Stellingen behorende bij het proefschrift

Monolithic Catalysts for Acylation and Esterification
door Annemarie Beers


3. Het mishandelen van een zeoliet kan effectiever zijn dan het zorgvuldig synthetiseren ervan, zie hoofdstuk 3b van dit proefschrift.

4. Een hydrofobe vaste zure katalysator is een contradictio in terminis.

5. Hoewel niet gepubliceerd, is het evident dat gesulfateerde oxidën in vloeistoffase reacties in de aanwezigheid van water ‘leachten’ en daarbij zwavelzuur vormen. Het is verbazingwekkend dat tegen beter weten in veel onderzoek wordt verricht om dit type katalysatoren toe te passen in dit soort milieus.

6. Koolstofgecoat monolieten zijn minder aantrekkelijk uit het oogpunt van terugwinning van actieve (edel)metalen.

7. Om het parkeerprobleem in grote steden op te lossen zou het gebruik van korte auto’s gestimuleerd moeten worden door, zoals in jachthavens al gebruikelijk, parkeergeld per meter te heffen.

8. Het feit dat de promotieven een boekenlegger toevoegt aan het proefschrift toont een misplaatst optimisme over de verwachting hoeveel er in de praktijk in het boekje gelezen wordt.

9. Fietsen door rood licht kan veiliger zijn dan fietsen door groen licht omdat men dan meer op zijn hoede is.

10. Het doel van de ICT (‘Information and Communication Technology’) sector om efficiënter te werken en zo een bijdrage te leveren aan een duurzame samenleving wordt grotendeels teniet gedaan door de verergering van de filevorming als gevolg van de slechte gewoonte in deze sector om grote aantallen leaseauto’s uit te delen.

11. Evenals roken zou het storende gebruik van mobiele telefoons in openbare gebouwen verboden moeten worden.
Monolithic Catalysts
for
Acylation and Esterification
Monolithic Catalysts
for
Acylation and Esterification

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K.F. Wakker,
voorzitter van het College voor promoties,
in het openbaar te verdedigen op dinsdag 15 mei 2001 om 10.30 uur

door

Annemarie Elisa Wilhelmina BEERS

doctorandus in de scheikunde
geboren te Curaçao, Nederlandse Antillen
Dit proefschrift is goedgekeurd door de promotoren:
Prof. dr. J.A. Moulijn
Prof. dr. F. Kapteijn

Samenstelling promotiecommissie:

Rector Magnificus, voorzitter
Prof. dr. J.A. Moulijn, Technische Universiteit Delft, promotor
Prof. dr. F. Kapteijn, Technische Universiteit Delft, promotor
Prof. dr. ir. H. van Bekkum, Technische Universiteit Delft
Prof. dr. ir. J.W. Geus, Universiteit Utrecht
Prof. dr. W.F. Hölderich, Rheinisch-Westfälische Technische Hochschule Aachen, Duitsland
Dr. R. Downing, Technische Universiteit Delft
Dr. ir. M.J. Groeneveld, Shell Global Solutions International

Dit onderzoek werd uitgevoerd in het kader van het Innovatiefgerichte Onderzoeks Programma
Katalyse (IOP Katalyse, nr. 96023a) met financiële steun van het Ministerie van Economische
Zaken.

Print: Offsetdrukkerij Ridderprint B.V., Ridderkerk

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ISBN 90-9014721-7
"Vecht, huil, bid, lach, werk en bewonder"
# Contents

**Chapter 1**  
Introduction  
1

**Chapter 2**  
The acylation of aromatics  
13

**Chapter 3**  
The development of an active catalyst for the acylation of anisole with octanoic acid  
Part A  Development of Nafion/silica composites  
47  
Part B  Modification of BEA by means of steaming and acid leaching  
69

**Chapter 4**  
Solid acid coated monoliths – preparation and characterization  
85

**Chapter 5**  
Performance of coated monoliths in the acylation of anisole with octanoic acid  
121

**Chapter 6**  
The kinetics of the SAC13 catalyzed esterification of hexanoic acid and 1-octanol  
135

**Chapter 7**  
Reactor configurations in esterification  
157

**Summary**  
173

**Samenvatting**  
177

**Dankwoord**  
179

**List of publications and presentations**  
181

**Curriculum Vitae**  
183
Introduction

Summary

A general introduction is given of the present study, in which the approach is described. The solid acid catalyzed reactions and the structured reactors (monoliths) that are studied in this thesis are introduced. Guidelines are presented for reactor selection in certain chemical processes.
Chapter 1

Introduction

In the fine chemical industry, there is an increasing pressure to develop safer, cleaner and more energy efficient processes. In this branch the amount of waste produced per kilogram of product (E-factor, (Sheldon, 1994)) is extremely high compared to the ratio of byproducts to products in other branches, with a value of 5-50 for fine chemicals and 25-100+ for pharmaceuticals compared to <1-5 for bulk chemicals and ~0.1 for oil refinery products (Sheldon, 1994). For example, Rhodia (a large fine chemicals producer, leader in vanillin production) has committed itself to reduce its waste production by 50% between 1990 and 2000. One way to achieve a minimization or elimination of waste production is by adjusting the existing production processes, but this often requires high investments (Ratton, 1998). Another way is to develop new processes, solving the problem at the source.

When improving a chemical process two important aspects need to be considered. On the one hand the chemistry of the reaction has to be studied, which will lead to improved catalysts with higher activity and selectivity. On the other hand, the technology of this chemical reaction is just as important. When a catalyst is rejected for its low activity or selectivity, an acceptable performance can still be obtained by considering the right process parameters or another reactor configuration.

This is illustrated with the following example; a chemical reaction between reactants A and B of which reactant A is strongly adsorbed on the catalyst surface, like the alkylation of iso-butane with alkenes. In this solid acid catalyzed reaction the alkenes will adsorb very strongly on the catalyst surface leading to oligomerisation which will deactivate the catalyst severely, this is schematically depicted in figure 1. The resulting very short catalyst life times can be increased by applying low olefin/paraffin feed and by using a continuously stirred tank reactor (CSTR) instead of a fixed bed (plug flow) reactor (de Jong et al., 1996).

Figure 1. The strong adsorption of a reactant on a catalyst surface, leading to inhibition of the active sites. Strong adsorption of reactant A preventing formation of desired products.
In the case of a reaction with a strongly adsorbing reactant leading to undesired side reactions such as oligomerisation, the injection and the mixing (on the micro- and macro-scale) of the reactants is extremely important in a slurry reactor. If the reactants are added at once to the solvent containing slurry catalyst - 'late-mixing' - locally the catalyst may encounter (too) high concentrations. This is depicted in figure 2. The reactants should be mixed before contacting the catalyst - 'early-mixing' - and local high concentration of reactant at the surface of the catalyst can be avoided.

Table 1. Some characteristic reactions and the reactor selection.

