Stellingen


1. Het vermelden van een druk zonder daarbij aan te geven of deze absoluut of relatief is (bara of barg), is zeker bij lage drukken onzinnig.

2. Het probleem met modelleren is dat de werkelijkheid een gegeven is en een model nooit beter kan zijn dan de onderstellingen.

3. Het gebruik van grootheden als ‘Gas Hourly Spave Velocity (GHSV)’, ‘uurverbruik’, *etc.* is strijdig met de regel ‘Grootheid = getal maal eenheid’.

4. De populariteit van het vak scheikunde zou gediend zijn met een heldere opgave van ingrediënten van consumenten-artikelen zonder potjeslatijn of geheimzinnige E-nummers.

5. De kwaliteit van wetenschappelijke literatuur in haar algemeenheid zou er aanzienlijk op vooruit gaan wanneer met betrekking tot nieuwheid, inventiviteit en met name nawerkbaarheid, dezelfde eisen zouden worden gesteld als nodig zijn voor het verkrijgen van octrooi.

6. Schrijven is zwijgend spreken.
7. Door alleen naar de tv te luisteren wordt men gewaar dat het beeld daarbij veelal overbodig is.

8. Het toestaan van reclameborden langs de openbare weg berust op de misvatting dat weggebruikers een overschot aan aandacht hebben.


10. Een gegeven paard in de bek kijken kan vervelende verrassingen voorkomen.

11. Het bestrijden van computervirussen is een overheidstaak.
Zeolitic Coatings applied in Structured Catalyst Packings
Zeolitic Coatings Applied in Structured Catalyst Packings

Proefschrift

ter verkrijging van de graad van doctor
aan de technische universiteit Delft,
op gezag van de Rector Magnificus prof. ir K.F. Wakker,
in het openbaar te verdedigen ten overstaan van een commissie,
door het College voor Promoties aangewezen,

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scheikundig ingenieur
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Summary

In this thesis the synthesis and application of a novel type of structured catalyst packings are described. These catalyst packings are prepared by crystallization of zeolites onto the surface of a macroscopically preshaped support. Due to their microporous structure, zeolites possess a very high internal surface. This, and the fact that the crystals have a well-defined shape and size, make them excellent catalysts. Moreover, by means of ion exchange, the zeolites can be loaded with cations to suit a specific conversion. The advantage of structured catalyst packings is that the shape of the catalyst module can be optimized for the envisioned process. In this way, for example the pressure drop, the flow profile, the mass- and/or heat transfer or the dispersion characteristics of the catalyst module can be optimized. The objective of this thesis is to investigate the practical value of combining these two features in a number of conversions.

The deposition of zeolite crystals on a support is carried out according to the in-situ synthesis method. In this method, the zeolite crystals are enabled to grow onto the support, which is submerged in the synthesis mixture. The support should be receptive for the zeolite crystals. The bonding between the zeolite crystals and the support is supposedly enabled by the presence of OH groups on the surface of the support. During their formation, the zeolite crystals, formed by growing and branching networks of Si-O and Al-O bonds, attach to the carrier surface. Earlier studies have shown that a variety of solid materials are suited for covering with a zeolitic coating in this way. Apart from metallic surfaces, such as stainless steel and other alloys, also ceramic substances can be covered successfully with the in-situ synthesis method. On the other hand, organic polymers are generally not suited as a carrier material. In the case of metal surfaces, a thin oxidic film is present to which the crystals are bonded.

In this work, it will be investigated whether the zeolitic coatings are really suitable to be applied as catalyst modules and whether their implementation as a reactor packing will lead to an understandable and controllable system.

First the synthesis of zeolitic coatings will be explored. A number of choices will be made in the combination of zeolite types and support materials depending on their application. Although the synthesis of zeolites onto solid supports has already received some attention in literature, these studies pertain mainly to small scale experiments (support surfaces < 1 cm²) and generally lack quantitative data with respect to the obtained coverage. For a practically useful catalyst system, quantification of the coverage is indispensable, as the amount of catalytically active material co-determines the final size of the reactor. Factors that may influence the coverage will be investigated and subsequently it will be attempted to optimize these factors. Optimal synthesis conditions are strongly related to the chosen combination of zeolite type and support material.

Combinations of zeolite type and support material that were investigated are zeolite Beta and zeolite ZSM-5 on various metallic and ceramic supports. Experiments with zeolite Beta are
Summary

mainly carried out using stainless steel supports and to a lesser extent with other alloys. This combination of zeolite type and carrier material resulted in coverages of ca. 20 g_{zeolite}/m^{2}_{support}. If applied to a 600 cpsi (channels per square inch) monolith structure this corresponds to a loading of ca. 40 kg_{zeolite}/m^{3}_{reactor}. ZSM-5 was grown on stainless steel and on various ceramic materials, among others α-alumina porous plates (‘ceramic foams’) and cordierite monoliths. The coverage on stainless steel was ca. 20 g_{zeolite}/m^{2}_{support} (ca. 40 kg_{zeolite}/m^{3}_{reactor}). For ceramic supports, coverages up to 100 g_{zeolite}/m^{2}_{support} (160 kg_{zeolite}/m^{3}_{reactor}) were obtained.

The prepared packings were tested in two applications. In the first place the selective catalytic reduction of nitric oxide (SCR) was investigated using both zeolite Beta and ZSM-5 grown on steel and ceramic supports. The deNOx reaction can benefit from this type of packings in that this reaction is catalyzed by metal exchanged zeolites and by the fact that in a practical deNOx installation the pressure drop and the sensitivity toward dust in the feed should be minimized. Initially the packings were tested on their chemical activity, using an internal recycle reactor. This type of reactor enables the investigation of the chemistry in the absence of temperature and concentration gradients. With these experiments, hydrocarbons were used as the reducing agent (methane and propene). From those experiments it could be concluded that the activity of zeolites is not influenced negatively by the fact that the crystals are immobilized in a layer. However, the activity of the SCR using methane is too low to be of value in a practical application. On a larger scale, two reactor configurations were investigated: the monolith reactor and the parallel passage reactor (PPR) where the zeolitic coating was deposited on ceramic foam supports. Ammonia was used as the reducing agent. From these experiments it was clear that ceramic supports were particularly suited as a substrate for zeolitic coatings. The conversions obtained were comparable to those of practical installations, while no major optimization had taken place.

Apart from SCR, also the liquid phase synthesis of ethyl tert-butyl ether (ETBE) was studied, in which stainless steel packings, covered with acidic zeolite Beta were used. The motivation for this part of research was the possible application of zeolitic coatings in catalytic distillation. Their implementation may contribute to more compact process equipment, as the reactor and separation column can be integrated into one process unit. These experiments were carried out on a small scale and the chemistry was studied only. Especially the selectivity appeared to benefit from the fact that the catalyst was present in a thin layer. Nevertheless, the maximal deposition of the zeolites on the packing turned out to be too low for sufficient conversion, indicating the need for higher coverages. An obvious way to achieve this is to apply the aforementioned ceramic foams.
Contents

Summary ................................................................. 3

Chapter 1 General Introduction ..................................... 9

1.1 What are Zeolitic Coatings? ........................................ 9
1.2 Goal and Scope of this Work ....................................... 10
1.3 Outline of the Thesis ............................................... 13

Chapter 2 Introduction to Zeolitic Coatings ....................... 15

2.1 Introduction ....................................................... 15
2.2 Zeolites, General Information .................................... 18
  2.2.1 Molecular Sieves and Zeolites .............................. 18
  2.2.2 Synthetic and Natural Zeolites ............................ 18
  2.2.3 Nomenclature and Structure of Zeolites .................. 19
  2.2.4 Zeolite Characteristics ..................................... 20
  2.2.5 Zeolite Synthesis ............................................ 21
2.3 Background of Zeolitic Coatings ............................... 24
  2.3.1 Synthesis Techniques ....................................... 24
  2.3.2 Orientation of Zeolite Crystals ............................ 25
  2.3.3 Growth Modes ............................................... 26
  2.3.4 Synthesis of Zeolitic Coatings ............................ 28
2.4 Zeolitic Membranes ............................................... 29
  2.4.1 Reported Zeolitic Membranes .............................. 29
  2.4.2 Permeability Studies ....................................... 30
  2.4.3 Supports Used for Synthesis of Inorganic Zeolitic Membranes 31
2.5 Pure Zeolitic Films ................................................ 33
  2.5.1 Reported Pure Zeolitic Films .............................. 33
  2.5.2 Synthesis of Pure Zeolitic Films .......................... 33
  2.5.3 Supports Used During Synthesis ........................... 34
  2.5.4 Calcination of Pure Zeolitic Films ........................ 34
  2.5.5 Crystallinity Distribution Across the Film / Steaming .... 35
2.6 Metal supported Zeolitic Coatings .............................. 36
  2.6.1 Reported Metal Supported Zeolitic Coatings .............. 36
  2.6.2 Synthesis of Metal Supported Zeolitic Coatings ......... 37
  2.6.3 Composition of the Metal Support ........................ 38
  2.6.4 Cleaning Procedure Prior to Zeolite Film Formation ..... 38
  2.6.5 Pretreatment of the Support ............................... 39
Contents

2.7  Zeolitic Coatings on Siliceous Supports  40
    2.7.1 Reported Zeolite Coatings on Siliceous Substrates  40
    2.7.2 Hydrogel Surface Condensation Versus Nucleation and Crystal Growth  41
    2.7.3 Increased Zeolite Coverage on the Substrate Surface, Effect of Aging  41
    2.7.4 Synthesis: Factors Influencing Zeolite Film Deposition  42
2.8  Applications of Zeolitic Coatings  45
    2.8.1 Electroanalysis and Sensor Devices  46
    2.8.2 Pervaporation  47
    2.8.3 (Catalytic) Membrane Reactors  48
    2.8.4 Catalytic Distillation  49
    2.8.5 Pollutant Emission Control: NOx-reduction  50
    2.8.6 Hydrocarbon Conversion Processes  51
2.9  Conclusion  53
2.10 References  53

Chapter 3 Optimized Synthesis of Zeolite BEA on Metal Supports  59

3.1  Introduction  59
3.2  Theory  61
3.3  Experimental  63
3.4  Results and Discussion  68
3.5  Conclusions and Recommendations  75
3.6  References  76

Chapter 4 Optimized synthesis of ZSM-5 on stainless steel foil carriers  79

4.1  Introduction  80
4.2  Experimental  82
    4.2.1 Varying Surface Area of Stainless Steel Carriers  82
    4.2.2 Repeated Synthesis  83
    4.2.3 Optimized Reaction Conditions  83
    4.2.4 Large Scale Synthesis  84
4.3  Results and Discussion  86
    4.3.1 Varying Surface Area of Stainless Steel Carriers  86
    4.3.2 Repeated Synthesis  88
    4.3.3 Optimized Reaction Conditions  89
    4.3.4 Large Scale Synthesis  93
4.4  Conclusions and Recommendations  95
4.5  References  96
Chapter 5 Synthesis of ZSM-5 on Ceramic Carriers

5.1 Introduction .......................... 97
5.2 Background of Ceramic Carriers 100
  5.2.1 Monoliths ......................... 100
  5.2.2 Ceramic Foams .................. 100
  5.2.3 Other Ceramic Supports ......... 103
5.3 Experimental ....................... 104
  5.3.1 Materials Used .................. 104
  5.3.2 Support and Equipment Pretreatment 105
  5.3.3 Preparation of Synthesis Mixture 105
  5.3.4 Synthesis ....................... 106
5.4 Results and discussion ............. 109
  5.4.1 General Considerations ......... 109
  5.4.2 Investigated Factors ............ 110
5.5 Conclusions ....................... 119
5.6 References ......................... 120

Chapter 6 Application of In-Situ Grown Zeolites as DeNOx Catalyst .............. 123

6.1 Introduction .......................... 123
6.2 Theory of Low Pressure Drop DeNOx Reactors 127
  6.2.1 Pressure Drop across Rectangular Channels with a Constant Cross Section 127
  6.2.1.1 Friction Factors for Laminar Flow 127
  6.2.1.2 Friction Factors for Turbulent flow 129
  6.2.2 Pressure Drop and Flow in the Parallel Passage Reactor 130
  6.2.3 Pressure Drop and Flow in the Monolith 131
  6.2.4 Reaction Kinetics of the SCR of NO with Ammonia 131
  6.2.5 Relations for Diffusion Coefficients 131
  6.2.6 Mathematical Models to Predict Conversion 133
    6.2.6.1 Modeling the Parallel Passage Reactor 133
    6.2.6.2 Modeling the Monolithic Reactor 135
6.3 Experimental ....................... 137
  6.3.1 Catalyst Choice and Preparation 137
  6.3.2 DeNOx Experiments with Hydrocarbons as the Reductant 138
  6.3.3 DeNOx Experiments with Ammonia as a Reductant — Bench Scale 141
    6.3.3.1 Bench Scale Experimental Set-Up 141
    6.3.3.2 Bench Scale Experimental Procedure 142
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4</td>
<td>Results and Discussion</td>
<td>144</td>
</tr>
<tr>
<td>6.4.1</td>
<td>DeNOx Experiments with Hydrocarbons as the Reductant</td>
<td>144</td>
</tr>
<tr>
<td>6.4.2</td>
<td>Bench Scale Experiments with Ammonia as the Reductant</td>
<td>149</td>
</tr>
<tr>
<td>6.4.2.1</td>
<td>Pressure Drop across the PPR</td>
<td>149</td>
</tr>
<tr>
<td>6.4.2.2</td>
<td>Pressure Drop across the Monolith</td>
<td>151</td>
</tr>
<tr>
<td>6.4.2.3</td>
<td>Initial deNOx Experiments in the PPR and Monolith covered with Cu-ZSM-5</td>
<td>151</td>
</tr>
<tr>
<td>6.4.2.4</td>
<td>DeNOx Experiments in the PPR — Comparison with Model</td>
<td>153</td>
</tr>
<tr>
<td>6.4.2.5</td>
<td>DeNOx Experiments in the Monolith Reactor — Comparison with Model</td>
<td>155</td>
</tr>
<tr>
<td>6.4.2.6</td>
<td>Comparing the PPR and the Monolith with Practice</td>
<td>156</td>
</tr>
<tr>
<td>6.5</td>
<td>Conclusions and Recommendations</td>
<td>157</td>
</tr>
<tr>
<td>6.6</td>
<td>Notation</td>
<td>158</td>
</tr>
<tr>
<td>6.7</td>
<td>References</td>
<td>159</td>
</tr>
</tbody>
</table>

**Chapter 7 Synthesis of Ethyl tert-Butyl Ether Using In-Situ Grown Zeolites**  

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>161</td>
</tr>
<tr>
<td>7.2</td>
<td>Background of Catalytic Distillation and ETBE</td>
<td>163</td>
</tr>
<tr>
<td>7.2.1</td>
<td>Properties of ETBE</td>
<td>163</td>
</tr>
<tr>
<td>7.2.2</td>
<td>Production of ETBE</td>
<td>164</td>
</tr>
<tr>
<td>7.2.3</td>
<td>Catalytic Distillation</td>
<td>167</td>
</tr>
<tr>
<td>7.3</td>
<td>Experimental</td>
<td>169</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Equipment</td>
<td>169</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Catalyst Preparation</td>
<td>170</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Experimental Procedure</td>
<td>170</td>
</tr>
<tr>
<td>7.4</td>
<td>Results and Discussion</td>
<td>171</td>
</tr>
<tr>
<td>7.5</td>
<td>Conclusions and Recommendations</td>
<td>176</td>
</tr>
<tr>
<td>7.6</td>
<td>References</td>
<td>177</td>
</tr>
</tbody>
</table>

**Conclusions**  

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>179</td>
</tr>
</tbody>
</table>

**Samenvatting**  

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>181</td>
</tr>
</tbody>
</table>

**Dankwoord**  

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>185</td>
</tr>
</tbody>
</table>

**Curriculum Vitae**  

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>187</td>
</tr>
</tbody>
</table>
General Introduction

1.1 What are Zeolitic Coatings?

The synthesis of zeolite crystals is a good example of the quest of man to control the physical world on an atomic level. Apart from copying zeolite types as they occur in natural mineral deposits, entirely new types of zeolites have been synthesized and their number is ever increasing. From a technological point of view, zeolites are important because they present a high specific surface area, due to their well-defined microporous structure. This surface area has already proven its value in a myriad of industrial and small scale processes, involving adsorption, catalysis and ion-exchange. The possibilities in catalytic applications are further extended by the fact that zeolites can be exchanged with a catalytically active cation. In this way a monatomic dispersion of catalytically active sites can be obtained. The advantages are that the cation can be chosen to meet the requirements for the specific reaction and that the high dispersion ensures an optimal utilization of the catalytic material.

Crystal sizes of synthetic zeolites are typically between 0.1 and 500 μm. In nature zeolite crystals of up to several millimeters have been found. Sometimes a small crystal size (ca. 1 μm) is desirable, e.g., when zeolites are applied as ion exchanger in detergent formulation. However, the size of synthetic zeolites is often too small to be handled in practical applications. The zeolite material obviously needs to be immobilized in some way to obtain a product that can be incorporated successfully as a catalyst, sorbent, etc., depending on the type of application. Straightforward ways of immobilizing zeolite crystals are to press them into particles or to extrude them, generally by using a binder. The apparatus in question can then be filled with these solid catalyst or sorbent particles to form a bed through which the fluid is forced. This approach is satisfactory as long as the amount of zeolites present in the unit is the only factor of concern. However, successful operation is not only governed by capacity alone. An ever increasing demand on process efficiency requires optimization of other process parameters, such as pressure drop, equipment dimensions, sensitivity to dust, etc. To this end, packings can be employed that are preshaped in a form that meet these auxiliary demands. In the last decades, structured catalysts have become increasingly important, both for automotive use and in industrial applications. If zeolite crystals are used, the question is how to incorporate or fix these crystals to these packings.

An aspect of zeolites that has been studied for several years at Delft University of Technology is their ability to form and grow onto solid surfaces. It was observed that different types of zeolite show a preference to nucleate and grow on a variety of solid surfaces present in the synthesis mixture, such as metals and oxides. Although the exact nature of the bonding mechanism of the
zeolite crystal to the surface remains as yet unknown, it has been shown that it is a strong bonding, resisting considerable thermal and mechanical stresses. This suggests that the bonding is chemical. Schematically the formation of this bond is illustrated in Fig.1.1. It is assumed that during their formation and development, the zeolite crystals form chemical bonds with OH groups present at the carrier surface. These OH groups stem from the oxide or from their oxide surface layer of the metal or steel.

Fig. 1.1 Impression of the bonding mechanism of a zeolite crystal on a solid surface.

Since the work described in this thesis is in a relatively new field of science, no generally accepted terminology and definitions exist. In this work a zeolitic coating is defined as a layer of zeolite material connected to a solid surface. The zeolitic coatings described in this work are all prepared by means of in-situ synthesis, i.e., by allowing the synthetic zeolite crystals to form and grow directly onto the supporting surface. Apart from this technique, two other (post synthesis) methods of preparing zeolitic coatings can be distinguished: the washcoating technique or the slurry coating technique. In the washcoating technique, the zeolite crystals are mixed with a liquid binder, that is subsequently hardened by heating, thus fixing the crystals. In the slurry coating technique, the zeolite crystals are suspended in a liquid. Upon evaporating the liquid the crystals coalesce and form a more or less continuous coating. Coatings prepared by the slurry coating technique are also referred to as binderless zeolite coatings.

1.2 Goal and Scope of this Work

In principle, the fact that zeolite crystals can be synthesized directly onto solid surfaces, could provide an answer to the question of fixing the zeolites to the surface raised above. In the broadest sense, the aim of this work is to investigate the application and more in particular, to
assess the feasibility of zeolitic coatings in practical processes. The work is limited to the application of zeolitic coatings as catalytic packings.

To meet the goal, it is important to explore, at least to some extent, the large field that all possible combinations of zeolite types and carrier materials offer. Roughly, the first half of the work described in this thesis is dedicated to finding some of these combinations. Different synthesis methods are employed to find factors that are important in optimizing the zeolite coverage of the carrier. Within this work the focus has been on two zeolites, both consisting of 3-dimensional crossing channels: ZSM-5 with a channel diameter of ~ 0.55 nm and zeolite Beta with channel dimensions of $0.76 \times 0.64$ nm and $0.55 \times 0.55$ nm, see Fig. 1.2. Initially, relevant synthesis parameters are studied by performing small scale syntheses (vessels of ca. 35 ml). Practical applications, however, require structures of a larger dimension (typically 1 liter). The scaling up of zeolite synthesis is studied for ZSM-5 on metal and ceramic carriers.

![Diagram of MFI and BEA zeolites](image)

**Fig. 1.2** Projection of the framework structure of ZSM-5 (MFI) and zeolite Beta (BEA) (top) and cross section of different channel types (bottom). Channel dimensions are given in nm.

To test the synthesized catalyst packings, careful choice of the test reactions is important. Choices for the investigated reactions were based on the assumption that an envisioned practical application should benefit from the two features that zeolitic coatings offer. First, obviously, the
Chapter 1

selected zeolites should be able to catalyze the envisioned reaction and secondly the use of a structured catalyst is required by the nature of the process. Two test reactions are chosen.

The abatement of nitrogen oxides from off-gases is a process that meets the aforementioned requirements. The NOx reduction is effectively catalyzed by metal exchanged zeolites. The economy of the industrial deNOx process, where large flows at low pressures are to be treated, requires that the pressure drop across this unit is kept as low as possible. When applied to non-stationary sources, a high pressure drop cannot be allowed since it would have a detrimental effect on engine performance. In this work zeolitic coatings will be tested in two typical low pressure drop configurations: a monolithic reactor and a Parallel Passage Reactor (PPR). A schematic representation of these reactor types is shown in Fig. 1.3.

![Diagram showing Parallel Passage Reactor (1) and Monolith Reactor (2)](image)

Fig. 1.3 The Parallel Passage Reactor (PPR) (1) and the Monolith Reactor (2).

Apart from testing the performance of these reactor configurations, an aspect that is at least as important to assess the feasibility of zeolitic coatings applied in catalyst packings, is the development of tools to predict essential process variables, like pressure drop and conversion, and their dependance on the reactor geometry and the zeolite loading.

The second process that has been investigated within this thesis is the synthesis of ethyl tert-butyl ether (ETBE) from ethanol and isobutene. On an industrial scale ETBE can be produced by means of catalytic distillation. Since the reaction is known to be catalyzed by acid zeolites, zeolitic coatings can be employed as catalytic distillation packings and can thus contribute to a cost-effective production route.
1.3 Outline of the Thesis

In Chapter 2 an overview of the literature on zeolitic coatings is given. The field of zeolite research is large and growing rapidly. Although the focus of the experimental work described in this thesis is on zeolitic coatings prepared by in-situ synthesis, the scope of the literature survey is somewhat broader and includes data on preparation and application of zeolitic coatings. In this way it is hoped for that a solid background on possibilities is obtained.

In Chapter 3 the growth of zeolite Beta (BEA) onto stainless steel carriers is reported. Chronologically, these were the first experiments performed. Zeolite Beta is an interesting catalyst due to its relatively large pores and three-dimensional pore structure. It is expected to become of large importance for hydrocarbon conversions.

In Chapter 4 the synthesis of ZSM-5 on stainless steel carriers is studied. This work is an extension of successful experiments conducted earlier at Delft University of Technology. Focus will be on the optimization of the synthesis mixture and on the efficiency of synthesis.

Chapter 5 also deals with the synthesis of ZSM-5, but here various ceramic structures are used as the carrier material. Novel materials like ceramic foams enable the design of new reactor types. Apart from this, a more conventional ceramic structure, the cordierite monolith is also subject of study.

Chapter 6 deals with the testing of the prepared catalyst packings in the deNOx reaction. First experiments on a small scale, using an internal recycle reactor are discussed. The studied reaction is the reduction of nitric oxide using hydrocarbons as the reductant. This is followed by experiments performed in a bench scale deNOx unit. As mentioned before, two reactor configurations, a PPR and a monolith were tested. Cerium-, cobalt- and copper-exchanged zeolites are used. Pressure drop experiments are compared with theoretical values obtained by solving the momentum balances. A simple kinetic model will be assumed to attempt to describe the measured conversions of both reactor types, starting from a set of conservation balances.

In Chapter 7 stainless steel carriers covered with zeolite Beta in the H-form are employed in the batch synthesis of ETBE from ethanol and isobutene. These are small scale experiments performed to check the chemical feasibility of this reaction using zeolitic coatings and should be regarded as the first step in a study that should eventually lead to the implementation in a catalytic distillation unit.

Finally, in Chapter 8 the general conclusions of the work described in this thesis will be given. This is followed by an outlook regarding opportunities for implementation of zeolitic coatings.
2 Introduction to Zeolitic Coatings

2.1 Introduction

Zeolite molecular sieves are crystalline materials that possess ordered and interconnected microporous channels. The discrete crystals are commonly synthesized or mined in powder form, with crystal sizes ranging from tens of nanometers to several millimeters. As a result of their microporous nature, zeolites find application in a wide range of important areas such as ion exchange, adsorption and catalysis. As the interest in natural and particularly synthetic zeolites has enormously increased in the last twenty years, a number of publications well exceeding fifty thousand have been published to date.

Since the end of the eighties, zeolitic coatings have been gaining a still increasing interest. Zeolitic coatings are defined here as composite materials, comprising a carrier onto which zeolite crystals are physically or chemically bonded. The envisioned application determines the type and shape of the supporting carrier. For example, membrane modules are produced by coating a porous substrate with zeolites enabling molecular transport across the resulting module, whereas application as structured catalytic reactor packing could require non porous parallel channelled structures.

The choice of zeolite presents another freedom of choice in the preparation of zeolitic coatings. With the number of different zeolite framework types exceeding one hundred and the actual number of zeolite types being a multitude of this, the topic of zeolitic coatings is a virtually unbounded fertile area of research whose exploration has only just begun. Zeolite crystals have already been grown or deposited on a variety of supports, substrates being of inorganic, organic, ceramic, metallic or siliceous origin.

The attachment of the zeolite material to the substrate can be performed in different ways. The use of a binder or glue is more or less straightforward and presents questions and problems of itself. Although many work on zeolitic coatings using binders has been conducted, it will not be given much attention here, since our prime interest is in binderless coatings. One of the main questions that need to be addressed is that of the nature of the bonding of the zeolite crystals to the support. It is interesting to see that in one of the first publications\(^1\) on zeolitic coatings (in 1967), where mechanical entrapping (‘lathing’) of zeolite crystals on artificially roughened metal surfaces is described, direct chemical bonding of the zeolite crystals to the surface was already surmised.
Chapter 2

In this chapter an overview will be given of the work already conducted in the field of zeolitic coatings. Apart from the composite materials already mentioned, this also includes pure zeolitic films, also referred to as 'self-assembling zeolite films'. It will be shown that during their preparation, a substrate of some kind is required to prepare pure zeolitic films, thus complying to our definition.

In order to review the considerable amount of publications in a structured way, the topics in this chapter have been arranged by the type of supports used as substrate, which partly overlaps with application of the final product (membrane, catalyst module, etc.), since a subdivision in zeolite type or (envisioned) application alone would lead to little coherence. Arrangement of the topics on the basis of bonding nature (chemical, physical or entrapped) would also not lead to a clear structure, since the actual nature of the zeolite bonding is not always known. Synthesis conditions of different authors often vary in most subtle but important details, making comparison between work of different authors awkward. Comparison is also difficult with respect to the resulting zeolitic coatings, as it is difficult to quantify the success of the final product. However, effort will be taken to extract the most relevant data.

The general lay-out of this chapter is as follows: first some general information on the formation of zeolites will be given with the focus on zeolitic coatings. This information is more or less generic for zeolitic coatings prepared by in-situ synthesis. Then zeolitic membranes will be discussed. Typical for zeolitic membranes is the porous nature of the substrate and the special requirements of the final product. Pure zeolitic films will be treated next, followed by metal supported zeolitic coatings. Zeolitic coatings on siliceous supports will be treated in a separate section since this field has received relatively much attention in literature. Moreover, zeolite synthesis on siliceous supports differs from that on other supports, in that the carrier itself is also a nutrient source for zeolite synthesis.

Most literature is obtained from a Chemical Abstracts literature search, which covers all literature from 1967 to February 16, 1996. The results of the search are graphically summarized in Fig. 2.1.
Fig. 2.1 Result of an on-line literature search on zeolitic coatings. The numbers refer to the total number of hits using the given keywords.

Disclosure of relevant literature proved difficult since zeolitic coatings form a relatively new area of research in which no generally accepted definitions exist. The lack of consensus is strongest in patent literature where terminology reflects the different backgrounds of the researchers involved. Terms from biochemical and electrochemical disciplines were excluded from the search as well as articles in Russian and Japanese language.
2.2 Zeolites, General Information

2.2.1 Molecular Sieves and Zeolites

Molecular sieves are microporous materials, with pores of the size of molecular dimensions, 0.3-3 nm. Examples of molecular sieves include carbons, glasses and oxides. Some are crystalline with a uniform pore size, such as zeolites, while others are amorphous, e.g. carbon molecular sieves. Commercial adsorbent types, for example zeolites A, X or Y possess a singular pore size, which distinguishes them from amorphous activated carbon and alumina adsorbents with a broader pore size distribution and a larger mean pore diameter.

The four most current types of molecular sieves, characterized by their different TO₃ tetrahedra are:

- **Silicas:** SiO₂
- **Silicates:** TO₂ⁿ⁻ SiO₂ with n = 1, 2
- **Zeolites:** AlO₂⁻ SiO₂ with Si / Al ≥ 1
- **Phosphates:** AlO₂⁻ PO₂⁻ or GaO₂⁻ PO₂⁺

Pure silicas are composed of SiO₂-units. Silicates consist of SiO₂ and TO₂ units, in which T stands for an equal or lower valency atom that partly substitutes Si. Zeolites are actually silicates that have Al³⁺ as the substituting T-atom. This is however a definition that is hardly met in literature; the term zeolites is often used for describing any kind of synthetic molecular sieve. Zeolites are typically defined as crystalline porous tectoaluminosilicates (or other metal oxides), where oxygen bridges two tetrahedrally coordinated framework atoms.

Another class of molecular sieves consists of Al₂O₅PO₃ units (AlPO₄’s) whose Al or P constituents optionally may be substituted by other elements such as Si (silicoaluminophosphates or SAPO’s), or metals (metaloaluminophosphates or MeAPO’s) or combinations thereof (metaloalumino-phosphosilicates, MeAPSO’s). As with aluminosilicates, the AlPO₄’s, SAPO’s, MeAPO’s and MeAPSO’s are crystalline and microporous.

2.2.2 Synthetic and Natural Zeolites

The word zeolite was given to the material by Cronstedt. It reflects the bubbling (Gr. zeon=to boil) that is observed when the large amounts of water captured in the micropores escape upon heating the powdered (Gr. lithos=stone) material.

Their three-dimensional structure is built up by [SiO₄]⁻ and [AlO₄]⁻ coordination tetrahedra that are linked by all their corners. The frameworks are generally very open and contain channels and cavities in which hydrated cations and additional water molecules can be located. The geometry of the channels can be one-, two- or three-dimensional. The cations often possess a high degree of mobility, giving rise to easy ion exchange. Water molecules are gradually lost upon heating.
and can be regained. This accounts for the well-known desiccant properties of zeolites. The atomic composition of zeolites is given by:

$$\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot y\text{SiO}_2 \cdot w\text{H}_2\text{O}$$

where $y$ is the SiO$_2$/Al$_2$O$_3$ ratio, $n$ is the cation valence an $w$ represents the water contained in the voids of the zeolite. M is a metal ion, such as Na$^+$ or Ca$^{2+}$.

Having porous bodies with a skeletal structure with pores of regular geometry, zeolites form an interesting subject of scientific research. An important feature of zeolites is that the chemical composition of the crystal and the geometrical parameters (shapes and dimensions) of the intracrystalline pores can be varied. Structural and chemical modification is possible and can be achieved by varying either the conditions of synthesis or the composition of the reaction mixture. In comparative studies of adsorption on various zeolites, the geometry of the intracrystalline channels and cavities and the geometry of the “windows” leading to these cavities are extremely important. For zeolites of the same structural type, the nature of the exchange cations, their quantity, and their spatial distribution in the crystal lattice are also important.

At the moment, more than one hundred different zeolite framework types are known. Zeolites occur as natural minerals in abundance. Deposits of natural zeolites have been found at many places in the world, their occurrence is assigned to geological systems such as mountainous areas. In 1938, Barrer was the first to produce synthetic zeolites. Nowadays, many of the natural zeolites can be produced synthetically and moreover, many crystalline aluminosilicates with framework structures with no known natural counterpart have been made in the laboratory.

2.2.3 Nomenclature and Structure of Zeolites

According to IUPAC Commission on Zeolite Nomenclature, structure type codes of zeolite consist of three capital letters that are derived from their original name. These structure type codes have been developed to create a short nomenclature and do not depend on their composition, kind of T-atoms, cell dimensions or symmetry.

As zeolites are rather complex and possess very diverse structures, it is difficult to give a clear description of their structural frameworks. This is the reason that a general system for describing zeolite structures was developed by the structure commission of the IZA (International Zeolite Association). Zeolite frameworks are thought to consist of finite or infinite (i.e. chain-like- or layer-like) component units. The finite units that occur in the tetrahedral frameworks are called Structural Building Units (SBU’s). Describing zeolite structures is easily done by assuming that the entire framework is made up of just one type of SBU, although in certain cases, combinations of SBU’s need to be used. Sixteen types of SBU’s have been specified, containing up to 16 T-atoms. The SBU’s are invariably non-chiral. When studying zeolite structures, also a more detailed description, using Structural Sub Units (SSU), will be needed. Extended information about zeolite structures is given by Van Bekkum et al.
The framework density (FD) is expressed as the number of T-atoms per 1000 Å³. Non-zeolitic framework structures generally have an FD of 20 to 21 T/1000 Å³, whereas zeolites exhibit a FD, ranging from 11.1 (structures with the largest pore volume) to 20.5 T/1000 Å³. The microporous structure is reflected in a lower FD.

When classifying zeolites, a division in pore sizes is made. The pore size is determined according to oxygen atom packing models:

- **small pores:** eight-ring pores (viz. 8 T-atoms and 8 oxygen atoms), free pore diameter 0.30-0.45 nm. (e.g. zeolite A)
- **medium pores:** ten-ring pores, free pore diameter 0.45-0.60 nm (e.g. ZSM-5 and ZSM-11)
- **large pores:** twelve-ring or larger pores, free pore diameter ~0.8 nm (e.g. zeolites X, BEA and UTD-1)

The selective sieving effect of the zeolite depends on the pore size. For example, linear molecules may enter an eight-ring pore system, while their branched variant will be rejected. Also the geometry of the oxygen ring atoms determines the form and the free diameter of the pore opening. Large pore phosphate based materials already existed. Their practical value was however limited, because of poor (hydro)thermal stability.

### 2.2.4 Zeolite Characteristics

The fact that zeolites are rather special compared to other inorganic oxides can be illustrated by a number of specific properties:

- their microporous character with uniform pore dimensions: they are selective on a molecular scale,
- their excellent ion-exchange properties allowing all sorts of ion exchange reactions,
- their ability to develop internal acidity, which makes them interesting for catalyzing organic reactions,
- their high thermal stability,
- their high specific area (e.g. zeolite ZSM-5 offers a specific area of ca. 450 m²/g).

Zeolites are ideally suited for typical modifications, because all their metal-oxygen tetrahedra are exposed to the internal zeolite surface. Main types of modifications are:

- tuning of acidity and basicity over a wide pH range,
- exchange or isomorphous substitution of charge-compensating cations: (reversible) ion-exchange reactions and mostly irreversible chemical reactions such as reactions of zeolite protons with silanes to change pore size or to influence acidity,
- replacement of Si and Al in the zeolite framework and rearrangement of Si and Al atoms in the fine-tuning of structural and acidic properties,
- substitution (Al ↔ Si),

20
• extraction (Al-removal),
• insertion reactions (Si-insertion),
• other metal atoms than Al and Si can be introduced in the framework, such as boron, iron, gallium or phosphorus,
• introduction of small metal particles: often applied in industrial syntheses of zeolite catalysts,
• possibility of entrapping metal crystallites and metal complexes within the microporous environment (isolated redox-centers in the lattice).

2.2.5 Zeolite Synthesis

The chemical sources for synthesis of aluminosilicates and their function are given in Table 2.1.

<table>
<thead>
<tr>
<th>Source</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>Primary building units of the (alumino)siicate framework</td>
</tr>
<tr>
<td>AIO$_2$-</td>
<td>Origin of the framework charge</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>Mineralizer</td>
</tr>
<tr>
<td>Alkali cation, template</td>
<td>Counterion of framework charge, guest molecule (mold)</td>
</tr>
<tr>
<td>Water</td>
<td>Solvent, guest molecule</td>
</tr>
</tbody>
</table>

$Molar\ composition:\ pAl_2O_3:qSiO_2:rK_2O:sNa_2O:TPr_3O:u\ H_2O$

$SiO_2$- and $AIO_2$: sources
The Si-source is important as it may favor a crystallization of a particular zeolite type. This is, for instance caused by a difference in the solvability of the sources used (mainly caused by differences in particle size). Zeolite synthesis is a very fragile process and the rate of dissolution can influence the crystallization process and therefore the quality of the product formed. The content of impurities of the Si-source may change the crystal form and chemical properties. Impurities also promote heterogeneous nucleation, i.e. the impurity serves as a nucleus and the zeolite is crystallizing by surrounding this nucleus. The $AIO_2$:source is not as critical as the $SiO_2$:source. Although dissolution is often difficult, the $Al_2O_3$:source is generally very pure and consists of small particles.

Alkali cation / template
The cations or templates function as a mold, around which the zeolite crystal structure is built. They may be either charged or neutral molecules and always contain a certain functional atom or group. Organic as well as inorganic cations show structure directing, i.e. water-ordering properties. The water molecules comprising a tetrahedral network in the first layer around the cation might be partly replaced by silica and alumina anionic tetrahedra. In this way, the clathrated cations serve as crystal building units. Inorganic templates used are alkaline or ammonium ions. Most templates encountered in zeolite synthesis are summarized by Jansen.\textsuperscript{10}
**Chapter 2**

**OH⁻**
Zeolite synthesis is generally carried out in a basic environment (pH >10), using OH⁻ as a mineralizing agent. Another substance, with a completely different nature, F⁻, may be used. ¹⁰ These F⁻-anions form the counterion of the organic and inorganic cations used in the synthesis. These mineralizing agents may contain certain impurities, such as Al³⁺ and Fe²⁺.

