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Catalysis Engineering on Three Levels

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Catalysis Engineering on Three Levels

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Abstract

The relevance of levels in space and time for chemical engineering are discussed. Catalysis Engineering is introduced as an emerging new discipline. In Catalysis Engineering three levels can be distinguished: the microlevel focusing on molecules and catalytic sites, the mesolevel focusing on the catalyst particle and the catalytic reactor, and the macrolevel considering the process as an integrated entity. On the level of particle and reactor fascinating developments are visible in the field of structuring of the space. A good example is the monolithic reactor. With the hydrogenation of alpha-methylstyrene as an example, it will be shown that structured reactors allow decoupling of hydrodynamics and chemical kinetics. This implies an extra degree of freedom. From a chemical engineering point of view the intrinsic scaleability of these reactors is intriguing. A case study on nitrous oxide abatement exemplifies the three-level catalysis engineering approach.

KEYWORDS: catalysis engineering, monolithic reactor, multilevel approach

1. INTRODUCTION

Chemical process technology has had a long, branched road of development. It was not until the 1910s and 1920s, that disciplines such as thermodynamics, material and energy balances, heat transfer, and fluid dynamics, as well as chemical kinetics and catalysis became (and still are) the foundations on which chemical process technology rests. In chemical process technology various disciplines are integrated. These can be divided according to their scale, as shown in Table 1.

Scale	Disciplines	
Scale independent	Chemistry, Biology, Physics, Mathematics	
	Thermodynamics	
	Physical Transport Phenomena	
Microlevel	Kinetics	
	Catalysis on a Molecular Level	
	Interface Chemistry	
	Microbiology	
	Particle Technology	
Mesolevel	Reactor Technology	
	Unit Operations	
	Scale-up	
Macrolevel	Process Technology and Process Development	
	Process Integration and Design	
	Process Control and Operation	

Table 1. Disciplines in chemical process technology organized according to their scale

In the development stage of a process or product all necessary disciplines are integrated. The role and position of the various disciplines perhaps can be better understood from Figure 1, in which they are arranged according to their level of integration. Process development, in principle, roughly proceeds through the same sequence, and the *x*-axis also to a large extent represents the time progress in the development of a process. The initial phase depends on thermodynamics and other scale-independent principles. As time passes, other disciplines become important, e.g. kinetics and catalysis on a microlevel, reactor technology, unit operations and scale-up on the mesolevel and process technology, process control, etc. on the macrolevel.

Of course, there should be intense interaction between the various disciplines. To be able to quickly implement new insights and results, these disciplines are preferably applied more or less in parallel rather than in series as can also be seen from the figure above.

An enlightening way of placing the Chemical Engineering discipline in a broader framework has been put forward by Villermaux. He made a plot of length and time scales, such as the one shown in Figure 2. From this figure it can be appreciated that chemical engineering is a broad integrating discipline. On the one hand, molecules, having dimensions in the nanometer range and a vibration time on nanosecond scale, are considered. On the other hand, chemical plants may have a size of half a kilometer, while the life expectancy of a new plant is 10 to 20 years. The atmosphere could also be envisaged as a chemical reactor and chemical engineers can contribute to predictions for temperature changes, etc. by modeling studies analogously to those referring to 'normal' chemical reactors.

So, the chemical engineer is active in a wide range of space and time scales. Traditionally, in research chemical engineers and chemists are active in a narrow field. In catalysis, examples of specialist areas are surface science, coordination chemistry, materials synthesis, chemical reactors and process design. Chemical engineering is based on integration and as such a narrow specialization is not useful. From now on let us focus on Catalysis Engineering.



Figure 1. Disciplines in process development organized according to level of integration.



Figure 2. Space and time scales according to Villermaux.

2. CATALYSIS ENGINEERING

2.1 Process Development

The term 'Catalysis Engineering' is meant to cover the realization of an optimal chemical environment for the catalytic events that are aimed at. The term is analogous to 'Chemical Reaction Engineering'. In Catalysis Engineering three levels are distinguished:

- the level of the process,
- the level of the catalyst particle and the catalytic reactor and
- the level of the molecules and the active sites of the catalyst.