<table>
<thead>
<tr>
<th>Reaction characteristics</th>
<th>Rule of thumb</th>
<th>Type of reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>A+B → Product(s)</td>
<td>Concentration of strongly adsorbing reactant has to be kept as low as possible.</td>
<td>Fed-batch or CSTR-type of reactor, with pre-mixing of the reactants</td>
</tr>
<tr>
<td>Strong adsorption of a reactant on catalyst surface leading to inhibition of reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A+B → Product(s)</td>
<td>Concentration of reactant has to be kept as low as possible</td>
<td>Fed-batch or CSTR-type of reactor, with pre-mixing; cross-flow reactors in which the inhibiting reactant is fed in stages.</td>
</tr>
<tr>
<td>Undesired (often 2nd order) parallel reactions due to adsorption of a reactant</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A+B → C+D</td>
<td>Product removal from the catalyst surface and from the reaction mixture during reaction.</td>
<td>Plug-flow (PF) reactor or better: Multifunctional reactors - with removal of products.</td>
</tr>
<tr>
<td>Strong adsorption (low rate of desorption) of products on catalyst surface leading to inhibition.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A → B → C</td>
<td>Product removal from the catalyst surface and from the reaction mixture.</td>
<td>Small catalyst particle diameter or egg shell catalyst; Multifunctional reactors – PF-type of reactor; with removal of products.</td>
</tr>
<tr>
<td>Undesired consecutive reactions due to strong adsorption of desired intermediate product (reaction order &gt;0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A+B ⇄ C+D</td>
<td>Product removal from the catalyst surface and from the reaction mixture.</td>
<td>Multifunctional reactors - PF-type of reactor; with removal of products.</td>
</tr>
</tbody>
</table>
Chapter 1

When selecting a reactor type for optimal performance of a reaction, basically three types of reactors are distinguished, the batch stirred-tank reactor, the continuous stirred tank-reactor (CSTR), and the plug flow reactor (PFR).

In table 1, examples are given of specific reaction characteristics and the guidelines for reactor selection in the case of isothermal operations. So heat effects are not considered.

Removal of the products can be done by for example a membrane, stripping, distillation, catalyst modification, chemical reaction, solvent extraction. In the case of undesired consecutive reactions or reversible reactions, local high concentrations of products which can react further have to be prevented. To achieve this a good transport away from catalyst must be provided.

Chemical reactions and industrial relevance

The chemical reactions studied here, are acid catalyzed reactions. These reactions are abound in the fine chemical industry. Considered are the acylation of aromatics with carboxylic acids and the esterification of carboxylic acids with alcohols (figure 3a and 3b). The acylation of aromatics (chapter 2) is the main route for the formation of aromatic ketones, important intermediates in the pharmaceutical, fragrance, flavour, and agrochemical industry. The esterification reaction (chapter 6) is an important reaction in the production of fragrances, flavours, and polymers.

a.  

\[
\begin{align*}
\text{R}_2 \text{C}_{6} \text{H}_4 \text{X} + \text{R}_1 \text{CO}_2 \text{H} & \rightarrow \text{R}_2 \text{C}_{6} \text{H}_4 \text{CO}_2 \text{R}_1 + \text{HX} \\
\text{X} &= \text{Cl, OH, OCOR}
\end{align*}
\]

b.  

\[
\begin{align*}
\text{R}_1 \text{CO}_2 \text{H} + \text{R}_2 \text{OH} & \rightarrow \text{R}_1 \text{CO}_2 \text{R}_2 + \text{H}_2\text{O}
\end{align*}
\]

Figure 3a. The acylation of aromatics. b. The esterification of carboxylic acids with alcohols.
Conventionally, these reactions are catalyzed by metal halides (like AlCl₃) and by strong mineral acids (like HF and H₂SO₄). Problems associated with the metal halides as a catalyst include the relatively strong complex formed between the ketone product and the metal chloride (Scheele, 1991) and the need to hydrolyse the complexes formed. Catalysts are therefore used in more than stoichiometric amounts. This leads to large corrosive waste streams, because the 'catalyst' cannot be regenerated. This type of 'catalyst' should rather be seen as a reactant and, moreover, halide-containing side-products are formed.

Solid acid catalysts

The use of a solid acid catalyst can overcome these disadvantages (Hölderich and van Bekkum, 1991). These catalysts can be separated from the reaction mixture and reused. Besides, these 'green' materials are not harmful for the environment, because they are not corrosive and do not produce corrosive side-products. Different types of materials can be considered for their applicability as solid acid catalysts. Examples are zeolites and ion-exchange resins.

Reactor configurations – slurry vs structured packings

In fine chemical industry, solid acids are generally used as slurry catalysts in a batch reactor. The main disadvantage of using these materials in liquid phase reactions, is the laborious and expensive separation of the catalyst particles from the reaction mixture. Also due to the high stirring speed for mixing attrition of the particles occurs. By fixing the catalyst in the reactor, for example in a fixed bed, separation is not necessary anymore. The disadvantage of a fixed bed, however, is that the particle size of the catalyst is increased to prevent pressure drop issues, leading to a lower catalyst effectiveness. By integration of the catalyst with the reactor using a structured support, separation and attrition problems are circumvented, so the catalyst can be used for a longer period. Coating the walls of a structured reactor with a thin layer of catalyst, leads to a high effectiveness and selectivity by reducing diffusional distances.

Furthermore, depending on the shape of the structure, the pressure drop decreases towards zero (Kapteijn et al., 1999). Another advantage of the structured packing is the fact that the reactants can be mixed before contacting the catalyst, to prevent the strong adsorption problems mentioned earlier in the introduction. In this way also the undesired side-reactions are suppressed, because local high concentrations of reactants are prevented.
Chapter 1

Reactants and Products

In both selected reactions, water is produced as the second product. Due to the hydrophilicity of the active (acidic) sites and of the catalyst itself, the formed water can adsorb on the surface of the solid acid catalyst, thereby inhibiting the active sites for reaction, see figure 4. So, to improve the performance of the solid acid catalyzed reactions in which water is formed, the water has to be removed from the surface of the catalyst, for example with a dry inert gas by means of stripping (figure 5).

![Figure 4. Strong adsorption of water on a solid acid catalyst, leading to inhibition of the active sites.](image)

For this in-situ removal of water, the use of a structured packing also has advantages. Besides the optimal mass transfer characteristics, these packings can be used in co- and counter-current stripping. Applying an inert gas flowing co- or counter-currently can remove (by)-products that are competitively adsorbed on the catalyst surface (Lebens et al., 1999a; 1999b; 1999c), like water in the mentioned solid acid catalyzed reactions. When operating in the counter-current mode, only structured packings can be applied or else flooding will occur (liquid entrainment by the gas in the wrong direction) (Kapteijn et al., 1999).

![Figure 5. The application of co- and counter-current flow of gas for removal of inhibiting products](image)
Chapter 1

Goal of the study

The aim of this study is to develop a structured reactor configuration with an improved performance for a solid acid catalyzed process, i.e. in which optimal activity and selectivity is achieved and catalyst filtration is eliminated. To achieve this goal chemistry and technology are combined.