**The Zeolite Reaction Process**
Zeolite formation is thought to take place by a low temperature process, prior to a high temperature process. The low temperature process takes care of the preparatory requirements, i.e. mixing of the reaction sources, resulting in a gel, sometimes followed by aging. Upon further heating of the synthesis mixture, gel rearrangements take place in which dissolution of the gel and silicate dissociation takes place. ¹⁰,¹¹

**The High Temperature Process**
The main event occurring in the synthesis mixture at the reaction temperature is the formation of zeolites from amorphous material. The high temperature process realizes the following chemical reactions:

1) further reorganization of the low temperature synthesis mixture,
2) followed by primary (homogeneous) and secondary (heterogeneous, seed crystals) nucleation,
3) and finally precipitation on the nuclei, as a form of crystallization.

**Nucleation**
When the reaction mixture is at its actual zeolite formation temperature, crystallization is expected after an induction period during which nucleation occurs. In the low temperature process, the gel and species in solution rearrange from a continuous changing phase of monomers to clusters of (poly)silicates and aluminosilicates. These clusters form and disappear by condensation and hydrolysis, under the influence of the higher temperature. In the course of this reorganization process, particles become stable and small nuclei (typically 10 Å for Na-A and 20 Å for ZSM-5) have been formed before the actual crystallization (‘growth’) starts.

**Crystallization**
Zeolite crystal formation can take place according to three different formation and crystallization mechanisms:

1) Crystallization from a **clear synthesis solution**: homogeneous nucleation, prior to crystallization. The driving force for crystallization is equal in all directions.
2) Crystallization in a reaction mixture containing a **highly dispersed gel** (of building clusters in water): heterogeneous nucleation occurs at the liquid-gel interface in the dispersed gel-solution mixtures. The driving force for crystallization is varying in all directions, the zeolite crystals may therefore adopt very specific forms. Besides, homogeneous crystallization will occur. In synthesis of zeolitic coatings, the varying driving force for crystallization is thought to be responsible for the orientation of the crystals on the support.
3) Crystallization in a heterogeneous reaction mixture containing a support, covered with a gel film: crystallization proceeds into the gel. Deviating crystal forms, compared to crystal forms from dispersed gel systems are observed.

In 2) and 3), dynamic equilibria between successive steps of dissolution, ion transportation and precipitation can be recognized. Especially the precipitation/crystallization step, i.e. the type of crystal building units and the way of crystal growth on the molecular level, has been subject of many studies.

**Nucleation-crystallization Kinetics**

Nucleation and crystallization events are generally described by characteristic S-shaped crystallization curves. The amount of crystalline material, plotted versus time, gives an impression of the nucleation and crystallization rates. As soon as the crystallization starts, the chemical nutrients are consumed for crystal growth. From then on, formation of new nuclei is almost completely suppressed. When the linear crystal growth rate and the rate of nucleation can be determined, based on crystal size and size distribution, more accurate information on the crystallization kinetics can be provided. Crystallization is however very sensitive to many external factors.

**Energy of Activation**

Most nucleation and zeolite crystallization processes take place at elevated temperatures, ranging from 60 to 250 °C. The rate of nucleation is taken to be the reciprocal induction period and the rate of crystal growth as the slope of this curve at 50% conversion. Activation energies can then be calculated from these rates recorded at different temperatures. Both activation energies depend strongly on Si/Al ratio and template used.
2.3 Background of Zeolitic Coatings

2.3.1 Synthesis Techniques

Different methods of preparation of zeolitic coatings can be distinguished, the main difference being whether the composite is prepared with or without using a binder. A binder will simply function as a glue, to keep the support and the already prepared zeolite crystals in contact. When no binder is used and the zeolite is grown directly onto the support surface, this is referred to as in-situ growth. Also other synthesis methods (e.g. from condensed hydrogel) are applied without using a binder.

The four main methods for preparation of zeolitic coatings are:

1) Dip-coating\textsuperscript{16,17}: covering of a support with already existing zeolite crystals with the help of glue (generally an aqueous binder), resulting in a composite consisting of three substances: the support, the binder and the zeolite layer. Dip-coating is an efficient and versatile technique for the deposition of thin layers of an oxidic material on all sorts of supports of various shapes. The bonding between the zeolite crystals and the metallic or oxidic support are formed by condensation reactions between the SiOH groups on the outer zeolite surface and hydroxyl groups on the support. It is therefore required that both the zeolite material and the support possess reactive surface groups. However, to increase the still rather weak interaction between the zeolite and the support, a precursor of an aqueous binder is usually added to the zeolite slurry. Upon curing, the binder assists in the formation of a strongly bonded zeolite layer on the support. The main shortcoming of dip-coating is that total coverage of the support surface with a closed layer of zeolite crystals will hardly be obtained. Therefore, dip-coating is generally not applied in membrane synthesis but could be useful in adsorption and catalysis.

2) Slurry coating\textsuperscript{16,17}: covering of a support with a zeolite layer by contacting it to a dispersion of zeolite crystals followed by evaporation of the liquid. Deposited crystals are left bonded to the surface by Van der Waals forces. The slurry coating technique can in potential provide a uniform surface coverage and also enables monolayer coverage but the main problem is to assure a homogeneous deposition of the zeolite crystals, since the formed film always suffers from evaporating liquid. The choice of the dispersion liquid is therefore critical. When choosing a liquid, the boiling point and the heat of vaporization of the substance are important. The solvent has to be of high purity, as nonvolatile impurities will be concentrated when the solvent is evaporated. This results in a change of physical properties of the suspension and in less uniformity of the coating. The main application of slurry coating of zeolite crystals is in the preparation of chromatography columns.

3) In-situ synthesis from a diluted reaction mixture solution\textsuperscript{18}: an (oriented) layer of zeolite crystals is directly grown onto the support surface, i.e. there is no gel layer functioning as an intermediate.

4) In-situ synthesis from a condensed hydrogel\textsuperscript{18}: growth of an (oriented) layer of zeolite
crystals on a support surface after a silica rich hydrogel has been condensed onto the support firstly. The gel forms the nutrient-rich environment for zeolite nucleation and crystallization. These processes find place at the gel-liquid interface and at the initial state of nucleation and crystallization, the zeolite is not directly connected to the support surface. In-situ synthesis will be treated in more detail in the next sections.

The films prepared by those methods may be different concerning:

- intercrystal porosity
- molecular accessibility to intercrystal micropores;
- orientation onto the support;
- bonding strengths between the crystals and the support;
- uniformity of coverage with respect to the support;
- degree of coverage of the support;
- thickness of the formed layer of crystals.

These differences are the results of:

- Dip-/slurry-coating: the concentration of the dipping/slurry-solution, the character of the binder, the number of repeated dipping, etc.
- Direct synthesis: the synthesis time and temperature, the composition of the reaction mixture, the support character, etc.

2.3.2 Orientation of Zeolite Crystals

The orientation of zeolite crystals can differ with respect to the support:

- random orientation: both axial and lateral orientation, often in combination with multilayer coverage. In general, mainly polycrystalline zeolite crystals (twinned and/or intergrown) are connected by an amorphous silica phase.
- axial orientation: MFI type zeolite crystals can be oriented with their c-direction perpendicular to the support, i.e. the crystals are ‘standing’, with their smallest face connected to the support surface. Axial orientation is especially desired, when the zeolitic composite is to be used for catalytic objectives. In this conformation, optimal exposure of the outer crystallite surface to the reaction mixture to be converted is obtained.
- lateral orientation: when MFI type zeolite crystals are oriented with their c-direction parallel to the support, the crystals are ‘lying’ on the surface. Perfectly closed laterally orientated crystal films are desired to let the composite function as a membrane. Some macroporous, intercrystal pores are allowed, as they lower the pressure drop across the membrane.

In general, random orientation will be obtained. Especially desired are axially oriented or laterally orientated films, depending on the application.
2.3.3 Growth Modes

Thin films are formed on a substrate by a process of nucleation and growth. The initial stage is the formation of small clusters of the film material from individual atoms or molecules. A (continuous) film is formed when time progresses and more clusters are nucleated that grow and coalesce.

The study of zeolite films can benefit from general theory on formation of coatings, which is reviewed briefly by Jansen et al. and where thermodynamic and kinetic aspects of film formation are discussed. A classification in different growth modes is made according to the type of film formed. The mode determines the morphology, structure and properties of the film surface.

**Table 2.2 Film growth modes and their resulting coverage**

<table>
<thead>
<tr>
<th>Growth mode</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer mode</td>
<td>Substrate coverage by one or a few mono atomic layers.</td>
</tr>
<tr>
<td>(Frank-van der Merwe mode)</td>
<td></td>
</tr>
<tr>
<td>Island mode</td>
<td>Substrate coverage by nucleation and growth of separate island-like crystallites of multi atomic height. Grain boundaries may be developed between the separate crystallites and the film may become polycrystalline.</td>
</tr>
<tr>
<td>(Volmer-Weber mode)</td>
<td></td>
</tr>
<tr>
<td>Layer-plus-island mode</td>
<td>Combination of layer and island growth, formation of one or more monolayers is followed by growth of island-like crystallites on top.</td>
</tr>
<tr>
<td>(Stranski-Krastanov mode)</td>
<td></td>
</tr>
<tr>
<td>Continuous</td>
<td>Substrate coverage by simultaneous filling of several monolayers. Filling is a random process and not nucleation mediated. Film is of low crystallinity or even amorphous.</td>
</tr>
<tr>
<td>(normal or liquid-like mode)</td>
<td></td>
</tr>
</tbody>
</table>

Types and characteristics of the most observed film growth modes are given in Table 2.2. Generally most desired is a uniform monolayer or multilayer coverage with a single crystal structure, formed according to the layer mode.

The reason for formation of different growth modes is still not fully understood. A thermodynamic explanation is given by Bauer. Before the formation of the film, a single substrate/solution (or gel) interface with specific free energy \( \sigma_s \) \((J/m^2)\) exists. After formation of a continuous, uniformly thick film, the specific energies of the film/solution (or gel) \( \sigma_f \) and the substrate/film \( \sigma_{sf} \) result in the following energy change: \( \Delta \sigma = \sigma_f + \sigma_{sf} - \sigma_s \), where \( \Delta \sigma \) represents the specific energy change of film formation. Two cases can be distinguished:

\( \Delta \sigma \leq 0 \): criterion for layer growth of the substrate by the liquid film, formation film as a continuous layer is energetically favorable. The interaction between a molecule of the film and a molecule of the substrate is stronger than or equal to the interaction between two molecules of the film, resulting in complete wetting.
\[ \Delta \sigma > 0: \] criterion for island growth as the system is in a lower energy state if the film is broken into separate parts (islands). A film-substrate molecular pair is then more weakly bound than two molecules of the film, resulting in incomplete wetting.

Venables and Price\textsuperscript{19} state that film formation is essentially a kinetic phenomenon that can be changed by varying the growth conditions. Existence of supersaturation, \textit{e.g.} a critical temperature or solution concentration, for growth mode transition has been observed in laboratory and computer experiments\textsuperscript{21}. The modes of thin film growth and the transitions between them can be analyzed solely with the aid of kinetic considerations. Kashchiiev proposed the theory of polylayer growth as a support for a kinetic analysis\textsuperscript{22}. In this theory, the modes of thin film growth are described and the condition for transition between them is obtained in a general form. Growth is assumed to be entirely determined by the growth conditions. The initially bare, atomically smooth substrate is supposed to possess nucleation-active sites due to, for example, edge dislocations, but is free of screw dislocations. Building up of the film occurs via simultaneous filling of a number of layers, not necessarily monoatomic layers, each of them being deposited only on top of the layer underneath.

When covering a surface, the film formation will roughly develop as represented by the S-shaped kinetic growth curve. Three well-specified regions, representing different stages of the deposition process, can be recognized:

In the initial stage, nucleation on the bare substrate surface will take place. First, holes or irregularities in the substrate surface will be filled up and the successive growth of zeolite grains to an experimentally observable size will follow. This period of film formation crucially depends on the gel composition and temperature as well as on the substrate surface quality and pretreatment mode.

In the second region, the film thickness linearly increases with time. It is therefore possible to define a constant deposition rate in terms of change of the film thickness with time measured by the slope of the linear part of the kinetic curve. The dominating growth finding place in this region is the approximate regular increase in the size of the zeolites crystals, formed in the nucleation period. This will finally result in (incomplete) monolayer coverage of the substrate surface. When the surface was not completely covered in the initial stage of the formation process, also secondary nucleation on the uncovered parts of the substrate surface may proceed during this stage. This is generally resulting in formation of zeolite crystals of a smaller size. It can also cause a change in the slope of the linear part of the kinetic curve.

The final period is characterized by a decrease of the film growth rate as a consequence of exhaustion of the synthesis gel. Exhaustion will show up when quasi-equilibrium conditions have been established between the formation and dissolution of zeolite crystals on the film surface.

From this it follows that surface cleaning and further pretreatment of the support is important, in that it affects the first and in lesser extent the second stage of film formation.
Chapter 2

2.3.4 Synthesis of Zeolitic Coatings

Pretreatment and Cleaning of the Support
Before synthesizing a zeolite film onto a support, the support has to be cleaned thoroughly. In addition, other forms of pretreatment can be carried out with the aim of increasing the number of sites for nucleation of the zeolite crystal precursors. This will produce more uniform and more tightly bounded zeolitic coatings.

Cleaning of the support is not much discussed in literature but is an important factor, as zeolite synthesis is very sensitive to contamination. Cleaning aims to remove organic and inorganic contaminations and it is desirable to leave hydrophilic surface sites. Generally, organic contaminants are removed by boiling in xylene or toluene. Inorganic contaminants are removed by washing with hydrochloric or hydrofluoric acid. In Chapter 3 the effects of cleaning a stainless steel surface with acetone prior to zeolite Beta synthesis is shown to have a positive effect on coverage. This is in agreement with results of Valtchev and Mintova\textsuperscript{23} who found a more continuous ZSM-5 film after acetone treatment. Probably this is to be attributed to the cleaning effect of acetone rather than to surface modifications that result from it. In any case, it clearly demonstrates the critical effect of surface pretreatment. Jansen et al.\textsuperscript{24} use a thorough cleaning procedure that involves steps used in semiconductor industry. In this procedure organic contaminants are removed in two steps followed by an inorganic contaminant removal step and ultra sonic treatment.

After cleaning the support surface, it can be pretreated chemically or heated in air or oxygen to produce an oxide film. The aim of this is to promote nucleation of zeolite crystals. An approach that has been taken by several authors is to attempt to form a bond between the support and the template molecule or mimic the template functionality prior to zeolite synthesis. Anderson et al.\textsuperscript{25} suggest that the positively charged Dabco polymeric template (polymer formed of 1,4-diazabicyclo[2.2.2]octane and 1,4-dibromobutane: \(\text{1-N}_{2} \text{C}_{2} \text{H}_{12} \text{Br}^{2-} \cdot \text{C}_{4} \text{H}_{8} \cdot \) ) used to prepare mesoporous films on PTFE substrates attaches to the substrate during synthesis. This is also the case in the work of Van der Pul et al.\textsuperscript{26} who increase zeolite Beta coverage by pretreatment with a dilute template solution which is assumed to form a bond with the substrate surface (see also Chapter 3). The possibility of linking template molecules to the substrate surface is most clearly demonstrated by Althof et al.\textsuperscript{27}: the expected mimic effect of the functionality of the tetra-\(\text{C}_{2}\)-propylammonium (TPA) template ion used for MFI synthesis by linking tri-\(\text{C}_{2}\)-propylammonium group through a thiol linker to a gold surface, proved to be effective. Most interesting with this respect is the work of Feng and Bein\textsuperscript{28} who succeed in growing zinco-phosphate (FAU framework structure) with almost perfect orientation on a self-assembled organophosphonate film formed on a gold substrate. Their approach is inspired by features of biomineralization and demonstrates elegantly the possibilities of in-situ zeolite synthesis.

Apart from treatment with chemicals, mechanical deformation and thermal annealing of the support are known to have a promoting effect. This is either caused by increased number of nucleation sites or by enhanced wetting of the support by the synthesis mixture\textsuperscript{29}.
2.4 Zeolitic Membranes

In the past decades, the application of membranes for separation on an industrial scale has largely increased, caused by the fact that membrane separations are often the fastest and most energy effective separation techniques. Under normal conditions, organic/polymeric membranes are used since inorganic membranes show disadvantages like high costs, brittleness and lower specific surface areas. However, under extreme conditions, inorganic membranes are especially desired, because of their resistance to temperatures exceeding 200°C, high pH levels and aggressive organic media. Also their higher life-time and their easy regeneration by high temperature treatment are advantageous. The synthesis of zeolite crystals onto the porous membrane surface was initiated by a demand for increased specific surface area and reproducible, narrowly defined pore sizes. By this, a more economical separation of gases, better filtration and also integration of separation and catalysis was expected to be enabled. The smallest pore size reported for industrial (non-zeolitic) membranes is 5 nm,\textsuperscript{30} which justifies the research after zeolite membranes where pore sizes could be that of the zeolite micropores (i.e., tens of nanometers) thus leading to the highest selectivities theoretically achievable, allowing the separation of molecules based on their size.

2.4.1 Reported Zeolitic Membranes

The history of zeolitic composites started by the technique of dip-coating\textsuperscript{11} which was later applied to production of zeolite covered membranes\textsuperscript{32}. A porous support was covered with an inorganic matrix, in which zeolite crystals were embedded. However, by this method it is not possible to produces membranes with a satisfactory degree of continuity, required for membrane selectivity. The first in-situ synthesis, of zeolite Na-A on a stainless steel support layer, was carried out by Suzuki \textit{et al.}\textsuperscript{33} This was followed by an increasing amount of other investigations, of which an overview is given in Table 2.3. Noble and Falconer\textsuperscript{34} briefly review silicalite-1 membranes, which constitute the majority of the membranes produced to date. In a more comprehensive review by Jansen and Coker\textsuperscript{35} also membranes formed of other zeolite types are discussed.
Chapter 2

Table 2.3 Summary of zeolite covered membranes

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Support</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite A</td>
<td>Stainless steel</td>
<td>33, 36-38</td>
</tr>
<tr>
<td>(Na-A)</td>
<td>α-Alumina with Zirconia</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>α-Alumina</td>
<td>38, 39</td>
</tr>
<tr>
<td></td>
<td>Alumina by slurry-coating</td>
<td>40</td>
</tr>
<tr>
<td>Analcime</td>
<td>α-Alumina</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Metakaolin</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Metakaolin on clay</td>
<td>41</td>
</tr>
<tr>
<td>Silicalite-1</td>
<td>Stainless steel</td>
<td>42-46</td>
</tr>
<tr>
<td></td>
<td>α-Alumina</td>
<td>47, 48</td>
</tr>
<tr>
<td></td>
<td>Ceramic clay</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Carbon hollow fibre</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>γ-Alumina by dip-coating</td>
<td>51</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>α-Alumina</td>
<td>44, 52-54</td>
</tr>
<tr>
<td></td>
<td>Carbon hollow fibre</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Pyrex glass plate (Borosilicate glass)</td>
<td>55-57</td>
</tr>
<tr>
<td></td>
<td>Cordierite monolith (MgO/Al₂O₃/SiO₂)</td>
<td>55-57</td>
</tr>
<tr>
<td></td>
<td>Mullite monolith (3Al₂O₃/2SiO₂)</td>
<td>55-57</td>
</tr>
<tr>
<td></td>
<td>Non-oxide ceramics by dip-coating</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>Alumina by slurry-coating</td>
<td>40</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Carbon hollow fibre</td>
<td>50</td>
</tr>
<tr>
<td>Ferrierite</td>
<td>α-Alumina</td>
<td>59</td>
</tr>
</tbody>
</table>

2.4.2 Permeability Studies

Table 2.4 lists permeation studies conducted on zeolite membranes. The first description of molecular flow through zeolite membranes was made by Barrer. Furthermore, some extensive studies about permeation behaviour of silicalite membranes were carried out by Kapteijn et al. and Geus et al. Both Fickian and Maxwell-Stefan diffusion models were considered and also behavior in different temperature and saturation regions was investigated. In general, transport through zeolitic membranes appears to be controlled by adsorption properties and indeed molecular sizes of the gas mixture.
### Table 2.4  Permeability studies performed on zeolitic membranes

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Subject of study</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicalite single crystal</td>
<td>Permeability studies on a single crystal membrane model, Henry region (silicalite crystal embedded in an epoxy resin) - H₂, N₂, O₂, CO₂ - CH₄, C₂H₆, n-C₄H₁₀</td>
<td>64</td>
</tr>
<tr>
<td>Silicalite-1/stainless steel</td>
<td>Single- and multi-component transport - noble gases - lower n-alkanes - butane isomers - CFC-12 - 2,3,4-trimethylpentane</td>
<td>43</td>
</tr>
<tr>
<td>Silicalite-1/ceramic clay</td>
<td>Permeation measurements (Henry region) - Ne, Ar - CH₄ - n-butane, isobutane</td>
<td>49</td>
</tr>
<tr>
<td>Silicalite single crystal</td>
<td>Time-lag measurements for intracrystalline diffusion of aromatics (silicalite crystal embedded in an epoxy resin) - benzene - toluene - o,p,m-xylene</td>
<td>65</td>
</tr>
<tr>
<td>Silicalite-1/stainless steel</td>
<td>Temperature- and occupancy dependent diffusion (Maxwell-Stefan model) - n-butane</td>
<td>62</td>
</tr>
<tr>
<td>Silicalite-1/stainless steel</td>
<td>Permeation and separation behavior for single and binary mixtures as a function of temperature (steady state) and time (transient) (Maxwell-Stefan) - H₂, CO₂ - n-butane</td>
<td>63</td>
</tr>
<tr>
<td>Silicalite-1/stainless steel</td>
<td>High-temperature membranes: preparation module construction and permeation (350°C) - Ne - CH₄ - n-butane, isobutane</td>
<td>66</td>
</tr>
</tbody>
</table>
Chapter 2

2.4.3 Supports Used for Synthesis of Inorganic Zeolitic Membranes

Requirements that have to be met for synthesis of zeolitic membranes are:

- high thermal stability,
- thermal expansion coefficients matching that of the zeolite deposited or being low enough to ensure the bonding is left intact (for example: ZSM-5: $\sim 1 \times 10^{-6} / ^\circ \text{C}^{67}$ vs. $\alpha$-alumina: 8.5 $10^{-6} / ^\circ \text{C}^{41}$ appears to ensure good bonding$^{68}$), upon thermal cycles,
- high chemical resistance,
- regular pore sizes,
- high mechanical strength and
- receptive towards zeolite synthesis, i.e., OH-groups at surface.

The supports used for synthesis are in the classes of:

- Oxide ceramics: e.g. alumina, silica, titania or zirconia,
- Non-oxide ceramics: carbides (e.g. silicon carbide),
- Stainless steel (e.g. AISI 316) or
- Microporous carbons.$^{50}$

Although stainless steel may not possess such thermal qualities as ceramics, it turns out to be a suitable and useful support for moderate temperature applications. Synthesis on supports consisting of carbon has not yet been investigated intensively but it is however a rather cheap alternative for expensive ceramics.
2.5 Pure Zeolitic Films

In the previous section composite zeolitic membranes were discussed. In such membranes, in addition to the presence of a zeolite phase, the membrane material always contains a second phase with distinctly different chemical, physical and morphological properties. The separation performance of composite membranes is therefore determined by the individual properties of the different phases and phase boundaries. The major restriction of composite membranes is that it is often difficult to match the two different components to obtain the desired properties (e.g. differences in thermal expansion coefficients or in thermal stability).

Self-assembling or self-supporting two-dimensional structures with molecular-sieving properties are expected to have a higher performance than the corresponding zeolitic membrane composites. These self-supporting zeolitic films (also called ‘pure molecular sieves’ or ‘non-composite zeolitic membranes’) possess unique molecular sieve and/or catalytic properties due to the well-defined pore structure of zeolites. They essentially consist of only one molecular sieve material, in contrast with composite membranes which contain molecular sieve material in combination with the support material. The membrane can be ‘mono-crystalline’, consisting of a single sort of zeolite crystal. When continuous intergrowth of different zeolite crystals is observed, the membrane is entitled ‘poly-crystalline’. Typical of pure zeolitic films is that it is possible to synthesize almost completely oriented films. Many attempts have been made to prepare oriented film sensor membranes of zeolites. However, with all these approaches, the preparation of oriented films is virtually impossible and almost completely oriented crystallite films have hardly been obtained yet.

2.5.1 Reported Pure Zeolitic Films

Different self-supporting zeolite films have been synthesized: perpendicularly oriented gmelinite-films, silicalite-1-films, and ZSM-5-films with non-uniform crystallinity and non-uniform SiO₂/Al₂O₃ distributions. Recently, also formation of a ZSM-5 membrane on a mercury surface has been reported. The membranes were all produced on non-porous substrate surfaces with the exception of the work of Sano et al. who use cellulose as a substrate that is removed by calcination afterwards.

2.5.2 Synthesis of Pure Zeolitic Films

The reported syntheses were carried out under hydrothermal conditions in different ways:

1) Growing the film on a non-porous support slab and removing it before or after calcination. This method of making pure zeolitic films is often applied. Reported were gmelinite films of one crystal thick and ZSM-5 films with thicknesses of ca. 30-100 µm and of 20-250 µm. The films of Tsikoyiannis and Haag were the only
pure zeolitic films that were subject of permeability studies. Permeability ratios as high as 17.2 (for \(n\)-hexane vs 2,2-dimethylbutane mixture) were reported, demonstrating the high quality of the prepared film.

2) Fehlner et al.\textsuperscript{99} reported synthesis mixture compositions for the formation of silicalite-1 and ZSM-5 films. Apart from film formation on walls of the autoclave, the possibility for film formation on the surface of the solution is mentioned. The silica sources used were silicone polymers: Silastic 590\textsuperscript{98}: polydimethoxysilane, contains vinyl groups attached to silicon atoms and finely divided SiO\textsubscript{2} powder dispersed in the polymer, 2-part formulation and Sylgard 184\textsuperscript{98}: unfilled silicon polymer. Also synthesis of compact pure molecular sieve objects in a basket like molding was presented.

3) Growing the film on a cellulose molding (\textit{e.g.} filter paper) was reported by Sano et al.\textsuperscript{72}. During calcination (500 °C, 20h), the molding was burnt from the composite, leaving an intact pure molecular sieve. Non-oriented ZSM-5 films were obtained with a large thickness of \(ca.\) 500 µm, and increased strength, compared to films synthesized by method 1). The advantage of using a cellulose molding is that it can be preshaped in several forms and, therefore, allows easy shape control of the ZSM-5 film. The obvious drawback is that the zeolitic film suffers from macroscopic defects.

### 2.5.3 Supports Used During Synthesis

To create the two-dimensional surface of the molecular sieve film, a non-porous, relatively inert (\textit{i.e.} forming no strong bonding with the zeolite film) support slab is needed. Required is that the formed film can be removed from the slab without breakage. In most cases fluorocarbon polymers ('Teflon', \textit{e.g.} PTFE, FEP) are used, because contamination and nucleation on the walls is minimized. Suitable metal support slabs are silver, nickel and mercury.\textsuperscript{76} Although also aluminum, stainless steel and silicon wafers were mentioned as adequate slabs,\textsuperscript{10,73,74} removal of intact films from these supports has not been achieved yet. The film strongly interacts with the support, because also composite layer growth was achieved with these supports (Section 2.6.1). Synthesis on metal coated glass was also mentioned.\textsuperscript{73,74}

The layer of formed crystalline material may be removed from the non-porous surface by various means, depending upon the material chosen for the forming surface. The layer can be separated from polymeric surfaces by mechanical means (scrapping, peeling). Removal from silver surfaces may be accomplished by wetting with acetone. Removal from stainless steel surfaces was not possible as the film bonding was too strong.\textsuperscript{75} With a support consisting of Teflon, metal or metallized material (\textit{e.g.} aluminum on glass), treatment with an aqueous mineral acid can be employed.
2.5.4 Calcination of Pure Zeolitic Films

The film is preferably removed before calcination, because wet films are extremely malleable and can be formed into various shapes. The dried film is rather brittle, because of its small thickness. Calcination has to take place in an inert atmosphere or in air. The temperature applied, is in the range of 200 °C to 700 °C, calcination time varies from 1 to 50 hours. A low calcination rate, of 1°C/min or less, is needed, because of the increasing fragility of the film during heating.

2.5.5 Crystallinity Distribution Across the Film / Steaming

Sano et al. found non-uniform alumina distribution across the ZSM-5 films synthesized on PTFE sleeves. Concentrated synthesis mixtures gave rise to formation of a non-coherent powdery zeolite film. In case a higher water content was used, films with thickness of 30-100 μm were obtained. The alumina concentration on the side originally connected to the support slab was higher than that on the side in contact with the reaction mixture. This may be caused by the lower solubility of the AlO₂-units in the reaction mixture. The crystals on the support side were packed more closely than on the mixture side and more polycrystalline aggregates were included with increasing crystallization time. To obtain a more regular alumina distribution, the films were brought in contact with water vapor at 170°C to induce recrystallization. It was concluded that recrystallization found place by reorganization of polycrystalline aggregates that were initially incorporated in the ZSM-5 layer.
2.6 Metal supported Zeolitic Coatings

Zeolitic coatings consisting of zeolite crystals bonded to a metal support is another field of zeolite science that is still gaining interest. Although the support can be porous, many non-porous surfaces are described. Metals are especially convenient for deposition of zeolite layers as they can be formed in various shapes, showing high thermal stability and rather high acid resistance.

At the moment, the main objectives for preparing metal supported zeolitic coatings are their applications in catalysis and sensor technology. For catalytic aims, often an axial orientation of the crystals is desired to reach maximum exposure of the zeolite crystals to the fluid flowing along the support. However, a not yet realized alternative system may require a perfectly closed and laterally oriented zeolite layer to achieve highly selective catalysis (see, for example, Van der Puil). The catalyst is deposited between the zeolite layer and the support, or the catalyst may be formed by the support metal itself.

2.6.1 Reported Metal Supported Zeolitic Coatings

A short overview of reported zeolitic coatings on metal supports is given in Table 2.5. A large difference in the quality of the publications was observed.

One of the first attempts to synthesize a zeolite-metal composite was made by Davis et al. The formation of zeolite Y on a copper support has extensively been described and a lot of analytical information was included. Synthesis of NaA and ZSM-5-type zeolites (silicalite) on several metal and silicon supports was also reported. Films with a thickness between 3 and 30 μm precipitated. The influence of the dilution of the reaction mixture on the orientation of ZSM-5 type zeolite crystals was studied by Jansen et al. Observed was, that at a dilution of H2O/Si=2800, the crystals adopted a lateral orientation. At dilutions higher than 6900, axial orientation seemed to be preferred.

The synthesis of mordenite on chromium powder was studied by Xu et al. The formed composite, HMOR/Cr proved to be a suitable catalyst for the isomerization of xylene. The synthesis was carried out at 170°C under autogeneous pressure by the so called 'vapor phase method'. The water and the amorphous gel/chromium mixture in the autoclave were separated by a filter.

Furthermore, the synthesis of ZSM-5 on stainless steel 316 wire gauzes is interesting, because it is one of the first reports about a practical application of a zeolitic coating. The Cu-exchanged composite was used for Selective Catalytic Reduction (SCR) of NOx with ammonia (see Chapter 6). Analytical information about the composite and also reactor performance data were included.
### Introduction to Zeolitic Coatings

Table 2.5  Summary of reported zeolite films on metal supports, numbers in bold face refer to literature containing extensive information.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Support</th>
<th>Film</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>Copper</td>
<td>+</td>
<td>23,24,29,79</td>
</tr>
<tr>
<td></td>
<td>Copper alloy (79.3%Cu; 20.7%Ni)</td>
<td>+</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Brass alloy (67.3%Cu; 32.7%Zn)</td>
<td>+</td>
<td>23,79</td>
</tr>
<tr>
<td></td>
<td>Tin coated copper</td>
<td>+</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Tin</td>
<td>—</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Tin alloy (80.3%Sn; 19.7%Pb)</td>
<td>—</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Nickel</td>
<td>+</td>
<td>23, 24</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td>—</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Chromium</td>
<td>—</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Titanium</td>
<td>+</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Aluminum</td>
<td>+</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Silver</td>
<td>+</td>
<td>23,79</td>
</tr>
<tr>
<td></td>
<td>Stainless Steel</td>
<td>+</td>
<td>80, 24</td>
</tr>
<tr>
<td></td>
<td>'Pig iron' (95.1%Fe; 2.8%C; 0.8%Si)</td>
<td>+</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>08KP Steel (a.o. 96-98% Fe)</td>
<td>+</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>4x28 H 12 Steel (a.o.18.0%Cr;13.0%Ni;65%Fe)</td>
<td>—</td>
<td>23</td>
</tr>
<tr>
<td>Zeolite Y</td>
<td>Copper</td>
<td>+</td>
<td>81, 82</td>
</tr>
<tr>
<td></td>
<td>Copper alloy</td>
<td>+</td>
<td>23,29,79</td>
</tr>
<tr>
<td></td>
<td>Brass alloy</td>
<td>+</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Tin coated copper</td>
<td>+</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>Tin</td>
<td>—</td>
<td>79</td>
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<tr>
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<td>Tin alloy</td>
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<td></td>
<td>Nickel</td>
<td>+</td>
<td>23</td>
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<tr>
<td></td>
<td>Lead</td>
<td>—</td>
<td>23</td>
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<tr>
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<td>Chromium</td>
<td>—</td>
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<tr>
<td></td>
<td>Silver</td>
<td>+</td>
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<td></td>
<td>'Pig iron'</td>
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<td>23,79</td>
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<td></td>
<td>08KP Steel</td>
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<td>23</td>
</tr>
<tr>
<td></td>
<td>4x28 H 12 Steel</td>
<td>—</td>
<td>23</td>
</tr>
<tr>
<td>NaA</td>
<td>Copper</td>
<td>+</td>
<td>18</td>
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<td></td>
<td>Nickel</td>
<td>+</td>
<td>18</td>
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<td></td>
<td>Titanium</td>
<td>+</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Stainless Steel</td>
<td>+</td>
<td>18</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Chromium</td>
<td>+</td>
<td>82</td>
</tr>
</tbody>
</table>

37
2.6.2 Synthesis of Metal Supported Zeolitic Coatings

The bonding of zeolites to the metal support is thought to be between the hydroxyl groups of the oxide layer of the surface and the connecting SiO₄ and AlO₄-tetrahedra of the zeolite. Zeolite growth is thus expected to start via a condensation mechanism, resulting in a chemical bonding of the crystal on the surface. The bonding will exist even after calcination and under most reaction conditions when the composite is used as a catalyst.

Synthesis is generally carried out hydrothermally. In the following sections, some factors that influence the film formation on metal supports will be described. They are important for the size, morphology and density of the zeolite crystal film.

2.6.3 Composition of the Metal Support

The composition of the support, viz., the chemical and structural properties of the metal surface determine the number of potential nucleation sites, and thus control the achievable zeolite loading. An attempt to study the suitability of some metal compositions for zeolite deposition was made by Valtchev et al. The zeolite film crystallization of zeolite Y and of ZSM-5 was studied, using pure metal substrates as well as different alloys (see Table 2.5). Film formation was observed on silver, copper and nickel substrates, whereas on lead, chromium and tin no results were obtained. The conclusions of these authors were:

1) The (chemical) nature of the metal support influences the rate of coating.
2) The metal support influences the dimensions of zeolite crystals and the thickness of the coating. Also the geometry of the crystal deposited is influenced. For example, a film of elongated ZSM-5 crystals was obtained on brass alloy, whereas isometric, cubic ZSM-5 crystals were deposited on tin coated copper.
3) Pretreatment may influence the nature of the films deposited.

2.6.4 Cleaning Procedure Prior to Zeolite Film Formation

As metal surfaces, besides ceramic surfaces, are rather strong, in comparison to siliceous surfaces, the support may be subjected to intensive cleaning. Cleaning procedures often applied are:

1) Etching, acid treatment: with etching, cleaning with a strong acid as HF, HCl or H₂SO₄ is meant. The acid can (partially) destroy the upper surface layer of the support, leaving an ‘etched’ (or activated) support, with more active nucleation sites than before. This may enhance the number of nuclei formed and will generally result in a more uniform coverage, with finer sized crystals.
2) Another intensive cleaning procedure is given by Jansen et al. This involves washing with a basic and an acidic solution consecutively, followed by an ultrasonic step. In this way organic, inorganic and particulate contaminants are removed.
3) A ‘soft’ procedure consists of cleaning the metal plates in acetone\textsuperscript{23} for 10 minutes in an ultrasonic bath, followed by ultrasonic cleaning in distilled water. Only organic contaminants will be removed, and the upper surface layer will not be destroyed.

2.6.5 Pretreatment of the Support

The major objective of pretreatment is to increase the number of potential nucleation sites by increasing the number of surface imperfections. Surface imperfections can be produced by thermal and mechanical pretreatment of the support:

**Thermal treatment:** thermal treatment of supports is thought to lead to migration of defects from the bulk to the surface, to an increase of the surface energy and to a stronger interaction between the film and the metal surface. Furthermore, thermal treatment in air or oxygen will lead to a surface oxide layer.

Thermal annealing, prior to zeolite synthesis (zeolite Y and ZSM-5) on a copper substrate was reported in\textsuperscript{29}. The substrate was heated in air at 700 °C during 4 hours, cooled to room temperature and cleaned with 24% sulfuric acid. The film deposited on the untreated support appeared to be bonded weakly to the surface and could be removed easily from a large area under mechanical treatment. In contrast, on a thermally treated, non sulfuric acid treated support, the zeolite film is destroyed only within the area of the mechanical impact, indicating a stronger interaction between the film and the metal support surface.

**Mechanical treatment (plastic deformation):** metal plates can be subjected to plastic deformation by rolling at room temperature until reduction of their initial thickness is reached (e.g. from 5 to 2.5 mm). Plastic deformation causes transport of vacancies and dislocations from the bulk of the substrate towards the surface and gives birth to new surface defects. This way of mechanical treatment also modifies the surface crystal structure and afterwards, the appearance of parallel relief lines can be observed.

Film formation of zeolite Y on copper was investigated by Valtchev \textit{et al.}\textsuperscript{29} When the substrate was not subjected to plastic deformation, the plate was homogeneously covered with zeolite crystals and no relief patterns or density fluctuations appeared. When synthesizing on plastically deformed plates, the surface morphology was replicated and a densification of the film, due to the growth of more zeolite crystals in the relief zones, was observed. Another difference in the coating formed after thermal annealing followed by plastic deformation, is the size of the crystals. The size of crystals deposited on unheated plates is 2-3 μm, while after thermal treatment a homogeneous film of fine zeolite crystals of sizes below the SEM resolution (< 0.1 μm) is formed.
2.7 Zeolitic Coatings on Siliceous Supports

Although the interest in zeolitic coatings on a wide variety of supports has increased rapidly, zeolite synthesis on glass or other siliceous materials did not receive much attention as the supports were expected to dissolve in the zeolite synthesis mixture. However, by fine-tuning the synthesis, deposition on glass appeared to be possible.