Figure 3 represents the relationship between the different levels. The plant level is the macrolevel. When one wants to focus on the chemical conversion, the reactor is the level of interest. When the interest goes down to the molecules converted, the microlevel is reached. The challenge, of course, is the realization of the optimal process, whereby all aspects are considered in an integrated manner.



Figure 3. Relationship between different levels of development for a hydrodesulfurization process (Moulijn *et al.*, 2001).

2.2 Microlevel

The microlevel focuses on the reactions and the active catalyst sites. The basis of a novel or improved process is a satisfactory catalyst formulation. The chemistry should be right and this means that the catalyst should be

sufficiently active and selective for the desired reaction, and also have sufficient stability. Understanding of the reaction mechanism and identification of the active sites in the catalyst is crucial at this level.

Figure 4 shows the order of activities in the development of a catalyst, starting with the new idea for a catalyst or process. These activities are partially carried out in series and partially in parallel. During the advancement of the development there will be continual feedback to other stages to optimize the catalyst and the process. The number of catalyst formulations will decrease during the progress, but the time expenditure and scale increase and, consequently, the costs involved. This calls for an efficient and proper approach for laboratory scale experimentation.

The generation of a good idea, and from that the first catalyst selection, is the basis of the catalyst development program. In practice it is not possible to develop a catalyst from theory based on basic principles. Inspiration based on literature (including patents), common sense, and experience and previous knowledge on the design of other catalysts is the start of the development of a new or improved catalyst.



Figure 4. Stages during a catalyst development program.

Screening must give the first data on the activity and selectivity of the various catalyst formulations as a function of their composition and preparation and pretreatment history. As there are many variables, numerous catalysts should be screened at a high throughput rate. A distinction can be made between primary and secondary screening. During primary screening a large number of catalyst formulations need to be prepared, characterized, and roughly compared with respect to their activity and selectivity. An elegant example is the work of Holwarth *et al.* (1998) and Reetz *et al.* (1998), in which IR-thermography was used for analysis. The reactor was a monolith-type reactor array of 69 parallel channels, each filled with a cylindrical catalyst pellet. This High-Throughput Screening of libraries of catalytic materials enables the rapid identification of potential 'lead' catalysts. However, such screening systems cannot efficiently address issues related to the time-dependent behavior of catalysts (e.g. deactivation), because they were designed for short reactant-catalyst contact. In addition, a well-defined flow patterns or mass- and heat-transfer characteristics are not accomplished. Therefore, these combinatorial methods can only serve as a qualitative identification.

In secondary screening, miniaturized and parallel-flow reactor systems with identification of reaction products are used for a more quantitative testing of potentially interesting catalysts from the primary screening stage. Secondary screening involves kinetic studies and often a first insight in the deactivation behavior, *i.e.* the catalyst stability, is obtained simultaneously. The time-consuming kinetics and mechanistic studies are indispensable for the

Stability tests are intended to test the catalysts during a prolonged time-on-stream, often on a bench or pilot scale with real feeds and recycle streams. The latter are included to investigate the effect of trace impurities or accumulated components that are not observed in laboratory-scale experiments. It is often desired to test the catalyst in the shape used for practical application. Here the need exists for experimental results that can be directly linked to commercial applications, and here also we enter the mesolevel (scale-up to pilot plant).

2.3 Mesolevel

The mesolevel usually refers to the catalytic reactor, but it is also possible to view the catalyst particle or a zeolite crystal as a reactor: reactants enter the particle and products leave, a real reactor! At this level, the dimensions and shape of the catalyst particles are important, in connection with mass and heat transfer, pressure drop and hydrodynamics. Various catalytic reactors are evaluated for the implementation of the catalyst, based on the design parameters and operating conditions.