Monolithic catalysts

An example of a structured reactor is a monolith or honeycomb (figure 6) in which the catalyst can be applied as a thin layer on the walls. A monolithic support consists of a macroporous material, often cordierite, that is structured in straight parallel channels. Advantages of such a system are that filtering of the catalyst is not necessary, attrition of the catalyst does not occur, the extremely low pressure drop, and the low internal diffusion resistance (more efficient use of the catalyst due to the thin catalytic layer) (Cybulski and Moulijn, 1994; Villermaux and Schweich, 1994; Kapteijn et al., 1999). Disadvantage is that there is still little experience in liquid phase applications.

Currently, the most well known application of the monolith is in the automotive industry as an exhaust gas converter (Bardhan, 1997; Geus and van Giezen, 1999). In the early 1960s, these catalysts were especially developed for this application mainly due to their low pressure drop. The material of which the monoliths are usually made of is cordierite (2MgO.2Al2O3.5SiO2) because of its insensitivity towards temperature changes (low thermal expansion, high thermal stability, and mechanical strength) and its favourable properties for extrusion (Williams et al., 1995). For other applications also other materials, like silica and alumina can be extruded into various monolithic shapes (Irandoust and Andersson, 1988).

Besides the exhaust gas treatment, monoliths are also applied in power stations as selective catalytic reduction catalysts of NOx with NH3 (Beretta et al., 1998), in airplanes for ozone destruction (Campbell and Sanders, 1999; Chang and Pluim, 1999), for effluent gas purification with monoliths consisting of activated carbons (Yates et al., 2000), for the oxidative dehydrogenation of propane to propylene (Capannelli, 1996a; 1996b), and for the commercial production of hydrogen peroxide via the hydrogenation of alkylated anthraquinone (Kapteijn et al., 1999).

Figure 6. A photograph of a monolithic structure.
Chapter 1

The applications in which monoliths are currently investigated are multi-phase reactions like the solid acid catalyzed liquid phase reactions (two-phase) and three-phase hydrogenation (Smits et al., 1996) and oxidation reactions (Kapteijn et al., 1999). In the hydrogenation of \( \alpha \)-methylstyrene (a very fast, often mass-transfer limited reaction), the monolithic reactor showed a higher productivity compared to a trickle-bed catalyst system (Nijhuis et al., 2001). In this study an activity of 22 mol/m\(^3\)\(_\text{reactor-s}\) was found for the monolithic system compared to an activity of 5 mol/m\(^3\)\(_\text{reactor-s}\) for the trickle-bed reactor at a similar geometrical surface area even with ten times lower amount of catalyst. The higher activity of the monolith is attributed to a higher mass transfer rate. From a model study (Edvinsson and Cybulski, 1994) in which a three-phase hydrogenation with a consecutive, three-phase hydrogenation with Langmuir-Hinshelwood-Hougen-Watson type of kinetics was studied, the performance of a monolithic reactor gave much higher selectivity towards the desired intermediate product than a trickle-bed reactor. The results of this modelling work were supported by the study of the selective hydrogenation of benzaldehyde towards benzyl alcohol (Nijhuis et al., 2001). This product can be further hydrogenated towards the undesired toluene. The experiments performed in a monolith resulted in a selectivity of 96% towards the benzyl alcohol compared to 73% in the trickle bed configuration at a conversion level of 50%. The higher selectivity of the monolithic configuration is attributed to both the shorter diffusion distance into the catalyst coating on the monolithic walls and the narrow residence-time distribution in the monolithic reactor.

Examples of patented industrial reactions performed in a monolith, are the hydrogen peroxide process (Kapteijn et al., 1999), the hydrogenation of dinitrotoluene to toluenediamine (Machado et al., 1999) and the Fisher-Tropsch process (Schanke et al., 1998). In the hydrogen peroxide process, alkylated anthraquinone is hydrogenated in a monolithic reactor to alkylated hydroanthraquinone followed by the oxidation via the endoperoxide to hydrogen peroxide and alkylanthraquinone. A concentrated solution of hydrogen peroxide is obtained after extraction (annual capacity 150,000 tons) (Kapteijn et al., 1999). In the hydrogenation of dinitrotoluene to toluenediamine, excellent reaction rates are claimed through high gas/liquid and liquid/solid mass transfer. Other advantages of the monolith are that the reaction can be performed without an additional solvent, the monolithic reactor can be applied in industry with minimal capital investments maintaining the advantage of fixed bed reactors, and eliminating the disadvantage of slurry phase reactors (Machado et al., 1999). The Fischer-Tropsch synthesis, the formation of higher hydrocarbon products from synthesis gas (CO and H\(_2\)), is a strongly exothermal reaction and effective heat transfer is a prerequisite for successful reactor operation. In the monolithic operation, high mass transfer characteristics are claimed and cooling is performed by direct heat removal by the production stream (Schanke et al., 1998).
Monoliths can also be applied in reactive distillation or stripping operations. By performing a co- or counter-current gas-liquid flow an inhibiting component can be removed from the liquid phase through the gas phase. This is a stripping type of operation and not reactive distillation because the liquid is not actually boiling and there is no applied temperature gradient over the reactor. For the application of counter-current stripping operations, a special type of monolith has been designed with larger channels, the so-called internally finned monoliths (figure 7). In the finned monolith the liquid phase is the reactive part and the gas phase the stripping part. The fins stabilize the counter-current flow, provide additional surface area for the deposition of the catalyst, and avoid flooding (Lebens et al., 1999a; 1999b).

An example of a study for efficient counter-current removal of a compound in internally finned monoliths (figure 7), is the removal of inhibiting H₂S in the hydrodesulfurization of gasoil (Lebens et al., 1999b; 1999d; Sie and Lebens, 1998).

![Cordierite structure](image1.png)

![Gas phase](image2.png)

![Liquid phase](image3.png)

Figure 7. An internally finned monolith; photographic and a schematic view of a cross-section.

Monoliths, and also many other ceramic structures, are usually produced by extrusion techniques (Lachman et al., 1981). Metal monoliths, however, are made by rolling up thin corrugated metal sheets. It is possible to vary the geometric parameters of the channels, like the channel shape, size and the wall thickness of the ceramic ‘classical’ monolithic structures. The various shapes that are produced are amongst others hexagonal, triangular, square, circular, and with fins in the corners and in the walls of the channels (Kapteijn et al., 1999). These latter, finned, monoliths are currently studied for their application in counter-current operations in liquid-gas reactions (chapter 7 of this thesis).

Mainly monoliths with square channels are considered. These monoliths are defined by their number of channels per cross sectional area (cell density), and by their wall thickness. The unit of the cell density is defined as the number of cells per square inch (cpsii). Monoliths are available in cell densities ranging from 5 to 1100. For some characteristics of the most common square channel monoliths see table 1.2. In the value for the void fraction or the open frontal area (OFA) the values of the wall thickness are taken into account.
Table 2. Characteristics of the most common square channel monoliths.