Nucleation of zeolites on amorphous silicon dioxide (glass) or other siliceous supports offers several advantages. Because of the high mechanical strength and thermal and chemical stability of glass, deposition of zeolites enables the pressure resistance of gaseous or gasified liquid reactants to be decreased by coating of suitable glass profiles. Furthermore, as the supports consist of SiO₂ or Si-units, studying of film formation on siliceous surfaces, might deliver a broader insight into the zeolite film formation on other support surfaces.

2.7.1 Reported Zeolite Coatings on Siliceous Substrates

In Table 2.6 an overview is given of reported zeolitic films deposited on siliceous supports.

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Support</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Fused silica glass</td>
<td>84</td>
</tr>
<tr>
<td>silicalite-1/ZSM-5</td>
<td>Silicon wafers</td>
<td>24</td>
</tr>
<tr>
<td>NaA</td>
<td>Surface oxidized silicon</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Silicon</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Quartz (plate and fiber)</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>Quartz (single crystal)</td>
<td>18</td>
</tr>
<tr>
<td>unknown</td>
<td>Capillary glass tubes</td>
<td>86</td>
</tr>
</tbody>
</table>

One or more layers of perpendicularly oriented silicalite can be synthesized hydrothermally on the surface of fused silica glass ⁸⁴ and on silicon wafers ¹⁸,²⁴. At the early stage of the reaction, a porous gel layer spontaneously condenses on the substrate surface, within which the zeolite crystals are nucleated and grown, mediated by the structure-directing agent. The zeolite crystals are preferentially orientated with their b-axis perpendicular to the substrate surface. The crystal orientation is strongly dependent on the roughness of the underlying surface and consequently on the thickness of the zeolite film. By control of the synthesis conditions, the individual crystals constituting the zeolite films can be prepared either smaller than 500 nm or as large as 30 μm.

Originally, the zeolite film formation on silica glass was thought to be initiated by dissolution of silica of the siliceous support. This should have been followed by formation of zeolite nuclei.
that required the gel environment of dissolved silica for their nucleation. However, film formation of ZSM-5, and probably also of other kinds of zeolites, does not involve dissolution of the silica support, but the gel is formed from the silica source present in the reactant mixture. Prior to the formation of a zeolite crystal, always a layer of amorphous hydrogel, condensed on the substrate surface, is observed. This layer is creating a nutrient rich environment for zeolite nucleation. The hydrogel condensation not only reduces the surface area of the silicate species, but also preorganizes the gel. This preorganization is necessary for the nuclei formation as mediated by the structure directing-agent and can be considered as the collection of the right silicalite building blocks in the right ratios, necessary for the start of the building of nuclei. The zeolite crystals nucleate within the gel layer which is supersaturated with silicate and TPA molecules.

In the beginning of film formation (after 2 hr of crystallization), the surface is covered with irregularly globule species, ranging from 20 nm to 100 nm and just a few cubic regular shaped crystals (400-600 nm) can be observed. However, it was shown that these crystals were embedded in a porous gel layer composed of aggregated globular species. When an insoluble silica source, such as TEOS, was used however, no surface coating on the silica glass could be observed. This implies that the hydrogel coating is not caused by dissolution of the fused silica substrate, but that the coating can be attributed to the formation of silicate gel layer and ZSM-5 crystals on the substrate that resulted from the condensation of the readily hydrolyzed TEOS.

2.7.2 Hydrogel Surface Condensation Versus Nucleation and Crystal Growth

The crystal growth on the substrate surface is possibly controlled by a solid-phase transformation process, in which the solid hydrogel is reorganized for the formation of zeolite crystals mediated by the structure directing agent. In the early stage of the reaction, the rate of surface condensation of the globular shaped hydrogel is much faster than that required for zeolite nucleation and growth and just a few nuclei were evolved from the supersaturated gel layer. After 2 hours of reaction, the gel layer starts shrinking and simultaneously, the zeolite nuclei start growing. After 4 hours of reaction, no gel layer was observable anymore.

When the reaction is prolonged, a maximum substrate coverage of less than 60% is observed, whereas the thickness of the film increases at a much faster rate by intergrowth or nucleation on the underlaying crystals.

The observation that the irregular particles which appeared at the early (2 hr) stage of nucleation had disappeared after 12 hours is attributed to the hypothesis, that the crystal growth possibly involves the diffusion of silicate and TPA species from the liquid phase to the nucleation site. The crystal growth at the initial stage is attributed to the solution-mediated transport mechanism that has been found responsible for homogeneous crystallization of zeolites.
2.7.3 Increased Zeolite Coverage on the Substrate Surface, Effect of Aging

Increased substrate coverage by the zeolite film, *i.e.* formation of a more continuous zeolitic coating (up to 90%), can be achieved by increasing the nucleation rates prior to the rapid growth of the crystals. This increase is said to be obtained by aging of the reaction mixture (15 hour, 50 °C), prior to the actual zeolite formation reaction at 165 °C. Generally, aging of the soluble silicate species provides a higher concentration of the soluble silicalite species and consequently results in a small and more homogeneous crystal layer. During aging of the precursor, three processes that are thought to be necessary for the formation of the nuclei in the solution may occur:

1) hydrolysis of the silica source,
2) good mixing, driven by concentration gradients of the Al- and Si- sources,
3) interaction of the TPA molecules with the soluble silicate species.

Aging will result in a more uniform monolayer coverage of zeolite crystals (2h), formed of more densely packed crystals and thinner zeolitic films.

Synthesis of both perpendicularly and axially oriented ZSM-5 type (silicalite-1) films on silicon wafers and axially oriented ZSM-5 on quartz was reported by Jansen *et al.*\(^2\) Especially the influence of dilution (H\(_2\)O) on the crystal orientation was described. Synthesis of axially oriented silicalite-1 films with a thickness of 10 μm on silicon wafers was also reported.\(^1\)

Single-crystal aligned silicalite crystals were ordered in two dimensions on a micro structured silicon wafer surface under subjection to an external electric field. Powdery silicalite crystals were ordered at a low frequency in the grids (width 30 μm) of the support and were heated at 80°C with tetramethoxysilane and water. The tetramethoxysilane and water reacted to silica, forming a binder between the crystals and the support.\(^9\)

Oriented zeolite A was synthesized on silicon wafers from diluted filtrate solution.\(^2,9\) Crystal sizes of 7 μm were obtained and the growth history of the continuous zeolite A film on a single crystal of quartz was presented by Jansen *et al.*\(^8\) Yamazaki and Tsutsumi prepared zeolite A films on three kinds of substrates with different characters: silicon plate, the surface of which was oxidized; quartz glass plate; and a filter of quartz glass fiber.\(^8\) The membrane syntheses were successfully performed by using the liquid phase separated from the hydrogel of the reactants. A well crystallized tight membrane on silicon oxide-film silicon and quartz plates was obtained. However, the quartz substrate was often corroded and therefore induced instability for the prepared membrane. Therefore, a 'multi-fold' crystallization, by using A-type zeolite powder as a seed, was carried out. This proved to be very effective and tight and compact membranes were obtained on the quartz fiber filter.

An unknown high alumina zeolite (SiO\(_2\)/Al\(_2\)O\(_3\) ~ 3) was synthesized on a not exactly specified etched glass support.\(^8\) The major aim of the syntheses was to elucidate the mechanism of film formation on glass surfaces and to create highly orientated coatings.
2.7.4 Synthesis: Factors Influencing Zeolite Film Deposition

Pretreatment of the Substrate Surface
As silicon supports are easily attacked by alkaline solutions, it is necessary to increase their stability to the reaction mixture by oxidation, prior to synthesis. The reactivity of the support may be enhanced by etching.

Composition of the Synthesis Mixture
Especially the dilution ratio, H₂O/SiO₂ is reported to be important. Jansen et al. found that the crystallization time varied inversely with the concentration of the synthesis mixture, whereas the final crystal size is smaller at higher concentrations. At a low dilution ratio (e.g. H₂O/SiO₂ is 80), and therefore at a high concentration of building sources, the speculation was made, that a gel layer was condensing rapidly onto the support. A crystallization time of 3.5 h resulted in mainly laterally oriented crystals. A high dilution ratio (e.g. H₂O/SiO₂ is 1680), no gel layer was thought to be formed. After a crystallization time of 20 h, a film with axially oriented crystals was obtained. From this the speculation was made, that crystals start with different orientations at different dilution ratio. The dilution ratio is thought to affect the orientation, because a lower pH gel layer (containing many charged building sources) may have other influences on nucleation and crystallization than a diluted, higher pH solution.

pH of the Reaction Mixture
When working with a concentrated reaction mixture, a gel with lower pH will readily condense onto the substrate surface, protecting the support against the higher pH environment of the reaction solution. This will result in reduced dissolution of the support. It is generally assumed, that in a condensed hydrogel environment, the surface dissolution will be negligible, as a consequence of the rapid condensation of the gel. Little dissolution however, cannot be avoided.

When working with the diluted reaction mixture solution, the support will not be protected by a gel layer, leading to relatively large surface dissolution. However, as the surface consists of silica groups, these may also react as building sources for the zeolite film formation. They may even allow easier film formation, as they are still in little connection to the support during dissolution. A high pH environment also increases the solution rates of the silica and alumina compounds, which enables a faster nucleation rate. The average crystal particle size will decrease, as a higher pH results in a larger number of nuclei. Narrowly investigated effects of the pH on zeolite film formation, concerning the influence of dissolution of the siliceous support, have not been reported yet. This may lead to more clear insights into the formation of the bonding between the support and the zeolite film.

Aging Time of the Reaction Mixture
Generally, a positive effect is attributed to the period of aging. As TEOS is furthermore readily soluble, synthesis will not be influenced by a long aging period. Aging is in particular important for powdery silica sources, as both dissolution (dispersion) and hydrolysis have to find place before synthesis. When colloidal or other silica sources are used, just hydrolysis has to be realized. A longer aging period may however also alter the type of zeolite formed.
crystallization times may sometimes facilitate the formation of crystals that consist of the same secondary building blocks but that possess a higher atomic density. This was investigated for the synthesis of zeolite A. At first, just zeolite A was formed, but when the reaction was proceeding, also chabazite, mordenite and faujasite were formed. Continuation even led to transformation of all zeolite A and chabazite to faujasite and mordenite. The influence that is attributed to the aging time is strange however, as no changes are thought to occur in the initial synthesis mixture, when all silica building blocks have been dissolved and hydrolyzed.

Formation of higher atomic density variants of a certain zeolite also depends on the dilution of the reaction mixture, the aging period, the pH and the reaction temperature. The former described transformation just occurred in the non-diluted liquid phase and not in the double-diluted liquid phase. This is probably due to the fact that a higher atomic density also requires more building atoms and these will be exhausted in an earlier stage in highly diluted reaction mixtures.

**Crystallization Temperature**

The crystallization temperature is of general importance, whether working with diluted or non-diluted reaction mixtures. Temperature influences the solubility constants of the reaction components and therefore the zeolite formation. Also the pH is subjected to temperature and consequently the dissolution of the rather sensitive siliceous supports.

Different crystallization mechanisms of zeolite A membranes were observed at 70°C and 110°C.85 However, as repeated syntheses at different temperatures were carried out (and as the support surface is rather unstable), drawing a valuable conclusion can not be entirely justified. It is uncertain whether the proposed mechanisms of zeolite A membrane formation at different temperatures are plausible, because too little is known about both different zeolite formation mechanisms and repeated crystallization.

**Effect of the Presence of Seed Crystals**

Seed crystals are known to play a significant role in the crystal growth process as they may induce zeolite formation in a fresh reaction mixture ('memory effects').85 Before synthesis, the substrate is immersed in an aqueous suspension of the desired zeolite crystals and dried. In the absence of seed crystals, nucleation occurs at the active sites which are formed by defect sites on the support surface. The nucleation however depends on the reactivity of the active sites. In the presence of seed crystals, these crystals will partially dissolve, but also serve as nucleation sites for the fresh nuclei to be formed. The nucleation step of synthesis is accelerated in this way, resulting in faster crystal formation. The nucleation onto a support immersed in a seed crystal solution will therefore be faster than nucleation onto a bare support. The crystal film may however be less uniform, because the support will not be completely covered with seed crystals and the size of the freshly formed crystals may not be equal to the size of the seeds.

The formation of a zeolite membrane was investigated on quartz fibers in the presence of A-type zeolite crystals.85 With proceeding crystallization, a well packed membrane of A-type zeolite could be obtained (70°C, 3h). As the crystal growth was carried out in succession on seeds, the void among the seed particles was filled up with badly crystallized or amorphous particles. However, from the viewpoint of well packed and compact membranes, crystallization with seed crystals turned out to be most useful.
2.8 Applications of Zeolitic Coatings

The development of zeolitic coatings is still in an exploratory phase. Examples of different studies applying zeolitic coatings are listed in Table 2.7.

The use of zeolitic coatings enables the possibility of transient processing\(^9\). The incentive is to operate beyond equilibrium conditions by creating a continuously driving force for reaching equilibrium (e.g. by continuously removing a product stream). Also hybrid systems\(^9\) become possible, in which different steps are integrated, resulting in bi-functional process units. For example, a reactor in which reaction (with a catalyst) and separation (e.g. by adsorption) take place simultaneously to enhance yields and selectivities. Hybrid systems and transient processing are often two inherently coupled terms. As for instance, a catalytic membrane is responsible for either conversion as separation (implying continuous removal of the product stream), the process will be operated under transient conditions as equilibrium will not be reached.

<table>
<thead>
<tr>
<th>Membrane reactor</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| Membrane consisting of a pure ZSM-5 film deposited on a microporous alumina support | • Catalytic conversion of cyclohexane to cyclohexanone and cyclohexanol. Catalyst: Molybdenum oxide/quartz  
• Conversion of cumene to propylene and benzene. Catalyst: HZSM-5 extrudates  
• Selective conversion of isobutane in a mixture of isobutane and n-butane. Catalyst: Vanadium(V)oxide  
• Conversion of isobutane to isobutene and hydrogen. Catalyst: Pt  
• Conversion of 1,3-pentadiene to isoprene. Catalyst: Pt/Alumina  
• Conversion of toluene and trimethylbenzene to toluene and xylene, with the desired p-xylene in an amount > 24%. Catalyst: H-ZSM-5 | 75   |
| Hybrid membrane reactor consisting of a silicalite/alumina tube membrane         | • Oxidative dehydrogenation of propane catalyst: V-Mg-O pellets in the inner compartment of the reactor | 92   |
| Membrane reactor composed of a silicalite-1 layer deposited on stainless steel (316) | • Permeation measurements of He, Ne, Ar, Kr, methane, n-butane, CCl\(_2\)F, isobutane, isoctane | 43   |
| Catalytic membrane reactor with a zeolitic membrane of silicalite-1/α-alumina    | • Dehydrogenation of isobutane                                          | 63   |
Chapter 2

2.8.1 Electroanalysis and Sensor Devices

In electroanalysis, the measurement of charge, current, or equilibrium potential is related to the concentration of the unquantified electrolyte. Zeolitic coatings are applied in electroanalysis in the form of zeolite-modified electrodes. The electroanalytical suitability\textsuperscript{93} of zeolite-modified electrodes is demonstrated by:

1) the use of the zeolite present in the electrode composite or coating to sequester the electrolyte (often via cation exchange with mobile extra-framework cations),
2) their ability to follow the pre-concentration step by sweeping the potential of the electrode to react the harvested analyte while measuring the amount of Faradaic current that flows,
3) their use in calibration curves, devised using known concentrations of the analyte (preferably in the same solution environment (matrix) as the unknown, to determine the concentration of the analyte).

The potential of the electoreaction is diagnostic of the identity of analyte, the faradaic current (or faradaic charge) permits quantitative analysis. A summary of preparatory methods for zeolite-modified electrodes is given by Rolison\textsuperscript{93}. For a review of the use of zeolite-modified electrodes for electroanalysis is referred to\textsuperscript{94}.

Bein and co-workers have grown thin zeolite composite films on piezoelectric devices, such as surface acoustic wave devices\textsuperscript{95} and they have achieved molecular sieving of gas-phase organic electrolytes. They also prepared quartz crystal microbalances, where the mass, due to sorbed gases, is monitored as a change in the frequency of the piezoelectric device.\textsuperscript{96} In the latter, microporous thin films composed of a molecular coupling layer, zeolite A crystals, and a porous silica overlayer, were formed on the gold electrodes of quartz crystal microbalances (QCM’s). The silica overlayer enhances the mechanical stability of the zeolite films, and results in additional surface area and porosity as characterized by the sorption isotherms and transient sorption of vapors with different molecular diameters and different polarities. The protecting silica glass layer is gas permeable such that the regular zeolite micropores with molecular sieving capability are still accessible in the composite film. A novel surface tailoring technique for the microporous thin films was developed, in which organosilane molecules were chemisorbed on the silica overlayer via siloxane linkages, forming a molecular ‘gate’ at the gas thin film interface. The adsorption of vapors into the microporous zeolite films is therefore controlled by the permeability of the gate layer. Selective adsorption based on kinetic or equilibrium exclusion from the microporous films could be achieved, as demonstrated by discrimination of molecules with similar polarity but different molecular diameters (water vs. ethanol), and effective exclusion of larger molecules such as $n$-hexane. As a result of the increase in the vapor sorption selectivity and reduction of the external surface area of the thin films, the modified QCM’s show high selectivity towards water over other molecules.
2.8.2 Pervaporation

Pervaporation is a combination of permeability and evaporation. In pervaporation, part of a liquid feed is separated by a membrane that is selectively permeable for that certain substance. On the other side of the membrane, a vacuum is present, causing the liquid to evaporate. The driving force for the membrane separation is the concentration gradient over the membrane. Because of the subsequent evaporation, the process will never reach equilibrium conditions and can be specified as a transient process. An example is the dehydration of alcohol, i.e., separation of a water/ethanol mixture. Water is preferentially sorbed in the hydrophilic (zeolite A) membrane material, diffuses through the membrane and evaporates in the vacuum at the permeate side of the membrane.

Proposed is that zeolitic coatings, deposited on the feed side of the membrane, can be useful in pervaporation processes as they will be able to select on a molecular scale. The membrane used may now be a less selective one, because separation of the liquid feed will be carried out by the zeolite molecular sieve. Required is, that the zeolite layer is completely covering the membrane surface. Mechanically stronger or cheaper membranes can be used, as they will just function as support and transport medium. Separation will not be their major task when a zeolitic coating is implemented.

2.8.3 (Catalytic) Membrane Reactors

Zeolitic membranes may play either a passive or an active role in catalytic (organic) conversion reactions and their potential applications in zeolite membrane reactors are quite promising. Both liquid phase and gas phase reactions may advantageously be carried out in a membrane reactor, and transport from the reaction zone is promoted by continuous removal of the permeating molecules. Selective removal of product molecules is beneficial in equilibrium limited conversion reactions, since the conversion per pass is enhanced and the downstream product purification is simplified. The membrane plays a passive role in case its main function is to:

- selectively remove product molecules or
- to supply an active component to the reaction zone.

The membrane plays an active role in case its function is to:

- catalyze the reaction and
- act as a carrier for the active catalyst component.

The membranes need to be permeation selective and thermostable (inorganic materials, carbon) and have to allow fluxes, that are proportional to the chemical conversion rates. Permeation selectivity is obtained if the pore size ranges from 10 nm down to molecular dimensions (zeolites). In these regimes, Knudsen diffusion, surface diffusion and zeolitic diffusion take place, allowing selective component transport.
Chapter 2

The use of membrane reactors has been advocated for a considerable number of reacting systems. In dehydrogenation reactions, the yield can be increased beyond thermodynamic equilibrium by selectively removing hydrogen from the reaction mixture. Moreover, a catalytic membrane offers the advantage of combining catalysis and separation in the same reactor. An example is the dehydrogenation of ethane\(^9\), using a porous alumina membrane tube covered with Pt crystallites. The catalyst enables reaction and the reaction products are continuously removed by diffusion through the membrane, causing the reaction to proceed far beyond its equilibrium.

Another increasingly important field of application for membrane reactors involves their use as distributors of reactants. In this case, the membrane is used to distribute one or more reactants which permeate to the reaction side. This can be useful in many instances of consecutive oxidation reactions with a valuable intermediate product. The selectivity towards the desired product is often favored when low oxygen concentrations are employed. Also for methane oxidative coupling, for most catalysts, the apparent reaction order for oxygen in the deep oxidation reaction is higher than in the coupling reaction.

Most processes using membrane reactors for methane oxidative coupling have employed solid electrolytes as the membrane material. This leads to a flux of ionic oxygen across the membrane when one of the sides is exposed to an oxygen-rich stream and the other to an oxygen-consuming reaction. On the other hand, even when electrochemical ionic pumping was applied, the fluxes of oxygen obtained were of a small magnitude, due to the low permeability of the materials involved. This gave rise to hydrocarbon yields that are usually below 10\% with this type of membrane.

A new type of reactor with a much higher permeability was developed by Coronas et al.\(^9\) For methane oxidative coupling, a modified porous ceramic microfiltration membrane was used as an oxygen distributor to a fixed bed catalytic reactor. The pore structure along the membrane was altered by deposition of silica in the tube wall of the \(\alpha\)-alumina membrane, in order to attain a controlled, non-uniform pattern of oxygen permeation. This appeared to have significant advantages for the reaction investigated, for example on the temperature profile. The different permeation arrangements employed were characterized, and compared in terms of the conversion and selectivity achieved. It is clear, that also deposition of zeolites on the surface and in the wall of the tube may result in other new applications.

In Table 2.8 several membrane processes that could benefit from implementation of a zeolitic coating are proposed. A review of membrane reactors was given by Eng and Stoukides.\(^9\)
2.8.4 Catalytic Distillation

Catalytic distillation involves a combination of distillation and catalysis in a single column. In industry, it is already applied in the production of MTBE and of cumene. Cumene is formed from benzene and propene:

\[ C_6H_6 + CH_3 - CH=CH_2 \rightarrow C_8H_{12} - CH(CH_3)_2 \] (exotherm)

Subsequent reactions are the formation of di- and triisopropylbenzenes (DIPB resp. TIPB). These secondary products can react back to cumene by disproportionation:

\[ \text{DIPB} + C_6H_6 \rightarrow 2 \text{cumene} \] (exotherm)

From this reaction it is clear, that the yield of cumene can be enhanced by recycling of the heavy products. Coating of the reactor packing of the column inner wall with catalyst exchanged zeolite crystals may provide a low pressure drop, dustproof operation, with a large catalytic surface. Besides, the formation of di- and tri-mers will be minimized, because of the steric hindrance in the zeolite channels.
2.8.5 Pollutant Emission Control: NOx-reduction

Cars and stationary engines are identified as the major sources of environmental pollution and photochemical smog. Their exhaust gases contain NOx, SOx, hydrocarbons and carbon monoxide. Selective Catalytic Reduction (SCR) of nitric oxide is an end-of-pipe process that requires a dustproof, low pressure drop reactor, to remove the pollutant. This is in conflict with the need for intensive contact between the gas flow and the catalyst. For this, special structured catalyst packings were developed, such as the Honeycomb Reactor and the Parallel Passage Reactor. The currently most widely used catalyst for SCR of NOx with ammonia consists of vanadia, often in combination with titania, on an amorphous silica or alumina carrier. The catalyst is present as a washcoat on the surface of the ceramic body of a Honeycomb Reactor (monolithic shape). Some typical NOx reduction studies using zeolites are given in Table 2.9.

<table>
<thead>
<tr>
<th>NOx-reduction process</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selective catalytic reduction of NOx in dustproof low pressure drop reactors</td>
<td>reductant: NH₃; catalyst: Cu-ZSM-5 deposited on stainless steel 316 wire gauzes temp.: 350 °C</td>
<td>100</td>
</tr>
<tr>
<td>Reduction of automotive NOx emissions in lean burn internal combustion engine exhaust</td>
<td>reductant: H₂C₂H₄CO= 1:1.2:3.1; catalyst: Cu-ZSM-5-clay aggregates temp.: 500 °C</td>
<td>101</td>
</tr>
<tr>
<td>Catalytic removal of NOx from total energy installation flue-gases</td>
<td>reductant: urea</td>
<td>102</td>
</tr>
<tr>
<td>Selective catalytic reduction of NOx</td>
<td>reductant: NH₃; catalyst: H-ZSM-5 deposited on alumina temp.: 350-550 °C</td>
<td>56</td>
</tr>
</tbody>
</table>

Calis et al.⁹⁰ proved the applicability of supported zeolite crystals as a catalyst in dustproof low pressure drop reactors. These authors developed a novel structured catalyst packing, consisting of ZSM-5 crystals grown in situ on a metal wire gauze, to be produced in any required shape. The mechanically strong packings resulted in an extremely low pressure drop across the packing and almost no dust particles were trapped. After incorporation of copper into the zeolites by ion exchange, testing of its suitability for an end-of-pipe process for SCR of NOx with ammonia at 350 °C from large flows of dust containing flue gas was carried out. Both the activity and selectivity of the catalyst packing proved to be superior to the conventional vanadia/titania a catalyst.

Another pollutant removal process is the cleaning of lean-burn flue gases of powerplants of greenhouses. The flue-gases could be used again for CO₂ fertilization in greenhouses, so that good vegetation is reached and energy is saved. The gases however contain too much pollutants to feed them to the plants directly. With the so called ‘Delft NOx/urea process’, lean-burn gases,
containing a rather low amount of NOx, will be cleaned by converting the NOx under decompositon of urea. Zeolitic coatings may be applied here as they enable a low pressure drop, dustproof process. Furthermore, zeolitic coatings on static mixers can be applied to minimize the risk of reductant slip.\textsuperscript{103}

2.8.6 Hydrocarbon Conversion Processes

Octane Yield Improvement in Catalytic Cracking

The octane and total yield in catalytic cracking (both fluid (FCC) and thermofo (TCC)) can be enhanced by using \textit{in-situ} crystallized ZSM-5 on a clay aggregate support.\textsuperscript{104} The silica/alumina ratio of the support should exceed 5, to preserve the crystallinity of the zeolite crystals during the extreme cracking conditions. It was found that zeolite composites, derived from clay aggregates were hydrothermally more stable than corresponding other composites. The steam may be present in the feed, produced as a reaction product, added to remove products and unreactive feed from the catalyst or generated during regeneration. The net result is an irreversible loss of catalytic activity. In coke aging, however, the catalyst can be restored to almost its fresh activity by conventional regeneration techniques where the carbonaceous coke deposits are removed by burning at elevated temperatures. The relative importance of coke versus steam deactivation depends on the particular process involved. As in catalytic cracking, steam stability is far more important than coke aging, the catalyst spends over about 80% of the total residence time in the regenerator at elevated temperatures in the presence of steam. Impregnation of the composite with silver may enhance the steam stability, however, the improved liquid selectivity (to gasoline) will be lost, although the resistance to hydrothermal deactivation is improved.

The Fischer-Tropsch Process

The hydrogenation of carbon monoxide by the Fischer-Tropsch process permits the synthesis of hydrocarbons ranging from methane to high melting point paraffin waxes, depending on the catalyst and process conditions. Cobalt based catalysts for Fischer-Tropsch synthesis have been extensively used during the first half century until the end of World War II. Nowadays, cobalt-containing catalyst are still being used in the Shell plant at Bintulu, whereas Sasol (South Africa) applies an iron based catalyst.

A composite catalyst comprising a water-gas shift catalyst, coated by a thin zeolite film, which, in turn, has a Fischer-Tropsch catalyst deposited on its outer surface.\textsuperscript{105} The zeolite has a gatekeeper function of allowing short chain hydrocarbons and steam into the water-gas shift catalyst and allowing the return of carbon monoxide and hydrogen products back to the Fischer-Tropsch catalyst at its outer surface.
Chapter 2

A stream of short chain hydrocarbons (e.g. C1-C4 alkanes or alkenes) and steam is passed to the catalyst composite where it diffuses past the Fischer-Tropsch catalyst through the zeolitic layer to the water-gas shift catalyst. At the surface, the short chain hydrocarbon reacts with water to produce carbon monoxide and hydrogen. These products then diffuse back to the zeolite covered surface where they react on the Fischer-Tropsch catalyst to produce hydrocarbon oligomers.

A zeolite Fischer-Tropsch catalyst has three advantages:

1) The Fischer-Tropsch function can be highly dispersed in the fresh catalyst, reducing the metal loading needed to attain a specific activity.
2) The zeolite can selectively modify (by acid catalyzed shape selective reactions) the primary Fischer-Tropsch product.
3) A water-gas shift function could be introduced into a molecular sieve based catalyst. For example, Co-APO-34 can be modified by Zn and Cu components to introduce the water gas shift activity.
2.9 Conclusion

In this chapter an overview of literature on zeolite coatings was given. It clearly demonstrates the breadth of the subject.

Zeolitic coatings can be prepared in a variety of ways, the most important and versatile method appears to be in-situ synthesis, since it offers possibilities like membrane synthesis, orientation of crystals and highly defined products. At the same time it is noted that most literature on preparation is often incomplete and consequently, most results might be difficult to reproduce.

There is still very little known about the processes taking place during the nucleation and growth of zeolite crystals on surfaces, but the increasing attention the subject receives will eventually lead to a better insight. Also, an inventory of realized and possible applications is given.

The majority of applications found in literature deal with zeolitic coatings applied as membranes, leaving the subject of structured catalyst packings almost completely untouched.

Acknowledgment

Gemaine Seijger is gratefully acknowledged for her substantial contribution to this chapter.

2.10 References

Introduction to Zeolitic Coatings


Introduction to Zeolitic Coatings

78. N. van der Puij; Development and catalytic testing of zeolitic coatings, Ph.D. Dissertation (Delft University of Technology, 1997).
Chapter 2

3

Optimized Synthesis of Zeolite BEA on Metal Supports

3.1 Introduction

For many catalytic applications important process characteristics such as pressure drop, selectivity and/or accessibility of catalytic sites may be improved by applying structured catalyst packings. Therefore it is preferable to have the catalyst material present as a thin film connected firmly to a pre-shaped carrier. In this chapter the preparation of binderless films of zeolite Beta (BEA) on metal supports is described, in order to produce catalyst packings with a stable, thin layer of BEA crystals.

Of the various types of zeolites, zeolite beta (BEA) is of special interest because of its twelve ring pore structure, which stretches out in three dimensions. The pores of BEA are large enough to accommodate commercially interesting hydrocarbons, allowing catalytic reforming, alkylation, dewaxing, cracking and synthesis of ethers such as ETBE and MTBE. BEA is unique in having Lewis sites on the inner surface, leading to high selectivity in MPV reduction\textsuperscript{1}. Furthermore BEA has shown high catalytic activity in inorganic conversions, such as selective catalytic reduction of nitrogen oxides\textsuperscript{2,3}.

An important aspect of using zeolites for catalytic processes is their shaping to obtain particles that are large enough to handle. Classical methods are extruding, granulating and spray-drying. A drawback of these methods is that the catalytic sites are contained within a matrix, which has often no catalytic activity and which by its size lowers catalytic efficiency, due to internal diffusion limitations. A more recent method is the application of thin zeolite coatings to structured supports, e.g. monoliths. This yields a catalytic reactor packing with many attractive properties, such as a well-defined fluid flow, a low pressure drop and a high selectivity and activity. The effect of the film characteristic on the selectivity of a simple consecutive reaction (A $\rightarrow$ B $\rightarrow$ C, first order kinetics) is illustrated in Fig. 3.1. In this figure the calculated selectivity for product B (defined as the production rate of B over the consumption rate of A, in the first part of a plug flow reactor) is plotted as a function of the dimensionless Damkohler number:

$$Da = L^2 \left( \frac{k}{D_{er}} \right)$$  \hspace{1cm} (3.1)
Fig. 3.1 Calculated selectivity for product B in a consecutive first order reaction $A \rightarrow B \rightarrow C$ as a function of Damköhler number.

with $L$ the film thickness, $k$ the first order reaction rate constant assumed to be the same for both $A \rightarrow B$ and $B \rightarrow C$ and $D_{eff}$ the effective diffusivity. It is noted that a high selectivity is promoted by thin films and high effective diffusivities.

Of importance to the feasibility of packings comprising BEA films is the accessibility and mechanical stability of the film, i.e., the bonding of the zeolite crystals to the support material. Two well-known methods to prepare zeolite films on supports are washcoating and slurrycoating, however, the mechanical stability of such films remains poor\(^1\). An improvement could be the hydrothermal synthesis of zeolites in the presence of a support material, which leads to preferential growth of zeolite on the support surface. This procedure, referred to as \textit{in-situ} synthesis, results in a binderless zeolite film on the support surface. Macroporous multilayers of zeolite without a binder are possible\(^2\). Absence of a binder increases the effective diffusivity in the layer, yielding a higher selectivity (see Fig. 3.1). Besides the mechanical stability of the film, also the mechanical stability of the support is important. In that respect metal supports, e.g., metal monoliths, are of particular interest. The use of metal supports may also be advantageous in strongly exothermic reactions as to prevent temperature gradients.

Consequently, the concept of catalytic reactor packings containing BEA films, \textit{in-situ} synthesized on metal packings seems to offer promising opportunities. However, to prove this concept, it is necessary to first prepare such packings on a laboratory scale and then to test their characteristics. An extensive literature search\(^3\) has revealed that preparation of this kind of catalytic modules has not been reported yet.
Optimized Synthesis of Zeolite BEA on Metal Supports

The aim of this work is to assess whether in-situ synthesis of BEA on metal supports is possible at all, and whether a catalytic packing can be obtained that could be feasible in a commercial process. To do so it is first tested whether BEA films on metal supports can be obtained by simply following literature recipes for normal, free phase BEA synthesis, i.e., not in the presence of a supporting surface. Next an investigation is made to determine which synthesis variables have a significant influence on the film characteristics. Based on these results, a recipe for in-situ synthesis of BEA on a metal support is developed.

In this paper, first the literature of free phase BEA synthesis is reviewed, as well as the literature on in-situ synthesis of zeolites on supports. This was taken as the starting point for the in-situ synthesis of BEA films on metal supports. Four series of experiments were carried out: a) experiments in which literature recipes for free phase BEA synthesis were used; b) experiments in which minor modifications were made to those literature recipes; c) experiments based on a rigorous statistical approach, in which the influence was tested of 14 synthesis variables; and d) experiments in which the best result of the first three series was used to screen different support materials.

3.2 Theory

As a starting point for the attempts to prepare in-situ synthesized films of BEA on metal carriers, literature data on BEA and its free phase synthesis will be discussed briefly, as well as literature on in-situ synthesis of zeolites on various supports. Furthermore several features of zeolite film packings will be discussed briefly.

The first report on BEA synthesis is a patent by Wadlinger\textsuperscript{9} from 1967. The synthesis procedure revealed in this patent is characterized by the use of tetraethylammonium hydroxide (TEA-OH) as a template, a Si/Al ratio of 20-30, a relatively low synthesis temperature (ca. 100°C) and a synthesis time of about three weeks.

The framework morphology of BEA was not elucidated until 1988\textsuperscript{10-11}. BEA turned out to be an intergrowth of at least two, and possibly three, polymorphs. It has 12-membered intersecting 2-D straight channels measuring $7.6 \times 6.4$ Å, which makes it a wide-pore zeolite. Moreover, a third sinusoidal channel ($5.5 \times 5.5$ Å) exists. The pores extend in three dimensions, resulting in a high accessibility of the internal surface. The crystals have a capricious morphology of intergrown polymorphs. BEA can be synthesized with Si/Al ratios from 5 up to infinity\textsuperscript{12}.

Although many reports were published on the free phase synthesis of BEA, all are merely variations on the original Wadlinger patent. In many reports only different silica and alumina sources were used, as well as higher synthesis temperatures (up to ca. 140°C). Of interest is the patent by Rubin\textsuperscript{13}, in which the original TEA\textsuperscript{+} template was replaced by the cheaper dibenzylidimethylammonium ion (DBDMA\textsuperscript{+}). Van der Waal \textit{et al.}\textsuperscript{14} introduced di(cyclohexylmethyl)dimethylammonium as a more stable variant of the Rubin template. In all cases, synthesis times of at least three days were necessary to obtain BEA in sufficient yields.
Chapter 3

In-situ synthesis of BEA films on supports has to the authors' best knowledge not been reported before. Several authors report the synthesis of other types of zeolites on various supports. Grasselli et al.\textsuperscript{15} claim in-situ synthesis of a wide range of zeolites on an even wider range of support materials. However, in the patent examples only in-situ synthesis of MFI on ceramic materials was treated, to produce a sorbent structure comprising a film of interconnected zeolite crystals. Reported coverages are typically 60 g/m\textsuperscript{2}.

Of the same date is a report by Jansen et al.\textsuperscript{16}, in which all-silica MFI was synthesized on silicon wafers. Here the high degree of dilution (H\textsubscript{2}O/Si > 700) leads to a preferential axial orientation of the crystals with respect to the support surface, which is of advantage for catalysis. Furthermore, films of mordenite, mordenite, and others have been reported. The majority of these reports deal with lateral growth aiming at the preparation of membranes using porous ceramic supports.

Valchev et al. describe explorative syntheses of ZSM-5 and zeolite Y on metal supports\textsuperscript{17-19} and cellulose fibers\textsuperscript{20} but give no quantitative data on coverage results.

Little is known about the formation of zeolites in general, let alone the formation of zeolite crystals on the surface of a support. In our view, two ways along which the formation of zeolites on the surface of a carrier can take place exist, depending on the concentration of the synthesis mixture. In a dilute mixture, crystallization is believed to proceed through direct nucleation onto the support, from which the crystals grow further. In a more concentrated synthesis mixture, a gel is formed, like in standard free phase synthesis. The gel phase consists of linked Si-O-Al-O-Si groups, forming a cross linked network with interlocked H\textsubscript{2}O. This network expands across the gel phase. In free phase synthesis this gel is continuous or dispersed in the aqueous phase. When a solid support is present, the gel particles will stick to the surface individually or coalesce to form a continuous gel layer, depending on their charge and number. Nucleation then takes place either in the bulk of the gel particles or gel layer or on the interface of the gel layer and the support surface. Although it has been confirmed repeatedly that the binding of the crystals to the support surface is strong, the nature of this bonding has not been elucidated yet. It is most probable that the terminal OH groups of the support condense with those of the zeolite, thus establishing a chemical bond between the support and the zeolite crystal. This is supported by the fact that different supports show different receptivity toward in-situ zeolite growth\textsuperscript{18,19} and no zeolite bonding occurs on essentially OH-free surfaces, such as PTFE.