The most important factors for the choice and design of a reactor for heterogeneous catalysis are:

- The number and type of phases involved, e.g. gas/solid, gas/liquid/solid. Much, though not complete, freedom exists in choosing the volume fractions of the various phases, the degree of mixing, and the contacting patterns. A fundamental difference between structured and random or chaotic reactors lies in the degree of freedom, which for the former type is larger than for the latter type. Details of contacting and hydrodynamics have a large impact on mass and heat transport between the phases.
- The kinetics of the main and side reactions. These determine the desired temperature and concentration profile, the residence time distribution (degree of mixing), etc.
- The heat of reaction. This is the most important parameter determining the measures to be taken for heat transfer.

Another issue that must be taken into consideration in the selection of the reactor is catalyst deactivation. The rate of catalyst addition and removal (periodically, continuously, etc.), and the possible need for regeneration are important design and engineering aspects.

For any particular situation, there usually are a large number of reactors to choose from, and the challenge is to make the optimal choice, keeping in mind the total process economics. A strategy such as put forward by Krishna and Sie (1994) is recommended. This strategy is based on decisions at three levels within the mesolevel. Level I concerns the catalyst design, in the case of solid catalysts ideal particle size, shape, pore structure and distribution of active material. Level II deals with the optimal contacting pattern of the phases, and Level III involves choices with regard to the hydrodynamic regime on the basis of mass and heat transfer characteristics, etc. Combining the decisions reached at each level will yield the most suitable reactor. Krishna and Sie (1994) argue that such a systematic approach may lead to innovative reactor configurations with a potential edge over conventional technologies.

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 (Pérez-Ramírez, 2002). Examples of structured reactors are monolithic reactors and parallel-passage reactors (Cybulski and Moulijn, 1998). The use of structured catalysts offers the advantage of decoupling the hydrodynamics, kinetics and transport phenomena (Kapteijn *et al.*, 1999).

There is a wide range of commercially available monolithic structures, which makes the selection of the monolithic reactor quite flexible. Cell density, expressed as cells per square inch (cpsi), and wall thickness are design parameters of monolithic reactors. Monolithic reactors offer a number of advantages, such as optimal catalyst

effectiveness, low pressure drop, good mechanical properties, dust and erosion resistance, and compactness (Cybulski and Moulijn, 1994; Cybulski and Moulijn, 1998; Heck and Farrauto, 1995). They have already found widespread use in gas-phase environmental applications such as automotive exhaust gas treatment and NO_x control (Cybulski and Moulijn, 1998) and are also increasingly considered for gas-liquid-solid applications, especially for fast reactions such as hydrogenations and oxidations. Section 3 offers an example of the advantage of three-phase monolithic reactors in this type of reactions.

2.4 Macrolevel

In Catalysis Engineering, the macrolevel concerns the integration of a catalytic unit in an existing or new chemical process. This requires a detailed technical knowledge of the process. At the level of the process all relevant aspects should be included. In the case of existing plants, the macrolevel often concerns the use of an improved catalyst formulation in an existing process or the addition of a catalytic unit for end-of-pipe environmental measures. Section 4 provides an example of such a situation.

When developing a new process, rather than integrating a catalytic reactor in the process, the process is 'built around the catalytic reactor'. At the start, nothing is known about the process yet, apart from the intended reaction and probably a rough selection of potential catalysts for this reaction. The reactor is also still a black box. The more information becomes available about the reaction during the microlevel studies, the more detailed the reactor and process design can become. A crucial aspect for a catalytic process is the influence of recycle streams (e.g. on catalyst stability). Usually complete conversion of all of the reactants is not possible or even desired (the higher the conversion the higher the reactor cost) and unconverted reactants need to be separated from the product and possibly recycled. Build-up of impurities in recycle streams may lead to catalyst deactivation in the long run and this should be investigated. It is important that there is interaction between the experiments and decisions on the three levels, and therefore an integrated approach is required.

3. MONOLITHIC REACTORS FOR THREE-PHASE SYSTEMS

3.1 Introduction

Conventional reactors for gas-liquid reactions over solid catalysts are trickle-bed reactors and slurry reactors. A potentially attractive alternative is the three-phase monolithic reactor (Figure 5).