<table>
<thead>
<tr>
<th>Cell density (cpsi; cells.cm(^{-2}))</th>
<th>Wall thickness (mm)</th>
<th>Channel diameter (mm)</th>
<th>Geometric surface area (m(^2).l(^{-1}))</th>
<th>Void fraction (\varepsilon)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>31</td>
<td>0.30</td>
<td>1.49</td>
<td>1.85</td>
</tr>
<tr>
<td>400</td>
<td>62</td>
<td>0.18</td>
<td>1.09</td>
<td>2.71</td>
</tr>
<tr>
<td>600</td>
<td>93</td>
<td>0.11</td>
<td>0.93</td>
<td>3.45</td>
</tr>
</tbody>
</table>

**IOP Catalysis**

This research has been carried out as part of the Innovation Oriented research Programme on Catalysis (IOP Catalysis), funded by the Dutch Ministry of Economic Affairs. The main task of the IOP Catalysis is to promote research and development in catalysis and at the same time encouraging the communication between universities and industry.

The research performed within the framework of the IOP Catalysis has its emphasis on the relevance in industry, in this study being the development of a structured reactor configuration with an optimal performance for two processes in fine chemistry. These are the acylation of aromatics and the esterification of alcohol with carboxylic acid. Replacement of the conventional catalysts by solid acid catalysts for these processes, leads to a cleaner process.

**Outline of the thesis**

The acylation of aromatics and the esterification of a carboxylic acid with an alcohol are studied in respectively chapter 2 and 6. In these chapters the existing literature, the chemistry and the kinetics are studied, and catalyst screening results are presented. Catalyst development is done by studying the preparation of silica/Nafion composite and by modification of BEA (chapter 3). As a structured reactor, the monolithic reactor is selected. To integrate catalyst and reactor, the preparation and characterisation of a solid acid coated monolith is studied (chapter 4). The performance of these coated monoliths is studied in the model acylation reaction (chapter 5). Finally, the obtained knowledge is applied for prediction and improvement of the performance using a reactor design approach in the esterification reaction (chapter 7).
Reference List


Chapter 1


The acylation of aromatics

Summary

The acylation of aromatics is of great importance for the synthesis of aromatic ketones which are applied in the production of pharmaceuticals, fragrances, and agrochemicals. In this chapter, a literature review is given of the solid acid catalyzed acylation reaction. The solid acid catalysts that have appreciable activity for aromatic acylations, are mainly ion-exchange resins such as Nafion and zeolites such as BEA and FAU.

In the acylation of anisole with octanoic acid, slurry catalyst screening experiments showed that the Nafion/silica composite SAC25, with 25 wt% of Nafion, exhibited the highest specific activity in the acylation of anisole with octanoic acid compared to zeolites BEA and USY. A particle-size dependency of the Nafion/silica composites indicated that this reaction is internally diffusion-limited in the composite particles. The Nafion/silica composites showed a batch-dependency in their performance, indicating that their production is not reproducible.

Water removal during reaction is advantageous for the reaction progress since it inhibits strongly. The kinetics of the BEA catalyzed acylation of anisole with octanoic acid are of an Eley-Rideal type. Cumene shows low activity in the acylation with octanoic acid. The acylation activity of veratrole is higher than that of anisole. No pronounced effect of the chain length of the carboxylic acids (C4-C12) is observed on the acylation activity of anisole.
Chapter 2

Introduction

The acylation of aromatics is a coupling reaction in which an aromatic substrate reacts with an acylating agent to form an aromatic ketone and a second product (figure 1).

\[
\begin{align*}
\text{R}_2\text{C} & + \text{X}\text{R}_1\text{C} & \rightarrow & \text{R}_2\text{C} & + & \text{HX} \\
\text{X} & = \text{Cl, OH, OCOR} & & & & \\
\end{align*}
\]

Figure 1. The acylation of aromatics.

In this chapter, a description will be given of the various solid acid catalyzed acylation studies described in literature, starting with the industrial relevance of the reaction and the products. Subsequently, the acylation of aromatics with carboxylic acids is studied. From an environmental point of view, the carboxylic acid forms the most attractive acylating agent, because water is formed as the only second product. In a model reaction (the acylation of anisole with octanoic acid) a comparison has been made of the catalytic performance of zeolites, ion-exchange resins and Nafion/silica composites. Also the effect of water, the kinetics, the effect of the chain length of the carboxylic acid and varying the aromatic substrate were studied.

History

Aromatic acylations and alkylations were already investigated in 1869 by Zincke (1869). The role of the metal chloride as a catalyst was studied in 1877 by Charles Friedel and James Mason Crafts (1877a; 1877b), and this is why these reactions are called 'Friedel-Crafts' reactions. During the following century the studies on the aromatic acylation are numerous, especially when Olah published an extensive overview handling the Friedel-Crafts (and related) reactions (Olah, 1963).

Industrial application of the acylation of aromatics

The Friedel-Crafts acylation (figure 1) is of great importance for the synthesis of aromatic ketones, because many fine chemicals of industrial interest contain an aromatic acylation step in their synthesis. The use of these compounds can be found in the production of pharmaceuticals, fragrances and agrochemicals. Numerous examples are found in the patent
literature by various companies like BASF (Henkelmann and Siegel, 1991; 1994; Wolf, 1994; Eggersdorfer et al., 1989), Bayer (Waldmann et al., 1991; 1999; Botta et al., 1989), Hoechst Celanese (Gupta, 1987), Rhodia (Spagnol et al., 1997), Uetikon (Vogt and Pfenninger, 1994), UOP (Kurek, 1991), and Zeneca (Newton, 1996).

The first industrial application of a zeolite catalyzed acylation reaction was introduced by Rhodia Chimie (Spagnol et al., 1997). The acylation of anisole and veratrole was performed with acetic anhydride in a recyle fixed bed reactor. The catalysts of this reaction are zeolites (FAU and BEA). They claimed a very high productivity compared with the conventional methods (AlCl₃). The advantages of the liquid phase system were that a multi ton scale set-up was possible, the product could easily be isolated and finally this all leads to an environmentally friendly process.

Several examples of important products which are synthesized via an acylation step are depicted in figure 2. Benzophenone (figure 2), a flavor component of grapes with a geranium-like odor (Bauer et al., 1999) has a variety of applications. It is used as an additive or intermediate in the preparation of medicinal substances, as a fixative in perfumes, and added as a catalyst to UV-cured polymers formulated to produce inks, adhesives and coatings. Benzophenone is also a precursor in the manufacture of pesticides. Furthermore, derivatives of benzophenone, like 2-hydroxy-4-methoxybenzophenone, can be applied in sun creams, because of their capacity to absorb UV-light.

Acetophenone, another aromatic ketone, is a component of a large number of foods and essential oils, see figure 2. It is used for perfuming detergents and is also an intermediate of other fragrance compounds. 4-Methylacetophenone, see figure 2, prepared by Friedel-Crafts acetylation of toluene has been identified in Brazilian rosewood oil and in pepper. It is used for blossom notes in mimosa and hawthorn type perfumes, especially in soap perfumes. The Friedel-Crafts acetylation of naphthalene yields methyl β-naphthyl ketone, see figure 2, which smells like orange blossom. This ketone is used as a fixative and in soap perfumes and detergents. Acetylation of indanes yield the musk fragrances which are used in perfumes and cosmetics. Two examples are given in figure 2 (Bauer et al., 1999).