Key parameters in assessing the feasibility of zeolite films on supports are:

1) the coverage expressed as grams of zeolite per gram support or square meter support,

2) the conversion expressed as the fraction of the Al or Si present in the initial synthesis mixture incorporated in the crystals present on the support after synthesis and

3) the selectivity of growth onto the support surface expressed as the ratio of weight of zeolite present on the support toward the total weight of zeolite formed both in mixture and free phase.
For zeolite BEA, a solid monolayer of crystals of 0.5 \( \mu \text{m} \) corresponds to a coverage of ca. 0.9 \( \text{g}_{\text{zeolite}}/\text{m}^2_{\text{support}} \). For any practical application knowledge of the reactor loading is important. Assuming the 0.5 \( \mu \text{m} \) monolayer of zeolite BEA to be present on a 600 csi (cells per square inch) monolith, this corresponds to a value of ca. 3.5 kg\( \text{g}_{\text{zeolite}}/\text{m}^3_{\text{reactor}} \). In spite of the high cell density of a 600 csi monolith, this loading is about 300 times lower than that of a randomly packed bed reactor and 50 to 150 times lower than loadings obtained for typical low pressure drop reactor packings, such as Parallel Passage Reactors, Lateral Flow Reactors, Radial Flow Reactors or washcoated monoliths. Unless the loading can be increased (e.g., by thicker layers) or the absence of a binder enhances catalytic activity considerably, the choice for a packing with \textit{in-situ} synthesized BEA is only justified for very specific processes. Examples are processes that strongly depend on the selectivity of the reaction, processes with a strong reaction heat effect, and processes in which the shape or morphology of the catalyst packing is important (e.g., during catalytic distillation).

### 3.3 Experimental

The synthesis procedure of zeolite films consists of five steps:

1. Preparation/shaping of the supporting material;
2. Pretreatment of this material to remove contaminations and/or to modify the surface morphology;
3. Preparation of the synthesis mixture;
4. Autoclaving of the mixture at synthesis temperature, in the presence of the support;
5. Post-treatment of the packing.

Four series of experiments have been performed:

**Series A**

In the first series of experiments, the choices to be made in steps 1 and 2 were based on earlier work in our group. Steps 3 and 4 were based on recipes for free phase BEA synthesis from literature.

Supports were manufactured by cutting strips of stainless steel (AISI 316) wire gauze (wire diameter 35 \( \mu \text{m} \), mesh 50 \( \mu \text{m} \), specific surface 0.0113 \( \text{m}^2/\text{g} \)) measuring 1.00 m \( \times \) 0.04 m. These strips were rolled up and cleaned in boiling ethanol for two hours, during which the ethanol was refreshed twice. Further cleaning was done by treatment with a 10% \( \text{H}_2\text{O}_2 \) solution at room temperature. After this, the carriers were dried in an oven at 140°C to restore the oxidic layer at the cut edges of the stainless steel. The synthesis mixtures were made according to literature\textsuperscript{21-23} with minor modifications, see Table 3.1.
Chapter 3

Table 3.1 Composition of synthesis mixtures in the experiments of series A (molar ratios relative to Al₂O₃).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>t [h]</th>
<th>SiO₂</th>
<th>Si type</th>
<th>H₂O</th>
<th>TE₆O₂</th>
<th>NaCl</th>
<th>total OH</th>
<th>K/(K+Na)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>96</td>
<td>32.7</td>
<td>TEOS</td>
<td>507</td>
<td>9.20</td>
<td>-</td>
<td>23.3</td>
<td>0.202</td>
</tr>
<tr>
<td>A2</td>
<td>144-216</td>
<td>34.6</td>
<td>HS-40</td>
<td>288</td>
<td>1.73</td>
<td>0.695</td>
<td>6.64</td>
<td>0</td>
</tr>
<tr>
<td>A3</td>
<td>16</td>
<td>49.9</td>
<td>Aerosil</td>
<td>1500</td>
<td>12.5</td>
<td>1.45</td>
<td>31.2</td>
<td>0.351</td>
</tr>
</tbody>
</table>

The carriers were placed in Teflon lined stainless steel autoclaves (50 ml) that were then filled with 35 ml of the synthesis mixture. The autoclaves were placed in an oven that was kept at 135°C, for 16 to 216 h. During the experiments the autoclaves were rotated at ca. 30 rpm. At the end of the synthesis, the autoclaves were left to cool to ambient and opened. The carriers were taken out and rinsed thoroughly with demineralized water. The resulting synthesis mixture was filtered to recover any particulate matter produced.

Series B

Because the crystal sizes obtained in the first series of experiments were very small (< 0.1 μm), it was attempted in the second series to increase the crystal size of the deposited BEA. This was done by varying the composition of the synthesis mixture, based on literature data and experience, the choice of the templating agent, and by varying the Si/Al and H₂O/Si ratio. As a template, dibenzyldimethylammonium chloride (DBDMA-Cl) was chosen. The synthesis mixture compositions and the synthesis conditions are listed in Table 3.2. The Si-source used was Aerosil 200, the Al-source was sodium aluminate (Riedel-de Haën) and the SiO₂/Al₂O₃ ratio was kept at 100. Synthesis temperature was 135°C.

Table 3.2 Composition of synthesis mixtures in the experiments of series B (molar ratios relative to Al₂O₃, SiO₂/Al₂O₃ = 100).

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<th>Exp</th>
<th>t [h]</th>
<th>H₂O</th>
<th>Tpl₂O</th>
<th>total OH</th>
<th>K/(K+Na)</th>
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<td>72'</td>
<td>2500 - 15000</td>
<td>40.2'</td>
<td>52.2</td>
<td>0.35</td>
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<td>B2</td>
<td>47-142'</td>
<td>1890.0</td>
<td>20</td>
<td>17.4</td>
<td>0.3</td>
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<td>B3</td>
<td>116'</td>
<td>570-1150</td>
<td>5-20</td>
<td>17.4</td>
<td>0.3</td>
</tr>
<tr>
<td>B4</td>
<td>120</td>
<td>570-1150</td>
<td>5-20</td>
<td>17.4</td>
<td>0.3</td>
</tr>
<tr>
<td>B5</td>
<td>72'</td>
<td>2300</td>
<td>10</td>
<td>17.4</td>
<td>0.3</td>
</tr>
<tr>
<td>B6</td>
<td>96'</td>
<td>2300</td>
<td>10</td>
<td>17.4</td>
<td>0.3</td>
</tr>
</tbody>
</table>

'r' : rotated during synthesis

'f': extra fine meshed gauze; wire diameter = 22 μm; 260 cm²/g

'r': TEAOH template

Series C

Compared with series A, series B yielded promising results. It was decided to investigate the effect of a number of variables systematically, using a rigorous statistical approach. A number
of variables, such as synthesis time and temperature, will obviously have an effect. These trivial variables were therefore not changed in this series. Fourteen other variables of which the effect on the synthesis result were uncertain were identified. In series C, only those variables were tested. This was done by choosing different settings for these variables. Because a very large number of combinations can be made in which fourteen variables can be varied independently (16384 if each variable would be tested at two levels), it was decided to use a so-called fractional factorial experimental design$^{24,25}$. In effect, only a small fraction of all possible combinations of variable settings needs to be tested by eliminating essentially redundant experiments in this way. Thirty-two experiments were performed in which fourteen variables were tested at the following levels (The silica source and the aluminum source were each tested at four levels, i.e., four different sources were used, marked 1 to 4. The remainder of the variables was tested at two levels, marked ‘+’ and ‘-’).

With respect to the synthesis mixture composition the variables included (the numbers and symbols between brackets refers to the notation used in Table 3.3):

1) Silica source: Aerosil 200 (1), sodium metasilicate (2), Ludox HS-40 (3) or tetraethyl orthosilicate (TEOS) (4).
2) Aluminum source: sodium aluminate (1), aluminum nitrate (2), aluminum hydroxide (3) or aluminum tri-isopropoxide (4).
3) Template: tetraethylammonium chloride (TEACl) (1) or dibenzylidimethyl ammonium chloride (DBDMACl) (2). The chloride form is used so as to keep the total OH$^-$ concentration fixed.
4) Si/Al: 20 (-) or 200 (+)
5) Template/Al: 2 (-) or 20 (+)
6) Water/Al: 1200 (-) or 3000 (+)
7) Total salt concentration: (Total contents of salts in the solution; this determines the solubility. To be changed by adding KCl or NaCl in amounts equal to KOH and NaOH on a molar base): low (-) or high (+) (KCl/NaCl added).

With respect to treatment of the synthesis mixture the variables were:

8) The time the synthesis mixture was stirred before the aluminum source was added. This was varied between ca. one hour (-) — the time needed for the mixture to become homogeneous — and two days (+).
9) The time the synthesis mixture is left to stir after the aluminum source was added. Less than 10 minutes (-) or 2 days (+).

With respect to pretreatment of the carrier prior to synthesis two variables were altered:

10) Cleaning with acetone for 1 hour (+) or not (-).
11) Pretreatment by dipping (1 min) in a diluted (0.18 M) solution (+) or not (-). The concentration of the solution was chosen low enough to prevent a significant increase in the template concentration in the autoclave caused by the extra amount of template added.
Chapter 3

With respect to synthesis and post-synthesis three variables were examined:

12) Rotating the autoclaves in the ovens during synthesis (+) or not (-).
13) Cooling: unforced (-) or forced (+). In forced cooling, the autoclaves are submerged in cold water after synthesis. In unforced cooling the autoclaves are left in open air to cool down to room temperature.
14) The autoclaves were opened either directly after synthesis (-) or were kept closed for two days (+) before opening.

The experiments were conducted as given in Table 3.3.

Table 3.3  Scheme used for generating experimental conditions of series C.

<table>
<thead>
<tr>
<th>Exp No</th>
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<th>4</th>
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</tbody>
</table>

Series D

In the fourth series of experiments, recipe C1c was used as a starting point to assess the reproducibility of the synthesis procedure and to investigate the effect of different support materials and morphologies. Rather than rolls of wire gauze, monoliths made of corrugated metal
foil were used as a support; see Fig. 3.2. Strips of metal foil measuring $1 \times 0.04$ m were cut, subsequently corrugated using a special cog wheel mill and winded as illustrated in Fig. 3.2. The packings were kept together by winding a small wire of the same material around it.

![Diagram of metal monolith construction](image)

**Fig. 3.2** Construction of metal monoliths; measures in mm.

The same recipe was used to prepare zeolite films on other types of stainless steel, other metals, or stainless steel that had been sandblasted to increase the specific surface area. The tested foils and their chemical bulk compositions are listed in Table 3.4.

<table>
<thead>
<tr>
<th>Table 3.4</th>
<th>Metal foils used in Series D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Composition</strong></td>
<td><strong>Thickness [µm]</strong></td>
</tr>
<tr>
<td>AISI 304</td>
<td>Cr: 18-20%; Ni: 8-10%; balance Fe</td>
</tr>
<tr>
<td>AISI 316</td>
<td>Cr: 16-18%; Ni: 10-14%; Mo: 2%; balance Fe</td>
</tr>
<tr>
<td>AISI 321</td>
<td>Cr: 17-19%; Ni: 9-12%; balance Fe</td>
</tr>
<tr>
<td>Brass</td>
<td>Cu: 63-69%; balance Zn</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni</td>
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</table>

Finally, the bonding strength between crystals and support was tested by subjecting the composite catalysts to high temperatures (550°C) for several hours, and by subjecting a composite to a severe thermal shock, by first heating it up to 100°C and then immersing it in liquid nitrogen (-196 °C).
Chapter 3

3.4 Results and Discussion

The results will be discussed in terms that are relevant to practical application of the supported zeolite films for catalytic processes. The coverage of the support and the selectivity for zeolite growth on the carrier are both determined by gravimetric analysis, i.e., measuring the mass gain of the packings due to the synthesis procedure. The characterization of the zeolite type formed in each experiment was done by XRD, IR, micropore analysis and visual observation with SEM. The four series of experiments will be discussed consecutively; the most relevant results are summarized in Table 3.5.

Table 3.5 Results of zeolite beta syntheses on metal carriers.

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Coverage [g/m²]</th>
<th>SiO₂ conversion [%]</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1-A3</td>
<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
<td>SEM Fig. 3.3</td>
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<tr>
<td>B1</td>
<td>0.486</td>
<td>0.33</td>
<td>Optimum at H₂O/Al₂O₃=10 000</td>
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<tr>
<td>B2</td>
<td>0.648</td>
<td>0.07</td>
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<td>B3</td>
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<td>C1c</td>
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<td>6.15</td>
<td>SEM Fig. 3.5</td>
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<td>DB Brass</td>
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Fig. 3.3  SEM picture of Exp. A2; SiO₂/Al₂O₃=35; scale bar is 10 μm.

Fig. 3.4  SEM picture of Exp. B3; SiO₂/Al₂O₃=100; template is DBDMACI; scale bar is 10 μm.

Fig. 3.5  SEM picture of Exp. C1c; SiO₂/Al₂O₃=20; scale bar is 10 μm.

Fig. 3.6  SEM picture of Exp. D304; SiO₂/Al₂O₃=20; scale bar is 5 μm.
Chapter 3

Fig. 3.7 SEM picture of Exp. Dbrass; SiO₂/Al₂O₃=20; scale bar is 10 µm

Series A
On the SEM picture of experiment A2 (Fig. 3.3), very small particles (< 0.1 µm) can be seen on the surface of the metal support, the morphology of the particles resembling that of BEA. Due to the low coverage and the small particle size, the identity of the particles could not be determined. However, XRD analysis performed on the particles formed in the free phase of that experiment confirmed that BEA was the only crystalline phase formed. Therefore, the material present on the carrier is considered to be BEA as well. However, the yield is too low for practical application, making improvement necessary.

Series B
The SEM picture of experiment B3 reveals a high, uniform coverage with particles showing typical BEA morphology. Attempts to characterize these crystals directly with XRD failed, since film thickness was too low. Therefore the transmission FT-IR spectrum of a single crystal of experiment B3 was compared with that of particles formed in the free phase of the same experiment, see Fig. 3.8. There is a good correspondence between the two spectra. XRD analysis on particles formed in the free phase proved them to be BEA. Therefore it is justified to assume that the material present on the carrier is indeed BEA.

The result of micropore analysis of sample B3 is given in Fig. 3.9. The characteristic micropore distribution for BEA is found. Comparing the coverage of this experiment with that of experiment A3, it was concluded that the change of template agent and the changes in Si/Al ratio and H₂O/Si ratio have resulted in a substantial improvement of the coverage. This conclusion formed the incentive for a systematic investigation of the influence of a larger number of synthesis variables (as done in series C).

Series C
In Table 3.5 experiments that yielded no crystalline material or that led to coverage with zeolite types other than BEA are omitted. Analysis was based on SEM for all cases and XRD where
possible, since not all experiments yielded material in the free phase. A clear impression was obtained about which synthesis factors were of influence.

**Figure 3.8** Comparison of the transmission FT-IR spectra of crystals formed on carrier and in free phase in Exp. B3.

**Figure 3.9** Horvath-Kawazoe micropore volume plot of sample B3.
Large differences occur in the final products from the settings of series C, both with respect to the zeolite type formed as well as the amount of coverage. In Fig. 3.10 a SEM picture of experiment C3c shows large analcime crystals grown to the wire. Settings that produced no BEA are summarized in Table 3.6

### Table 3.6  Non-BEA material formed in series C

<table>
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<tr>
<th>Exp. No.</th>
<th>Material formed</th>
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<tr>
<td>1b, 2c, 3c, 7a, 8d</td>
<td>Analcime</td>
<td>Si-source is sodium metasilicate</td>
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<tr>
<td>6a, 3d</td>
<td>ZSM-12</td>
<td>Si-source is sodium metasilicate</td>
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<tr>
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<td>Al-source is Al(OH)_3</td>
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<tr>
<td>4a, 4d</td>
<td>amorphous</td>
<td>multiple</td>
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</table>

The average coverage for all experiments in Table 3.5 is 0.709 g/m². The coverage was set to zero g/m² for experiments that yielded no BEA. From replicated experiments the reproducibility in the mean coverage is estimated to be 15%. The most important variables are now easily found by comparing their effect to the mean coverage. The effect of cleaning with acetone for example, is given by the difference of the mean value of all experiments with acetone and that of all experiments without acetone. For the acetone variable this yields a value of -0.394 g/m² which is large when compared to the mean coverage. Other important main effects are: the Si/Al ratio
(effect on coverage +0.305 g/m²), the total salt concentration (+0.182 g/m²), cooling (+0.134 g/m²) and rotating (+0.132 g/m²). Coverage was highest when TEOS was used as silica source (mean coverage for these experiments is 1.60 g/m²) but also Ludox HS-40 and Aerosil are suitable (0.738 and 0.399 g/m² respectively). The mean coverage for sodium metasilicate however, is very low (0.096 g/m²), since this silica source leads to the formation of mainly non BEA product. The choice of alumina source does not appear to have a strong effect on coverage. Apart from these main effects there is an interaction effect between pretreatment with template solution and cleaning with acetone, indicating that results are better when the gauzes are first cleaned with acetone and subsequently pretreated with a 0.18 M template solution, provided that the template is DBDMACl. The details of this can be found elsewhere.27

Fig. 3.11 XRD spectra of sample D316 (a), C8d using 316 foil (b) and particles formed during synthesis of the latter.

Series D
Series D showed again a profound increase in the amount of zeolite material deposited on the carrier when compared with the previous series. The coverages well exceeded that of a monolayer of 0.5 μm thickness, which was estimated to be 0.9 [E_{zeolite}/m² support]. This is to be attributed to the different starting materials from which were used in series D (foil instead of gauze). Also the shape of the metal monoliths was better defined and more accessible for the synthesis mixture than the rolled up gauzes used in previous series. An interesting phenomenon was that very little or no particulate matter was formed during synthesis. This implies that the selectivity for growth on surface is much higher in case foil is used than for gauzes. An explanation for this could be the difference in atomic surface structure as a result from production history. Metal foil is milled whereas the gauzes are produced from drawn steel wires. The crystals formed are relatively large in size (ca. 5 μm).

XRD was performed directly to the supported material and showed next to BEA another crystalline phase (Fig. 3.11a), which is also visible on SEM. This is probably ZSM-12. Additional synthesis on AISI 316 foil, using synthesis conditions from experiment C8d resulted
Chapter 3

in pure BEA coverage (Fig. 3.11b and c).

The results of the tests with various types of metal supports reveal a significant effect of the type of support, as can be seen in Table 3.5. The coverage of 304 stainless steel is higher than that of the other two grades, indicating that an increasing amount of chromium leads to higher coverage. Also the difference in coverage of the brass and nickel foil indicate that the formation of a zeolite film on a metal support is not merely a physical process, but that chemical groups on the support surface, presumably OH groups, intermediate in the bonding of the zeolites. In order to fully understand the differences, detailed knowledge about the outermost atomic layer of the different supports is required. The hypothesis that the zeolites are chemically bonded to the support surface is supported by the results of the heat treatment, the thermal shock treatment and the ultrasonic bath treatment. Neither of the severe treatments resulted in any measurable decrease of coverage. This justifies the conclusion that the crystals are indeed firmly attached to the metal support. Nevertheless, this work was not aimed at elucidating the exact nature of the interaction between zeolites and support surface, which remains a topic for future research.

As can be seen in Fig 3.7, surface roughness of the scale of the crystals can have a strongly promoting effect on the coverage. This leads to the conclusion that a further investigation of the effect of surface morphology modifications caused by physical or chemical treatment is worthwhile.
3.5 Conclusions and Recommendations

Although the use of literature recipes for free phase BEA synthesis in the presence of a metal support, can result in some coverage of a support with BEA crystals, the coverage is generally too low for any practical application (\(\ll 1 \text{ g/m}^2\)). It was the aim of this work to assess relevant synthesis parameters so that optimization of the coverage could be performed. From this the following conclusions can be drawn. The silica source should be preferably Ludox. Furthermore, the addition of NaCl, pretreatment of the carrier by dipping in a 0.18 M template solution and rotating the autoclaves during synthesis have a positive influence on the resulting coverage. Finally, cleaning with acetone only leads to better results when the carrier is pretreated with DBDMACl solution.

A coverage of 27 g/m\(^2\) is obtained when the conditions of experiment C1c are applied to stainless steel 304 foil. The coverages of the foil carriers were generally much higher than that of metal gauzes of the same bulk composition. This is caused by the higher selectivity for surface growth in case foil is used, \(\text{viz.}\), little material is formed in the free phase. This is either to be attributed to the morphologies of the structures used or difference in chemical surface structure as a result of differences in production history.

Based on the results of this study it is anticipated that structured catalytic packings containing up to 40 kg\(_{\text{BEA}}\)/m\(^3\) can be obtained (as a 600 csi monolith). This loading is low compared with alternative reactor systems, so application of \textit{in-situ} grown BEA films on metal packings seems only justified for specific processes, \(\text{viz.}\) for very fast reactions or reactions where selectivity is an issue. The mechanical stability of the film is sufficient. Further research is needed to elucidate the mechanism of the zeolite growth on the support surface, as well as the nature of the bonds between the zeolites and the support surface.

Future work should focus on the assessment of the catalytic activity of the prepared packings. Because of the absence of a binder of some sort, it is possible that due to the enhanced accessibility of the active sites inside the zeolite crystals, the performance of \textit{in-situ} grown zeolites is higher than that of its pelletized counterparts.
List of suppliers of used chemicals

Aerosil 200: Degussa: Germany
sodium metasilicate: CMC, Delft, The Netherlands
Ludox HS-40: DuPont, Belgium
tetraethyl orthosilicate (TEOS): Acros Organics, Belgium
sodium aluminate (NaAlO$_2$): Riedel-deHaën, Switzerland
aluminum nitrate (Al(NO$_3$)$_3$): J.T. Baker BV, The Netherlands
aluminum hydroxide (Al(OH)$_3$): J.T. Baker BV, The Netherlands
aluminum tri-isopropoxide (Al(OCH(CH$_3$)$_2$)$_3$): J.T. Baker BV, The Netherlands
tetraethylammonium chloride (TEACl, (C$_2$H$_5$)$_4$NCl): J.T. Baker BV, The Netherlands
dibenzylidimethylammonium chloride (DBDMACl, (C$_6$H$_5$)$_2$CH$_2$N): ex laboratory

3.6 References

bonded to substrates, structures and uses thereof", US Pat. 5310714 (1994).
4

Optimized synthesis of ZSM-5 on stainless steel foil carriers

During their formation zeolite crystals show the tendency to form bonds with solid surfaces, such as ceramic or metal structures, if present in the synthesis mixture. In this way preshaped structures can be obtained with a high degree of coverage of zeolite crystals.

In this chapter it is shown experimentally that the formation of bonded crystals prevails over that of non-bonded crystals. In order to gain insight in the process of bonded zeolite growth on surfaces (in-situ zeolite synthesis), ZSM-5 syntheses in the presence of stainless steel carriers with different surface areas were performed, thus varying the ratio of amount of synthesis mixture to carrier surface area present. Although it was expected that the coverage expressed in g/m² will become independent on the provided surface area when the surface area is low, this was not confirmed by our experiments. In the investigated range of 0.025 - 0.075 m² for the carrier surface area, the coverage increased when the provided surface area was decreased and the amount and composition of the synthesis mixture was maintained constant.

When syntheses were performed on carriers which already had been covered (repeated synthesis), the amount of zeolite material deposited was larger than the mass increase of the previous step. Coverages of up to 19 g/m² were obtained.

Apparent activation energies for nucleation and crystal growth were found to be 11.7 kJ/mol and 17.0 kJ/mol respectively, indicating that under the conditions studied the crystal growth rate onto the surface is determined by diffusion of reactants.

EDX analysis showed a large variation in the Si/Al ratio in the film formed. The trend being that Si/Al ratios near the support surface are lower than in the regions formed later.

Synthesis variables were varied to find optimal conditions for in-situ synthesis at 125°C of ZSM-5 on stainless steel carriers. This resulted in a synthesis method for preparing stainless steel packings with coverages of up to 2.4 g/m².

Finally, a large scale stainless steel monolithic structure was covered with ZSM-5 and the distribution in coverage was investigated. Although synthesis conditions were not optimized, a coverage of 3.5 g/m² was obtained at a synthesis temperature of 170°C. Analysis of the covered surface with SEM showed a considerable amount of scatter in the coverage of the zeolite crystals, demonstrating the need for mixing during synthesis, especially in syntheses on a larger scale.
Chapter 4

4.1 Introduction

As the need for cleaning off-gases produced by power plants and vehicles has grown increasingly, the use of monolithic structures as reactor packings for carrying catalytic material has experienced a considerable growth in the last two decades. Structured catalyst packings as a reactor packing offer advantages, such as a low pressure drop and dust resistant operation that are not met by packed bed reactors. Common procedure so far in covering monoliths or otherwise pre-shaped carriers has been to fix catalyst material to the packing's surface by the use of a binder. In this work a new technique is presented which applies to zeolites as catalyst materials and in which a binder is absent. Zeolite ZSM-5 (alumina containing MFI) has been studied extensively and proved to be an active and selective catalyst for a.o. reduction of nitric oxides. The deNOx reaction is an interesting application for this purpose, since it allows the combination of two relatively new fields of research, viz., that of zeolites used as catalyst for this reaction and that of binderless coating applied to the preparation of low pressure drop catalyst modules.

By growing zeolites in autoclaves in the presence of a carrier it was found that zeolite crystals show the ability to form a strong bond with the carrier, thus providing a reliable catalytic system. However, the modest knowledge of in-situ growth of zeolites (see Chapter 2) is still of very explorative and qualitative nature. Moreover, in most literature where in-situ ZSM-5 synthesis is claimed silicalite-1 (all silica MFI) is obtained. For application as a catalyst it is very important that alumina containing MFI is deposited on the carriers surface, since silicalite-1 has limited exchange capability and cannot be modified to a strongly acidic catalyst.

Stainless steel is expected to be an ideal material for application as catalyst module since different types of stainless steels already find large application in chemical, pharmaceutical and foodstuffs industries. However, the chemistry, and more specifically, the corrosion behavior is not well understood, especially with respect to the effect of surface treatment and application at high temperature. Critical to the corrosion resistance of stainless steel is the formation of a so-called passive layer which is a chromium oxide or chromium hydroxide layer (depending on the amount of chromium present in the bulk material). Since the passive layer is only a few atoms thick, chemical analysis of the surface is very difficult. Moreover, it makes stainless steels very sensitive to surface modifications, such as scratching or deformation. The unresolved questions of the chemistry of the surface of stainless steel make understanding of the nature of the bonding of the zeolite crystal to the support surface difficult. In spite of this lack of theoretical knowledge, the growth of zeolites on stainless steel has been investigated by several authors and successful applications of zeolite covered stainless steel are reported in adsorption modules, membrane separation and as deNOx catalyst.

It is the aim of this chapter to investigate the synthesis conditions that influence improvement in this system. To this end we will focus on zeolite ZSM-5 grown on stainless steel AISI 316.

The effects of synthesis time, synthesis temperature and gel composition on the resulting covered
Optimized synthesis of ZSM-5 on stainless steel foil carriers

packing will be investigated. Points of interest in this respect are the coverage and the quality of the coating produced and the conversion of the synthesis mixture to zeolite material in the coating.

The first problem that needs to be addressed is the selectivity of growth on the surface. It has been found repeatedly\textsuperscript{5,9,10} that zeolites grow preferentially on a stainless steel surface. However, during synthesis also zeolite crystals can be formed in solution, depending on the amount of surface area present. In our study we first performed experiments with identical synthesis mixtures — as to composition and amount — but with varying carrier surface area. It is expected that when the surface area of the carrier is too high to be covered by a monolayer, considering the synthesis mixture potential, the coverage \([\text{g/m}^2]\) will decrease when the carrier surface area is increased, the deposited amount being constant. On the other hand, at very low surface areas, the coverage is expected to be constant when changes in carrier surface area are low.

Since the volume of the autoclaves used was given and limited, the only way to increase coverage beyond the potential of the mixture present is by means of repeated synthesis in which packings already covered with a ZSM-5 layer are used as a carrier for a subsequent synthesis.

A more preferable approach would be to scale up the equipment used for \textit{in-situ} ZSM-5 synthesis. As will become clear in this chapter, by increasing the volume of the synthesis autoclave (from 35 ml to 2 liter) inhomogeneities in the local conditions during synthesis throughout the autoclave give rise to a non-homogeneous coverage of the carrier. Proper controllable mixing can only be obtained by circulating the synthesis mixture through the autoclave using a pump which is at synthesis temperature. In doing so, it is necessary to operate at lower synthesis temperatures. In view of planned large scale experiments, small scale syntheses were performed to find optimal conditions for the case that the synthesis temperature is limited to 125\textdegree{C}. 

4.2 Experimental

4.2.1 Varying Surface Area of Stainless Steel Carriers

Stainless steel foil (AISI 316, thickness 50 μm, supplied by Knight’s Strip Metal Ltd, UK) was cut in strips with varying length and width of 30 mm. The resulting surface area of the strips ranges from 0.025 - 0.075 m². These strips were processed to metal monoliths by forcing them through a cog wheel mill, thus corrugating half of the total length of the strip and winding it subsequently around the center of the strip (see Fig. 4.1). The channels in the monoliths were sinusoidal shaped in cross-section with dimensions of 4.0 mm (base) by 2.0 mm (height). The packings were cleaned by boiling in toluene for two hours, dried overnight in air at 240°C and subsequently weighed.

![Figure 4.1 Construction of metal monoliths. Measures in mm.](image)

Synthesis mixtures were prepared by adding tetraethyl orthosilicate (TEOS, Acros) to a stirred mixture of tetrapropylammonium hydroxide and tetrapropylammonium bromide (TPAOH, TPABr, Chemische Fabrick Zaltbommel) and sodium aluminate (Riedel-deHaën) to form a mixture with molar composition: 1.0 Al₂O₃ - 83.2 SiO₂ - 10200 H₂O - 8.36 TPA₂O - 5.22 OH⁻. The packings were placed in Teflon-lined autoclaves which were subsequently filled with 35 g of the synthesis mixture. The autoclaves were then placed in an oven and the synthesis was carried out at a temperature of 170°C for 26 hours. The syntheses were carried out statically, i.e. without rotation of the autoclaves. After synthesis, the packings were removed and washed thoroughly with de-ionized water and dried at 140°C. The coverage was measured by weighing the packings again.

The coverage of the packings is defined as the mass increase per unit surface area [g/m²]. Conversion is expressed as the ratio of the amount of silica incorporated in the zeolite film to the amount of silica originally present in the synthesis mixture.

Coverage in time was monitored by removing autoclaves from the oven at certain intervals.
4.2.2 Repeated Synthesis

Preparation of packings and synthesis mixture was carried out as described in the previous paragraph and synthesis conditions were the same. After the first synthesis the covered packings were subjected to ultrasonic cleaning to remove non-bonded material if present. This was done by placing the packings in polyethylene bottles filled with de-ionized water and submerging the bottles in an ultrasonic bath, operating at 25 kHz. After drying, the covered packings were then used again as carrier for a next synthesis. Three syntheses were performed subsequently in this way.

![Figure 4.2 Rotation of autoclaves: a: 35 ml autoclave, b: clamp, c: horizontal axis of rotation](image)

4.2.3 Optimized Reaction Conditions

To investigate optimal synthesis conditions at 125°C, five factors were varied:

- the molar Si/H₂O ratio,
- the amount of template in the synthesis mixture,
- the pH of the synthesis mixture, controlled by using different ratios of TPAOH and TPABr,
- the molar Na/Al ratio, controlled by adding appropriate amounts of NaBr,
- static synthesis or rotation of autoclaves during synthesis. This was performed by rotating the autoclaves a full 360° turn per minute followed by a static interval, see Fig. 4.2.

The experiments were arranged in a 2⁵-1 fractional factorial design as listed in Table 4.1. The (+) and (-) signs in Table 4.1 are used for the calculation of the effects of changes in the variables. Changes in synthesis mixture compositions were chosen to be around the settings used in the previous experiments. Synthesis time was 59 hour and temperature was 125°C.
Chapter 4

Table 4.1 Synthesis conditions used in the optimization experiments.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>H₂O/Si [mol/mol]</th>
<th>(Si+Al)/TPA [mol/mol]</th>
<th>pH</th>
<th>Na/Al [mol/mol]</th>
<th>rotation [rpm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90(-)</td>
<td>2.5(-)</td>
<td>12(-)</td>
<td>1(-)</td>
<td>1(+)</td>
</tr>
<tr>
<td>2</td>
<td>150(+))</td>
<td>2.5</td>
<td>12</td>
<td>1</td>
<td>0(-)</td>
</tr>
<tr>
<td>3</td>
<td>90</td>
<td>7.5(+)</td>
<td>12</td>
<td>1</td>
<td>0</td>
</tr>
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<td>4</td>
<td>150</td>
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<tr>
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<td>90</td>
<td>2.5</td>
<td>13(+)</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>150</td>
<td>2.5</td>
<td>13</td>
<td>1</td>
<td>1</td>
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<tr>
<td>7</td>
<td>90</td>
<td>7.5</td>
<td>13</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>150</td>
<td>7.5</td>
<td>13</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>90</td>
<td>2.5</td>
<td>12</td>
<td>2(+)</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
<td>2.5</td>
<td>12</td>
<td>2</td>
<td>1</td>
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<tr>
<td>11</td>
<td>90</td>
<td>7.5</td>
<td>12</td>
<td>2</td>
<td>1</td>
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<tr>
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<td>150</td>
<td>7.5</td>
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<td>0</td>
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<td>150</td>
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<td>150</td>
<td>7.5</td>
<td>13</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

4.2.4 Large Scale Synthesis

In addition to the previous experiments, an attempt was made to cover a large sized monolith (height × O.D. = 0.1 m × 0.1 m, volume 785 ml) with ZSM-5. The monolith was constructed as described previously from a strip of 5 m × 0.1 m yielding a monolith with an outside surface area of 1.0 m². The dimensions of the sinusoidal channels were 7.5 mm (base) by 4.0 mm (height). Cleaning and drying was performed as described in paragraph 4.2.1.

Synthesis was performed using a mixture of molar composition 1.0 Al₂O₃ - 80.0 SiO₂ - 160000 H₂O - 36.5 TPA₂O - 75.4 OH. Synthesis time was 48 h at a temperature of 170 °C. The position of the monolith is depicted in Fig. 4.3. To investigate the coverage distribution, two test strips of the same material were placed inside the central channel and a wall channel of the monolith, as indicated in Fig. 4.3. The test strips were as long as the monolith height and were approximately 2 mm wide.
Figure 4.3  Positioning of 1 m²-monolith in autoclave. a: stainless steel autoclave, b: 2 liter Teflon insert, c: monolith, d: liquid level, e: supporting table (Teflon). The arrows indicate the position of the test strips (see text).
4.3 Results and Discussion

4.3.1 Varying Surface Area of Stainless Steel Carriers

After removing the packings from the autoclaves, no particulate matter was found, neither in the synthesis mixture nor on the packing after rinsing. In Fig. 4.4 the coverage of packings (expressed in g/m²) is given as a function of available carrier surface area and in Fig. 4.5 SEM micrographs of a small and a large surface area packing are shown. When varying surface area, even at very low values a further decrease still resulted in a higher coverage.

![Graph showing coverage vs. Foil Surface Area](image)

Figure 4.4 Dependence of coverage (●) and Si-conversion (▲) on available foil surface area.

This indicates that at a high available surface area a film is formed with thickness of one crystal. These initially formed crystals are bonded to the support surface. When the surface area decreases, this gradually changes to a layer of multiple crystals that form bonds with the crystals already connected to the surface. This process already starts when there are still uncovered areas on the support, demonstrating that under the current conditions formation of a complete monolayer of zeolite crystals is not possible. A somewhat paradoxical image is obtained from this: on one hand crystals show a distinct preference to grow on the surface of the metal support, while on the other hand, at a certain surface area this process is dominated by crystals showing preference to grow on crystals already present, leaving parts of the carrier uncovered, while no crystal growth in the solution was observed.

This indicates that the growth process under these conditions is determined by diffusion of reactants and not by the formation of the zeolite crystals. In order to check this hypothesis, apparent activation energies were calculated.
Optimized synthesis of ZSM-5 on stainless steel foil carriers

Figure 4.5 SEM pictures of ZSM-5 coverage on 0.0256 m² foil (a) and of 0.0708 m² foil (b). Scale bars represent 100 μm. Synthesis conditions are given in section 4.2.1.

Apparent activation energies for nucleation ($E_{n,n}$) and for crystal growth ($E_{c,g}$) were calculated from the growth curves recorded at 125°C and 170°C, given in Fig. 4.6. From the nucleation time and the rate of crystallization at half of the total conversion and by assuming first order kinetics in SiO₂ concentration both activation energies can be calculated: $E_{n,n} = 11.7$ kJ/mol and $E_{c,g} = 17.0$ kJ/mol.

Figure 4.6 Conversion of SiO₂ used to calculate $E_a$

According to Chao et al. these values should be 25 and 29 kJ/mol respectively. In general these relatively low activation energies are characteristic for diffusion limited systems.
Fig. 4.7 SEM pictures of repeated synthesis experiments. Packing after first (a and b) and second (c and d) step at different magnifications. Scale bars represent 100 µm.

4.3.2 Repeated Synthesis

Here too the formation of non-bonded material was negligible. In Table 4.2 the results of repeated synthesis are given. Ultrasonic cleaning after each step had only a small effect on coverage, weight decrease being less than 5% of the amount present. An XRD spectrum of the final product is given in Fig. 4.8. After each synthesis the weight gain of the packings increased. As can be seen in Fig. 4.7 the surface is already covered completely after the first synthesis. Weight gain of the second synthesis step should therefore partly be attributed to the increase in size of the ZSM-5 crystals and partly to the deposition of new small crystals on top of the existing ones, as can be seen in Fig. 4.7d. The crystal shape becomes more rounded as a result of repeated synthesis, indicating that the crystals dissolve on the sharpest edges first. After the first synthesis the surface is almost completely covered, leaving only some small uncovered areas. The empty spots are completely covered after the second synthesis in which all nutrients are refreshed. The remainder of the nutrients in the synthesis mixture is used for growth on the already existing film. This process is continued in the third cycle.
Table 4.2 Coverage of foil upon repeated synthesis.

