegepast om materialen te onderzoeken die worden toegepast als bijvoorbeeld adsorbentia of ionen-wisselaars, met inbegrip van andere klei-achtige materialen.

Zoals weergegeven in *Hoofdstuk 7* zijn gemengde metaaloxide, die zijn afgeleid van een oorspronkelijk hydrotalciet-structuur, zeer actief in de katalytische omzetting van N₂O. Helaas vertonen deze materialen in de aanwezigheid van andere gassen, zoals NOₓ, H₂O, and SO₂, een veel lagere activiteit: met andere woorden, er vindt remming plaats. Dit wordt ook waargenomen bij vele andere typen katalysatoren, zoals gedragen katalysatoren gebaseerd op edelmetalen (Rh, Ru, en Pd) of overgangsmetalen (Co, Cu, Ni).

7.3. Ex-framework FeMFI katalysatoren

*Bereiding en karakterisering*. Een nieuwe (‘ex-framework’) route is ontwikkeld om FeMFI katalysatoren te synthetiseren. Deze methode gaat uit van de bereiding van zogenaamd isomorf gesubsituteerd FeMFI, gevolgd door calcinering en extractie van Fe door activering in stoom. Een gedetailleerde beschrijving van fysisch-chemische veranderingen in het materiaal en de structuur van de ijzer-functionaliteiten wordt gepresenteerd in *Hoofdstuk 5* voor FeZSM-5. Deze beschrijving is gebaseerd op een uitgebreide karakterisering van de materialen door middel van verschillende (nieuwe) technieken.

*Nieuwe karakteriserings methoden*. *Hoofdstuk 6* beschrijft een nieuwe, unieke voltammetrische methode om heterogene katalysatoren te karakteriseren. In deze zogenaamde vaste-fase electrochemische methode, worden verschillende metalische componenten gedefinieerd aan de hand van een karakteristieke electrochemische respons. Deze is afhankelijk van de oxidatie toestand van de te analyseren component, alsmede van de chemische structuur. Deze methode levert een substantiële bijdrage aan de karakterisering van complexe katalytische systemen. Er wordt een snelle 'vingerafdruk' van de katalysator-samenstelling verkregen, met name ten aanzien van de structuur van de aanwezige ijzerfase zoals in de onderzochte FeMFI katalysatoren.

*Mechanistische aspecten van omzettingen betreffende N₂O*. De opmerkelijke katalytische eigenschappen van *ex-framework* FeZSM-5 in de verschillende ontleidings- en toepassingsgerichte reacties van N₂O, wordt nader toegelicht in *Hoofdstuk 7*. Het promotering effect van NO en SO₂ op de N₂O ontleiding over dit type katalysatoren is opmerkelijk, omdat in het algemeen een omgekeerd effect wordt waargenomen. Het mechanisme van de promotie is nader onderzocht, en de resultaten worden beschreven in *Hoofdstuk 8*. In het bijzonder wordt de NO-geassisteerde N₂O ontleiding over *ex-framework* FeZSM5 nader toegelicht aan de hand van 'steady state' activiteiten metingen, *in situ* transiente infrarood metingen, en Multi-Track metingen (een geavanceerd TAP apparaat). Inzicht is verkregen in de *fundamentele aspecten* van de verschillende reacties met N₂O.
De desorptie van zuurstof van het oppervlak van de katalysator via recombinatie van zuurstofatomen is de snelheidbepalende stap in de ontleding van N₂O over ijzerkatalysatoren. In aanwezigheid van sporen NO wordt dit proces enorm versneld over verschillende typen ijzerkatalysatoren (zeolieten en niet-zeolitische). Er zijn kennelijk geen specifieke active plaatsen nodig voor dit effect. Deze promotie geldt niet voor alle typen reacties met N₂O. In de selectieve oxidatie of reductie met koolwaterstofrennt NO de omzetting van N₂O, tengevolge van een ander reactiemechanisme. Uit vergelijking met andere reacties kan in het algemeen gesteld worden dat NO een component is die atomair zuurstof helpt overdragen.