In the pharmaceutical industry, an important example of the acylation of aromatics is the production of the analgesic Ibuprofen (figure 2), a competitor of aspirin. This product has a large worldwide production of 7-8 ktons/y. For the production of this drug the two main process routes are given in literature (Moulijn et al., 1993). In both cases the Friedel-Crafts acylation of isobutylbenzene is the first step. In the classical route, developed by Boots, the
Chapter 2

acylation is performed with aluminium chloride as a catalyst. In another route, developed by Hoechst-Celanese, HF is used as a catalyst (Sheldon, 1996).

By acylating 2-methoxynaphthalene with an acyl group an intermediate for another important anti-inflammatory drug, (S)-Naproxen (year sales of $1.05 billion in 1995), is formed (Aslam et al., 1994; Kim et al., 2000; Gunnewegh et al., 1996a; Harrington and Lodewijk, 1997), see figure 2.

![Chemical structures](image)

Benzophenone  acetophenone  methylacetophenone  methyl-β-naphtyl ketone

5-acetyl-1,1,2,3,3,6-hexamethylindane
Trade name: Phantolide (PFW)

4-acetyl-1,1-dimethyl-6-tert-butyldindane
Trade name: Celestolide (IFF)

Naproxen  Ibuprofen

Figure 2. Industrially relevant products in fine-chemical industry, produced through an acylation step.

Acylating agent

As acylating agents acyl halides, acid anhydrides and carboxylic acids can be used. In general, acyl halides are used due to their high activity compared to the other acylating agents, but as the second product is dependent on the nature of the acylating agent (figure 1), HCl is produced in this reaction, which is very corrosive and environmentally unfriendly.

The reactivity of the acyl halides is higher than that of the acid anhydrides, while these latter are more active than carboxylic acids. Also the anhydrides have corrosive properties, but in
Chapter 2

the case of the carboxylic acids water is formed. The chain length of the linear carboxylic acid was found to show an optimum in the Ce-Y catalyzed acylation of toluene for 12 carbon atoms (Chiche et al., 1986).

Aromatic substrate

The aromatic compound to be acylated is a (substituted) benzene. The acylation reaction, being an electrophilic substitution reaction, is facilitated by an electron-donating substituent (Kouwenhoven and van Bekkum, 1997). This results in an order of activity of the aromatic substrates of (for example) anisole > toluene > benzene. A broad range of aromatic substrates have been studied in their ability to be acylated, like veratrole (Spagnol et al., 1996), anisole (Gunnewegh et al., 1996b; Corma et al., 1989; Gaare et al., 1997; Ma et al., 1997), toluene (Chiche et al., 1986), benzene (Olah, 1964; 1971; Singh and Pandey, 1997), heterocyclic compounds (benzofuran) (Richard, 1996a; 1996b), 2-methoxynaphthalene (Kim et al., 2000; Harvey and Mäder, 1992; Gunnewegh et al., 1996a), and phenol (Subba Rao et al., 1995; Neves et al., 1992; 1994; Gunnewegh et al., 1995; van Bekkum et al., 1994). For example, Gunnewegh et al. (1996b) investigated the acylation of anisole (an activated substrate) and toluene (a non-activated substrate) with octanoic acid catalyzed by zeolite HBEA. The acylation of anisole resulted in a conversion of the acid of 21%, while for toluene a conversion of only 2.5 % to the aromatic ketone was measured.

Thermodynamic considerations

The thermodynamics of the acylation of benzene with acetic acid and with acetic anhydride are considered here for evaluation of the question whether thermodynamics allows the acylation with carboxylic acids. The gasphase thermochemical data, ΔG at 400K, were used from the software program HSC Chemistry for Windows, version 4, and listed in table 1. The two overall reactions are:

\[
\begin{align*}
&\text{Benzene} + \text{Acetic acid} \rightarrow \text{Acetophenone} + \text{H}_2\text{O} \\
&\text{Benzene} + \text{Acetic anhydride} \rightarrow \text{Acetophenone} + \text{Acetic acid}
\end{align*}
\]
Table 1. The thermodynamic properties of the compounds for acylation of benzene with acetic acid and with acetic anhydride.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔG\textsubscript{f} at 400K (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid (g)</td>
<td>-549</td>
</tr>
<tr>
<td>Acetic anhydride (g)</td>
<td>-733</td>
</tr>
<tr>
<td>Benzene (g)</td>
<td>-26</td>
</tr>
<tr>
<td>Water (g)</td>
<td>-318</td>
</tr>
<tr>
<td>Acetophenone (g)</td>
<td>-238</td>
</tr>
</tbody>
</table>

![Figure 3. A schematically presentation of the thermodynamic calculation of the two acylation processes. Left: The acylation of benzene with acetic acid. Right: the acylation of benzene with acetic anhydride.](image)

The thermodynamic calculation can be sketched in a two step process. First, the change from benzene to acetophenone, which is the same for both reactions. This step yields a ΔG\textsubscript{r} of -212 kJ/mol. Secondly, the additional change from either acetic acid to water or from anhydride to acid. These steps yield a ΔG\textsubscript{r} of respectively 231 kJ/mol and 184 kJ/mol. The thermodynamic calculation of the acylation reactions is depicted in figure 3. For the acylation of benzene with acetic acid (producing water as second product), an overall ΔG\textsubscript{r} of 19 kJ/mol is calculated (left), whereas the ΔG\textsubscript{r} of the acylation of benzene with acetic anhydride shows a value of -28 kJ/mol (right). This would indicate that the acylation of benzene with acetic acid is thermodynamically not feasible. However, the acylation of benzene with acetic anhydride resulting in acetophenone and acetic acid has a negative ΔG\textsubscript{r}, implying that this reaction is thermodynamically achievable. The question remains whether benzene can be acylated with the carboxylic acids with a longer carbon chain than acetic acid. Unfortunately, the thermodynamics of these reactions cannot be calculated, due to lack of data of the acylated products that are formed. The effect of a substituted benzene (like toluene or cumene) on the thermodynamics of the acylation reactions cannot be calculated for the same reason (lack of thermodynamic data of the product). The 'estimation methods' often used for the calculation of the thermodynamics on the basis of group contributions of the molecules, are hard to apply here because they result in a large error. This is especially crucial in the present case where a high accuracy is required since the ΔG\textsubscript{r} does not differ much from zero.

Experimental results described in this study and also in other studies revealed that it is possible to perform the acylation of anisole with carboxylic acids. The acylation, being a nucleophilic substitution reaction is facilitated by the presence of the methoxy group. But here again insufficient thermodynamic information is available.
In general, it is concluded that the thermodynamics of these reactions are poorly or not at all established, but the available information indicates that the acylation of certain aromatics with carboxylic acids may not be thermodynamically feasible. Therefore a lot of emphasis has been put on the use of anisole.

**Reaction mechanism**

The Friedel-Crafts acylation can proceed via a Lewis acid catalyst or a Brønsted acid catalyst. For the homogeneous Lewis acid catalyst, like for example AlCl₃, the generally accepted reaction mechanism is formulated by Olah (1963) and is depicted in figure 4.