<table>
<thead>
<tr>
<th>cycle</th>
<th>coverage [g/m²]</th>
<th>cumulative coverage [g/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.28(5.03)</td>
<td>5.03</td>
</tr>
<tr>
<td>2</td>
<td>6.91(6.76)</td>
<td>11.79</td>
</tr>
<tr>
<td>3</td>
<td>7.25</td>
<td>19.02</td>
</tr>
</tbody>
</table>

1) Coverage after ultrasonic cleaning is given between brackets.

Figure 4.8 XRD of repeated synthesis sample. Si/Al=40. Vertical bars are reference for MFI.

4.3.3 Optimized Reaction Conditions

SEM pictures of experiments 1-16 are given in Fig. 4.9. There is large difference in the film obtained, both with respect to coverage as well as crystal size and morphology. High coverages (experiments 6, 8, 15 and 16) are accompanied by flat shaped crystals with rounded edges. Twinned MFI crystals only appear when crystallization on the carrier is apparently unfavorable. When crystal growth on the carrier surface is favorable, a homogeneous film is readily formed. Settings that result in a high and homogeneous coverage include a lower template concentration and pH = 12.8.
Fig. 4.9 SEM pictures of optimization experiments, cf. Table 4.1 for synthesis conditions. Scale bars represent 10 μm.
Table 4.3  Results of optimization experiments. Conditions are given in Table 4.1.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>coverage [g/m²]</th>
<th>conversion [%]</th>
<th>Si/Al [-]</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.031</td>
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<td>4</td>
<td>0.224</td>
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<tr>
<td>5</td>
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<tr>
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<td>7</td>
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<tr>
<td>8</td>
<td>1.051</td>
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<td>9</td>
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<td>0</td>
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<tr>
<td>10</td>
<td>0.078</td>
<td>1.6</td>
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<td>0</td>
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<td>0.3</td>
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<td>13</td>
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<td>16-23</td>
</tr>
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<td>14</td>
<td>0.26</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.587</td>
<td>19.8</td>
<td>31-∞</td>
</tr>
<tr>
<td>16</td>
<td>2.362</td>
<td>46.4</td>
<td>42-53</td>
</tr>
</tbody>
</table>

The advantage of using a factorial design for the experimental set-up is twofold. On one hand different settings are screened, some of which are not obvious, and this may lead to new settings. On the other hand, quantitative interpretation of the data becomes possible by assigning values to the effect of the factors investigated. The effect of a factor is defined as the difference in response (i.e. the coverage) between the mean value of the resulting coverage of the experiments conducted with the factor at the (+) level and the mean value of the response at the (-) level.\(^1\)

In Table 4.3 coverage and conversion are given for all experiments. Normal plots of the effects indicate that only two effects are distinguishable from noise:

- The pH effect is 0.88 g/m², indicating that on average the high setting for pH leads to a higher coverage;
- The interaction between template concentration and rotating is -0.21 g/m². This implies that on average a combination of rotating and a low template concentration lowers the coverage, as can be seen from experiments 4, 7 and 11.

In general, the synthesis is most sensitive to pH, template concentration and rotation. Other factors investigated did not show clear effects in the investigated range.

Si/Al ratios given in Table 4.3 were measured by EDX. There are considerable variations in these values, the general trend being that closer to the surface the Si/Al ratio is lower. This is in
contrast with the results of Sano et al.\textsuperscript{16} who report a quite extreme Al-distribution in ZSM-5 films formed on Teflon, but opposite to our findings, the Al-rich species are being formed later in the growth process.

In case rotation of the autoclaves is applied, Si/Al ratios varied less and are more close to that of the synthesis mixture.
4.3.4 Large Scale Synthesis

The coverage of the large monolith was 3.5 g/m². As can be seen in Fig. 4.10, there is a considerable distribution in the coverage throughout the monolith. There appears to be no specific trend in the differences of the coverage, suggesting that the maldistribution is the result of random inhomogeneities and it is to be attributed to a lack of mixing during synthesis.

![Coverage distribution](image)

**Fig. 4.10** Coverage distribution encountered in ZSM-5 synthesis on a large monolith (100 mm O.D.). Scale bars represent 100 μm.
Chapter 4

Although the stainless steel monolith proved to be useful as a catalyst module (see Chapter 6), some loss of coverage was observed after a period of several months, after it had undergone calcination. This was also the case with the small covered monoliths that had been subjected to calcination and were left at ambient conditions for a period of several months. Although AISI 316 steel is expected to be applicable at temperatures exceeding 550°C, changes in color of the surface are observed after heating at these temperatures. Although the material maintained its stainless quality (no severe oxidation is observed, at least no color changes were observed), chemical changes in the passive layer must have taken place upon heating. This proved to be critical for the application of binderless zeolite carrier in some cases, since the zeolite crystals are bonded to the outermost surface layer. As mentioned before, the passive layer is very critical for the corrosion resistance of the stainless steel and the possibility that the presence of zeolite crystals disturbs the formation or reorganization upon heating should not be ruled out.3

In order to prevent the stainless steel from surface corrosion, a lower calcination temperature (350°C) is suggested. To ensure the complete decomposition of the template from the framework, an oxidizing atmosphere such as ozone should be applied. In later syntheses with zeolite Beta on stainless steel carriers this was done and no color changes of the modules were observed.
4.4 Conclusions and Recommendations

Synthesis conditions for successful preparation of zeolitic films on stainless steel carriers were found and optimized, indicating that a higher pH improves coverage and thereby synthesis efficiency. The bonding of the crystals with the surface is strong, as ultrasonic treatment at 25 kHz of the packings resulted in low (< 5 wt%) loss of zeolite material.

The maximum pH at which syntheses were performed was 12.8. No indications were found that the metal carrier suffered from the synthesis conditions, so a further improvement could be to increase pH beyond this. The metal surface did suffer from the high temperatures applied in calcination, which is a necessary step in producing a catalyst. As a result of the calcination step the formed films lost their stability in some cases, but only after a longer period of time (several months). To this respect it would be interesting to monitor the chromium distribution in the zeolite layer with time, to check wether the chromium remains in the passive layer or diffuses into the zeolite crystals. Apart from applying milder conditions for the calcination step, which proved to be effective in later syntheses, an other option to prevent loss of zeolite material would be to use different carrier materials, such as the aluminum rich Kanthal A® (5% Al) or Fecralloy® (4.7% Al and 0.3% Y) metals. These metals are known to have superior oxidation resistance due to the formation of an alumina scale when oxidized at elevated temperatures. Furthermore, Kanthal A showed promising results as carrier material for in-situ grown zeolites.

The experiments with varying surface area give insight in the formation process of zeolitic films on stainless steel carriers. Initially crystals show a preference to grow onto the support. This is followed by formation of crystals that are less rich in aluminum and show a decreased preference for growth on a surface, leaving some of the area even uncovered. From repeated synthesis experiments it is concluded that this decreased preference for surface growth is not a result from the formation chemistry, but more likely to be the result of variations in the local concentration of the synthesis mixture, which locally becomes exhausted of nutrients. This is confirmed by the relatively low apparent activation energies that were calculated, indicating that at the current configuration the synthesis process is governed by diffusion limitation of the reactants and mixing is required.

The necessity of mixing is further demonstrated by the inhomogeneities found in covering a large scale monolith. The difficulty with rotating, apart from being impractical with larger autoclaves, is that it disturbs the crystallization process as much as it helps to form optimal distribution of the zeolite coverage. Mixing should therefore be conducted with great care and from this point of view a set-up which enables the circulation of the synthesis mixture in plug flow is much to be preferred above mixing by means of a stirrer. Future experiments should point out what the optimal refreshment rate to this respect is.

Acknowledgment

Mark Ketting is gratefully acknowledged for his contribution to this chapter.
4.5 References

5 Synthesis of ZSM-5 on Ceramic Carriers

5.1 Introduction

In the previous chapters metal surfaces were used as supports for in-situ zeolite synthesis. Although stainless steel and other metals present marked advantages, some qualities of ceramic structures, like their high thermal resistance and their porous open structure, are unmatched. Cordierite and other ceramic monoliths have proven their value in a variety of practical applications, ranging from deNOx-ing of electricity plant off-gases to fat hardening in margarine production. It is expected that in-situ growth of zeolites on ceramic structures yields valuable catalyst systems.

The specific surface of most ceramic catalyst carriers is too low for practical purposes (< 1 m²/g). Common procedure in increasing the specific surface area of both monoliths and ceramic foams is application of a washcoat. By this method the surface area is increased to 30 m²/g or more. The amount of washcoat that can be applied successfully is limited by the thickness that will adhere without cracking of the coating and by the spacing of the channels in the ceramic structure. By applying the in-situ grown zeolite technique, it is expected that the specific surface can be increased to at least 50 m²/g, depending on the coverage of the zeolite material. Parameters like the amount of zeolite material deposited on the carrier surface, the synthesis time, the dilution ratio of the synthesis mixture, to name but a few, are of particular relevance to assess the practical value of these zeolite covered ceramic structures applied as catalyst modules. The selectivity towards growth on the surface proved difficult to investigate, since reproducible collection of non-bonded material after synthesis was not possible. But it was already seen in the previous chapter that this is hardly an issue, since growth takes places preferentially on the carrier surface. In most cases this seems justified for ceramic carriers as well.

The little that is known in literature about in-situ synthesis of ZSM-5 and other zeolite types on ceramic carriers has already been mentioned in Chapter 2: growth of silicalite on clay¹, on fused silica glass² and of zeolite A and ZSM-5 on alumina filters³,⁴ has been reported. However, this literature is poor in quantitative data with respect to the prepared packings. Some quantitative data on in-situ zeolite synthesis on ceramic carriers is given in a patent by Grasselli et al.⁵ who cover Pyrex glass plate, cordierite and mullite monolith with ZSM-5.
Chapter 5

This chapter aims to investigate the relevant parameters encountered in the synthesis of ZSM-5 on different ceramic carriers. The factors of which the effect on the amount and the quality of the film formed was studied, can be summarized as follows:

1. Rotating of the autoclaves. Previous work with stainless steel carriers showed a large influence of rotation. It is expected that when ceramic foams are used, this effect will become more pronounced because of the brittleness of the carrier material. From this it is expected that a high rotation rate would lead to loss of material, which is subsequently interpreted as a lowered coverage. The necessity of rotating the autoclaves during synthesis remains open to debate. If rotation is required to ensure a homogeneous coverage with zeolite crystals, the speed of rotation is expected to show an optimum. Due to experimental limitations two modes of operation were subject of research: continuous rotation in which the autoclaves were rotated at a speed of 1 revolution per second and pulsewise rotation in which the autoclaves were rotated 180° per each 30 minutes.

2. Dilution of the synthesis mixture (expressed as H₂O/Si ratio). This is especially important from a practical point of view. Early work by Jansen et al. describes in-situ ZSM-5 synthesis at very high dilutions (H₂O/Si = 13000). This implies that for covering a monolith or other type of carrier, impractically large autoclaves would be required. For this reason, the focus has been on lowering the amount of water.

3. Feed-to-surface-ratio. As discussed in Chapter 4, surface loading is expected to be a function of the amount of Si present in the synthesis mixture per unit surface area of carrier material. It is relevant to know how much support surface can be covered. This value can be expressed as the amount of silica offered (feed) per unit area of support, expressed in mol Si/m² support. The experiments were carried out with a constant amount of reaction mixture and varying the available support surface area.

4. Si/Al ratio. The zeolite’s Si/Al ratio is known to influence the zeolite growth rate. Although most literature claims in-situ synthesis of ZSM-5, in most cases silicalite is really obtained. For most catalytic applications, the presence of framework alumina is essential, since it determines the cation exchange ability of the zeolite obtained. On the other hand, a too high alumina content decreases the hydrothermal stability of the zeolite. In this work, for most experiments the Si/Al-ratio in the synthesis mixture was kept at 40. Some experiments were performed at a Si/Al ratio of 14 to investigate the effect on the formed layer.

5. Determination of the support loading as a function of synthesis temperature and time. Synthesis of homogeneous ZSM-5 crystals is normally carried out at temperatures of 150-200°C. In the present work syntheses were carried out at 110, 150 and 160°C and the mass increase was recorded as a function of time at fixed temperatures.

6. Upscaling. Large scale syntheses were performed with synthesis conditions that were found to be optimal in the small scale experiments.

7. The type of carrier material. The majority of the experiments were performed on α-alumina foam but also cordierite monolith, α-alumina tubes and other foam materials were tested.
The arrangement of the experiments by carrier type and the factors investigated are summarized in Table 5.1.

<table>
<thead>
<tr>
<th>Table 5.1</th>
<th>Overview of conducted experiments by carrier type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45 ppi(^{(1)})</td>
</tr>
<tr>
<td></td>
<td>α-Al(_2)O(_3) foam</td>
</tr>
<tr>
<td>Rotation of autoclaves</td>
<td>●</td>
</tr>
<tr>
<td>Si/H(_2)O</td>
<td>●</td>
</tr>
<tr>
<td>Feed ratio</td>
<td>●</td>
</tr>
<tr>
<td>Si/Al</td>
<td>●</td>
</tr>
<tr>
<td>Temperature/time</td>
<td>●</td>
</tr>
<tr>
<td>Large scale synthesis</td>
<td>●</td>
</tr>
</tbody>
</table>

1) The pore size of a ceramic foam material is usually expressed in pores per linear inch (ppi).

Only zeolite ZSM-5 will be subject of research in this chapter. The composition of the synthesis mixture was not further optimized since first syntheses already yielded promising amounts of ZSM-5 deposited on the carrier.

Before discussing the conducted experiments and their results, first some general background information on ceramic foams as structured catalyst packing and on monoliths will be given.
Chapter 5

5.2 Background of Ceramic Carriers

5.2.1 Monoliths

Ceramic monolithic structures find already wide application in process industries, their main purpose being in end-of-pipe processes and automotive exhaust gas cleaning. Monoliths can be obtained in many different shapes and sizes and with a wide range of channel diameters, from as coarse as 50 cpsi (Cells Per Square Inch, this corresponds to a channel pitch of 3.6 mm for square channels) to as fine as 600 cpsi (pitch = 1 mm). The higher the ppi number, the more compact the resulting reactor generally can be, albeit at the expense of a higher pressure drop. Among the advantages of monoliths are their low price and the ease of modeling their flow and performance.

Since monoliths have been in use now for several decades and have been subject of extensive research, many publications exist on the topic. An excellent review is given by Cybulski and Moulijn and a very recent overview of the state of the art, discussing all possible applications, present and future, is given by Farruto.

5.2.2 Ceramic Foams

Ceramic foams are open macroporous structures with interconnected pores, see Fig. 5.1. They found originally application in the filtration of molten metals. However, in recent years increasing attention is paid to the use of these foams as a structured catalyst packing.

![Image of ceramic foams](image)

**Fig. 5.1** a: Ceramic foam plates of varying composition and pore sizes. From left to right: 1. SiC (7.5 ppi), 2. SiC (10 ppi), 3. α-Al₂O₃/ZrO₂ (25 ppi), 4. α-Al₂O₃ (10 ppi), 5. α-Al₂O₃ (45 ppi), 6. ZrO₂ (45 ppi). Scale bar represents 200 μm. b: Magnification of α-alumina foam (45 ppi). Scale bar represents 200 μm.

In general, in this type of application the reactant stream is forced through the macroporous channels in the foam. By contrast, ceramic foams can be used as a catalyst reactor packing by
placing them parallel in the stream, as depicted in Fig 5.2., thus forming a parallel passage reactor (PPR).

![Diagram of porous ceramic plates in parallel passage reactor (PPR)](image)

**Fig. 5.2** Arrangement of porous ceramic plates in a parallel passage reactor (PPR) configuration

In the PPR the reactants enter the porous plates by diffusion/dispersion, which is perpendicular to the main gas flow direction.

Ceramic foams can be produced in a number of ways. Generally polyurethane (PUR) foam is used as lost material, acting in fact as a template. The PUR-foam is impregnated with an aqueous slurry of inorganic particles. After that, the PUR-foam is burnt out and at the same time the foam is calcined by heating at 1500°C. In this way the positive image of the PUR-foam is obtained. A different approach to produce ceramic foams is by in-situ polymerization, in which the image of an aqueous foam is captured in the ceramic particles by in-situ polymerization of a mixture of monomers and the ceramic particles and removing the formed polymer subsequently by calcination. This method yields foams with finer pores and enables the possibility to shape the foams before the calcination step$^{11}$. By using a regularly shaped packed bed, well-defined ceramic foams with a high regularity can be obtained$^{12}$ of which the main advantage is the increased mechanical strength.

Among the typical advantages of ceramic foams, used as catalyst carrier, are their high porosity and the wide range of shapes that is available due to their preparation methods. Furthermore, the more tortuous nature of the porosity improves reactant mixing and favors surface reactions as well as radial dispersion within the monolith. The most important disadvantage is presented by their limited mechanical strength.

The foams are characterized by their number of pores per linear inch (‘ppi-number’). For a given ppi-number and porosity, parameters like the average pore- or cell diameter, the density, the
specific surface area (\(\text{m}^2/\text{m}^3\)) or \([\text{m}^2/\text{g}]\)) and the pressure drop are determined. The relation between some of these parameters for a typical ceramic foam is given in Fig. 5.3.

![Graph showing pore diameter and specific surface area as a function of ppi number for alumina foam with 92% porosity.](image)

**Fig. 5.3** Pore diameter (---) and specific surface area (—) of a ceramic foam as a function of ppi number for alumina foam with 92% porosity. After Sweeting et al.\textsuperscript{13}

Ceramic foams exhibit structural properties that make them suitable as a catalyst carrier. Because of their large pore structure (0.04-1.5mm) and high porosity (80-90%), dust accumulation will not lead to plugging of the pores easily.

**Known Applications of Ceramic Foam as a Catalyst Support**

Although the use of ceramic foam as a catalyst support has not broadly been investigated yet, some experimental data on use as a catalyst are available from literature. In general, the surface of the foam increases by washcoating, after which it is loaded with metals or oxides. No literature appeared about \textit{in-situ} synthesis of zeolites onto ceramic foams. However, two related patents are known about loading of the applied washcoat with zeolites\textsuperscript{14} and carbon\textsuperscript{15}, respectively. In this way, the specific surface area increases significantly. In Table 5.2., some typical bench scale studies of reactions with ceramic foam catalysts, often in comparison with pellets and honeycombs, are summarized.
Table 5.2  Bench scale investigations of ceramic foams applied as catalysts.

<table>
<thead>
<tr>
<th>Process / Catalyst</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalytic combustion of soot</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Cu, Fe-La₂O₃-Pt, Co-La₂O₃-Pt / alumina</td>
<td>Ceramic foam showed best performance</td>
<td>16</td>
</tr>
<tr>
<td>Comparison between honeycomb, pellets and ceramic foam supported catalysts.</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HCN production (ammoniation):</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄ + NH₃ + 1½ O₂ → HCN + 3 H₂O</td>
<td>Selectivity HCN: 80%</td>
<td>17</td>
</tr>
<tr>
<td>• Pt-10% Rh on α-alumina foam</td>
<td>Conversion NH₃/CH₄: 80%</td>
<td></td>
</tr>
<tr>
<td><strong>Olefins by oxidative dehydrogenation of higher alkanes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>• Pt on α-alumina foam</td>
<td>Selectivity Olefins: 70%</td>
<td>17</td>
</tr>
<tr>
<td><strong>Methane partial oxidation (syngas production)</strong></td>
<td>Hydrocarbon conversion: 80%</td>
<td></td>
</tr>
<tr>
<td>• LaₓSr MnO₃ (Perovskite) on mullite foam (x=0.2-0.8)</td>
<td>Conversion: 10-85%</td>
<td>18</td>
</tr>
<tr>
<td>Comparison between ceramic foam supported perovskite and unsupported perovskite</td>
<td>GHSV: 7000 h⁻¹</td>
<td></td>
</tr>
<tr>
<td>• Rh and Pt / α-alumina foam</td>
<td></td>
<td>17, 19-21</td>
</tr>
</tbody>
</table>

5.2.3 Other Ceramic Supports

The application of ceramic carriers enables reactor layouts not conceivable before. An example of this is the polythix reactor in which catalytically active rods are placed in a fixed array to produce an open structure, much like a static mixer module, thus minimizing pressure drop for the flowing fluid and maintaining radial dispersion. The polythix reactor could be loaded with rods of catalytic material but also with in-situ zeolite covered ceramic rods, which will have the advantage of having a higher mechanical stability than pure catalytic material.
Chapter 5

5.3 Experimental

5.3.1 Materials Used

The different supports that were used for zeolite synthesis and their properties are listed in Tables 5.3 and 5.4. It is noted that the SiC foam contains large amounts of aluminum, in contrast to its specifications, indicating that the material is either contaminated or even contained no SiC at all.

Table 5.3 Specifications of the ceramic supports used in synthesis.

<table>
<thead>
<tr>
<th>Support type</th>
<th>EDX Composition</th>
<th>Density [kg/m³]</th>
<th>Porosity [%]</th>
<th>BET-Surface area [m²/g]</th>
<th>Spec. Surface area, (a_s) [m²/m³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)-Alumina foam 45 ppi</td>
<td>94.8 (\alpha)-Al₂O₃, 5.2 SiO₂</td>
<td>586</td>
<td>83</td>
<td>(\leq 2)</td>
<td>8000*</td>
</tr>
<tr>
<td>Zirconia foam 20 ppi</td>
<td>(\sim 18.0) ZrO₂, (\sim 2.6) Y₂O₃</td>
<td>652</td>
<td>-</td>
<td>(\leq 1)</td>
<td>3600*</td>
</tr>
<tr>
<td>Silicon Carbide foam 16 ppi</td>
<td>26.3 SiC, 31.6 Al₂O₃, 3.1 MgO, 39.0 C</td>
<td>304</td>
<td>-</td>
<td>(\leq 1)</td>
<td>3000*</td>
</tr>
<tr>
<td>(\alpha)-Alumina tubes (d_{\text{ave}} \times d_{\text{ave}} = 2 \times 3.9) mm</td>
<td>94.0 (\alpha)-Al₂O₃, 6.0 SiO₂</td>
<td>449</td>
<td>26.3</td>
<td>(\leq 1)</td>
<td>931</td>
</tr>
<tr>
<td>Cordierite honeycomb 1 (\times 1) mm channels; 286 cpsi</td>
<td>22.0 (\alpha)-Al₂O₃, 55.5 SiO₂, 22.5 MgO</td>
<td>480</td>
<td>44.4</td>
<td>(\leq 1)</td>
<td>2250*</td>
</tr>
</tbody>
</table>

*According to Sweeting et al.\(^{13}\); see Fig. 5.3. *According to Cybulski and Moulijn.\(^{*}\)
Table 5.4 Chemical compositions of the supports used in synthesis.

<table>
<thead>
<tr>
<th>Support</th>
<th>Elemental analysis [atomic %]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>α-Alumina foam</td>
<td>33.8</td>
</tr>
<tr>
<td>α-Alumina tubes</td>
<td>33.9</td>
</tr>
<tr>
<td>ZrO$_2$/Y$_2$O$_3$ foam</td>
<td>2.97</td>
</tr>
<tr>
<td>SiC foam</td>
<td>14.0</td>
</tr>
<tr>
<td>Cordierite monolith</td>
<td>11.4</td>
</tr>
</tbody>
</table>


5.3.2 Support and Equipment Pretreatment

Supports were cut to pieces of ca. 1 cm$^3$, depending on the type of experiments and were then cleaned by boiling in toluene for 1 hour with reflux. Subsequently, they were dried at 130°C overnight. Prior to each synthesis, the Teflon-lined 50 ml autoclaves were cleaned with a 4M NaOH solution at synthesis temperature. During synthesis the supports were mounted in the autoclaves as depicted in Fig. 5.4.

![Fig. 5.4 Positioning of ceramic supports in 50 ml autoclaves. a: stainless steel autoclave, b: Teflon insert, c: Teflon supporting rod, d: Teflon wire and e: ceramic material.]

5.3.3 Preparation of Synthesis Mixture

Aqueous mixtures were made from tetraethyl orthosilicate (TEOS, 98% in water, Acros Organics), tetrapropylammonium hydroxide (TPAOH, 40% in water, CFZ, Zaltbommel) and
sodium aluminate (NaAlO₂, Riedel-de Häıhn) with molar compositions in the ranges of: 1.0 Al₂O₃ - 40.0 SiO₂ - 2.3 (TPA)₂O - 800 H₂O, pH = 13.3-13.7. The syntheses were carried out under hydrothermal conditions at temperatures between 110 and 175°C. The synthesis time was between 2 and 130 h. During synthesis most syntheses autoclaves were rotated 180° pulsewise with a frequency of once every 30 min. After synthesis the supports were washed with demineralized water and subsequently dried overnight at 120°C.

5.3.4 Synthesis

Syntheses were grouped to investigate the following factors.

Rotating of autoclaves
Three types of experiments were performed:

1. Static.
2. Semi-continuous rotation (one 180° turn every 30 min).
3. Continuous rotation at ca. 60 rpm.

The (semi-continuous) rotation is performed as described in the previous chapter in section 4.2.2.

Dilution of the synthesis mixture
The effect of dilution of the synthesis mixture, i.e. the H₂O/Si ratio, was investigated by operating at two different concentrations: H₂O/Si=20 and 140 and using two different types of support: ZrO₂/Y₂O₃ and SiC.

Feed ratio — varying the amount of carrier
Experimentally, this is accomplished by varying the amount of surface, i.e., the weight of the supports present in the autoclave, while keeping the amount of reacting mixture constant. The weights of the carriers employed ranged from 0.3 - 8 g, while the amount of synthesis mixture was kept at 35 g. The effect of the feed ratio was investigated for three carrier types: Cordierite monolith, α-Alumina foam (45 ppi) and α-Alumina tubes, see Table 5.5.

Si/Al ratio
The Si/Al-ratio for most experiments was kept at 40. However, to investigate the influence, some experiments using α-alumina 45 ppi foam as a carrier where conducted with a Si/Al ratio of 14. The rest of the synthesis conditions was kept constant.

Temperature and time
Determination of the support loading as a function of temperature and time was performed using three different carriers: α-alumina foam, ZrO₂/Y₂O₃ foam (170°C) and SiC foam (160°C). Growth curves were recorded by removing autoclaves from the oven after predefined time intervals.
Large scale syntheses
Experiments in a large 2 liter autoclave were performed using a 0.5 dm³ cordierite monolith and α-Al₂O₃ 45 ppi foam plates (see Fig. 5.1) of approximately the same volume as support. A unique feature of the 2 liter autoclave is the sealing of the lid. Normally, sealing of the autoclave is obtained by pressing the lid of the insert tightly on the insert itself by screwing the lid of the metal autoclave. In this way a sealing at the rim of the insert is obtained and as a result only the Teflon insert is at autogeneous pressure. The autoclave employed in large scale syntheses was designed to seal at the lid of the autoclave by means of an O-ring. The Teflon insert merely contains the synthesis mixture. Upon heating, the pressure in the entire autoclave will become equal to the vapor pressure of the liquid phase inside the Teflon insert. As a result of this construction, rotating was not possible. The conditions applied followed from previous small scale experiments.

The type of carrier material
The arrangement of the experiments is given in Table 5.5. Part of the experiments coincided with the experiments already discussed in the previous sections.
Table 5.5  Overview of conducted experiments and results. The reported coverages are based on the weight gain prior to calcination.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>molar composition relative to Al$_2$O$_3$ SiO$_2$/TPA/H$_2$O</th>
<th>pH</th>
<th>support</th>
<th>time</th>
<th>T</th>
<th>coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[h]</td>
<td>[°C]</td>
<td>[wt%] [g/m$^2$]</td>
</tr>
<tr>
<td>1. rotation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>82/8.5/1785</td>
<td>13.32</td>
<td>α-Alumina, 45 ppi</td>
<td>23.3</td>
<td>169</td>
<td>6.7</td>
</tr>
<tr>
<td>p</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>25.7</td>
</tr>
<tr>
<td>s</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>29.8</td>
</tr>
<tr>
<td>2. dilution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>81/9.6/1773</td>
<td>13.36</td>
<td>SiC, 20 ppi</td>
<td>24.33</td>
<td>160</td>
<td>33.3</td>
</tr>
<tr>
<td>(H$_2$O/Si=21.8)</td>
<td></td>
<td>45.33</td>
<td>&quot;</td>
<td>&quot;</td>
<td>47.6</td>
<td>92.2</td>
</tr>
<tr>
<td></td>
<td>80/51.3/11600</td>
<td>13.33</td>
<td>SiC, 20 ppi</td>
<td>45.33</td>
<td>160</td>
<td>9.5</td>
</tr>
<tr>
<td>(H$_2$O/Si=146.0)</td>
<td></td>
<td>73.20</td>
<td>&quot;</td>
<td>&quot;</td>
<td>11.2</td>
<td>12.8</td>
</tr>
<tr>
<td></td>
<td>82/9.7/1787</td>
<td>13.36</td>
<td>ZrO$_2$/Y$_2$O$_3$, 20 ppi</td>
<td>20.5</td>
<td>170</td>
<td>26.5</td>
</tr>
<tr>
<td>(H$_2$O/Si=21.8)</td>
<td></td>
<td>49.83</td>
<td>&quot;</td>
<td>&quot;</td>
<td>26.6</td>
<td>65.8</td>
</tr>
<tr>
<td></td>
<td>81/51.1/11400</td>
<td>13.33</td>
<td>ZrO$_2$/Y$_2$O$_3$, 20 ppi</td>
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<td>170</td>
<td>5.0</td>
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<tr>
<td>(H$_2$O/Si=141)</td>
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<td>43.08</td>
<td>&quot;</td>
<td>&quot;</td>
<td>4.2</td>
<td>8.0</td>
</tr>
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<td></td>
<td></td>
<td>49.50</td>
<td>&quot;</td>
<td>&quot;</td>
<td>5.9</td>
<td>11.4</td>
</tr>
<tr>
<td>3. feed to surface ratio</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>86/23.6/5028</td>
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<td>α-Alumina, 45 ppi</td>
<td>26.67</td>
<td>170</td>
<td>11.7-20.6</td>
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<tr>
<td></td>
<td>82/9.5/1977</td>
<td>13.35</td>
<td>Cordierite monolith</td>
<td>46.42</td>
<td>160</td>
<td>18.7-31.9</td>
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<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>α-Alumina, 45 ppi</td>
<td>22.67</td>
<td>160</td>
<td>17.0-32.6</td>
</tr>
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<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>α-Alumina, tube</td>
<td>23.00</td>
<td>160</td>
<td>5.5-8.5</td>
</tr>
<tr>
<td>4. Si/Al ratio</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>44/9.2/593 (Si/Al=14)</td>
<td>13.75</td>
<td>α-Alumina, 45 ppi</td>
<td>34.00</td>
<td>160</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td>79/9.2/1763 (Si/Al=40)</td>
<td>13.35</td>
<td>α-Alumina, 45 ppi</td>
<td>34.00</td>
<td>160</td>
<td>27.2</td>
</tr>
<tr>
<td></td>
<td>27.8/9.6/610 (Si/Al=14)</td>
<td>13.75</td>
<td>α-Alumina, 45 ppi</td>
<td>24.00</td>
<td>175</td>
<td>14.0</td>
</tr>
<tr>
<td>5. temperature / time</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>79/9.8/1769</td>
<td>13.37</td>
<td>α-Alumina, 45 ppi</td>
<td>21.16</td>
<td>110</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>113.75</td>
<td>&quot;</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>81/9.4/1778</td>
<td>13.35</td>
<td>α-Alumina, 45 ppi</td>
<td>2.00</td>
<td>150</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>47.92</td>
<td>&quot;</td>
<td>28.2</td>
</tr>
<tr>
<td>6. large scale</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>81/8.5/1773</td>
<td>13.32</td>
<td>α-Alumina, 45 ppi</td>
<td>49.00</td>
<td>170</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>81/11.7/1773</td>
<td>13.42</td>
<td>α-Alumina, 45 ppi</td>
<td>49.00</td>
<td>160</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>78/8.1/1745</td>
<td>13.32</td>
<td>α-Alumina, 45 ppi</td>
<td>53.25</td>
<td>160</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>95/8.4/1748</td>
<td>13.30</td>
<td>Cordierite monolith</td>
<td>46.58</td>
<td>162</td>
<td>15.1</td>
</tr>
</tbody>
</table>

1) 'c': continuous, 'p': pulsewise and 's': static.
5.4 Results and discussion

5.4.1 General Considerations

The stability of the supports during synthesis is an important issue, since success of synthesis is mainly assessed by measuring the weight gain of the substrate. Therefore, prior to synthesis, test runs were performed, using synthesis mixtures lacking the silica source. In this way the stability of the ceramic carriers under synthesis conditions was checked. The results of these experiments encouraged the use of all the ceramic carriers available, weight decreases being smaller than 2 wt% for continuously rotated experiments and less than 0.25 wt% for static experiments.

The weight gain before calcination of the supports upon synthesis is taken as the key parameter to assess the success of a synthesis, cf. Table 5.5. This introduces some uncertainty because the coverage thus assessed might well result from deposition of non-crystalline material. A better means would be the use of XRD crystallinity, see Fig. 5.5 and comparing the peak areas originating from ZSM-5 and that of the foam. However, this is a cumbersome method, which would take an impractical amount of time. Moreover, it will still remain doubtful whether the crystallinity is to be attributed to accessible ZSM-5 crystals.

\[ \text{Fig. 5.5 XRD of ZSM-5 on } \alpha \text{-alumina foam (a), compared with empty foam (b) and calculated spectrum for ZSM-5 (c)\textsuperscript{23}.} \]

This problem is best overcome by measuring BET surface areas and assuming the BET surface for powdery ZSM-5 crystals to be 435 m\(^2\)/g. The BET surface of the bare supports is negligible. This comparison was performed for a selected number of experiments only, to check the assumption that weight gain can be attributed to crystalline material. The coverage on the basis of BET surface area was always within 3% of that based on weight gain of calcined samples.
Another assumption that is made is that the crystals are bound firmly to the surface. In Fig. 5.6 it is demonstrated that this assumption is indeed justified. A crack formed in the support material after synthesis is clearly able to split the bonded zeolite crystal, indicating that the bond between the carrier and the zeolite crystals is stronger than the zeolite crystal itself.

5.4.2 Investigated Factors

The type of carrier material
Comparison between different zeolite coated ceramic foams is best done in terms of the coverage in g/m², were the surface area is the bare foam’s specific surface area.

All ceramic materials investigated proved to be very suitable as a carrier for in-situ growth of ZSM-5 crystals.

Surprisingly, SiC showed the highest coverage in terms of g/m², up to 100 g/m². Assuming a specific surface area for the zeolite crystals of 435 m²/g, this means that the specific surface area of the ceramic material has been increased from less than 1 m²/g to more than 200 m²/g, a value that is much higher than obtained with a washcoating technique (ca. 40 g/m² for a 20 wt% washcoat¹). In the case of SiC, this is mainly to be attributed to the low bulk density of the carrier material, which gives rise to a high coverage in terms of wt%, from which the value in g/m² is subsequently calculated. The exact nature of the SiC material and its surface (presumably oxygen-containing) remains unknown and although coverage of the coated material is high, its practical use is very limited, since the material proved to be extremely brittle after synthesis.

Differences in coverage are expected to be caused by mainly two mechanisms:
1. Differences in chemical receptivity of the carrier surface.
2. Differences in the accessibility due to different pore structures.

Rotation of Autoclaves

Rotating of the autoclaves was investigated because it was expected to have influence on the distribution of the resulting zeolite film. On the other hand rotating is expected to have a negative impact on the coverage due to:

1. Reduced nucleation of zeolite crystals.
2. Attrition of the formed film.

Thus it is expected that an optimum rate of rotation exists, in which the negative and positive effects are balanced.

The effect of the speed of rotation is clearly demonstrated in the SEM pictures given in Fig. 5.7. In case continuous rotation is applied (Fig. 5.7a), crystal growth appears to be inhibited giving rise to low coverage with irregularly shaped ZSM-5 crystals. Pulsewise rotation (180° rotation every 30 min) yields a much more homogeneous coverage (Fig. 5.7b).

![SEM pictures of ZSM-5 crystals](image)

**Fig. 5.7** Predominant morphology of ZSM-5 crystals grown on α-alumina foam with continuous (a) and with pulsewise rotation (b). H₂O/Si=20, Si/Al=40, T=170°C, synthesis time is 24 h. Scale bars represent 10 μm.

From Table 5.5 it follows that the syntheses performed statically yield the highest coverage (31 g/m²). The coverage of the pulsewise rotated synthesis is somewhat lower than this (25 g/m²) and that of the continuously rotated synthesis is very low (5.2 g/m²). This together with the SEM pictures, clearly illustrates the negative effect of rotating on growth of ZSM-5 zeolite under the present conditions. The reason for investigating rotation was the expected maldistribution of coverage as it was encountered in the previous chapter. However, since the static samples did not show any signs of this, on the contrary, the coverage on the more remote inner parts of the ceramic foam samples did not show any difference from that on the outer parts, it can be
concluded that rotating is not necessary under the studied experimental conditions. Apparently, the foam is better accessible to the synthesis mixture than the metal carriers.

Dilution of the synthesis mixture
The dilution ratio influences the time needed for reaching complete coverage of the surface by ZSM-5. At higher dilution ratios, deviating crystal shapes were formed (‘submarines’) and the time needed for complete coverage was much longer. The optimal $\text{H}_2\text{O}/\text{Si}$ ratio appeared to be around 20. In less than 20 hours a close uniform coverage was formed at $160^\circ\text{C}$.

For example, in Fig. 5.8a (ZSM-5/SiC foam), complete coverage was obtained after 24 hours. The applied dilution ratio was 20. After 45 hours, the loading amounted to 92 g/m², and multiple twinned crystals were formed (Fig. 5.8a). When a dilution ratio of 146 was applied, thick rounded crystals are formed and the support is still not completely covered after 45 hours. The loading amounted to 11 g/m² (Fig. 5.8b). Only after 73 hours, the support was completely covered, but the coverage remained far below that of the concentrated synthesis mixture (13 vs 94 g/m²).

![Image of ZSM-5 on SiC foam at different dilution ratios](image1)

**Fig. 5.8** ZSM-5 on SiC foam at different dilution ratios: $\text{H}_2\text{O}/\text{Si}=20$ (a) and $\text{H}_2\text{O}/\text{Si}=146$ (b). Synthesis conditions: $\text{SiO}_2/\text{Al}_2\text{O}_3=80$, $160^\circ\text{C}$, 45 h. Scale bars represent 10 µm.