Figure 5. Schematic of a three-phase monolithic reactor with continuous gas flow and batch liquid operation.

Monoliths can be good alternatives for both trickle-flow and slurry reactors because of the short diffusional distance in the catalytically active layer, the excellent mass transfer that can be achieved for two-phase flow in capillaries (Kreutzer *et al.* (2001), the low energy requirements due to the low-pressure drop (Heiszwolf *et al.*, 2001) and the absence of a catalyst separation step.

3.2 Mass-Transfer Characteristics of a Three-Phase Monolithic Reactor

External mass transfer is an important mesolevel issue in three-phase reactors. The hydrogenation of α -methylstyrene to cumene over a palladium on γ -alumina catalyst



is a well-known model system for the determination of three-phase reactor performance under mass-transfer limited conditions (Cini and Harold, 1991; Frank *et al.*, 1999; Khadilkar *et al.*, 1996) because of its high intrinsic reaction rates. The reaction is zero-order in α -methylstyrene until the concentration drops to too low a value, which indicates strong adsorption of α -methylstyrene on the catalyst, and first order in hydrogen.

3.2.1 Stability tests: Kreutzer *et al.* (2001) studied this system in a monolithic reactor with continuous hydrogen flow and batch operation for the liquid α -methylstyrene/cumene mixture. Figure 6 shows the result of an experiment to determine the catalyst stability. The linear decrease of the amount of α -methylstyrene present in the reaction mixture indicates that the catalyst does not deactivate during an experiment. It also shows that at the reaction conditions applied the reaction is zero order in α -methylstyrene. External mass transfer is not rate limiting, because then the reaction would have appeared to be first order in α -methylstyrene.



Figure 6. Determination of the catalyst stability during a long run at constant operating conditions. Reprinted from Kreutzer *et al.*, Copyright (2001), with permission from Elsevier.

3.2.2 Mass transfer: Kreutzer *et al.* (2001) have developed a model for the prediction of the overall external mass transfer coefficient in monolithic reactors. Measurements were performed at a number of temperatures to make sure

that experiments were performed in the external mass-transfer limited regime. If external mass transfer limitations strongly dominate, the apparent activation energy is negligible, because the mass-transfer coefficient (which is the observed rate constant) is fairly independent on temperature.

In the case of internal diffusion limitations the apparent activation energy is half the true activation energy. Germain *et al.* (1974) have determined the true activation energy of the hydrogenation of α -methylstyrene in a slurry reactor with small particles at moderate temperatures and found a value of 42 kJ/mol.

Figure 7 shows the observed reaction rate constant as a function of the reciprocal temperature. The apparent activation energy is obtained from the slope of the plot.



Figure 7. Arrhenius plot of the first order rate constant, based on reactor volume. Catalyst: 400 cpsi monolith 1.8% Pd/γ -Al₂O₃, d = 0.01 m, L = 0.75 m, $u_L = 0.15$ m/s , $u_G = 0.2$ m/s. Reprinted from Kreutzer *et al.*, Copyright (2001), with permission from Elsevier.

From the slope at low temperatures (323 - 373 K) the reaction activation energy was determined to be 20 kJ/mol, indicating internal diffusion limitations. Only when the temperature becomes higher than 373 K a transition can be seen and the reaction becomes limited by external mass transfer. The observed reaction rate constant in this region is slightly larger than 1 s⁻¹. This is also the value of the overall external mass-transfer coefficient at the indicated gas and liquid velocities. This is high compared to the mass transfer rates obtained in slurry and trickle-bed reactors ($k_L a = 0.01 - 0.6$ and $0.01 - 0.08 \text{ s}^{-1}$, respectively).