![Reaction mechanism diagram](Image)

Figure 4. The reaction mechanism of the Lewis acid catalyzed acylation with acid chlorides.

The Lewis acid forms a stable complex with the acylating agent which interacts with the substrate to form an aromatic ketone. The formed product/catalyst complex is very stable and needs to be hydrolyzed with water, after which the catalyst cannot be reused anymore (Olah, 1963). This produces highly corrosive waste streams. The metal halides are also applied with a more than stoichiometric amount compared to the reactants, resulting in a substantial amount of inorganic byproduct (more than 4 mol chloride per mol of produced ketone). In the case of the AlCl₃ catalyzed acylation with carboxylic acids as acylating agents, according to Olah (1963), even more than two mol of AlCl₃ are required for each produced aromatic ketone. The explanation for this is that instead of a direct acylation, an acyl halide is formed followed by a Friedel-Crafts acylation (Olah, 1963).

For the heterogeneously Brønsted catalyzed acylation reaction it is assumed that the mechanism proceeds through an acylimium intermediate which is formed via an attack of the proton of the Brønsted acid site to the nucleophilic carbonyl group of the acylating agent (figure 5). The acylimium ion reacts with the aromatic substrate giving a Wheland type intermediate. This intermediate reacts subsequently into the corresponding ketone (Kouwenhoven and van Bekkum, 1997; Olah, 1963). In the search for elucidating the intermediate, an acylation was performed of benzene and toluene in strongly Brønsted acidic media.
Chapter 2

By using spectroscopic methods, the acylum ion was not detected. From these studies it was therefore concluded that in these highly Brønsted acidic reaction conditions, the major active species is not the acyl cation, but the protonated acyl cation (Sato et al., 1995; Roberts and Sadri, 1983). In the case of a solid acid catalyzed reaction the question remains whether the surface of the catalyst is truly acylated.

\[ \text{R}_2\text{C}^{-}\text{X} + \text{H}^+\text{cat} \rightarrow \text{R}_2\text{C}^+\text{cat} + \text{HX} \]

\[ \text{R}_2\text{C}^{-}\text{H} + \text{H}^+\text{cat} \rightarrow \text{R}_2\text{C}^+\text{H}^{-}\text{R}_1 \]

Figure 5. The reaction mechanism of the Brønsted acid catalyzed acylation.

When performing the reaction between benzene and a carboxylic acid, such as acetic acid, both benzene and the acylum ion from the carboxylic acid are very stable due to the presence of resonance. Reaction between two of such stable species is therefore not very likely to occur. Apparently, this acylating agent has to be ‘activated’ before it can react with the aromatic substrate. In the case of the Lewis acid this proceeds via the complex shown in figure 4, and in the case of the Brønsted acid catalyzed reaction the acyl cation is protonated before reaction. Of course, this also shows the enhancing effect of substituting the aromatic substrate.

Solid acid catalysts in general

A way to overcome all the difficulties of the conventional ‘catalysts’, is to use a solid acid catalyst. A solid material is also less corrosive and more safe to handle. Different types of solid acids have been considered for their applicability as catalysts in the acylation of aromatics. Examples are ion-exchange resins (Olah, 1964; 1978; Heidekum et al., 1999), zeolites ( Gunnewegh, 1996b; van Bekkum et al., 1994; Chiche et al., 1986; Corma et al., 1989; Gaare and Akporiaye, 1995), clays ( Cornélis et al., 1990; Selvin et al., 1999; Choudary
et al., 1998; Chiche et al., 1987a), and heteropoly acids (de Castro et al., 1998). Even graphite was shown to exhibit activity in the acylation of active aromatic compounds with the active acid halides (Kodomari et al., 1997).

Sulfonated zirconia (ZrO$_2$-SO$_4$) and other oxides are also reported to be very active (Arata et al., 2000; Goto et al., 1990; Hino and Arata, 1985; Yadav and Pujari, 1999), but as these catalysts can give leaching problems in the presence of water in liquid phase applications (Corma, 1995), these catalysts will not be discussed further.

**Ion-exchange resins in acylation**

The earliest example of a solid-acid catalyzed acylation reaction was reported in 1978 by Olah and co-workers (1978). In this study yields of 80% and higher were achieved in the acylation of (substituted) benzenes with aryl chlorides catalyzed by Nafion. This is the trade name for a strongly acidic ion-exchange resin produced by DuPont. It is a perfluorinated ion-exchange polymer, prepared as a copolymer of tetrafluoroethylene and perfluoro-2-(fluorosulfonylethoxy)propyl vinyl ether. Although Nafion is not a covalently crosslinked polymer, it has a highly ordered structure, analogous to that of proteins. The $-\text{CF}_2\text{CF}_2\text{SO}_3\text{H}$ groups are far more hydrophilic than the fluorocarbon backbone. What makes Nafion catalytically useful is its superacidity in the protonated form, Nafion-H. The Hammett acidity value, $H_0$, for Nafion-H is approximately $-12$. This value is comparable to that of 96-100 % sulfuric acid. Another feature that makes Nafion-H an attractive catalyst is its chemical stability. Unfortunately, a disadvantage of Nafion is its low surface area (typically 0.02 m$^2$/g or less) (Waller and Warren van Scoyoc, 1987). To overcome this, researchers at DuPont have developed a Nafion/silica composite in which small (20-60 nm) Nafion resin particles are embedded within a porous silica matrix (Harmer et al., 1996). These materials showed promising activity in the acylation of aromatic substrates with acid halides (Heidekum et al., 1999). Another example of an ion-exchange resin is Amberlyst-15. This is a bead-shaped, strongly acidic sulfonated polystyrene resin with a macroreticular structure. Resin particles having this structure possess a high degree of porosity. Unfortunately the thermal stability of this catalyst (maximum applicable temperature of 423K) is relatively low (Waller and Warren van Scoyoc, 1987).

**Zeolites in acylation**

In literature, a large number of zeolite catalysts has been described to be active in acylation reactions. The most studied zeolites for acylation are FAU (Gaare and Akporiaye, 1996; Isaev and Fripiat, 1999); Chiche et al., 1986; Wang et al., 1996), BEA (Gunnewegh et al., 1996b),
and MFI (Corma et al., 1989; Harvey et al., 1993; Freese et al., 1999; Heinichen and Hölderich, 1999; Ma et al., 1997; Gunnewegh et al., 1996b; Smith et al., 1998). In Table 2 the most common zeolites for acylation reactions are presented with their characteristics.