Feed-to-surface-ratio
Fig. 5.9 shows the ZSM-5 coverage on the $\alpha$-alumina 45 ppi foam as a function of feed to support ratio for two different reaction mixture dilutions. Surprisingly, the data suggest an optimum in the coverage at a feed ratio of 2-4 mol Si/m² support. The same trend is observed in similar experiments using a cordierite monolith and the $\alpha$-alumina pipes as support (Fig. 5.10). The highest coverage for the cordierite monolith is obtained at a ratio of around 8 mol Si/m² support. For the $\alpha$-alumina tubes, the effect is less pronounced.
**Fig. 5.9** Coverage of 45 ppi α-Alumina foam as function of feed to support ratio, at high (●) and low (○) dilution.

**Fig. 5.10** Coverage of α-Alumina tubes (●) and cordierite monolith (○) as a function of feed to support ratio.

On the left hand side (corresponding to high available surface) of the observed optimum, the coverage diminishes due to exhausting of the synthesis mixture. The surface to be covered simply becomes too large. This is reflected in the conversion of the synthesis, expressed as the ratio of the amount of Si incorporated in the bonded zeolite's framework to the amount of Si present in the original mixture:

$$\xi_{\text{synthesis}} = \frac{\text{(mol Si, in zeolite crystals, on support)}}{\text{(mol Si, originally in synthesis mixture)}}$$

For the lower feed-to-surface-ratio values, $$\xi_{\text{synthesis}}$$ approaches 100%, indicating that the synthesis mixture becomes exhausted. On decreasing the available surface area, the conversion of synthesis...
Chapter 5

drops, partly due to formation of non-bonded zeolite crystals, but as mentioned before, this was only in small amounts and in a few cases. Therefore, it can be stated that the selectivity of the synthesis, expressed as the ratio of the amount of bonded crystals to the total amount of crystals (bonded and formed in liquid phase) was difficult to establish in some cases but close to 100% for most syntheses. The low values of the coverage must therefore mainly be attributed to exhausting of the synthesis mixture.

As expected, the coverage becomes independent of the available surface area at low values of surface area (right hand side of optimum in Figg. 5.9 and 5.10, corresponding to low available surface). The amount of zeolites deposited is constant and around that of a monolayer of ZSM-5 (calculated to be 30-60 g/m² for a ZSM-5 monolayer with thickness of 20 μm, template included).

Si/Al ratio

As can be seen in Table 5.5, the Si/Al ratio in the synthesis mixture has a considerable influence on the coverage: 6.9 vs 27.3 g/m² for Si/Al = 14 and 40 respectively. The reason for the lower coverage is the difference in crystal size, as can be seen in Fig. 5.11. The alumina-rich crystals (Fig. 5.11a) are much smaller in size (< 0.5 μm) than the more siliceous ones (Fig. 5.11b, ca. 10 μm). In an attempt to improve the coverage with low Si/Al ZSM-5, the synthesis temperature was increased to 175°C, since this was expected to have a positive influence on the solubility of the alumina species. However, this led to comparable coverages as that of the synthesis at 160°C. Analysis with SEM (Fig. 5.12) showed complete coverage with the same small crystals, as well as larger sized undefined crystalline material,
Fig. 5.11 Results of changing Si/Al ratio in ZSM-5 synthesis on 45 ppi α-Al₂O₃ foam: a: Si/Al = 14 and b: Si/Al = 40. Synthesis conditions: H₂O/Si = 20, 160°C, 34h. Scale bars represent 5 μm.

Fig. 5.12 Non-ZSM-5 crystals on 45 ppi α-Al₂O₃ foam for Si/Al = 14. Synthesis conditions: H₂O/Si = 20, 175°C, 34h. Scale bars represent 10 μm.
Temperature and time

As can be seen in Fig. 5.13, the difference in coverages obtained at synthesis temperatures of 150 °C and 160 °C is small. The syntheses at 110 °C yield lower coverage and give rise to substantial spread in the coverage result. For bulk synthesis of ZSM-5 a temperature of 170 °C or higher is often employed. However, the few experiments that were performed at this temperature gave rise to a lower selectivity, viz., more crystallization in the free phase instead of growth on the support. But it has to be noted that the collection of all non-bonded material in a reproducible manner proved to be very difficult.

From the SEM pictures in Fig. 5.14 it follows that the small crystals observed after 2 hours are too small to give a substantial rise in the weight of the carrier. From that point onwards, the coverage of the surface proceeds very quickly. After 5 h the surface is already completely covered. The gain in weight that follows from that point onward is to be attributed to (i) the growth of the size of the crystals already present and (ii) the nucleation of new crystals on already existing ones, as can be seen in Fig. 5.14 after 14.8 h.
Synthesis of ZSM-5 on Ceramic Carriers

Fig. 5.14 Coverage of 45 ppi α-alumina foam with ZSM-5 after varying synthesis times at 150°C. Scale bars represent 10 μm.

Large scale syntheses

The scaling up of the small scale syntheses to cover large α-alumina 45 ppi foam plates (dimensions: 15x7x1 cm, cf. Fig. 5.1) and a cordierite monolith (dimensions: 7x7x15 cm) was performed without difficulties. Although no rotation of the autoclaves was possible, there was little variation in the coverage of the ceramic structures. This is in contrast with the results obtained with the metal carriers (previous chapter). The most probable reason for this is the porous nature of the ceramic structures which leads to a better wetting of the supports. Indeed, in most experiments crystals were found not only on the surface that was directly exposed to the synthesis mixture, but also inside the smaller pores that make up the foam and monolith walls. This clearly demonstrates that crystallization is not easily limited by blocking of pores, and that the mixture is able to find it's way through the walls.

In some experiments it could not be avoided that part of the carrier was above the liquid level of the synthesis mixture. This led to the surprising result that even these parts of the carrier that could not have been submerged during synthesis, upon SEM analysis showed a coverage that was indistinguishable from the coverage of the parts that were submerged during synthesis. An
Chapter 5

explanation for this could be that the porous nature of the ceramic carriers gives rise to capillary forces that enhance the wetting of the support by the synthesis mixture.

Moreover, the fact that rotating is not necessary is very fortunate, since it was shown already that rotating had a negative effect on the coverage.
5.5 Conclusions

Ceramic materials are obviously very suitable as carrier material for in-situ grown zeolites. Consequently, both ceramic monolithic structures and ceramic foams encounter an increasing interest in chemical industry.

The porous nature of the ceramic carriers leads to coverages of almost 100 g/m², which corresponds to a specific surface increase from less than 1 m²/g to more than 200 m²/g. This is much higher than could be achieved by washcoating, where typical values of 40 m²/g are reported.\textsuperscript{13}

It is shown that rotating of the autoclaves is not required and is even undesired since it lowers the resulting coverage. The porous nature of the investigated ceramic materials ensures a good distribution of the synthesis mixture on the support. It appears that capillary forces also contribute in this respect.

A dilution ratio of H₂O/Si=20 was found to be optimal. This high concentration also presents advantages from a practical point of view, since syntheses from more concentrated mixtures require smaller autoclaves.

Variation of the feed-to-support-ratio for different carrier materials all showed a distinct optimum in coverage. The exact explanation for this remains subject of study, but it is clear that the presence of a ceramic carrier surface has a positive effect on the formation of zeolite crystals.

Of the different Si/Al ratios in the synthesis mixture studied, Si/Al=40 yielded the highest coverage. This is to be attributed to the easier formation of high silica zeolites.

Optimal synthesis temperature for the formation of ZSM-5 on ceramic carriers was found to be 150-160 °C. This is somewhat lower than the 170 °C that is usually employed in normal (free phase) ZSM-5 synthesis. When the temperature is too high, formation of free phase crystals will predominate. Optimal synthesis times are about 40 h.

There were clear differences in achievable coverages found when different supports were used. Whether this is caused by chemical or morphological differences remains subject of study.

Acknowledgments
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ECN in Petten (NL) kindly supplied the α-alumina ceramic materials.
Chapter 5

5.6 References


Chapter 5
6 Application of *In-Situ* Grown Zeolites as DeNOx Catalyst

6.1 Introduction

The growth of worldwide economic activity and the recognition of the burden it imposes ultimately on the environment has led to many different approaches in reducing the effect of industrial and automotive exhausts. Obviously, the best approach would be to prevent the formation of these noxious compounds (such as carbon monoxide, volatile organic compounds and nitrogen oxides) at the source. As this is not always possible, conversion of these compounds to less harmful products by means of heterogeneous catalysis is the most attractive approach from several points of view. The most important advantage seems that principally something is gained for nothing; by its mere physical presence the catalyst is able to bring about the desired conversion without being consumed itself. Although in practice the removal of noxious compounds from off-gases is more difficult, catalytic removal of nitrogen oxides and other compounds has become of large importance in the last thirty years. The search for suitable catalysts should be carried out on at least two different fronts: from a chemical point of view, the material should show sufficient activity. On the other hand the catalyst packing should be shaped or shapable in a form that results in desired operation, *i.e.*, it should provide good contact between catalyst and gas stream and it should yield a low pressure drop. Particularly pressure drop is an important issue. Additional demands on the catalyst comprise low sensitivity to dust in the feed and resistance to thermal shock.

In this chapter the zeolite coated packings described previously, will be tested as a catalyst for the selective catalytic reduction of nitric oxide. The choice of the deNOx reaction as a test reaction for this chapter is not a coincidence. By the nature of the source that generates a NOx containing gas (often processes in which fossil fuels are combusted, with near atmospheric exhaust pressures) and the negative added value of the deNOx step, it follows that pressure drop is a key issue. For a deNOx unit in a car exhaust system or power plant it should typically be below 10-20 mbar. From the other (chemical) viewpoint, zeolites are among the most promising materials for the removal of NOx, due to their very high activity and selectivity at relatively low cost. It is therefore expected that packings based on *in-situ* grown zeolites can contribute to removal of NOx in practical applications. Sufficient stability under high temperature/steam conditions will be an important issue here.
Chapter 6

In this chapter the focus will be on the selective catalytic reduction (SCR) of nitric oxide (NO) using different reducing agents, to assess the value of the catalytic materials prepared according to the previous chapters. It is believed that in-situ grown zeolites can be applied to form a structured catalyst that provides good flow characteristics on one hand and sufficient NO conversion on the other. Two types of reducing agents will be subject of study:

1. Hydrocarbons, limited to methane and propene.
2. Ammonia, a reducing agent that has found widespread application in deNOx practice already.

Denoxing with added hydrocarbons is expected to be of importance for lean burn (excess oxygen) engines, such as stationary gas engines or automotive diesel engines. The generalized equation for this reaction is:

\[ \text{NO} + \frac{1}{a} \text{C}_n\text{H}_m \rightarrow \frac{m}{a} \text{CO}_2 + \frac{1}{2} \text{N}_2 + \frac{n}{2a} \text{H}_2\text{O} \] \hspace{1cm} (6.1)

with \( a = 2m + n/2 \),

or, when the NO reduction proceeds via a mechanism were oxygen is required:

\[ \text{NO} + \frac{1}{2} \text{C}_n\text{H}_m + \frac{n}{8} \text{O}_2 \rightarrow \frac{m}{2} \text{CO}_2 + \frac{1}{2} \text{N}_2 + \frac{n}{4} \text{H}_2\text{O} \] \hspace{1cm} (6.2)

Parallel to this reaction, (undesired) oxidation of the hydrocarbon by oxygen will occur:

\[ \text{C}_n\text{H}_m + (n/4 + m) \text{O}_2 \rightarrow m \text{CO}_2 + n/2 \text{H}_2\text{O} \] \hspace{1cm} (6.3)

The two hydrocarbons used in this study are methane and propene. Methane is an interesting reducing agent because it is cheap and abundantly available. The SCR of NOx with methane using zeolite catalysts has gained interest in recent years. Of the variety of other hydrocarbons, propene is chosen as a second option, because it is reported to be the most active when compared with other hydrocarbons.¹

Because of the explorative character of the present study, the reactions with hydrocarbon reductants will be carried out on a small scale, i.e., with several grams of catalyst.

To test the feasibility of structured catalyst packings in more realistic configurations, the selective catalytic reduction of NO with ammonia is chosen.

\[ 4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \] \hspace{1cm} (6.4)

This reaction has the advantage that it has already been proved in practice, so comparison with existing facilities can be made. Of great importance for practical application is the availability of models that adequately predict the performance of the catalyst packing. Two different configurations will be investigated. One in which the zeolite is grown onto porous ceramic foam plates that are arranged parallel to the flow ('Parallel Passage Reactor' or PPR, see Fig. 6.1). The results

124
of these experiments will be compared with those of a reactor type that is more usual in low pressure drop applications: the monolith. The ceramic monolith used is also covered with ZSM-5 crystals by the in-situ technique. The aim of these experiments is to check whether different configurations of the PPR can be described adequately in terms of the most important variables, such as pressure drop and conversion. Also, pressure drop and conversion predicting methods can be used to compare the performance of the PPR with the monolith reactor. Moreover, comparison of the zeolitic coated carriers with a practical deNOx facility is possible. For successful implementation, adequate tools that can predict the performance of the PPR reactor are indispensable; the dimensions of the reactor have to be chosen as to optimize the trade off that exists between pressure drop and catalyst efficiency and of course capital costs.

![Parallel Passage Reactor (PPR) with four catalytic plates.](image)

The catalysts studied here will be limited to copper-, cobalt- and cerium-exchanged zeolites of the ZSM-5 and Beta (BEA) type. Copper exchanged zeolite is one of the most promising catalysts for the removal of NO in that it appears to be a cheap and active catalyst for the decomposition. In the presence of reducing agents such as ammonia or hydrocarbons the rate of NO conversion can be increased further. Cobalt exchanged zeolite appeared most active for SCR with methane. Cerium exchanged zeolite also shows good activity, and, what is more important, shows no SO₂ oxidation.

The questions that need to be answered in this respect are:

1. Does the catalytic activity of in-situ grown zeolites differ from powdered zeolite material?
2. What is a suitable configuration for implementing the prepared zeolite-covered materials?
Chapter 6

3. Are the governing equations with respect to pressure drop and conversion known or can they be derived?
4. Can the performance of a reactor operated with zeolite-covered modules be predicted adequately?
5. Finally, would these reactor types qualify as practically feasible reactors?

Part of the experimental work pertains to reaction/catalyst systems treated extensively in literature, such as deNOx with ammonia using Cu-ZSM-5. Apart from this, some new zeolite catalysts will be subject of research in this chapter.

The approach that will be followed in this chapter is:

- Discussion of pressure drop models and reaction kinetics. Although much of the theory of pressure drop can be found in textbooks on transport phenomena, it is convenient to have these subjects summarized and applied to the reactor types under investigation, since it enables a better understanding of the typical problems that are involved in practical situations.
- Derivation of models that predict reactor performance.
- Investigation of the activity of in-situ grown zeolites for the deNOx reaction. It is already known that copper exchanged ZSM-5 packings based on in-situ technology show a high activity in the deNOx reaction when ammonia is used as a reductant. Therefore, first attention will be focused on the performance of hydrocarbons as a reductant. Hydrocarbons have not been studied extensively yet and have distinct advantages over ammonia.
- The activity of in-situ grown zeolites will be compared to that of pelletized zeolite powder to check if the expected lower diffusion path for the in-situ grown zeolites gives rise to higher activity or that other phenomena typical for this system are to be taken into account.
- Finally, a bench scale set-up (ca. 0.5 liter of catalyst packing) will be used to test covered ceramic carriers in a PPR and a monolithic configuration. The experimental data will be compared with the theoretical models.
6.2 Theory of Low Pressure Drop DeNOx Reactors

Bench scale experiments were carried out in two types of reactors. A parallel passage configuration consisting of porous ceramic slabs ordered in a parallel array and a conventional cordierite monolith, both covered with ZSM-5 zeolite crystals by the in-situ technique. To model these reactor concepts, relations for transport of momentum and mass are required. Therefore the theory of pressure drop across rectangular channels will be treated first and applied to both reactor concepts. As stated before, much of the theory of pressure drop can be found in text books on transport phenomena but the application to rectangular ducts is somewhat more specific and it is treated here for convenience.

In order to predict conversions, a kinetic model has to be assumed, which is also discussed in this section.

Finally, a mathematical model is derived that should be able to predict both pressure drop and conversion for both reactor types.

6.2.1 Pressure Drop across Rectangular Channels with a Constant Cross Section

In laminar flow pressure drop is caused by momentum losses due to friction with the wall. When the flow is turbulent, energy dissipation by eddies contribute to additional momentum losses. The pressure drop across a channel will depend on flowrate through that channel, the channel geometry, the roughness of the channel walls (in turbulent flow) and the fluid characteristics like viscosity and density. When an incompressible fluid flows through a channel, the pressure drop (Δp) follows from the pressure gradient in the direction of flow (v) that is given by:

\[- \frac{dp}{dy} = 4f \frac{1}{D_h} \frac{1}{2} \rho \langle v \rangle^2\]  \hspace{1cm} (6.5)

Where \( D_h \) is the hydraulic diameter that is given by:

\[ D_h = \frac{4A}{W} \]  \hspace{1cm} (6.6)

In these equations \( A \) is the cross sectional flow area, \( W \) the wetted perimeter, \( \rho \) the fluid density and \( \langle v \rangle \) the average velocity. As can be seen, the problem of predicting pressure drops is a problem of predicting the friction factor \( 4f \) and its dependance on the Reynolds number.

6.2.1.1 Friction Factors for Laminar Flow
Chapter 6

For incompressible laminar flow the friction factor for a given geometry can be found by solving the Navier-Stokes equation:

\[ \rho \left( \frac{\partial v_y}{\partial t} + \nu \nabla v_y \right) = -\frac{dp}{dy} + \eta \nabla^2 v_y \] (6.7)

Where \( \eta \) is the dynamic viscosity.

Under assumption of fully developed non-compressible flow, steady state and no flow perpendicular to the main flow direction, Eq. (6.7) reduces to a Poisson type equation:

\[ \nabla^2 v_y = \frac{dp}{dy} \frac{1}{\eta} \] (6.8)

For a rectangular duct with dimensions \( b \times d \) and the following boundary conditions:

\[ x = \pm \frac{h}{2}; v = 0 \]
\[ z = \pm \frac{h}{2}; v = 0 \]

Eq. (6.8) can be solved analytically to yield:

\[ v(x,z) = -\frac{1}{2\eta} \left( \frac{dp}{dy} \right) \left[ \frac{1}{4} b^2 - z^2 - \frac{8}{b} \sum_{n=0}^{\infty} \frac{(-1)^n}{\lambda_n^3} \cosh(\lambda_n z) \frac{\cosh(\lambda_n b)}{\cosh(\lambda_n d)} \cos(\lambda_n x) \right] \] (6.9)

With:

\[ \lambda_n = (n + \frac{1}{2}) \pi/b \] and \( n = 0, 1, 2, ... \)

In all calculations that were performed, deviations were smaller than 0.1% for \( n = 0 \ldots 10 \). Integrating the velocity profile of Eq. (6.9) over the cross sectional flow area, with a given pressure drop, yields the total flow through the rectangular duct from which the mean velocity is calculated. From Eq. (6.5) the geometry parameter \( C \) can be calculated, defined as \( C = (4\eta \text{Re})_{\text{lam}} \):

\[ C = (4\eta \text{Re})_{\text{lam}} = \frac{\frac{dp}{dz} D_h^2}{\frac{2}{\eta} \langle v \rangle} \] (6.10)

The Reynolds number is based on the hydraulic diameter of the duct. This geometry parameter is a constant for a given geometry, i.e., width-to-depth ratio \( (b/d) \). In Fig. 6.2 the calculated geometry parameters for varying width to depth ratios are given.
Fig. 6.2 Calculated geometry parameters for a rectangular channel as a function of
dimensionless channel width (●) and the polynomial fit, Eq. (6.11) (- - - - )

For convenience, the calculated data is fitted with a fourth order polynomial (for $0.01 \leq (b/d) \leq 1$ accurate within 1%):

$$C = 96.30 - 133.5 \frac{(b/d)}{} + 190.5 \frac{(b/d)^2}{()} - 141.8 \frac{(b/d)^3}{()} + 45.50 \frac{(b/d)^4}{()}$$

(6.11)

6.2.1.2 Friction factors for Turbulent Flow

Under practical conditions the low pressure drop reactor types discussed here are operated in the
laminar flow regime, where pressure drop increases linearly with flowrate. In the turbulent flow
regime the pressure drop dependence on flowrate becomes second order, which is unfavorable
for low pressure drop operation. Wall roughness is the key parameter in determining both the
onset point of turbulence and friction factor relations for turbulent flow. However, no predicting
equations for the Reynolds number at which flow in rectangular channels becomes turbulent are
found in literature and they must therefore be established experimentally. In the fully turbulent
regime the friction factor has become independent of the Reynolds number. A relation for the
friction factor in this case is given by:

$$\frac{1}{\sqrt{f}} = 1.737 \ln \frac{D_h}{2h} + 3.48$$

(6.12)

Where $h$ is the height of roughness.

From this equation it follows that in fully developed turbulent flow in a channel with constant
cross section the friction factors is not dependant on the channel’s geometry.
6.2.2 Pressure Drop and Flow in the Parallel Passage Reactor

In the parallel passage reactor the gas flows through a number of parallel rectangular channels. The pressure drop relations serve two purposes. First they obviously can be used to predict the pressure drop across the PPR for a given flowrate. On the other hand it follows that the pressure drop across each channel has to be the same, regardless its dimensions, since there can be no pressure gradients in the cross sectional area at the entrance and exit points. Eq. (6.10) can be used to calculate the flow distribution through the respective channels.

![Diagram](image)

**Fig. 6.3** Schematic representation and definitions in the PPR reactor with four ceramic slabs.

Two types of channels can be distinguished in the PPR configuration. Channels enclosed by two catalytic slabs will be referred to as central channels and the channels in which the gas flows between a catalytic slab and a reactor wall will be referred to as wall channels (see Fig. 6.3). With respect to the central channels, it is obvious that the ideal configuration is such that flow through each central channel is equal. The optimal dimensions of the wall channels, however, are found by the prerequisite that conversion over these channels should be equal to that of a central channel. However, this requires, apart from knowledge of the amount of flow through these channels, also an estimate of the catalyst utilization. This cannot be known on beforehand, i.e. when the PPR module is constructed. Therefore a choice is made here to let the flow through a wall channel equal half of the flow through a central channel. It is important to realize that, under these assumptions, any deviations from this ideal configuration will result in lower overall conversions. Furthermore, it should be noted that these problems are of less importance in large size practical applications of the PPR concept, were far more catalytic plates are employed.
6.2.3 Pressure Drop and Flow in the Monolith

In monoliths, flow is laminar under most practical conditions (with the exception of entrance effects). The theory presented for pressure drop in rectangular ducts also holds for the monolith. The monolith consists of a large number of square duct channels. If flow is laminar, the geometry parameter $C$ will be 56.92 for a square duct ($b/d = 1$). This value can be used to predict the pressure drop. Since the dimensions of each channel in the monolith are the same, the flow through one channel can easily be calculated by dividing the total flow by the number of channels.

6.2.4 Reaction Kinetics of the SCR of NO with Ammonia

In selective catalytic reduction (SCR) of NO by NH$_3$, nitrogen oxides are reduced by ammonia with the assistance of a catalyst. The essential SCR reaction is:

$$4 \text{NO} + 4 \text{NH}_3 + \text{O}_2 \rightarrow 4 \text{N}_2 + 6 \text{H}_2\text{O} \quad (6.4)$$

Possible side reactions are:

$$\begin{align*}
4 \text{NO} + 2 \text{NH}_3 + \text{O}_2 & \rightarrow 3 \text{N}_2\text{O} + 3 \text{H}_2\text{O} \\
2 \text{NH}_3 + 2 \text{O}_2 & \rightarrow \text{N}_2\text{O} + 3 \text{H}_2\text{O} \\
4 \text{NH}_3 + 3 \text{O}_2 & \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O} \\
2 \text{NH}_3 + 2 \text{O}_2 & \rightarrow 3 \text{H}_2\text{O} + \text{N}_2\text{O} \\
4 \text{NH}_3 + 5 \text{O}_2 & \rightarrow 6 \text{H}_2\text{O} + 4 \text{NO} \\
2 \text{NO} & \rightarrow \text{N}_2 + \text{O}_2 \\
\end{align*}$$

When Cu-ZSM-5 is used as a catalyst, the side reactions are expected to be negligible at temperatures below 400 °C. At higher temperatures the ammonia oxidation reaction can become significant, especially if a stainless steel reactor is used, because stainless steel catalyzes this reaction.

A simple expression for the reaction rate can be used when there is an excess of oxygen, ammonia and no water in the reaction mixture, which are the conditions used throughout the bench scale experiments. Another simplification is assuming the NO reaction to be first order in NO. This results in the following rate expression:

$$-r_{\text{NO}} = k_{i,T} C_{\text{NO}} \quad (6.15)$$

6.2.5 Relations for Diffusion Coefficients

To model the transport of mass in both the PPR and the monolith reactor, relations describing diffusion in the gas phase and in the pores of the solid phase as a function of temperature and
pressure are required. Calis et al. present methods to obtain diffusivities in a PPR configuration. Free diffusion coefficients $D_{\text{free}}$ can be calculated using the equation given by Fuller et al.:

$$D_{\text{free}} = 1.013 \times 10^{-7} T^{1.75} \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \sqrt{\frac{P}{\left( \Sigma_A v_i \right)^{1/2} + \left( \Sigma_B v_i \right)^{1/2}}} \quad (6.16)$$

$(\Sigma_A v_i)$ is the sum of the diffusion volume coefficients for component A, $M$ is the molar mass. Diffusion in a porous slab is governed by both free diffusion and Knudsen diffusion. The Knudsen diffusion coefficient $D_{Kn}$ can be calculated using the following equation:

$$D_{Kn} = \frac{16}{3} \frac{\varepsilon_p}{\rho_p S_g} \left( \frac{R T}{2 \pi M} \right) \quad (6.17)$$

The effective diffusivity is calculated by taking the harmonic mean of both contributions and by taking into account the effects of tortuosity and voidage:

$$D_{\text{eff}} = \frac{\varepsilon}{\tau} \left( \frac{1}{D_{\text{free}}} + \frac{1}{D_{Kn}} \right)^{-1} \quad (6.18)$$

The tortuosity factor $\tau$ contributes for the increased diffusion path as a result of the complexity of the pore structure. In general a higher value corresponds to a more complex structure as is the case in more dense porous media. A typical value of $\tau = 2$ is often used and will be used here as well. Furthermore, $\varepsilon_p$ is the porosity and $S_g$ the specific surface area. Knudsen diffusion will only play a role if the mean pore radius of the porous material is very small, viz. of a molecular scale.

Mass transfer in a porous slab can be described with the effective diffusion coefficient if the gas phase in the slab is stagnant. However, if there is a gas flow parallel to a porous slab, entrainment might occur, as a result of eddies in the flow. Furthermore pressure gradients across the slab can result in convective transport in the slab as well. This effect can be taken into account by adjusting the effective diffusion coefficient and replacing it by an overall dispersion coefficient in the slab: $D_{\text{slab}}$. This coefficient is made up of two contributions, $D_{\text{eff}}$ resulting from diffusion and $D_{\text{conv}}$ the convective contribution resulting from dispersion:

$$D_{\text{slab}} = D_{\text{eff}} + D_{\text{conv}} \quad (6.19)$$

The convective contribution in this equation depends on the average velocity of the gas stream next to the slab and on the shape of the slab. Kalthoff and Vortmeyer give the following relation for estimating the convective contribution:

$$D_{\text{conv}} = \frac{d_p}{1.1 K} <v> \quad (6.20)$$
Application of In-Situ Grown Zeolites as DeNOx Catalyst

This relation is derived for a bed of particles with a particle diameter \( d_p \) and a velocity \(<v>\) through the bed. The factor \( K \) accounts for the porosity differences that are encountered in packed beds due to the presence of a wall and is given by:

\[
K = 8 \left( 2 - \left( 1 - \frac{2}{(d_{slab}/d_p)} \right)^2 \right) \tag{6.21}
\]

However, in porous ceramic foams this wall effect is considered to be negligible and a value of \( K = 8 \) can be used. Eq. (6.20) then becomes:

\[
D_{conv} = 0.11 \ d_p \ <v> \tag{6.22}
\]

This equation is valid under the assumption that the porous slab can be described as a bed of spheres.

6.2.6 Mathematical Models to Predict Conversion

6.2.6.1 Modeling the Parallel Passage Reactor

To model the PPR a two dimensional unit cell is defined for both channel types (wall and central) in which the governing equations hold. Assuming symmetry of the concentration profile across the catalytic slab, the wall unit cell can be described by a wall channel and half a catalytic slab. The concentration profile is also symmetrical with respect to the central channel. The central unit cell is therefore defined by half a central channel and half a catalytic slab. The definition of the unit cells is given in Fig. 6.4.
Each unit cell has two regions. In the bulk region, the gas stream will be laminar and mass transport is a result from concentration gradients and free diffusion. In the slab region there will be diffusion/dispersion as well as reaction.

The concentration profile in the bulk region is governed by the following partial differential equation that results from a mole balance across an infinitesimal volume element:

$$\frac{\partial}{\partial x} \left( D_{\text{free}} \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_{\text{free}} \frac{\partial c}{\partial y} \right) - v_y \frac{\partial c}{\partial y} = 0 \quad (6.23)$$

and in the catalytic slab by:

$$\frac{\delta}{\delta x} \left( D_{\text{slab}} \frac{\partial c}{\partial x} \right) + \frac{\delta}{\delta y} \left( D_{\text{slab}} \frac{\partial c}{\partial y} \right) - k \ c = 0 \quad (6.24)$$
If the ratio $b$ to $d_{\text{channel}}$ is large, the flow in the channel can be described as a flow between two plates. Under laminar flow conditions the velocity profile in a central unit cell is then given by:

$$v_y = \frac{3}{2} \langle v \rangle \left( 1 - \frac{x^2}{\left( \frac{1}{2} d_{\text{central}} \right)^2} \right)$$  \hspace{1cm} (6.25)

The velocity profile in the wall channel is defined in a similar way to meet the condition that $v_y = 0$ at the wall and slab surface. The average velocity follows from the volumetric flow rate through the channel $\varphi$. The channel cross sectional area is equal to $d_{\text{central}} \times b$ for a central channel and $d_{\text{wall}} \times b$ for a wall channel.

### 6.2.6.2 Modeling the Monolithic Reactor

The monolith consists of square channels with width $d_{\text{channel}}$ and length $l$, separated by small walls of ceramic material with width $d_{\text{wall}}$. The region bounded by half the wall thickness around one channel can be approximated by a cylindrical segment with inner radius $R_1$ and outer radius $R_2$, see Fig. 6.5. This makes it possible to describe the monolith channel with a two dimensional model.

![Fig. 6.5](image)

*Fig. 6.5* Simplification of the geometry of a monolith channel to describe it with a two dimensional model.

The approximation is done by assuming the flow area of the square monolith channel to be equal to the flow area of a cylindrical channel, and the amount of catalytic material to be the same for both geometries:

$$\pi R_1^2 = d_{\text{channel}}^2$$  \hspace{1cm} (6.26)

$$4 \frac{1}{2} d_{\text{wall}} (d_{\text{channel}} + \frac{1}{2} d_{\text{wall}}) = \pi R_2^2 - \pi R_1^2$$  \hspace{1cm} (6.27)

The concentration profile in the bulk region is then given by:

$$\frac{1}{r} \frac{\partial}{\partial r} \left( D_{\text{free}} r \frac{\partial c}{\partial r} \right) + \frac{\partial}{\partial y} \left( D_{\text{free}} \frac{\partial c}{\partial y} \right) - v_y \frac{\partial c}{\partial y} = 0$$  \hspace{1cm} (6.28)
Chapter 6

And in the catalytic slab:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( D_{slab} \ r \ \frac{\partial c}{\partial r} \right) + \frac{\partial}{\partial y} \left( D_{slab} \ \frac{\partial c}{\partial y} \right) - k \ c = 0
\]  

(6.29)

with:

\[
v_y = 2 \ <v> \left( 1 - \frac{r^2}{R_1^2} \right)
\]  

(6.30)
6.3 Experimental

The experimental work comprised laboratory scale and bench scale experiments. The small scale experiments were performed using an internal recycle reactor set-up using hydrocarbons (methane or propene) as a reductant. The bench scale experiments were performed in a set-up that could be fitted with either a PPR or a monolithic module and used ammonia as a reductant.

6.3.1 Catalyst Choice and Preparation

The small scale experiments with methane and propene were performed using cobalt or cerium exchanged zeolites ZSM-5 and Beta (BEA). The bench scale experiments with ammonia as a reductant were performed using copper exchanged ZSM-5 on ceramic foam or on a cordierite monolith as the catalyst. The zeolites were applied in four different configurations:

1. Stainless steel monoliths covered with in-situ grown ZSM-5 or zeolite Beta. The preparation of these packings is described in Chapters 3 and 4. The zeolites on these packings were exchanged with cobalt, copper or cerium.
2. α-Alumina foam pieces covered with in-situ grown ZSM-5. The preparation of this type of packing is described in Chapter 5. The zeolites on these packings were exchanged with cobalt or copper.
3. A 300 cpsi cordierite monolith covered with in-situ grown ZSM-5 (Chapter 5) and exchanged with copper.
4. Cobalt or cerium exchanged commercial zeolite powder was pressed to pellets that were used for comparison experiments. The zeolite samples used as starting materials were ZSM-5 (sodium form, obtained from PQ-Zeolites, Si/Al=29) and zeolite Beta (sodium form, obtained from Uetikon, Si/Al=13). Zeolites are coded by giving the exchanged cation, the zeolite type, the Si/Al ratio and the exchange percentage, e.g., Co-BEA-(13)-88 refers to a sample of cobalt exchanged zeolite Beta with a Si/Al ratio of 13 and an exchange ratio of 88%.

Comparison of carried and non-carried zeolites was difficult since obtaining identical Si/Al ratios for the zeolite in the pellets and the in-situ grown zeolites could not be obtained. The in-situ growth was dictated by the synthesis conditions for optimum coverage. Moreover, as discussed in the previous chapters, setting the Si/Al ratio for the synthesis mixture does not guarantee that the obtained zeolite material deposited on the carrier follows this composition. Collecting non-bonded zeolite crystals from the in-situ synthesis was in most cases not possible due to the clear preference for growth on surface and apart from this, even if free phase crystallization had occurred, the Si/Al ratios differed still from that of the bonded crystals.

Ion exchange was performed at 80°C in sealed polyethylene bottles to avoid evaporation. The aqueous solutions used were 0.016 M of the acetate salt of the corresponding metal ions. The exchange process lasted 24 hours, during which the solution was refreshed 4 times. After this, the solids (zeolite powder or packings) were washed with deionized water and dried. The
exchange level was determined by ICP-AAS and is expressed as amount of Al\(^{3+}\) framework ions balanced by the exchanged cation. The zeolite powders were subsequently pressed, crushed and sieved to the desired size.

6.3.2 DeNO\(_x\) Experiments with Hydrocarbons as the Reductant

The activity of metal and ceramic supports covered with zeolite ZSM-5 and Beta was measured in an internal recycle reactor set-up and comparisons were made with pelletized zeolite. This type of reactor is exceptionally well suited for kinetic experiments since it behaves like an ideally stirred tank reactor so that the reaction rate is directly related to the conversion, the volumetric flowrate and the catalyst weight:

\[
-r_{\text{NO}} = \frac{\varphi_v (c_{\text{NO}_{\text{in}}} - c_{\text{NO}_{\text{out}}})}{W_{\text{cat}}}
\]

(6.31)

The reason for using a reactor of this type is the enhanced mixing of the gas that is necessary to ensure that all parts of the external catalyst surface are subjected to the same bulk concentrations.

---

![Diagram](image.png)

**Fig. 6.6** Experimental set-up used for small scale experiments.

The experimental set-up is depicted in Fig. 6.6. It consisted of a gas dosing section, the internal recycle reactor and an analysis section. Constant gas flow was provided by Inacom Mass Flow Controllers (MFC’s). Water was fed to the system by means of a peristaltic pump through a vaporizer. The water flowrate was checked by monitoring the mass of the water supply with a
balance. The gas mixture was either led through the reactor or bypassed to check the feed composition. Part of the reactor effluent/bypass stream was fed to a water column filled with 1 m water, to ensure a constant system pressure of 0.1 barg. The reactor was a stainless steel internal recycle reactor (internal volume 0.7 dm³). A cross section of the reactor is given in Fig. 6.7.

![Internal recycle reactor diagram](image)

**Fig. 6.7** Internal recycle reactor with 1: catalyst compartment, 2: temperature measurement, 3: pressure measurement, 4: graphite bearing, 5: magnetic shaft, 6: gas feed, 7: gas outlet, 8: rotor with labyrinth seal and 9: stator with labyrinth seal. The grey arrows indicate gas flow. The dark shaded parts are driven by a DC current motor to rotate at ca. 3000 rpm. This generates a pressure drop across the catalyst compartment, resulting in a recycle flow.

Hydrocarbon concentrations were measured with a gas chromatograph (Hewlett Packard P5890A) equipped with a flame ionization detector. NO concentrations were measured with a chemiluminescence NOx analyzer (Signal 4000).

The set-up was fully automated by a process computer that also performed the data acquisition. Series of experimental runs were programmed in the computer so that the set-up could run
unattendedly. Each run differed in composition of the gas feed and/or temperature of the reactor and started with flushing of the equipment with nitrogen, followed by a calibration. Then the NO and hydrocarbon stream were switched on and the reactor effluent was measured. Finally the reactor was bypassed to check the feed composition.

The use of the internal recycle reactor imposed limitations on the operating temperature, which had to be below 550°C to operate without problems. Most experiments were performed in the temperature range of 350-550°C. Feed composition was within the following ranges: 200 - 1000 ppmv NO, 200 - 1000 ppmv hydrocarbon (methane or propene), 2-5 %v oxygen and 0 - 5 %v water vapor.

Fig. 6.8 Experimental set-up used for bench scale experiments.
6.3.3 DeNOx Experiments with Ammonia as a Reductant — Bench Scale

Nitric oxide conversion experiments were conducted using two reactor concepts: the parallel passage reactor and the monolithic reactor. In the parallel passage reactor (PPR) the catalyst packing was formed by four ceramic foam plates, placed parallel to the flow direction. In the monolithic reactor a large number of square channels were separated by thin ceramic walls. The set-up was constructed around a universal reactor housing which could be fitted with either the PPR module or the monolith. The reactor housing had two measurement points that were used to monitor entrance and effluent gases and to measure pressure drop.

Kinetic experiments were performed using a sample from the catalytically active material. Cu-ZSM-5 covered α-alumina was used in the PPR and Cu-ZSM-5 covered cordierite for the monolithic reactor. These samples were crushed and a 0.8-1 mm sieve fraction was put in a quartz tube with an internal diameter of 8 mm to a height of approximately 10 mm.