Based on mass-transfer experiments overall activities can be determined. Nijhuis *et al.* (2001) compared the activities of a monolithic and trickle-bed reactor for the hydrogenation of α -methylstyrene over a nickel catalyst at 373 K and 10 bar hydrogen pressure. They found values of 6.2 and 4.6 mol/m³_{reactor}/s for the monolithic and the trickle-bed reactor, respectively, which signifies that the volume of the monolithic reactor can be considerably smaller than that of the trickle-bed reactor for the same productivity.

3.3 Concluding Remarks

Monolithic reactors show very good mass-transfer characteristics. As a result, despite the lower amount of catalyst per unit volume of reactor, the productivity of monolithic reactors is larger than that of trickle-flow reactors (Nijhuis *et al.*, 2001). The productivity can be increased by using higher cell densities of up to 1100 cpsi. This is possible because of the extremely low pressure drop of monolithic reactors. Therefore, monolithic reactors are an important contribution to Process Intensification (Stankiewicz and Moulijn, 2001).

4. THREE-LEVEL CATALYSIS ENGINEERING IN N₂O ABATEMENT

4.1 Introduction

Nitrous oxide (N_2O) has been identified as a greenhouse gas and a contributor to the depletion of ozone in the stratosphere (Rodhe, 1990; Kroeze, 1994; Centi *et al.*, 1999; Pérez-Ramírez, 2002). As regulations will become more and more stringent, there is a strong incentive towards N_2O emission control.

Direct catalytic decomposition of N_2O into N_2 and O_2 is an attractive option. However, so far none of the proposed catalysts show the desired combination of activity and stability for the conversion of N_2O under realistic conditions of tail gas composition and space velocities (Centi *et al.*, 2000; Kapteijn *et al.*; 1996, Pérez-Ramírez, 2002 and references therein). Therefore, the development of a versatile catalyst for direct catalytic decomposition of N_2O present in the different tail gases is indispensable. The primary requirements of such a catalyst are activity at low temperature and resistance towards deactivation.

Nitric acid production is the largest source of anthropogenic N_2O emissions and as such is a good candidate for N_2O abatement. Pérez-Ramírez (2002) has investigated the direct catalytic decomposition of N_2O in simulated tail gas from nitric acid plants. We will discuss the catalysis engineering aspects starting with the macrolevel, via the mesolevel to the microlevel instead of *vice versa*, because the basis of catalyst development is an existing plant in which the catalytic N_2O decomposition unit has to be incorporated.

4.2 Macrolevel: Process Selection

The macrolevel involved the study of the different options for installing the catalytic unit in a relatively complex process responsible for generating N₂O. Various abating options were identified (Smit *et al.*, 2001; Pérez-Ramírez, 2002), of which two options are considered as cost-effective control measures in existing plants. These are 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 the tail-gas expander, as shown in Figure 8. The reader is referred to Smit *et al.*(2001) and Pérez-Ramírez (2002) for a schematics of the nitric acid process.



Figure 8. Schematic representation of the (a) in process-gas catalytic N₂O decomposition and (b) the tail-gas catalytic N₂O decomposition upstream of the expander in nitric acid plants; the range of typical operating conditions is indicated (Pérez-Ramírez, 2002).

Direct N_2O decomposition in the tail gas upstream the expander (Figure 8b) offers the great advantage of not influencing the nitric acid production process, since no modifications have to be made to the ammonia converter. An additional advantage is that in principle 100% N_2O removal can be achieved, as there is no physical limit to the amount of catalyst that can be installed. Possible problems concerning the maximum allowable pressure drop can be overcome by proper reactor design (mesolevel, see Section 4.3). The most important issue is the temperature range (from 525 K to 775 K, and even higher in modern dual-pressure plants). Catalyst studies on the microlevel (see Section 4.2.3) have shown that a high N_2O conversion is feasible at temperatures above 725 K, which in practice means that about 50% of the N_2O emissions from nitric acid plants can be prevented in a cost-effective manner (Pérez-Ramírez, 2002).

4.3 Mesolevel: Reactor Selection

At the mesolevel proper reactor design, in the case of tail-gas treatment especially with respect to maximum allowable pressure drop, is very important. The particle size and shape are crucial aspects in obtaining reliable design data for full-scale implementation of catalytic N_2O abatement units in nitric acid plants.