<table>
<thead>
<tr>
<th>Informal name</th>
<th>Official abbreviation</th>
<th>Description of pore structure</th>
<th>Size of channels (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta</td>
<td>BEA</td>
<td>3-dimensional with intersecting elliptical channels</td>
<td>0.76 x 0.64</td>
</tr>
<tr>
<td>Faujasite, Y</td>
<td>FAU</td>
<td>3-dimensional cage structure</td>
<td>0.76</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>MFI</td>
<td>2-(3)-dimensional with intersecting channels</td>
<td>0.53 x 0.56</td>
</tr>
</tbody>
</table>

BEA and FAU are often reported to show high activity when compared to MFI (Harvey et al., 1993). Often MFI does not show any activity at all in acylation reactions, which is ascribed to the 10-ring pores which are probably too small for penetration of the aromatic substrate or formation of the transition state (Freese et al., 1999). However, in the work of Wang et al. (1995) MFI proved to be an effective catalyst for the reaction between anisole and various carboxylic acids performed in a liquid phase reactor. Extremely large amounts of catalysts were used (3-10 g catalyst with 0.1 mol of reactant), however. High activities were also obtained with zeolite USY (Ma et al., 1996a) and FAU (Wang et al., 1996) in the same reactions. When considering the 12-ring pores of BEA and FAU comparable activities might be expected, but BEA often shows to be the most active catalyst, like in the acylation of anisole with acetic anhydride (Freese et al., 1999). BEA also showed its ability to activate aliphatic carboxylic acids for acylation reactions in the intramolecular acylation of 4-phenylbutyric acid (Gunnewegh et al., 1996b).

The first zeolite catalyzed liquid-phase acylation reaction reported in literature is the acylation of toluene and xylene with various carboxylic acids catalyzed by rare-earth (Ce) modified FAU zeolites (423 K, 48 hours) performed by Chiche et al. (1986) at very high catalyst/reactant ratios (333 \( g_{\text{cat}}/\text{mol}_{\text{acid}} \)). By increasing the chain length of the carboxylic acid from 2 to 22, a optimum yields were found with acids in the range octanoic to palmitic acid. The decrease in yield with larger carboxylic acids than palmitic acid is attributed to the shape selective properties of the zeolites. According to the authors, the increasing activity with increasing chain length is attributed to an increase in hydrophobicity. No activity was observed with acetic acid. Comparable results were found for cation-exchanged montmorillonites (Chiche et al., 1987a), but in all cases more than stoichiometric amounts of solid were applied. The researchers also studied the reaction mechanism of this Ce-Y zeolite catalyzed acylation and found that the mechanism is an electrophilic substitution in which the
transition state resembles the Wheland intermediate (Chiche et al., 1987b), according to the mechanism as depicted in figure 5. The effect of cation-exchanging the zeolite on the acylation activity remains unclear. In the acylation of toluene with varying carboxylic acids catalyzed by Ce-Y, high activities are obtained. However, in the work of Smith et al. (1998), no improvement in activity was found when ion-exchanging the BEA zeolites in the acylation of anisole with acetic anhydride.

The nature of the active sites of zeolites is not so clear in the acylation of aromatics. In the case of the Lewis catalysts like AlCl₃, it is assumed that the nature of the active sites is purely of the Lewis type. However, strong Brønsted acid sites can be formed from the Lewis acid sites by reaction with water. In the case of the strong mineral acids of course the nature of the active sites has to be of the Brønsted type. It is well-known that zeolites contain both types of sites. Which type is responsible for the acylation reactions has also been under investigation, but leads to contradictory results. Most of the studies ascribe the activity to Brønsted acid sites, such as the studies of Freese et al. (1999), Corma et al. (1989), and Fang et al. (1995). Also Gauthier et al. (1989) concluded that Brønsted acid sites are responsible for the acylation reaction, by comparing the activities of different cation exchanged zeolites in two different reactions (acylation of toluene and dehydration of cyclohexanol). However, in the work of Ma et al. (1996b; 1997) the activity of the FAU zeolite is entirely attributed to the Lewis acid sites present in this zeolite, in contrast to MFI in which the activity is ascribed to very strong Brønsted acid sites. The Brønsted acid sites with moderate strength are said to be inactive.

While most of the studies described in literature (see previous) attribute the acylation activity to Brønsted acid sites, in the case of halide containing acylating agents the activity is attributed to Lewis acid sites. Like for example, in the case of the acylation of thiophene with butyryl chloride a correlation was found between the initial rates of the reaction and the number of Lewis sites, whereas no correlation was found between initial reaction rate and number of Brønsted sites. From this result the authors concluded that acylation is Lewis acid catalyzed, which contradicts the above-mentioned reported Brønsted dependency of the reaction (Isaev and Fripiat, 1999). It could be that the nature of the active sites in the acylation with halide containing acylating agents is different than the nature of the active sites in the acylation with anhydrides and carboxylic acids.

In the work of Freese et al. (1999) dealumination of HBEA yielded a higher initial activity in the acylation of anisole with acetic anhydride, which was ascribed to changes in pore distribution leading to lower mass transfer limitations. Harvey et al. (1993) also observed a positive effect of dealuminating the zeolites. In the work of Heinichen and Hölderich et al. (1999), the formation of extra framework alumina species was demonstrated to be
beneficial for the catalytic activity of BEA in the acylation of xylene and anisole. Also in the
case of halide containing reactants, the non-framework alumina species formed after
dealumination contributes considerably to the overall activity. According to Fang et al.
(1995), this is due to interactions with benzoyl chloride or HCl formed during reaction. The
explanation for the beneficial effect of dealuminating a zeolite by steaming or acid leaching is
still not entirely known. This aspect is studied in chapter 3B.

In literature, contradictory results have been published regarding the influence of the Si/Al
ratio of the zeolites. Smith et al. (1996) reported only a slight effect of the Si/Al ratio in the
BEA catalyzed acylation of anisole with acetic anhydride. These results were also found by
Corma et al. (1989) and by Harvey et al. (1993). However, in the study of Gaare and
Akporiaye (1996) a strong -linear- relation was found between the yield and the Si/Al ratio of
zeolite FAU in the acylation of anisole with acetyl chloride, which was attributed to the
increased hydrophobicity of the dealuminated zeolites.

Stability of zeolites in acylation reactions

Various studies investigated the stability of zeolites in the acylation of aromatics. Deactivation
occurring during reaction is either ascribed to the formation of coke (Rohan et al., 1998a;
Harvey, 1993), or to sorption phenomena (Gunnegwegh et al., 1996b). By adsorption
measurements Gunnegwegh et al. (1996b) showed that in the acylation of toluene with octanoic
acid, the acid adsorbs much stronger on the surface of the zeolite than toluene. This
unbalanced adsorption behaviour is attributed to play a role in the low activity for this
reaction.

In the study of Janssens et al. (1996), the acylation of toluene with acetic anhydride led to
deactivation of the (FAU) zeolite. However, in the same acylation on anisole the zeolites
showed to be very stable. The difference in stability behaviour is ascribed to the more polar
character of anisole compared to toluene, which leads to a stronger competition with the acyl
product on the surface of the zeolite, lowering the possibility of the product to undergo
consecutive reactions which lead to deactivating bulky products (Janssens et al., 1996).