6.3.3.1 Bench Scale Experimental Set-Up

A flow sheet of the experimental set-up used is given in Figure 6.8. The set-up was fully automated, control and data acquisition was performed with a personal computer. The set-up can be divided in a gas supply system, the reactor and an analysis section.

Pure ammonia, 2v% NO diluted in Ar or N₂, air and nitrogen were fed to mass flow controllers (Inacom Instruments). Downstream of the mass flow controllers, first the nitrogen and air flows were mixed and led through a preheater. To avoid oxidation of ammonia and reaction of NO on the elements of the preheater, the remainder of the gases was added downstream of the preheater, after which the mixture was fed to the reactor.

The reactor had a volume of 10 dm³. Diffusors with a top angle of 8° were used to connect the reactor with the supply and the exhaust pipes, to minimize swirls in the entrance and exit parts of the reactor. In the central, straight square part of the reactor the catalyst module could be placed. The volume occupied by the module was 0.5 dm³ for both the PPR unit and the monolith. The reactor shell was made of 316 stainless steel and the complete reactor was placed in a closed oven. The reactor temperature was kept constant with a cascade PID controller using thermocouples in the reactor and oven to adjust the output to the preheater and oven heating elements. Properties of the applied catalyst modules are given in Table 6.1.

Pressure drops were measured with two differential pressure transmitters for the ranges of 0-60 Pa and 0-600 Pa (Validyne Engineering). Three different types of analyzers were used, a chemiluminescence analyzer to measure NO (Envico Environmental Control), a microwave process analyzer to measure NH₃ (MIPAN) or, alternatively, a Fourier transformed infrared spectrometer (FTIR, Siemens) to analyze both compounds.
Table 6.1 Properties of PPR and monolith covered with Cu-ZSM-5. Preparation of the modules is described in Chapter 5.

<table>
<thead>
<tr>
<th></th>
<th>Parallel Passage Reactor</th>
<th>Monolithic Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of slabs/channels</td>
<td>4</td>
<td>2017</td>
</tr>
<tr>
<td>Material</td>
<td>α-alumina</td>
<td>cordierite</td>
</tr>
<tr>
<td>Porosity (covered) / [m$^3$$_{vold}$/m$^3$poucing]</td>
<td>0.73</td>
<td>0.16</td>
</tr>
<tr>
<td>Total Cu-ZSM-5 coverage / [g]</td>
<td>70.1</td>
<td>60.5</td>
</tr>
<tr>
<td>Cu content / [wt%]</td>
<td>0.53</td>
<td>0.24</td>
</tr>
<tr>
<td>Dimensions slabs or wall thickness / [mm]</td>
<td>13 × 65 × 105</td>
<td>0.3</td>
</tr>
<tr>
<td>Width channels / [mm]</td>
<td>2.5 (wall) / 5 (central)</td>
<td>1.23</td>
</tr>
<tr>
<td>Total slab or wall volume / [m$^3$]</td>
<td>3.55×10$^{-4}$</td>
<td>3.12×10$^{-5}$</td>
</tr>
<tr>
<td>Module dimensions / [mm]</td>
<td>70 × 70 × 102</td>
<td>70 × 70 × 105</td>
</tr>
<tr>
<td>Total module volume / [dm$^3$]</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Density (covered) / [kg/m$^3$]</td>
<td>850</td>
<td>1551</td>
</tr>
<tr>
<td>Total module mass / [g]</td>
<td>304.6</td>
<td>270</td>
</tr>
</tbody>
</table>

6.3.3.2 Bench Scale Experimental Procedure

Pressure drops across the catalytic modules were measured using compressed air at ambient temperature. Gas flowrates were varied between 50-600 dm$^3$/h.

Each conversion experiment was preceded by a calibration step in which NO and NH$_3$ calibration gases were led to the analyzers. Then the mass flow controllers were set to obtain the desired gas composition. The NO and NH$_3$ concentrations before and after the catalyst module in the reactor were monitored, from which the conversions were calculated.

The specifications of the mass flow controllers constrained the flowrate and the concentrations that could be applied. The temperature that could be reached was limited by the power of the preheater. The experimental conditions are listed in Table 6.2.

Table 6.2 Experimental conditions used in bench scale experiments.

<table>
<thead>
<tr>
<th></th>
<th>PPR</th>
<th>Monolith</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature / [°C]</td>
<td>200 - 350</td>
<td>125 - 370</td>
</tr>
<tr>
<td>Oxygen concentration / [%]</td>
<td>0 - 15</td>
<td>0 - 15</td>
</tr>
<tr>
<td>NO concentration / [ppmv]</td>
<td>50 - 500</td>
<td>50 - 500</td>
</tr>
<tr>
<td>NH$_3$/NO ratio / [¥]</td>
<td>0 - 2.5</td>
<td>0 - 2.5</td>
</tr>
<tr>
<td>Flowrate / [dm$^3$/min]</td>
<td>10 - 70</td>
<td>40 - 210</td>
</tr>
</tbody>
</table>

The experimental conditions that were used to obtain the kinetic parameters for the PPR and the monolith, using crushed catalyst in a quartz tube are listed in Table 6.3.
Table 6.3  Experimental conditions used to measure kinetic parameters in laboratory scale experiments.

<table>
<thead>
<tr>
<th></th>
<th>covered α-alumina (PFR)</th>
<th>covered cordierite (monolith)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of material in reactor / [g]</td>
<td>0.45</td>
<td>0.559</td>
</tr>
<tr>
<td>Gas flowrate / [dm³/min]</td>
<td>0.478</td>
<td>0.243</td>
</tr>
<tr>
<td>Temperature / [°C]</td>
<td>350</td>
<td>275</td>
</tr>
<tr>
<td>NH₃/NO ratio / [-]</td>
<td>1.25</td>
<td>1.5</td>
</tr>
<tr>
<td>O₂ concentration inlet / [%]</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
6.4 Results and Discussion

First the result of the laboratory scale deNOx experiments using methane and propene will be discussed, followed by the results obtained in the bench scale set-up and the modeling of its performance.

6.4.1 DeNOx Experiments with Hydrocarbons as the Reductant

Experiments with Methane

The reduction of NO with methane proceeds via Eq. (6.2):  
\[ 2 \text{NO} + \text{CH}_4 + \text{O}_2 \rightarrow \text{N}_2 + \text{CO}_2 + 2\text{H}_2\text{O} \]  

(6.32)

The selectivity of methane towards this reaction is defined as:

\[ S_{\text{CH}_4} = \frac{1}{2} \frac{\xi_{\text{NO}} C_{\text{NO},in}}{\xi_{\text{CH}_4} C_{\text{CH}_4,in}} \]  

(6.33)

Fig. 6.9 Conversions (left axis) of NO (●) and methane (○) and methane selectivity (□, right axis) as a function of temperature for 2 g Co-BEA-(13)-88, 3.5 mm pellets. GHSV=12500 h⁻¹, flowrate = 46 dm³/h. Inlet concentrations: no water, 945 ppm methane, 680 ppm NO, 2.5% oxygen and balance nitrogen.
Application of In-Situ Grown Zeolites as DeNOx Catalyst

In Fig. 6.9, typical conversions for SCR with methane are given for different temperatures. Space velocities were chosen such that the NO conversion was kept well below 100%. In this way the influence of temperature and of other factors could be monitored.

At 400°C the selectivity of methane towards the reduction of NO is 75%, proving the selectivity of the cobalt exchanged zeolite. At higher temperatures the oxidation of methane starts to prevail, lowering the selectivity to 26% at 500°C.

In Fig. 6.10 the NO conversion for different feed ratios of reductant to NO are given and the effect of the addition of oxygen and water is tested. No decomposition in the absence of methane and oxygen was observed. This is in accordance with literature were also no decomposition was observed for other cobalt exchanged zeolite types\textsuperscript{13}. The conversion with oxygen in the feed is higher, indicating that oxygen is required in the reduction reaction. This is also in accordance with findings of other authors\textsuperscript{16,17} and indicates that NO is oxidized to NO\textsubscript{2} and subsequently reduced by the hydrocarbon. Addition of 2% water to the feed led to a substantially lower NO conversion but this appeared to be a reversible process (i.e. inhibition rather than deactivation).

![Graph](image)

**Fig. 6.10** Influence of the amount of methane on the NO conversion at T=450°C. 2 g Co-BEA-(13)-88 3.5 mm pellets. GHSV = 30,000 h\textsuperscript{-1}, flowrate=46 dm\textsuperscript{3}g\textsuperscript{-1}h. Feed composition all experiments: NO=250/500 ppm, CH\textsubscript{4}=250/500 ppm, (\textbullet): 2.5% O\textsubscript{2}, no water; (▲): no O\textsubscript{2}, no water; (●): O\textsubscript{2}=2.5%, 2% water and balance N\textsubscript{2}.

Furthermore, the influence of the particle size of the pellets was investigated and a comparison was made between the pelletized zeolites and the packings covered with the in-situ grown zeolites (Table 6.3). The lower NO conversion of the 3.5 mm BEA particles compared to that of the 1.4 mm particles (11.0 vs. 12.4%) could indicate that the reaction is limited by internal diffusion limitation. The higher conversion of the metal monolith (16.1%) does seem in accordance with this. However, when the differences in Si/Al ratio and cobalt loadings are taken into account, as is reflected in the Turn Over Frequency (T.O.F., see Table 6.3), the pelletized
samples appear to be more active than the BEA on stainless steel carrier. However, the Si/Al ratio and the exchange ratio could not be obtained by AES because the zeolite crystals could not be removed from the carrier. The data in Table 6.3 is therefore based on EDX analysis, in which large concentration gradients of both alumina and cobalt were observed. The metal carried BEA zeolite shows a higher conversion at cost of a lower selectivity, compared to the pelletized reference zeolite.

The opposite holds for the ZSM-5 on alumina foam, where the conversion is lower than that on the pelletized zeolite (5.9 vs. 9.4%) but selectivity is clearly higher. The BEA zeolite is more active than the ZSM-5 zeolite. When comparing the results of stainless steel with alumina foam, the differences in selectivity are most obvious. Promotion of the direct oxidation of methane by stainless steel is not likely, since the majority of the set-up is constructed of stainless steel and no influence was detected there. The most obvious explanation should therefore be the differences of the Si/Al ratios and the differences in exchange level. Apart from the problem of establishing the correct exchange ratio, also the considerable over exchange of the ZSM-5 pellets (856%) indicates that the exchange procedure was not performed properly. Overall, the NO conversions with methane as reductant are too low to be of practical interest.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Form</th>
<th>$\xi_{\text{CH}_4}$</th>
<th>$\xi_{\text{NO}}$</th>
<th>$S_{\text{CH}_4}$</th>
<th>T.O.F. [10$^{-4}$mol$<em>{\text{NO}}$/mol$</em>{\text{Co, s}}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-BEA-(13)-88</td>
<td>3.5 mm pellets</td>
<td>10</td>
<td>11</td>
<td>26</td>
<td>6.10</td>
</tr>
<tr>
<td>Co-BEA-(13)-88</td>
<td>1.4 mm pellets</td>
<td>10</td>
<td>12.4</td>
<td>30</td>
<td>6.87</td>
</tr>
<tr>
<td>Co-BEA-(5)-80</td>
<td>SS304 monolith</td>
<td>32.5</td>
<td>16.1</td>
<td>12</td>
<td>4.39</td>
</tr>
<tr>
<td>Co-ZSM-5-(29)-856</td>
<td>1.4 mm pellets</td>
<td>29</td>
<td>9.4</td>
<td>7.8</td>
<td>1.77</td>
</tr>
<tr>
<td>Co-ZSM-5-(41)-28</td>
<td>$\alpha$-alumina foam</td>
<td>7.2</td>
<td>5.9</td>
<td>20</td>
<td>47.3</td>
</tr>
</tbody>
</table>

T = 450°C, GHSV=30000 h$^{-1}$, 2 g zeolite, flowrate=46 dm$^3$ h$^{-1}$. Inlet concentrations: 500 ppm methane, 240 ppm NO and 2.5% oxygen.

1) Notation: Exchanged metal-Zeolite type-(Si/Al ratio)-exchange level (mol%)

**Experiments with Propene**

Since the conversions with methane were too low to be of practical value, additional experiments were conducted using propene as the reductant. Table 6.4 lists the results of initial experiments with excess of propene using Co exchanged ZSM-5 catalysts. The activity towards NO reduction is higher than that with methane as a reductant. Considering the larger hydrocarbon excess (and the higher carbon and hydrogen content per molecule) the selectivities are low. This is certainly connected to the more easy oxidation of propene compared to methane.

Considering that the exchange level of the in-situ grown zeolite is much lower than that of the pelletized zeolite, the results are very promising. This is most clearly reflected in the T.O.F.
given in Table 6.4. The effects of water and oxygen on the NO conversions are also significantly lower for the packings than for the pellets.

<table>
<thead>
<tr>
<th>zeolite type</th>
<th>form</th>
<th>T (°C)</th>
<th>ξ_{CH₆} [%]</th>
<th>ξ_{NO} [%]</th>
<th>S_{C₅H₄} [%]</th>
<th>T.O.F. [10^9 mol NO/(mol Co-s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-ZSM-5-(14)-209</td>
<td>α-alumina foam</td>
<td>375</td>
<td>94</td>
<td>83</td>
<td>11.8</td>
<td>11.0</td>
</tr>
<tr>
<td>Co-ZSM-5-(29)-856</td>
<td>1.4 mm pellets</td>
<td>375</td>
<td>94</td>
<td>79</td>
<td>11.2</td>
<td>5.06</td>
</tr>
<tr>
<td>Co-ZSM-5-(15)-44</td>
<td>SS316 monolith</td>
<td>450</td>
<td>96</td>
<td>7.7</td>
<td>1.08</td>
<td>5.16</td>
</tr>
<tr>
<td>Co-ZSM-5-(35)-376</td>
<td>SS316 monolith</td>
<td>375</td>
<td>85</td>
<td>34</td>
<td>5.37</td>
<td>5.94</td>
</tr>
</tbody>
</table>

GHHSV 10,000 h⁻¹, 2% oxygen, 2% water, 820 ppm propene, 220 ppm NO

An attempt was made to provide an empirical rate expression for the NO reduction with propene. The generalized rate expression is:

\[-r_{NO} = k_0 e^{-\frac{E_a}{RT}} c_{NO}^p c_{C_5H_6}^q c_{O_2}^r c_{H_2O}^s\]  

(6.34)

With: \(-r_{NO}\) the reaction rate of NO to N₂, in [mol/kg•zeolite s], \(k_0\) the kinetic rate constant, \(E_a\) the activation energy in [J/mol], \(R\) the gas constant in [J/mol/K], \(T\) the temperature of the reaction in [K], \(c\), the concentration of component \(i\) in [mol/m³] and \(p, q, r, s\) the reaction orders.
### Table 6.5 Settings used and measured conversions for SCR with propene

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>NO [ppm]</th>
<th>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; [ppm]</th>
<th>O&lt;sub&gt;2&lt;/sub&gt; [%]</th>
<th>H&lt;sub&gt;2&lt;/sub&gt;O [%]</th>
<th>T [°C]</th>
<th>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt; conversion [%]</th>
<th>NO conversion [%]</th>
<th>binderless pellets</th>
<th>pellets binderless</th>
<th>pellets</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>1000</td>
<td>5</td>
<td>5</td>
<td>400</td>
<td>96</td>
<td>66</td>
<td>61</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td>1000</td>
<td>200</td>
<td>2</td>
<td>2</td>
<td>400</td>
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<td></td>
</tr>
<tr>
<td>10</td>
<td>200</td>
<td>200</td>
<td>2</td>
<td>2</td>
<td>350</td>
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<td>94</td>
<td>51</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>11</td>
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<td>1000</td>
<td>1000</td>
<td>2</td>
<td>2</td>
<td>350</td>
<td>71</td>
<td>87</td>
<td>60</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>15</td>
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<td>5</td>
<td>350</td>
<td>65</td>
<td>79</td>
<td>71</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>200</td>
<td>1000</td>
<td>5</td>
<td>2</td>
<td>350</td>
<td>88</td>
<td>92</td>
<td>74</td>
<td>77</td>
<td></td>
</tr>
</tbody>
</table>

GHSV = 10,000 h<sup>-1</sup>. In-situ: Co-ZSM-5-(14)-209 on α-alumina foam. Pellet: Co-ZSM-5-(29)-856.

The kinetic expression (6.34) can be fitted by finding the experimental rates for different sets of concentrations and temperatures. This was done for both pelletized zeolite and a comparable in-situ covered packing. The experiments were organized according to a ½·2<sup>3</sup> factorial design scheme as given in Table 6.5.

Although there were not enough measurements to yield a adequate fit of the model, the so called main effects of the investigated factors could be calculated and are given in Table 6.6. A main effect is the difference of the measured response variable (viz. the conversions) resulting from changing the value of one of the factors. It is obtained by taking the average value of the response variable at similar settings of the investigated factor<sup>18</sup>. From Table 6.6 it follows that the NO conversion for the binderless zeolite is comparable to that of the pelletized sample (49.19 vs. 46.25%). This is supported by the fact that the response to the different factors is also comparable, although, in general, the effects for the pelletized sample are more pronounced. The strongest effect on NO conversion is that of the propene concentration. However, it should be noted that this is arbitrary, since the levels at which the factors are varied include settings where there are substoechiometric amounts of propene present and this obviously leads to dramatic results with respect to the NO conversion.
Table 6.6  Main effects of the factorial design experiment for SCR with propene

<table>
<thead>
<tr>
<th>Effect</th>
<th>C₃H₆ conversion [%]</th>
<th>NO conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>binderless pellets</td>
<td>binderless pellets</td>
</tr>
<tr>
<td>Average</td>
<td>91.06</td>
<td>49.19</td>
</tr>
<tr>
<td>NO</td>
<td>1.125</td>
<td>-12.875</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>-8.625</td>
<td>38.5</td>
</tr>
<tr>
<td>O₂</td>
<td>6.375</td>
<td>-3.125</td>
</tr>
<tr>
<td>H₂O</td>
<td>-0.625</td>
<td>-1.3125</td>
</tr>
<tr>
<td>T</td>
<td>8.625</td>
<td>-4.375</td>
</tr>
<tr>
<td>Estimated</td>
<td>0.215</td>
<td>0.894</td>
</tr>
<tr>
<td>standard error (σ)</td>
<td>0.215</td>
<td>0.765</td>
</tr>
</tbody>
</table>

As with the methane experiments, the difficulty in comparing carried zeolites with pelletized zeolites is that the zeolite must be of comparable composition (Si/Al ratio and exchange ratio) and crystal size distribution to rule out differences caused by diffusion limitation. This condition is not easily met. Using commercial zeolite powder with the same Si/Al ratio would result in different crystal sizes, while the crystals that originate in the free phase during in-situ synthesis (often a small amount) are of different Si/Al ratio and particle size, since conditions for in-situ growth were not met for these crystals.

6.4.2 Bench Scale Experiments with Ammonia as the Reductant

As discussed previously, bench scale experiments were performed using ammonia as the reductant, since this made higher conversions possible and in this way no major modifications to the set-up were necessary. Prior to conversion experiments, pressure drop experiments were done. This was done for two reasons. First, it was necessary to check if flow conditions were indeed laminar, so that the used conversion models would be valid. Secondly, it had to be checked whether prediction of the measured pressure drops was possible.

In this section, first the pressure drop experiments of the PPR and of the monolith will be given and the comparison with theory will be discussed. Then the conversion experiments will be discussed and the results of the modeling will be given.

6.4.2.1 Pressure Drop across the PPR

In Figure 6.11 the pressure drop across the PPR as a function of the Reynolds number is given. The differential pressure transmitter used in this experiment had a range of 0-60 Pa (accuracy of 2 Pa). However at values below 5 Pa no reliable measurements could be done. The GHHSV is based on the flowrate at normal conditions and the total volume of the PPR module (volume of the four ceramic slabs and volume of the five channels). Since the Reynolds number has a
different value in each channel, the average Reynolds number is taken, based on the channel’s hydraulic diameter. Pressure drops were measured using air at ambient conditions.

![Graph showing pressure drop vs Reynolds number](image)

**Fig. 6.11** Measured pressure drop across 4 plate PPR module (●) vs Reynolds number and theoretical values: turbulent flow with fitted roughness height \( h = 2.4 \) mm (solid line); laminar flow (dotted line). The corresponding GHSV’s range from 0 - 43 000 h\(^{-1}\).

From the experimental points in Figure 6.11 it follows that flow ceases to be laminar at relatively low Reynolds numbers. For circular ducts, the laminar flow regime is generally expected to end at Reynolds numbers above *ca.* 2100. For the PPR this figure is around 500. The difference in transition Reynolds number is most likely to be attributed to the mounting structure at the packing inlet that contains edges that protrude in the flow and/or the roughness of the ceramic foam, leading to disturbance of the flow.

The lowest possible measurable pressure drop was 5 Pa, which was measured at a Reynolds number of 700. This corresponds to a flow of 108 dm\(^3\)/min and a GHSV of 13 000 h\(^{-1}\). The highest flowrate used in the conversion experiments was only 70 dm\(^3\)/min, which corresponds to a Reynolds number of 225. From Figure 6.11 it is safe to assume that the conversion experiments were indeed performed at laminar flow conditions.

Relations to predict pressure drop in the turbulent flow regime for channels with geometries other than circular are not easily found in literature. On the other hand, channel geometry has little influence in turbulent flow through channels with constant cross section. Eq. 6.12, which is derived for channels with circular geometry, was used to describe the experimental data. A good fit was obtained when a roughness height, \( h \), of 2.4 mm was used. The fact that this is too large (the channel dimensions are only 2.5 to 5 mm) should be attributed to the fact that this relation does not hold for the PPR geometry. Nevertheless, the fitted equation describes the measured data in a convenient way and moreover, the turbulent flow regime is not expected to be of practical interest.

150
6.4.2.2 Pressure Drop across the Monolith

Pressure drop experiments and calculations for the monolith were performed similarly to those of the PPR. The results are given in Figure 6.12. It follows that the laminar model does predict the measured pressure drops well for the monolith. The model over-predicts by an average of 4%, which is within the accuracy of the differential pressure transducers. The flowrates used in the monolith conversion experiments corresponded to GHSV's between 5000 and 30000 h⁻¹, which is within the range of the pressure drop experiments, so it can be assumed that conversion experiments were performed under laminar flow conditions.

![Graph showing pressure drop (Δp) vs Reynolds number (Re)](image)

**Fig. 6.12** Measured pressure drop across monolith module (●) vs Reynolds number and theoretical values for laminar flow (straight line). The corresponding GHSV's range from 0 - 76 000 h⁻¹.

6.4.2.3 Initial deNOx Experiments in the PPR and Monolith covered with Cu-ZSM-5

Experiments were performed to investigate the influence of temperature, NH₃/NO ratio, oxygen concentration and NO entrance concentration on the measured NO conversion. These results were used to obtain results that could be fitted by the simple kinetic model presented in Eq. (6.15). To comply with the first order kinetics, the conversion should be dependant on NO concentration alone. It was expected that this would hold for a limited range of the investigated factors. To be able to model the performance of the reactor it is necessary to operate in this window.

In Figure 6.14 the influence of temperature on NO conversion is given for the PPR and the monolith. From this, a temperature of 350 °C was chosen for further experiments for the PPR and 275 °C for the monolith. The conversion is near its optimum at these temperatures for the
monolith and seems to approach its optimum for the PPR. This ensures that small temperature changes would not have a drastic impact on the measured NO conversions. During the experimental work these temperature deviations were limited to 5 °C.

![Graph showing NO conversions vs temperature](image)

**Fig. 6.14** Measured NO conversions for a Cu-ZSM-5 covered PPR (●) and monolith (■) as a function of temperature. Conditions: 5.5 %v oxygen, excess NH₃. For PPR: $\Phi_r=3360$ dm³/h, GHSV=3294 h⁻¹, 195 ppm NO. For Monolith: $\Phi_r=10$ 380 dm³/h, GHSV=20353 h⁻¹, 130 ppm NO, excess NH₃

The influence of the NH₃/NO ratio on NO conversions in the PPR and the monolith is given in Figure 6.15. From this the excess amount of ammonia required to rule out influence of ammonia concentrations on the reaction rate was taken. From the results in Figure 6.15 it was concluded that an NH₃/NO ratio of 1.5 was sufficient. Furthermore it appears that the PPR shows a NO conversion that is considerably higher than in the monolith reactor when no ammonia is present (NH₃/NO = 0). By monitoring other oxides of nitrogen in the effluent, it was found that this is to be attributed to NO₂ formation. However, the formation of NO₂ disappeared completely when ammonia was added in stoichiometric amounts or higher.

Further experiments comprised the influence of oxygen and NO entrance concentration. The influence of the oxygen concentration in the range of 2-14 %v was negligible for both the PPR and the monolith. The influence of NO entrance concentration proved to follow first order kinetics very closely, which was checked using the method of Ostwald-Noyes⁹. This yielded a reaction order of 0.95.
Measurement of the ammonia concentration showed that the NH₃ conversion is about 10% higher than NO conversion for typical settings (i.e. 5% O₂ and NH₃/NO = 1.5). To check the formation of other oxides of nitrogen, experiments using only ammonia were performed. These showed that only a small part of the ammonia was oxidized to N₂O, the remainder was not detected and was probably converted to N₂ via NO.

6.4.2.4 DeNOₓ Experiments in the PPR — Comparison with Model

In modeling the PPR the following assumptions were made:

1. The SCR of NO with NH₃ is the only reaction to take place. It has been shown that this is, under the conditions mentioned above, a valid assumption.
2. Flow is assumed to be completely developed, non compressible, one directional and laminar. From the performed pressure drop experiments it was concluded that these assumptions are valid.
3. The reactor is isothermal. No deviations from the setpoint temperature are assumed to take place. (During experiments the temperature was constantly monitored, and deviations were within a range of 5 °C.)
4. The models use an experimentally determined value for the reaction rate constant which has an accuracy of about 10%.
5. From the specifications of the experimental equipment used, it was estimated that the conversion could be determined with an accuracy of 6%. Some experimental series
Chapter 6

were replicated. This resulted in a difference of less than 2% of the calculated conversion.

![Graph](image)

**Fig. 6.16** Measured NO conversions for the PPR vs GHSV (●). T = 350 °C, 5 % v O₂, 200 ppmv NO, 300 ppmv NH₃, fitted model ( — ) and theoretical conversion for 100% catalyst efficiency (- - -).

In Figure 6.16 the experimentally determined NO conversions at different GHSV’s are given and compared with the conversions from the mathematical model and the conversion for full catalyst utilization \( (E = 100\%) \).

The theoretical conversion from the model was obtained by solving the microscopic mass balances given in Equations (6.23) and (6.24) numerically, using a PDE solver package\(^\text{20}\). Integration of the concentration profiles at the outlet of the PPR module yields the conversion. The diffusivity in the slab was corrected for the forced flow through the pores, according to Eq. 6.20. As mentioned, flow in the PPR channels causes an entrainment effect in the porous slab. This results in enhanced mixing that is a function of pore sizes in the slab. Although Eq. (6.20) was derived for packed beds, whereas the ceramic foams used are more or less the inverse of a packed bed, the use of a particle diameter of 1.75 mm produced the best fit, as given in Figure 6.16. With this, the model is not fully predictive any more. On the other hand, the value of 1.75 mm could be regarded typical for the 45 ppi ceramic foam used, which has an average pore diameter of 0.5 mm (Figure 5.3 in the previous chapter).

The line for 100% effectiveness is obtained when all the catalyst is assumed to be utilized in the reaction and the module were to be operated as an ideal plug flow reactor. From Figure 6.16 it follows that the configuration of the PPR is far from ideal. The effectiveness of the PPR module is estimated to be ca. 17%.

Additional calculations showed that the configuration of the PPR module \( (i.e., \) slab thickness and channel diameters) is of critical importance. From a construction point of view, especially the
equally spaced positioning of the ceramic plates to obtain an ideal configuration is very important. Small deviations in the order of 1 mm were inevitable in these experiments. According to the calculations this could already result in conversion losses of up to 10%. In order to increase catalyst effectiveness, it is necessary to reduce the slab thickness. If an effectiveness of 90% is acceptable, slabs of 1 mm thickness would be required. With the 45 ppi ceramic foams used in this work this would not be feasible, due to the lack of mechanical strength. This clearly illustrates the advantage of a monolith structure, which can be finer meshed.

6.4.2.5 DeNOx Experiments in the Monolith Reactor — Comparison with Model

In Figure 6.17 the experimental and theoretical NO conversions as a function of the GHSV are given for the monolith module. It is seen that the monolith (60.5 g Cu-ZSM-5) makes much better use of the catalyst than the PPR (70.1 g Cu-ZSM-5). The monolith converts 80% NO at a GHSV of 18 000 h⁻¹, the PPR reaches this conversion at a GHSV of 3000 h⁻¹.

The $E$=100% line lies below the experimental points, which is theoretically not possible. The explanation for this must be in the determination of the kinetic rate that is used to calculate the 100% effectiveness. Although SEM analysis of the zeolite coverage on the monolith showed that it was homogeneously covered, laboratory scale experiments present always the difficulty of obtaining a representative sample.

![Fig. 6.17 Measured NO conversions for the monolith vs GHSV (●). $T = 275\, ^\circ\text{C}$, 8 %v $\text{O}_2$, 80 ppmv $\text{NO}$, 120 ppmv $\text{NH}_3$, model (— ) and theoretical conversion for 100% catalyst efficiency (— — —).](image)

The microscopic mass balances for the monolith were solved using the kinetic data obtained from the kinetic experiments of the ceramic foams. In principle the active phase, Cu-ZSM-5, is the same on both carriers. And although the kinetic experiments were performed at different
temperatures, the theoretical values in Figure 6.17 are in good agreement with the experimental points. It can be concluded that the conversion of the monolith can be well predicted without the use of fit parameters, provided that the correct kinetic data are available.

Parameter sensitivity analysis for the monolith model indicated that varying the diffusion coefficients hardly influences the predicted conversions. This also follows from effectiveness calculations which showed that the reaction is controlled by reaction kinetics and not by mass transfer. Therefore it is concluded that it is not relevant whether the zeolite crystals are present inside the ceramic monolith walls, or at the surface of the walls.

6.4.2.6 Comparing the PPR and the Monolith with Practice

Performances of the both reactor concepts, including the catalyst efficiency, \( E \), can be compared with typical data from practical deNOx installations, see Table 6.7.

<table>
<thead>
<tr>
<th></th>
<th>NO conversion [%]</th>
<th>GHS V [h(^{-1})]</th>
<th>( E ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPR</td>
<td>80</td>
<td>3000</td>
<td>17</td>
</tr>
<tr>
<td>monolith</td>
<td>80</td>
<td>18000</td>
<td>~ 95</td>
</tr>
<tr>
<td>practice(^{21})</td>
<td>&gt;80</td>
<td>4000</td>
<td>n.a.</td>
</tr>
</tbody>
</table>

n.a.: data not available

Table 6.7 shows the GHSV at which the reactor is able to convert 80% NO. It seems that the monolith used in this work performs very well. It should be noted that this comparison is not completely fair since no account is given for catalyst deactivation and the (idealized) experimental conditions used in this work (clean gas, no water, excess NH\(_3\), smaller monolith channels than in practice). However, it is concluded that the application of zeolitic coated structures to deNOx processes is very promising and deserves further study (cf. section 6.5).
6.5 Conclusions and Recommendations

In this chapter an attempt was made to assess the value of in-situ grown zeolites for application in deNOx processes. It has been shown that the activity of covered ceramic and metallic packings is not different from pelletized zeolites, thus opening the possibility for application on a larger scale.

Furthermore, the activity of zeolite catalysts in the SCR reaction has been investigated using different reductants. The activity of methane is much lower than that of propene. The activity of propene, in turn, is lower than that of ammonia. It depends on various practical parameters such as equipment size and availability of reductants which reductant is to be favored.

The performance of the monolithic and parallel passage reactor was predicted reasonably well using relatively simple methods and simple kinetic data, which required only one fit parameter for the PPR. This implies that the processes taking place in heterogeneous chemistry with zeolitic coatings is well understood and shows no unexpected phenomena.

Some aspects that have not been subject of research yet, include durability tests and further optimizing of the catalyst system, especially the stability against water is a topic that must be considered in applying zeolitic catalysts, but these issues were beyond the scope of this work.

The simple predicting mathematical methods proved to be valuable for describing the tested configuration. This opens the possibility for optimizing the design of the parallel passage reactor with respect to plate thickness and distance. From the data obtained in this work it can be concluded that if the objective is to minimize reactor volume, the thickness of the reactor packings should be smaller than that of the foam plates used (< 13 mm) but larger than that of commercially obtained monoliths (> 0.3 mm). The spacing can then be optimized so as to yield a minimal pressure drop while obtaining just full catalyst efficiency.

Acknowledgment
Alexander Boekhorst and Edwin Maaskant are gratefully acknowledged for their contributions to this chapter.
6.6 Notation

\[ \begin{align*}
a & \quad \text{stoichiometric constant} \\
A & \quad \text{cross sectional flow area} \quad [\text{m}^2] \\
b & \quad \text{width of a rectangular channel} \quad [\text{m}] \\
C & \quad \text{geometry parameter} \quad [-] \\
c_{A,in} & \quad \text{inlet concentration of A} \quad [\text{mol}/\text{m}^3] \\
c_{A,out} & \quad \text{outlet concentration of A} \quad [\text{mol}/\text{m}^3] \\
d & \quad \text{depth of a rectangular channel} \quad [\text{m}] \\
d_{\text{central}} & \quad \text{distance between plates in a PPR} \quad [\text{m}] \\
d_{\text{wall}} & \quad \text{distance between plates and wall in a PPR} \quad [\text{m}] \\
d_{\text{lab}} & \quad \text{slab thickness in a PPR} \quad [\text{m}] \\
D_{\text{conv}} & \quad \text{convective contribution to diffusion coefficient} \quad [\text{m}^2/\text{s}] \\
D_{\text{eff}} & \quad \text{effective diffusion coefficient} \quad [\text{m}^2/\text{s}] \\
D_{\text{free}} & \quad \text{free diffusion coefficient} \quad [\text{m}^2/\text{s}] \\
D_h & \quad \text{hydraulic diameter} \quad [\text{m}] \\
D_{Kn} & \quad \text{Knudsen diffusion coefficient} \quad [\text{m}^2/\text{s}] \\
E & \quad \text{catalyst efficiency factor} \quad [-] \\
\eta & \quad \text{friction factor} \quad [-] \\
h & \quad \text{roughness height} \quad [\text{m}] \\
K & \quad \text{constant used in Eq. (6.20)} \quad [-] \\
m & \quad \text{stoichiometric constant} \quad [-] \\
M & \quad \text{molar mass} \quad [\text{kg}/\text{mol}] \\
n & \quad \text{stoichiometric constant} \quad [-] \\
p & \quad \text{pressure} \quad [\text{Pa}] \\
p/\rho & \quad \text{pressure gradient} \quad [\text{Pa}/\text{m}] \\
r & \quad \text{radial coordinate} \quad [\text{m}] \\
R & \quad \text{gas constant} \quad [\text{J}/(\text{mol K})] \\
-r_A & \quad \text{reaction rate} \quad [\text{mol}/\text{kg s}] \\
Re & \quad \text{Reynolds number} \quad (\rho v d / \eta) \quad [-] \\
S_p & \quad \text{particle specific surface area} \quad [\text{m}^2/\text{kg}] \\
T & \quad \text{temperature} \quad [\text{K}] \\
v & \quad \text{fluid velocity} \quad [\text{m/s}] \\
v & \quad \text{average fluid velocity} \quad [\text{m/s}] \\
W & \quad \text{wetted perimeter} \quad [\text{m}] \\
W_{cat} & \quad \text{catalyst weight} \quad [\text{kg}] \\
x & \quad \text{Cartesian coordinate} \quad [\text{m}] \\
y & \quad \text{Cartesian coordinate} \quad [\text{m}] \\
z & \quad \text{Cartesian coordinate} \quad [\text{m}] \\
\Delta p & \quad \text{pressure drop} \quad [\text{Pa}] \\
\varepsilon_p & \quad \text{particle porosity} \quad [-] \\
\end{align*} \]

Greek letters

158
Application of In-Situ Grown Zeolites as DeNO\textsubscript{x} Catalyst

\[ \eta \] dynamic fluid viscosity [Pa s]
\[ \lambda, \] eigenvalues of Eq. (6.9) [-]
\[ \xi \] conversion [-]
\[ \rho \] fluid density [kg/m\textsuperscript{3}]
\[ \Sigma_v \] sum of the diffusion volume coefficients for component A [m\textsuperscript{3}/s]
\[ \varphi_v \] volumetric flowrate [m\textsuperscript{3}/s]

6.7 References


20. PDEase 2D Pro Macsyma, Inc, Arlington, Massachusetts 02174, USA, Part of Macsyma Front End Package, v.2.6.1 c (1997)

7 Synthesis of Ethyl tert-Butyl Ether Using In-Situ Grown Zeolites

7.1 Introduction

Modern automotive fuels contain a considerable amount of octane enhancers to increase the octane number of gasoline blends to acceptable levels. Formerly lead additives such as tetra ethyl lead were used to comply this need. Environmental legislation has forced the use of oxygenates (alcohols and tertiary ethers) for gasoline blending to phase out lead additives that could poison three-way catalysts. Moreover, the addition of oxygenates also contributes to reduce exhaust emissions like benzene, ozone and carbon monoxide. The U.S. Clean Air Act Amendments of 1990 (EPA, 1992) state the basic guidelines for future transportation fuel composition and require the manufacture of oxygenated and reformulated fuels. The EPA, under the “2-2.7 % oxygen in fuel” definition, permits 12-15 vol% of these oxygenates in unleaded gasoline. The annual production of gasoline based fuels is over 10 billion liters in the Netherlands only, showing the huge market for oxygenates.

Candidates most suitable to be employed as oxygenated compounds in gasoline-based fuels, are alcohols and their derivatives, especially tertiary ethers, like methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE). MTBE is currently the industrial standard and is already produced in large amounts and applied in gasolines worldwide. In fact it has been the fastest growing major chemical of the 90’s and its demand is expected to rise to 29 million metric tons by the end of the millennium. ETBE has superior qualities as an octane enhancer compared to MTBE. The key difference between MTBE and ETBE is the nature of the starting materials. Tertiary butyl ethers are produced by an addition reaction of isobutene with an alcohol. For the production of MTBE, methanol is used which is obtained industrially from natural gas. ETBE could be produced from bioethanol, which is a renewable.