The first reactor type to look at is the conventional fixed-bed reactor with shaped particles (Figure 9a) because it is the simplest type of reactor for gas-phase reactions and has a high catalyst load per unit volume of reactor. However, the high pressure drop when using small catalyst particles, which are required for a high catalyst effectiveness and good mass and heat transfer, is a major disadvantage. A promising alternative is a monolithic reactor with structured packing (Figure 9b), which allows the separate optimization of the kinetics, transport properties, and hydrodynamics.



Figure 9. Schematic representation of (a) a fixed-bed reactor and (b) a monolithic reactor.

Pérez-Ramírez (2002) has compared the fixed-bed reactor and the monolithic reactor for the catalytic decomposition of N₂O. For the calculations the activity data of the steam-activated *ex*-FeZSM-5 catalyst in the simulated tail-gas mixture in Figure 13a were used. Other data used were a volumetric flow rate of the tail gas of $2 \cdot 10^5$ Nm³ h⁻¹, a maximum allowable pressure drop of 200 mbar and a reactor diameter of 2 m. The targeted N₂O conversion was 80% at a reaction temperature of 750 K. Pressures upstream of the expander of 4 and 10 bar were used.

Figure 10 shows the effectiveness factor and pressure drop in the fixed-bed reactor for a number of extrudate sizes. Due to the high intrinsic reaction rates, he reaction in the extrudates exhibits severe diffusion limitations, leading to a low effectiveness factor (Figure 10a); only the outer part of the particles is used.

For the effectiveness factor to be high the particles should be small, but this results in a large pressure drop. In fact, at a pressure of 4 bar none of the particle sizes used satisfies the maximum pressure-drop criterion (marked area in Figure 10b). At a pressure of 10 bar (not shown), the use of particles with a diameter of 4 mm and over results in an acceptable pressure drop, but with an effectiveness factor < 0.4 (Pérez-Ramírez, 2002).



Figure 10. (a) effectiveness factor and (b) pressure drop for different extrudate size in a fixed-bed reactor; P = 4 bar, T = 750 K and X = 0.8.

Figure 11a shows the effectiveness factor of the extruded monolith as a function of the wall thickness. The effectiveness factor is much higher then in the fixed-bed reactor. Figure 11b shows the pressure drop for different wall thickness and cell density. Due to the relatively large open frontal area in the channels and the straight route the gas can follow, the pressure drop is much lower than in the fixed-bed reactor.



Figure 11. (a) Effectiveness factor as a function of the wall thickness δ and (b) pressure drop for different cell density and wall thickness of the extruded monolith; P = 4 bar, T = 750 K and X = 0.8.

The optimal reactor designs based on effectiveness factor and pressure drop were a fixed-bed reactor with extrudates of 6 mm diameter and an extruded monolithic reactor with a cell density of 200 cpsi and a wall thickness of 0.4 mm (a quite standard geometric design). These are compared in Table 2. This table shows the superior behavior of the monolithic reactor in tail-gas treatment. The monolithic reactor combines a high intrinsic activity, high catalyst effectiveness and low pressure drop. In spite of the lower amount of catalytic active material per unit volume of reactor as compared to the fixed-bed reactor, the monolithic reactor still has a smaller reactor volume.

Parameter	Fixed-bed reactor		Monolithic rector	
Туре	Extrudates		Extruded monolith	
Geometry	Diameter: 6 mm		Cell density: 200 cpsi, square channels	
			Wall thickness: 0.4 mm	
Pressure (bar)	4	10	4	10
Reactor volume (m ³)	5	3	2.2	1
Bed height (m)	0.8	0.5	0.7	0.3
Catalyst effectiveness η (-)	0.33	0.21	0.95	0.88
Pressure drop (mbar)	630	160	60	10

 Table 2. Comparison of reactors for direct N₂O decomposition over *ex*-FeZSM-5 in tail gas of nitric acid plants.