Katalysator optimalisering en structuur van de actieve centra. In Hoofdstuk 9 wordt de nieuwe ex-framework route toegepast op andere samenstellingen van het MFI-type zeoliet (combinaties van Fe, Ga of Al, en Si). Karakterisering van deze katalysatoren laat zien dat opnieuw een heterogeen systeem wordt verkregen, waarbij de samenstelling van de ijzerdeeltjes met name wordt beïnvloed door het stoom-procedé. De katalytische activiteit, gekoppeld aan de resultaten van de toegepaste karakteriserings-methoden, laat een verband zien tussen de katalysator samenstelling en de katalytische activiteit. Extra-framework ijzer functionaliteiten zijn belangrijk voor een hoge N₂O ontledingsactiviteit, terwijl Lewis- of Brønsted-zure groepen een minder belangrijke rol vervullen. Gebaseerd op de resultaten beschreven in Hoofdstuk 8 zijn oligonucleaire zuurstof-ijzer clusters goede kandidaten voor de actieve centra in de kanalen van de katalysator. Geïsoleerde Fe-ioniën zijn waarschijnlijk minder actief in N₂O ontleding, aangezien de recombinatie van zuurstof atomen noodzakelijk is om molecular O₂ te vormen. Deze recombinatie is eenvoudiger bij Fe-clusters dan bij geïsoleerde ionen. Het is niet erg waarschijnlijk dat er één generieke actieve plaats is voor alle processen met N₂O die over FeZSM5 plaats vinden, omdat het reactiemechanisme van bijvoorbeeld een oxidatiereactie van alkanen heel andere snelheidsbepalende stappen kan hebben. Veel aannemelijker is het dat verschillende Fe-structuren in de zeolieten een rol spelen, afhankelijk van het proces. Elke reactie moet apart worden bestudeerd, om op grond hiervan de gewenste structuur van de actieve fase vast te stellen. Er bestaat niet zoiets universeels als de active plaats.

8. Wrap up... Het gehele werk, zoals beschreven in dit proefschrift, wordt uitgebreid samengevat in Hoofdstuk 10, waar ook de implicaties voor de wetenschap van de heterogene katalyse nog eens worden benadrukt.

J. Pérez-Ramírez

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Oral presentations


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About the Author

Javier Pérez-Ramírez was born on October 28, 1974 in Benidorm, Spain. He attended Colegio Nuestra Señora de los Dolores (Benidorm) from 1978 to 1987 and Colegio Lope de Vega (Benidorm) from 1987 to 1991. After high school, he studied Chemical Engineering at the University of Alicante (Alicante, Spain), from which he graduated in February 1998 with Suma Cum Laude and Extraordinary Master's Degree Award. During his undergraduate studies Javier participated in research projects related to the optimization of bubble caps distillation columns and catalytic removal of SO$_x$ with calcium in moving-bed reactors. His graduation project dealt with the design of wastewater treatment plants in food processing industries. In March 1998, he moved to Delft University of Technology, Section Industrial Catalysis (Delft, The Netherlands) to start his Ph.D. project with thesis advisors Prof. dr. F. Kapteijn and Prof. dr. J.A. Moulijn. Since March 1999, Dr. G. Mul was also involved in his research activities. His main research topic covered the development of novel catalysts for abatement and utilization of nitrous oxide (N$_2$O). The most representative results are included in this dissertation. During his Ph.D. studies he was also active in NO$_x$ reduction with hydrocarbons, adsorption and diffusion in zeolites, magnetic properties of layered compounds, and post-synthesis modification of microporous and mesoporous materials. Since March 2002 he has been appointed as visiting scientist in Norsk Hydro, Oil & Energy Department, Section for Hydrocarbon Processes and Catalysis in Porsgrunn (Norway). His current interests are in catalyst development for high-temperature applications.