Commercial scale syntheses of MTBE and ETBE as well as most of the laboratory scale syntheses are carried out using acidic ion-exchange resins, such as Amberlyst or Lewatit. During the last decade, zeolites have gained attention as suitable catalysts for MTBE\(^{7-11}\) and ETBE\(^{12-17}\) production. Acid zeolites show activity for the gas phase synthesis of MTBE that is comparable to conventional Amberlyst-15 catalysts, while the selectivity is much higher.\(^{11}\)

The synthesis of tertiary ethers is limited by thermodynamic equilibrium. An elegant and cost effective approach to circumvent this difficulty in the production of ETBE could be the application of catalytic distillation, also referred to as, in a broader sense, reactive distillation.\(^{18}\)
Chapter 7

Successful synthesis of ETBE by means of catalytic distillation on a laboratory scale has been reported by Thiel et al.\textsuperscript{19}

These two observations — the successful use of zeolites in ETBE synthesis and the fact that catalytic distillation appears to be a favorable means of doing so — combine elegantly when in-situ grown zeolites are applied as a catalytic distillation packing.

By the nature of the process, catalytic distillation packings need to be a compromise between the two functions they must fulfill. This compromise is limited by the poor shapeability of most catalysts. On one hand they must contain a sufficient amount of catalyst, while on the other a maximum surface area is necessary for optimal gas/liquid contact that is required for the distillation function. To date most catalytic distillation units operate with packings that consist of a number of containers filled with catalyst particles. These containers are packed in the column as gas-liquid contacting device. It is difficult to remove the product from such a reaction zone promptly and, because of the structure, different from original distillation packings, the tower is difficult to operate. Therefore it is expected, that an operation configuration, involving catalytically active zeolitic coatings on structured packings in the reaction part of the distillation unit, could offer advantages with respect to overall efficiency:

- Optimal access to active sites due to coating thickness.
- Thin coating is expected to enhance product selectivity.
- Distillation packing structure remains unchanged, thus optimal gas-liquid mass transfer is obtained.
- Size reduction of the reaction zone in order to remove the product promptly.
- Catalyst packing is easily made.

Yet little is known about the chemical activity of zeolites in general in the aforementioned reaction and even less is known about the feasibility of the implementation of catalytic packings of binderless zeolitic coatings in the catalytic distillation process.

It is the aim of this chapter to investigate whether the two features can be combined, \textit{viz.}, if the (stainless steel) covered packings, produced as described in the previous chapters, can be successfully applied as catalytic distillation column packings to be used in the production of ETBE. The experimental work will be limited to the chemistry of the ETBE reaction in the liquid phase using zeolitic packings. Before (pilot scale) catalytic distillation experiments are started, it is important to know if the zeolitic packings perform as expected and if the system can be adequately described. The ETBE synthesis experiments will be conducted in small (250-300 ml) autoclaves that are fitted with a reciprocating agitator that carries the catalytic packings. To investigate the feasibility of in-situ grown zeolitic packings, a comparison will be made between commercial Amberlyst-15 and zeolite H-BEA, the latter both as powder and as zeolitic coating, as a catalyst for ETBE synthesis. Prior to the experimental work, background information on catalytic distillation and the current technology in ETBE production will be discussed.

162
7.2 Background of Catalytic Distillation and ETBE

7.2.1 Properties of ETBE

In order to comply with legislation and public demand, fuels will in the future consist, at least to some extent, of alcohols and their derivatives. Among the requirements for these blends are a sufficiently high octane number, a low volatility to prevent organic compound emissions during handling and storing of the fuel and a low emission of toxic products after combustion.

<table>
<thead>
<tr>
<th>Property</th>
<th>MeOH</th>
<th>EtOH</th>
<th>MTBE</th>
<th>ETBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular mass [g/mol]</td>
<td>32</td>
<td>46</td>
<td>88.2</td>
<td>102.2</td>
</tr>
<tr>
<td>Oxygen [wt%]</td>
<td>49.9</td>
<td>34.7</td>
<td>18.2</td>
<td>15.7</td>
</tr>
<tr>
<td>Density at 20 °C, [kg/m³]</td>
<td>797</td>
<td>797</td>
<td>740</td>
<td>740</td>
</tr>
<tr>
<td>Normal boiling point [°C]</td>
<td>64.4</td>
<td>78</td>
<td>55.2</td>
<td>72.8</td>
</tr>
<tr>
<td>Normal freezing point [°C]</td>
<td>-97.8</td>
<td>-117.3</td>
<td>-108.6</td>
<td>-94.0</td>
</tr>
<tr>
<td>Vapor pressure (25 °C) [kPa]</td>
<td>17.6</td>
<td>5.87</td>
<td>32.7</td>
<td>17.3</td>
</tr>
<tr>
<td>Reid vapor pressure [kPa]</td>
<td>32</td>
<td>17.2</td>
<td>53.6</td>
<td>17.1</td>
</tr>
<tr>
<td>ΔH_{ap} [kJ/kg]</td>
<td>992</td>
<td>921</td>
<td>321</td>
<td>311</td>
</tr>
<tr>
<td>ΔH_{comb} [kJ/mol]</td>
<td>19950</td>
<td>26690</td>
<td>35150</td>
<td>36020</td>
</tr>
<tr>
<td>H₂O in compound solubility (20 °C) [wt%]</td>
<td>∞</td>
<td>∞</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Compound in H₂O solubility (20 °C) [wt%]</td>
<td>∞</td>
<td>∞</td>
<td>4.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Air/fuel stoichiometry</td>
<td>6.4</td>
<td>9.0</td>
<td>11.7</td>
<td>12.2</td>
</tr>
<tr>
<td>Azeotropes with hydrocarbon</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>RON</td>
<td>105</td>
<td>104</td>
<td>115</td>
<td>118</td>
</tr>
<tr>
<td>MON</td>
<td>92</td>
<td>92</td>
<td>98</td>
<td>105</td>
</tr>
<tr>
<td>(RON + MON)/2</td>
<td>98.5</td>
<td>98</td>
<td>106.5</td>
<td>111.5</td>
</tr>
<tr>
<td>Flammability limits [vol%]</td>
<td>6.7-36.0</td>
<td>4.3-19.0</td>
<td>1.7-8.4</td>
<td>—</td>
</tr>
<tr>
<td>Ignition temperature [°C]</td>
<td>470</td>
<td>362.8</td>
<td>460</td>
<td>—</td>
</tr>
<tr>
<td>Flash point [°C]</td>
<td>11</td>
<td>21</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Price [US$/m³]</td>
<td>156</td>
<td>307</td>
<td>287</td>
<td>—</td>
</tr>
</tbody>
</table>

RON, Research Octane Number, determined in an engine normalized at 600 rpm (ASTM D-2722); MON, Motor Octane Number, determined in an engine normalized at 900 rpm (ASTM-2723).

Ethers, for example MTBE, ETBE and tert-amyl methyl ether (TAME) are preferred above alcohols, such as methanol, ethanol and tert-butanol for several reasons. Because alcohols are hygroscopic, their addition to gasoline can result in the separation of an organic and an aqueous phase. Moreover, alcohols have a lower research octane number (RON), a lower heat of combustion and a higher blending vapor pressure than ethers. Table 7.1 lists some important properties of common oxygenated compounds.
ETBE shows some distinct advantages compared to MTBE. The effect of ETBE in gasoline with regard to the octane number is larger than that of MTBE: the lower the octane number of the base fuel, the higher the resultant increase is with ETBE. Furthermore, the higher boiling point of an ETBE-gasoline blend and its lower vapor pressure, combined with the absence of azeotrope formation with hydrocarbons, results in a lowered tendency to engine vapor lock and less loss due to evaporation. The lower blending Reid vapor pressure makes ETBE especially suitable for use in regions where summer temperatures are high and consequently the use of MTBE is critical.\textsuperscript{21} With respect to phase separation when water is present, ETBE is also more effective than MTBE due to its extremely low solubility in water and vice versa, as can be seen in Table 7.1. Because of the lower oxygen content in ETBE a higher dilution effect can be reached (17.3 vol\% vs. 15 vol\% for MTBE, to achieve 2.7 wt\% oxygen level), which allows a greater reduction in concentration of aromatics, sulfur and benzene and thus results in cleaner gasolines. No modifications of the carburetor have to be made when ETBE is used instead of MTBE, because of the higher air-fuel stoichiometric ratio.\textsuperscript{6} The higher heat of combustion (Table 7.1) could result in a reduction in fuel consumption while maintaining power. Given the lower heat of vaporization of ETBE it can be expected that no ignition problems occur, and that no ice will be formed in the carburetor.\textsuperscript{6,22}

### 7.2.2 Production of ETBE

The production of ETBE depends critically on the availability of its reactants, isobutene and ethanol. Given that isobutene is used in both MTBE and ETBE production, the controlling factor for selection of either product is the alcohol. The price of ethanol depends even more than that of methanol on local market factors, such as availability and tax regulations. Nevertheless, the use of ETBE would reduce the dependence on methanol and oil imports and create additional markets for agricultural products. Ethanol for use in gasoline is given a tax grant in the US to promote the production and market of ETBE.\textsuperscript{23} Furthermore a cost-competitive process for obtaining bio-ethanol from biomass might be possible by the year 2000.\textsuperscript{21,24} MTBE on the other hand is produced from methanol, derived from natural gas.

ETBE can be manufactured in various ways, but is still not commercially available on a large scale. It can be produced in the gas phase as well as in the liquid phase at moderate pressures and temperatures, by reaction of ethanol with either isobutene or tert-butyl alcohol:

\[
C_2H_5OH + H_2C=C(CH_3) = C_2H_5—O—C(CH_3)_3 \quad \Delta H^\circ = -35 \text{ kJ/mol (7.1)}
\]

\[
C_2H_5OH + HOC(CH_3)_3 = C_2H_5—O—C(CH_3)_3 + H_2O \quad (7.2)
\]

The equilibrium-controlled reaction is acid catalyzed by either homogeneous or heterogeneous catalysts. Main side reactions are the dimerization of isobutene and the formation of tert-butyl alcohol, due to the presence of water as impurity. Knifton et al. have reported methods for liquid-phase alkyl tert-butyl ether synthesis by using tert-butanol and alcohol as feed. The temperature ranges from 40-140°C and the pressure range is 1-70 bar. The catalyst used is acidic alumina or
silica\textsuperscript{25}, HF treated zeolites\textsuperscript{26,27}, fluorophosphoric acid-treated zeolites\textsuperscript{28} and pentasil type zeolites (e.g. ZSM-5)\textsuperscript{29}, resulting in 40-70% yield and 65-95% selectivity. Interestingly, the claims of Knifton \textit{et al.} only pertain to ETBE synthesis when zeolite BEA is used as a catalyst.\textsuperscript{13,14}

![Graph 1](Fig. 7.1 Calculated equilibrium ETBE formation as a function of temperature for different molar feed ratios.)

![Graph 2](Fig. 7.2 Selectivity towards ETBE for different catalysts: H-ZSM-5 (○), fluorocarbonsulfonic acid polymer (●), Amberlyst-15 (□) and Amberlyst-35 (■).\textsuperscript{12})

The most frequently used and investigated method of obtaining ETBE, however, is the liquid phase reaction of isobutene, or a C\textsubscript{4}-cut containing isobutene, with ethanol under moderate pressure (10-50 bar) and temperature (50-90 °C) in the presence of an acid ion-exchange resin\textsuperscript{30,31} (Eq.7.1). Most frequently used is a sulfonic acid resin, like the commercially available Amberlyst-15, which is also used world wide in the synthesis of MTBE. Under stoechiometric feed conditions and temperatures between 50-60 °C the equilibrium conversion is found to be ca. 90% (Figure 7.1) with a selectivity towards ETBE of above 95%. Kinetics\textsuperscript{6,29,31} as well as thermodynamics\textsuperscript{1,32} have been studied.

In order to achieve higher selectivities, several catalysts were tested, including several ion-exchanged resins and H-ZSM-5\textsuperscript{21,33}, (modified) zeolite HY and several other zeolites, such as BEA, ZSM-5,-8,-11,-12, -23 and -35.\textsuperscript{15,21,34} The zeolitic catalysts are thermally stable, give no acid effluent and seem less sensitive to the reactant ratio, which is important because it enables the use of a mixed feedstock. The superior thermal stability of zeolites is especially of importance when comparing to sulfonic acid resins, such as Amberlyst-15. These catalysts become thermally unstable above 100 °C and, more importantly, may give off acidic fumes. Apart from being a hazard to process equipment due to their corrosive nature, these acid gases will continue to catalyze the reaction, which is an equilibrium reaction. If downstream process temperatures favor the reverse reaction, this can have disastrous effects on the overall performance. In Figure 7.2 selectivities for different catalyst types are given as a function of feed reactant ratio.
Chapter 7

The optimal process configuration has been subject of several studies. The conventional process consists of one or two fixed-bed reactors with resin catalyst particles and a (reactive) distillation tower to separate the product from the non-converted reactants and inerts. This is also used for MTBE production and often a combined process or a retrofit is suggested. Nowadays reactive distillation is suggested as a means to boost the conversion. In this process several configurations of the reaction section are possible. A schematic representation of two configurations is shown in Figure 7.3.

![Diagram of ETBE production process](image)

**Fig. 7.3** Two possible configurations for the production of ETBE: conventional process (1) and Catacol™ Process (2).

The main difference between the conventional catalytic distillation process and the Catacol process is the separation of functions. The Catacol process thus aims to further optimize the catalytic and separating function.

Some important aspects of the ETBE process are:

- The feed ratio of the reactants.
- The impurities in the reactants (1-butene in isobutene and water in ethanol) and their influence on selectivities.
- The high non-ideality of the reaction mixture, due to the alcohol.
- The selectivity of the catalyst.
- The amount of catalytic sites.
- Reaction temperature.
- The existence of azeotropes in the T-p region of synthesis and distillation.
7.2.3 Catalytic distillation

Catalytic or reactive distillation is a unit operation which combines chemical reaction and physical separation. By continuous separation of products from reactants and inerts, much higher conversions of equilibrium-limited reactions than in conventional processes can be obtained.\textsuperscript{18,23} Requirements for applying a reactive distillation system are:

- The temperature range of distillation has to match or at least overlap the reaction temperature range.
- The reaction rate has to match residence time in the reaction section.
- At least one of the desired products has to be either the highest or the lowest boiling component in the mixture, in order to move equilibrium in the desired direction.
- The reaction can be either exothermic or endothermic, with a moderate heat of reaction, in order to keep isothermal operation of the reaction section. Exothermic reaction can benefit the most because the heat can be utilized for the distillation.
- The mechanical stability of the catalyst packing should be high enough to ensure problem free operation.

The design aspects of a reactive distillation column are complicated. On top of the requirements of refluxer and reboiler, the number of stages, the position of the feed streams and process control, additional aspects are important. The two most important ones are the catalyst system used and the configuration of the reaction section within and/or outside the column. The catalyst system has to be active and selective within the temperature and pressure range required for distillation. Furthermore it should have a high concentration of active sites per unit volume of reactor, a high external surface for optimal vapor-liquid mass transfer, low pressure drop and it has to be easy to regenerate. A system of a zeolitic coating on a structured stainless steel carrier could in principle comply with all these requirements.

![Diagram of conventional and catalytic distillation](image)

**Fig. 7.4** Conventional (1) and catalytic distillation process (2).\textsuperscript{18}

The configuration of the reaction section depends on the type of reaction and reaction mixture. In the case that purification is required (ETBE) or breakage of azeotropes (methyl acetate
process), part of the distillation column is not reactive and used to accomplish purification or azeotrope breakage. Figure 7.4 shows an example of a possible configuration.

Because the ETBE reaction complies in principal with all requirements needed to apply reactive distillation successfully, use of this concept could result in several advantages when compared to a conventional process:

- Reduction of expensive recycle volumes, because near-stoechiometric feed composition can be used. Reactant ethanol is normally added in excess, to ensure the absence of side-reactions.
- Size reduction of main reactor and auxiliaries, because part of the reaction takes place in the distillation column itself (see figure 7.4).
- Elimination or size reduction of purification section.
- In case of exothermic reactions, the heat of reaction is used for vaporization, hence no equipment is needed for heat-transfer.
- Lower operating costs due to higher conversion per pass.
- Less limitations due to azeotropes.

In the present work exploratory experiments were carried out to study the batchwise ETBE synthesis, using carried zeolites as the catalyst.
7.3 Experimental

7.3.1 Equipment

The ETBE syntheses were carried out in two different types of reactors. The first series of experiments were carried out in a 250 ml Parr autoclave (Parr 4842) made of Hastelloy C, agitated with a pitched blade turbine agitator. The reactor was equipped with a temperature controller actuating on a heating jacket and an electromagnetic valve, that controls the air flow for internal cooling. The second series of experiments were conducted in a 300 ml Hastelloy B autoclave, agitated with an electromagnetic driven reciprocating stirrer. Stainless steel packings with zeolite could be attached to this stirrer. This reactor was fitted with a temperature controller actuating on a heating jacket. Both reactors were equipped with a pressure indicator and with a 1 ml sample tube for taking samples manually. A 150 ml stainless steel bottle was used to release the pressurized isobutene in the reactor. Figures 7.5a and b show schematic drawings of the reactors with auxiliaries.

Fig. 7.5a Parr autoclave set-up used for ETBE synthesis with powder catalyst. 1: stirrer, 2: sample tube, 3: cooling air flow control, 4: temperature control, 5: heating jacket, 6: charge tube, 7: pressure indicator and 8: isobutene charge.

Fig. 7.5b Autoclave with magnetic vertical stirrer used for ETBE synthesis using structured catalysts packing. 1: electromagnet, 2: pressure indicator, 3: N\textsubscript{2} vent flush connection, 4: temperature control, 5: heating jacket, 6: catalyst packing, 7: sample tube, 8: stirrer and 9: isobutene charge.
Chapter 7

7.3.2 Catalyst Preparation

The catalysts used and their properties are listed in Table 7.2. The BEA covered packings with were produced as described in Chapter 3. Mordenite (MOR) covered stainless steel packings were obtained under similar conditions using a synthesis mixture of the following molar composition: \( \text{Al}_2\text{O}_3 - 30.8 \text{ SiO}_2 - 22.2 \text{ OH}^- - 1880 \text{ H}_2\text{O} - 3.1 \text{ DBDMA}_2\text{O} - 7.7 \text{ Na}_2\text{O} - 3.8 \text{ K}_2\text{O} \). The silica source was Ludox HS-40 and the alumina source was \( \text{Al(OH)}_3 \) (Fisher Scientific).

Table 7.2 Catalysts used in ETBE synthesis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Manufacturer</th>
<th>Particle size [µm]</th>
<th>Surface area [m²/g]¹</th>
<th>Acidity [meq H⁺/g]¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-BEA powder Si/Al = 12.2</td>
<td>Uetikon A.G.</td>
<td>0.2-0.4</td>
<td>700</td>
<td>1.261</td>
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<tr>
<td>H-BEA powder Si/Al = 56</td>
<td>ex laboratory</td>
<td>0.2-0.4</td>
<td>654</td>
<td>0.26</td>
</tr>
<tr>
<td>H-BEA-coating/stainless steel</td>
<td>ex laboratory</td>
<td>0.1-0.3</td>
<td>654</td>
<td>1.80</td>
</tr>
<tr>
<td>9-14 g/m², Si/Al = 8</td>
<td>ex laboratory</td>
<td>1.3</td>
<td></td>
<td>1.49</td>
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<tr>
<td>H-MOR-coating/stainless steel</td>
<td>ex laboratory</td>
<td>27 g/m², Si/Al = 8.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ Based on resin or zeolite weight.

7.3.3 Experimental Procedure

The starting procedure for both autoclaves involved flushing the reactor with nitrogen after introduction of the appropriate amounts of ethanol (Nedalco B.V., ≥ 99.8 vol%) and catalyst (in most cases 1.35 g, dried overnight at 80°C to minimize the adsorbed water content), and closing the autoclave. Then a stainless steel bottle was filled with the balanced amount of isobutene (Air Products, ≥ 99.5 wt%). The isobutene was forced into the autoclave with nitrogen up to a pressure of 20 bar. The agitator was switched on (1000 rpm for the Parr autoclave and 90 vertical strokes per minute for the magnetic stirrer) and the mixture was heated with 6-10 °C/minute to the set point. At predefined times samples of ca. 1 ml were taken from the liquid mixture by means of a liquid nitrogen cooled sample tube. The sample tube was emptied in Eppendorf bottles and kept at ca. 8 °C to await analysis. The samples taken from the syntheses with powder catalyst had to be centrifuged first to remove traces of catalyst.

The samples were analyzed with a Varian star 3400 Gas Chromatograph over a CP sil 5 column (50 m x 0.53 mm), using nitrogen as a carrier gas. The GC was equipped with a Flame Ionization Detector (FID). Calibration for ETBE, ethanol, diisobutene, tert-butanol and diethyl ether was done in order to calculate conversions and selectivities.
7.4 Results and Discussion

The experiments with Amberlyst-15 were carried out in the Parr autoclave. Lowering the stirring speed did not influence the measured conversion, which rules out the existence of external mass transfer limitations. A control experiment with Amberlyst was done in the magnetic vertical stirrer autoclave, leading to similar conversions for both autoclave types. From this it was concluded that both systems were adequately mixed at the mixing speeds given above.

Apart from the reactants and products, diethyl ether, diiso-butylene and tert-butanol were formed as byproducts. Since direct measurement of the isobutene concentration with GC was not possible due to its high volatility, it was calculated from the concentration of the other components.

In Figure 7.6 the temperature influence on isobutene conversion using stoechiometric reactant ratios is given for different catalysts. In most cases the conversion was close to the equilibrium conversion, except when BEA coatings were used. The latter is presumably due to the fact that the amount of zeolite crystals was so low that the reaction was kinetically limited rather than equilibrium limited. The measured conversions for the BEA packing in Figure 7.6 were obtained after 17 h (90°C) and 58 h respectively and were still increasing but in view of experimental planning the experiments had to be stopped. Since the isobutene conversion is calculated from the concentrations of the other components, assuming no side reactions take place, the formation of diisobutene and tert-butanol gave rise to isobutene conversions that exceed the theoretical equilibrium conversion.

![Graph showing isobutene equilibrium conversions as a function of temperature](image)

**Fig. 7.6** Isobutene equilibrium conversions as a function of temperature for 1.35 g of different catalyst types at stoechiometric reactant ratios: Amberlyst-15 (■), H-BEA powder, Si/Al=12.2 (—■—), H-BEA powder, Si/Al=56 (○), H-MOR on packing (Δ) and H-BEA on packing (●). The dashed line represents the equilibrium conversion.
In Figure 7.7 the selectivity of the different catalysts is given as a function of temperature. At 90°C the selectivity of the tested zeolites is higher than 98%. The selectivity of the BEA coating is even 99%. The selectivity increases with increasing aluminum content of the zeolite. Furthermore, the selectivity of the BEA coating remains high as the temperature increases up to 100 °C, which can be attributed to the small layer thickness of the coating which prevents undesired conversion of the ETBE product.

![Graph showing selectivity of different catalysts as a function of temperature.](image-url)

**Fig. 7.7** Isobutene to ETBE selectivity as a function of temperature for 1.35 g of different catalyst types at stoichiometric reactant ratios: Amberlyst-15 (■), H-BEA powder, Si/Al=12.2 (□), H-BEA powder, Si/Al=56 (○), H-MOR on packing (Δ) and H-BEA on packing (●).
In Figure 7.8 the initial reaction rate is given as a function of temperature. The reaction rates for all catalyst types are optimal at around 90°C.

From Figure 7.8 it follows that the zeolite BEA powder with Si/Al=56 shows the highest activity per H⁺ site. The low aluminum content results in a low polarity of the surface and at the same time in an increased acidity. This favors the adsorption of isobutene while the adsorption of ethanol is lowered. Since ethanol is the strongest adsorbing species of the two the overall result is that higher Si/Al ratios lead to a more balanced adsorption and thus to higher activities. Although the initial reaction rate of the zeolitic coatings is lower than that of the powdered zeolites, the selectivity was shown to be higher in case the zeolitic BEA coating is used and this could be of importance for use in a practical application.

Another important parameter in the synthesis of ETBE is the reactant ratio. In Figure 7.9 the influence of the reactant ratio on isobutene conversion is given. The conversions for most experiments increase with temperature and are higher than the equilibrium conversion, due to side reactions. This is not the case for the experiments conducted with the BEA coating where no equilibrium was established.
**Chapter 7**

**Fig. 7.9** Isobutene conversions at varying reactant ratios for different catalyst types: Amberlyst-15 at 80°C (■), H-BEA powder, Si/Al=12.2 (□), H-BEA powder, Si/Al=56 (○), H-MOR on packing (Δ) and H-BEA on packing (●). Temperature is 90°C for all other experiments. The dashed line represents the equilibrium conversion.

**Fig. 7.10** Isobutene to ETBE selectivities at varying reactant ratios for different catalyst types: Amberlyst-15 at 60°C (■), H-BEA powder, Si/Al=12.2 at 90°C (□), H-BEA powder, Si/Al=12.2 at 75°C (○), H-BEA powder, Si/Al=56 at 90°C (○), H-MOR on packing at 90°C (Δ) and H-BEA on packing at 90°C (●).
In Figure 7.10 the selectivity for ETBE formation is given as a function of reactant ratio. The dependance of selectivities shows a similar trend for all catalyst types. At low EtOH concentrations the dimerization of isobutene lowers the formation of ETBE. The selectivities of the BEA powder are higher for all investigated ratios at 75°C.
7.5 Conclusions and Recommendations

Ethyl tert-butyl ether (ETBE) was successfully synthesized in the liquid phase using different catalysts in batch autoclave experiments. All zeolitic catalysts showed activities that were comparable to or higher than the activity of the conventional Amberlyst-15 catalyst.

Zeolite BEA appears to be an active and stable catalyst for the production of ETBE and shows the highest activity for ETBE synthesis, since it can be used at higher temperatures. The BEA coated stainless steel carriers showed a high selectivity, although conversions were below equilibrium due to limitations in the set-up.

The amount of in-situ coated BEA packing that could be fitted in the reactor was too low to provide equilibrium conversion in an acceptable amount of time. To assess the feasibility of binderless zeolitic packings more thoroughly, a more sophisticated set-up is required but the results so far indicate that the zeolitic coating concept can be applied successfully. The packings used showed no sign of deactivation and there were no influences observed from the carrier material.

For application in catalytic distillation more parameters have to be taken into account than catalytic activity alone. However, the advantages of zeolitic coatings, their shapeability, their robustness against high temperature excursions and the increased selectivity, and the results so far, are encouraging for further research on a larger scale.

Acknowledgment
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7.6 References

Conclusions

The objective of the work described in this thesis was to investigate the feasibility of zeolitic coatings applied as catalyst packings. To this end syntheses of zeolite Beta (BEA) and ZSM-5 on metal and ceramic carriers were carried out, to obtain structured packings with a binderless coating of zeolite material. Subsequently, the catalytic activity of these packings was tested in the selective catalytic reduction of nitrogen oxide and the synthesis of ethyl tert-butyl ether (ETBE).

Both stainless steel (grades 304, 316 and 321) and ceramic materials (particularly cordierite, α-alumina and zirconia) are suitable materials to be covered with a zeolitic coating by means of the in-situ growth method.

In a single step, stainless steel packings can be coated with coverages of more than 20 g/m² of either BEA or ZSM-5. When applied in a practical set-up, such as a metal monolith containing 600 cells per square inch, this corresponds to reactor loadings of ca. 40 kg_{zeolite}/m³_reactor. In most cases, stable and durable coatings are obtained, resistant to severe thermal shocks and ultrasonic treatment.

The synthesis of BEA coatings appears to be most sensitive to variations of synthesis conditions. Composition of the synthesis mixture, mixing during synthesis and pretreatment of the carrier with template solution are factors that have significant effects in the synthesis of BEA coatings. Moreover, the chemical composition of the metal carrier is important; highest coverages were obtained with grade 304 stainless steel (18-20% Cr; 8-10% Ni; balance Fe).

The synthesis of ZSM-5 coatings on stainless steel can greatly benefit from repeated synthesis, where a second coating is allowed to form on top of an existing one by repeating the complete synthesis procedure. Here the coverage appears to increase more than linearly with the number of applied synthesis steps. Synthesis of zeolitic coatings on a larger scale (packing volume larger than 0.5 dm³) requires mixing of the synthesis mixture during synthesis. The way of mixing as well as the intensity of mixing should be carefully optimized, since too strong mixing has a detrimental effect on the resulting coating.

The ZSM-5 coverages of the ceramic carriers are substantially higher than those of metal carriers. This is probably caused by the surface area of the uncovered material, which is higher for the ceramic materials. A cordierite monolith was covered with 100 g/m², which corresponds to a reactor loading of ca. 160 kg_{zeolite}/m³_reactor when applied in a 600 cpsi monolith. The bonding of the crystals to the ceramic surface appears to be excellent, even stronger than the zeolite crystals themselves.
Chapter 8

Cordierite monolith and α-alumina ceramic foam covered with ZSM-5 by the in-situ technique, can be successfully applied as a structured deNOx catalyst. Both the monolithic structure and the ceramic foams (which were arranged as a Parallel Passage Reactor or PPR) show deNOx activities that can compete with that of practical applications. Moreover, the performance of these reactor concepts can be described well by using simple equations. In case of the PPR, only one fit parameter is required. The value of this parameter can be linked to the pore geometry of the ceramic foam.

Metal monoliths covered with a BEA coating were employed in the liquid phase synthesis of ETBE. The zeolitic coatings show activities comparable to or higher than those of conventional catalysts. The BEA coated stainless steel carriers show a high selectivity towards ETBE formation and no deactivation is observed. Although the properties of the covered packings as a distillation unit have not been subject of study, it is expected that the freedom of choices of the shape of the packing provides a distinct advantage over conventional catalytic distillation packings.

Altogether, it has been shown that both the amount of zeolites that can be bonded to a structured surface in a zeolitic coating as well as the mechanical and thermal stability of this zeolitic coating are sufficient to make these catalyst modules suitable candidates in the design of more compact and functional, and ultimately more cost effective chemical reactor design.
Zeolietcoatings Toegepast in Gestureerde Katalysatorpakkingen

Samenvatting

In dit proefschrift wordt de synthese en toepassing van een nieuw type gestureerde katalysatorpakking beschreven. Deze katalysatorpakkingen zijn gemaakt door zeolieten te laten kristalliseren op het oppervlak van een op macroscopische schaal voorgevormde drager. Zeolieten kunnen uitstekend toegepast worden als katalysator in tal van chemische omzettingen omdat zij door hun microporeuze opbouw een zeer hoog intern oppervlak hebben. Een andere aantrekkelijke eigenschap wordt gevormd door de goedgedefinieerde vorm en afmetingen van de zeolietkristallen. Bovendien kunnen de zeolieten door ionwisseling voorzien worden van kationen die specifiek katalytisch actief zijn voor een gewenste omzetting. Het voordeel van gestureerde katalysatorpakkingen is dat de vorm ervan geoptimaliseerd kan worden voor het beoogde proces. Op deze wijze kan bijvoorbeeld de drukval, het stromingsprofiel, de stof- en/of warmteoverdrachtsnelheid of de dispersiegraad van het beoogde katalytische proces geoptimaliseerd worden. Het was het doel van dit proefschrift om te onderzoeken in hoeverre de combinatie van deze twee gegevens kan leiden tot bruikbare systemen voor een aantal reacties.

Het aanbrengen van de zeolietkristallen op de drager gebeurt volgens de zgn. in situ synthese-methode. Bij deze methode wordt de kristallen de mogelijkheid geboden tijdens hun vorming vanuit een synthemengsel te hechten aan het oppervlak van een drager die in het synthemengsel is ondergedompeld. De drager dient als eigenschap te hebben dat deze receptief is voor de zeolietkristallen. Waarschijnlijk verloopt het binden van de zeolietkristallen aan het dragermateriaal via OH-groepen die aan het oppervlak van de drager aanwezig zijn. Vormende zeolietkristallen, die ontstaan door groeiende en zich daarbij vertakkende netwerken van Si-O en Al-O-bindingen, kunnen zich hierdoor verankeren aan het drageroppervlak. Eerdere studies hebben aangetoond dat een grote variëteit aan vaste stoffen geschikt is om op deze wijze met een zeolietcoating bedekt te worden. Naast tal van metallische oppervlakken, zoals roestvast staal en andere legeringen, blijken ook keramische oppervlakken goed te bedekken met behulp van de in situ synthemethode. Anderzijds zijn organische kunststoffen in het algemeen niet geschikt als drager. Bij groei op metalen wordt gedacht aan een dunne oppervlakte-oxide film waaraan de zeolietkristallen gehecht kunnen zijn.

In dit werk is onderzocht of zeolietcoatings ook werkelijk kunnen worden ingezet als katalysatorpakking en of dit leidt tot een reactorconfiguratie waarvan de eigenschappen verklaarbaar en controleerbaar zijn.
Samenvatting

In de eerste plaats is de synthese in kaart gebracht. Verschillende keuzes worden gemaakt voor combinaties van zeoliettype en dragermateriaal met het oog op bepaalde toepassingen. Hoewel in de literatuur al iets bekend is over het groeien van zeoliëten op drager betreft dit voornamelijk kwalitatieve studies op kleine schaal (drageroppervlakken < 1 cm²). Voor een praktisch bruikbaar katalysatorsysteem is het nodig om de bedekking te kwantificeren, omdat de mate van bedekking met katalytisch actief materiaal de uiteindelijke afmetingen van de reactor mede bepaalt. Daarom wordt onderzocht welke factoren van invloed zijn op de uiteindelijke bedekking en of de bedekking geoptimaliseerd kan worden. Het blijkt dat de optimale synthesecondities sterk afhankelijk zijn van de gekozen combinatie van zeoliettype en dragermateriaal.

Onderzochte combinaties van zeoliettype en dragermateriaal zijn zeoliet Bêta en ZSM-5 op verschillende metalen en keramische dragers. Experimenten met zeoliet Bêta zijn vooral uitgevoerd met roestvast staal als dragermateriaal en in mindere mate met andere legeringen. Uiteindelijk zijn pakkingen bereid bestaande uit zgn. metalen monoliëten met een bedekking van ca. 20 g zeoliet/m² pakking. Indien toegepast in een monoliëtstructuur van 600 cpsi (kanalen per vierkante inch) komt dit overeen met een belading van ca. 40 kg zeoliet/m³ reactor. ZSM-5 is gegroeid op roestvast staal en diverse keramische materialen waaronder poreuze α-alumina platen (‘keramische schuimen’) en corderiet monoliëten. De opbrengsten op roestvast staal bedroegen ca. 20 g zeoliet/m² reactor (ca. 40 kg zeoliet/m³ reactor). Op keramische dragers werden bedekkingen tot 100 g zeoliet/m² pakking behaald (ca. 160 kg zeoliet/m³ reactor).

De gemaakte pakkingen zijn getest in een tweetal toepassingen. In de eerste plaats is de Selectieve Katalytische Reductie (SCR) van stikstofoxide onderzocht, gebruikmakend van zowel zeoliet Bêta als ZSM-5 gegroeid op roestvast stalen en keramische pakkingen. De deNOx-reactie kan voordeel ondervinden van het feit dat deze reactie wordt gekatalysed door metaalgewisselde zeoliëten en van het feit dat in een praktische deNOx-installatie de drukval en gevoeligheid voor stof geminimaliseerd dienen te worden. Dit kan worden bewerkstelligd door het juist kiezen van de macrostructuur van de pakking. In eerste instantie zijn de pakkingen onderzocht op hun chemische activiteit. Hiervoor is een zgn. internal recycle reactor gebruikt die het mogelijk maakt om de chemie te bestuderen in afwezigheid van temperatuur- en concentratiegradienten. Bij deze experimenten zijn koolwaterstofen (methaan en propeen) als reductiemiddel gebruikt. Uit deze experimenten is gebleken dat de activiteit van zeoliëten geen nadeel ondervindt van het feit dat de kristallen in een laag zijn aangebracht. Niettemin is de activiteit van de SCR met methaan te laag om voor een praktische toepassing interessant te zijn. Op grotere schaal zijn twee reactorconfiguraties onderzocht: de monoliëtreactor en de Parallel Passage Reactor (PPR) waarbij de zeolietcoating is aangebracht op platen van keramisch schuim. Het hier gebruikte reductiemiddel was ammoniakgas. Uit deze experimenten is gebleken dat met name de keramische dragers zeer geschikt zijn als substraat voor zeolietcoatings; de behaalde conversies zijn vergelijkbaar met die van praktische installaties, zonder dat vergaande optimalisatie van de geteste configuraties vooraf had plaatsgevonden.

In de tweede plaats is de vloeistoffasesynthese van ethyl-tert-butylether onderzocht, waarbij gebruik werd gemaakt van roestvast stalen pakkingen bedekt met zeoliet Bêta in de zure vorm. De achterliggende gedachte is hier dat zeolietcoatings toegepast kunnen worden in katalytische destillatie en, doordat de reactor en de scheidingskolom geïntegreerd worden in één apparaat, bij
kunnen dragen aan compactere procesapparatuur. De experimenten zijn op kleine schaal uitgevoerd en alleen de chemie is bestudeerd. Met name de selectiviteit wordt gunstig beïnvloed door het feit dat de katalysator in een dunne laag aanwezig is. Niettemin bleek de maximale belading van de pakkingen met zeoliet te laag om bevredigende conversies te halen. In de toekomst kan dit ondervangen worden door de zeolietbelading van de pakkingen te verhogen. Een voor de hand liggende manier om dit te bereiken is door gebruik te maken van de eerder genoemde keramische schuimen.
Samenvatting
Dankwoord

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Dankwoord
Curriculum Vitae

Otto Leonard Oudshoorn werd geboren op 5 juni 1965 te Leiden.


Aansluitend werd begonnen met de studie Scheikundige Technologie aan de Technische Universiteit in Delft. Het afstudeeronderzoek naar drukval in de kralenreactor werd verricht bij prof. ir Cock van den Bleek van de sectie Chemische Reactorkunde (vakgroep Chemische Procestechnologie). In april 1993 werd het ingenieursdiploma behaald.

In augustus van dat jaar werd begonnen met het onderzoek naar de toepassing van zeolietcoatings in gestuctureerde katalysatorpakkingen. De resultaten van dit onderzoek staan beschreven in dit proefschrift. Het promotieonderzoek is uitgevoerd bij prof. Herman van Bekkum (vakgroep Organische Chemie en Katalyse) en prof. Cock van den Bleek (vakgroep Chemische Procestechnologie) aan de Technische Universiteit Delft.

Sinds 1 augustus 1998 is Otto Oudshoorn werkzaam bij de Vereenigde Octroibureaux te 's-Gravenhage.