 Adapted from (Pérez-Ramírez *et al.*, 2002b)

Basis of design: Tail-gas flow = $2 \cdot 10^5$ Nm³ h⁻¹, Temperature = 750 K, Pressure upstream the expander = 4 or 10 bar, N₂O conversion = 80%, reactor diameter = 2 m.

4.4 Microlevel: Catalyst Selection

The microlevel, which is related to the development of the catalyst formulation, is crucial for the feasibility of the overall process. High-throughput screening, quantitative testing, stability tests and kinetic investigations in a fully PC-controlled six-flow reactor (Figure 12) were all part of the selection procedure for a suitable N₂O decomposition catalyst. The catalyst should be able to operate in the presence of other gases in the tail gas, such as NO and H₂O, which in many catalyst formulations lead to strong inhibition and/or deactivation. Pérez-Ramírez (2002) has evaluated promising catalysts (especially FeZSM-5) under simulated real process conditions.



Figure 12. Basic scheme of the six-flow reactor for fast catalyst screening and kinetic studies (Pérez-Ramírez *et al.*, 2000)

4.4.1 Catalyst preparation, characterization and screening: During the first stage of catalyst development, within one month around 100 catalyst formulations were prepared and tested. The catalysts included supported oxides, zeolites and mixed oxides derived from hydrotalcites (Pérez-Ramírez, 2002, Pérez-Ramírez *et al.*, 2002b). The screening identified a number of FeZSM-5 catalysts, amongst which one prepared via a novel *ex*-framework route

(Pérez-Ramírez *et al.*, 2003), and Rh-based catalysts (especially *ex*-Co-Rh,Al-HTlc) as promising candidates for the direct catalytic N_2O decomposition. These catalysts were further examined in activity and stability studies.

The *ex*-framework route for the preparation of FeZSM-5 catalysts was developed by Pérez-Ramírez *et al.* (2003) to overcome limitations of FeZSM-5 catalysts prepared by other methods, in particular ion exchange. This steam activation method is of vital importance for the catalyst performance, as will be shown in the following section. In contrast with zeolite catalysts prepared by other methods, *ex*-framework FeMFI zeolites have a well-defined active site architecture. Tailoring the nature of iron sites by optimizing the steam treatment ultimately determines the catalyst performance.

A multi-technique approach was used for the characterization of the catalysts. For Fe-zeolites this involved the integration of traditional techniques and a novel voltammetric response method based on solid-state electrochemistry to unravel the nature of iron species in the catalyst (Pérez-Ramírez *et al.*, 2002, 2002a, 2003).

4.4.2 Activity and stability tests: The performance of the best catalysts from the screening stage was tested in simulated tail gas from nitric acid plants containing N_2O , O_2 , NO and H_2O . Figure 13a shows the conversion of *ex*-FeZSM-5 as a function of temperature in a number of different gas mixtures.



Figure 13. N₂O conversion versus temperature in simulated tail gas from nitric acid plants over (a) *ex*-FeZSM-5 and (b) *ex*-Co-Rh,Al-HTlc. Conditions: (\blacklozenge) 4.5 mbar N₂O, (\diamondsuit) 4.5 mbar N₂O + 70 mbar O₂, (\blacklozenge) 4.5 mbar N₂O + 1 mbar NO, (\circ) 4.5 mbar N₂O + 15 mbar H₂O, (\blacktriangle) 4.5 mbar N₂O + H₂O; balance He; *P* = 3 bar; *GHSV* = 60,000 h⁻¹ (Pérez-Ramírez *et al.*, 2002b).

With a N₂O/He feed the catalyst shows a large N₂O conversion at temperatures above 700 K. Addition of O₂ hardly affects the conversion. The most remarkable result is that NO considerably enhances the reaction rate, shifting the reaction to lower temperatures. H₂O severely inhibits the reaction, but in the complete gas mixture (N₂O + O₂ + NO + H₂O) the activity of *ex*-FeZSM-5 is still significantly higher than in N₂O alone.

This promoting effect of NO is what distinguishes ex-FeZSM-5 from other N₂O decomposition catalysts, such as ex-Co-Rh,Al-HTlc (Figure 13b) and other Rh catalysts. In these catalysts NO inhibits the N₂O conversion. It should be mentioned, however, that with Rh catalysts a higher conversion is obtained at a certain temperature than with ex-FeZSM-5, even in the complete simulated tail gas mixture.

However, not only the activity is important, but also the stability. Figure 14 shows the results of a stability test during 600 h for *ex*-FeZSM-5 and *ex*-Co-Rh,Al-HTlc. The Fe catalyst shows a remarkable stability at both 675 and 725 K. The N₂O conversion is higher in the tail-gas mixture than in the N₂O/He mixture, as was already shown in Figure 13a. In the tail-gas mixture, at 675 K the Rh catalyst shows a higher initial activity than the Fe catalyst, but this activity decreases to below the level obtained with the Fe catalyst within about 100 h on stream. After 300 h, the Rh catalyst has already lost 60% of its activity. The conversion rapidly increases to 80% after switching to a N₂O/He

feed, but this conversion is lower than the conversion obtained in an earlier experiment with the same catalyst (see Pérez-Ramírez (2002)), which indicates deactivation. After switching back to the tail-gas mixture again the conversion continues to decrease. This deactivation behavior limits the practical application of *ex*-Co-Rh,Al-HTlc (and other Rh catalysts showing similar behavior) for N₂O abatement in nitric acid plants.



Figure 14. N₂O conversion versus time on stream over (a) *ex*-FeZSM-5 and (b) *ex*-Co-Rh,Al-HTlc in (\bullet, \bullet) 4.5 mbar N₂O and (\circ, \diamond) 4.5 mbar N₂O + 70 mbar O₂ + 1 mbar NO +15 mbar H₂O; balance He; *P* = 3 bar; *GHSV* = 60000 h⁻¹. Temperatures are indicated in the figure. (Pérez-Ramírez *et al.*, 2002b).

4.5 Concluding Remarks

A nitrous oxide abatement process for nitric acid plants has been developed via catalysis engineering on three levels. On the macrolevel a choice had to be made regarding the position of a catalytic N_2O decomposition unit. Reactor studies on the mesolevel revealed that for this reaction an extruded monolithic reactor is superior to a fixed-bed reactor filled with extrudates. Finally, on the microlevel an intriguing feature of FeZSM-5 catalysts came to light, namely that NO significantly enhances their activity, while the opposite effect is usually observed for other catalytic systems based on noble metals or transition metal oxides. In addition, *ex*-framework FeMFI catalysts show superior performance for direct N_2O decomposition in real tail gases from nitric acid plants compared to other catalysts, including FeZSM-5 catalysts prepared by other methods, especially with respect to stability.

5. CONCLUSIONS

The monolithic reactor can be an important contribution to process intensification. This was shown, by comparing the productivity of a monolithic reactor and a trickle-flow reactor for a fast three-phase hydrogenation reaction. As a result of the good mass transfer characteristics, using a monolithic reactor can reduce the required reactor volume by over 25%. The monolith structure has intrinsic scaleability in that it can be tailored by choosing different wall thicknesses and cell densities.

Monolithic reactors also play a part in catalysis engineering on three levels. This multilevel catalysis engineering approach is very useful in the rapid development of a catalytic process, as was shown for the case of N_2O abatement.

NOTATION

a	specific surface area, m^2/m^3
cpsi	cell density (cells per square inch), 1/inch ²
d	diameter, m
E_A	apparent activation energy, kJ/mol
GHSV	gas hourly space velocity, 1/h
k_L	gas-liquid mass transfer coefficient, m/s
k_{v}	reaction rate constant, 1/s
L	length, m
Р	pressure, bar
t	time, s
Т	temperature, K
и	superficial velocity, m/s
Χ	conversion

Greek letters

- δ wall thickness, m
- η effectiveness factor

Subscripts

- G gas
- L liquid

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