The kinetic study of Moreau et al. (22000) of the reaction of veratrole (1,2-
dimethoxybenzene) with acetic anhydride over FAU revealed an Eley Rideal type of
mechanism, where the adsorbed acetic anhydride reacts with veratrole in the liquid phase. In
this case also a significant inhibiting effect was observed of the aromatic substrate veratrole
and the reaction products. Also in the work of Derouane et al. (1999) and Rohan et al.
(1998b), deactivation of the catalyst is ascribed to competitive adsorption of reactants and

24
products, because an inhibiting effect was observed of the product of anisole with acetic anhydride (p-methoxyacetophenone). This product inhibition could be described with a Langmuir-Hinshelwood model.

It can be concluded that the deactivation of zeolite catalysts in acylation reactions could be due to 'coke' formation, but it seems more likely that in many cases deactivation is due to sorption phenomena of reactants and products on the surface of the zeolite. To enhance the performance of the zeolite in the acylation of aromatics catalytic reactor configurations should be applied in which these competitive adsorption effects are minimized.

Experimental

Materials

Anisole (Fluka), cumene (Acros), and veratrole (Aldrich) were used as aromatic substrates. Acetic acid, propanoic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, decanoic acid and dodecanoic acid were purchased from respectively Aldrich, Merck, JT Baker Aldrich, Merck, Aldrich, Fluka, Aldrich and Aldrich. Hexadecane was purchased from Merck. The chemicals were used as received from the supplier, without additional drying.

The zeolites investigated in this reaction were H-BEA, H-FAU, H-USY, and H-MFI. BEA zeolites with a Si/Al ratio of 12.5, 25, and 50 were obtained from Südchemie AG and had a crystal size of 15-20 nm and a particle size distribution of 5-20 μm due to the clustering of the crystals. The FAU had a crystal size of 1 μm. Both FAU zeolites (Si/Al ratios of 5 and 80, crystal size of 1 μm), and BEA zeolites with a Si/Al ratio of 12, 37.5, and 75 were kindly provided by Zeolyst International (particle size distribution 5-20 μm). USY (Si/Al of 5, crystal particle size of μm) and MFI zeolites with Si/Al ratios of 48, 78, and 113 (particle size ~ 50 μm) were kindly provided by the Department of Organic Chemistry and Catalysis of the Delft University of Technology. For a comparison with other solid acid catalysts also ion-exchange resins (Amberlyst-15, Nafion) were studied. The particle size of the resins was respectively 0.28-0.8 mm for Amberlyst-15 and 0.5-2 mm for Nafion (as received). Additionally, Nafion was also tested as a composite with silica (SAC13 and SAC25 with respectively 13 wt% and 25% of Nafion). Both Nafion/silica composites were tested with a particle size of 50-100 μm. From these Nafion/silica composites three batches were obtained in the course of this project. Amberlyst-15 and Nafion were purchased from Aldrich and the Nafion/Silica composites
Chapter 2

were kindly provided by DuPont and Engelhard. All catalysts studied were in the acidic H-form. The Mg-saponite was prepared according to Vogels (1996).

Testing procedure

The activity of the catalysts was measured batchwise in the acylation of anisole with octanoic acid (figure 6) in 6 reflux slurry (figure 7) reactors that operate in parallel. On top of the cooling section a drying tube is placed, which is filled with silica gel. The amount of catalyst used was 0.3 g, the molar ratio of aromatic/acid was 40 and the total reaction volume 50 ml. This corresponds with a concentration of 0.2 mol/l acid in anisole. The reaction temperature was the boiling point of anisole (428 K), the pressure was atmospheric and the stirring speed was 500 rpm. Prior to the activity measurement, the ion-exchange resins were dried at 383K for 15 h (overnight), and the zeolites were calcined at 723K for 4 h (heating rate 5K/min).

Figure 6. The acylation of anisole with octanoic acid.

Liquid samples (~ 100 μl) were taken manually at regular time intervals. Analysis was done by gas chromatography on a Chrompack CP9001 gas chromatograph with FID-detection equipped with a CP9050 autosampler and a CP Sil 8CB column (length 50 m, internal diameter 0.25 mm, film thickness 0.12μm). n-Hexadecane was used as an internal standard. The loss of liquid volume due to sampling is assumed to be negligible.

To investigate the effect of water on the acylation reaction, some experiments were also performed in a closed system. In this system, a micro-autoclave with a swinging capillary as a mixing device (Tajik et al., 1990), the amount of catalyst used was 60 mg, the total reaction volume was 10 ml, and the molar ratio of aromatic/acid was 40; the same as in the above described ‘open’ system. A pressure of 10 bar was applied with nitrogen for sampling. Temperature was 428K.
Activity and selectivity are defined as described below. For the kinetic study, the initial reaction rate (mol.h\(^{-1}\).g\(_{\text{cat}}\).l\(^{-1}\)) is defined as the slope of the concentration vs time plot (mol.l\(^{-1}\).h\(^{-1}\)), normalized for the catalyst concentration (g\(_{\text{cat}}\).l\(^{-1}\)).

**Results and discussion**

**Definition of activity and selectivity**

A typical catalyst screening result is shown in figure 8, in which the conversion of octanoic acid in the SAC25 catalyzed reaction is plotted as a function of time (figure 8a). After approximately 240 minutes 100% conversion of the octanoic acid is reached. For the determination of the activity, first order dependency was assumed. The concentration evolution can then be described as in formula [1]. Integration gives formula [2]. The plot of ln(C\(_0\)/C) against time (first order plot) will give a straight line through the origin. After normalizing the slope (in h\(^{-1}\)) for the catalyst concentration (in g\(_{\text{cat}}\).l\(^{-1}\)) the first order rate constant \(k\) (l.g\(_{\text{cat}}\).h\(^{-1}\)) is obtained.

\[
\frac{dC}{dt} = -k \cdot \frac{g_{\text{cat}}}{V_{\text{reactor}}} \cdot C \quad [1]
\]

\[
-ln \left( \frac{C}{C_0} \right) = k \cdot \frac{g_{\text{cat}}}{V_{\text{reactor}}} \cdot t \quad [2]
\]

The "first order plot", ln(C\(_0\)/C) as a function of time, of the SAC25 catalyzed acylation of anisole with octanoic acid is given in figure 8b. A straight line is observed for nearly all experiments, indicating an observed first order reaction in all cases. Selectivities (%) were calculated as the molar ratio of the acylated aromatic substrate para-octanoyl anisole and total amounts of products at 50% of conversion.

![Figure 8a](image1)

*Figure 8a.* A characteristic result of the acylation of anisole with octanoic acid (SAC25 catalyzed, standard conditions; 428K, 0.2 mol/l octanoic acid/anisole). a. The conversion of octanoic acid.

![Figure 8b](image2)

*Figure 8b.* a. First order plot.
Chapter 2

Catalyst screening

The results of the activity measurements are given in figure 9. The zeolites BEA and FAU, and the ion-exchange resins Nafion and Amberlyst-15 gave average activity values of 0.026-0.055 l. g_{cat}^{-1}.h^{-1}, with the highest activities for BEA with Si/Al 37.5 and 50. When increasing the Si/Al ratio of the BEA zeolites an optimum in activity is observed. FAU shows an opposite effect. With an increasing Si/Al ratio the activity decreases. Since the Si/Al ratio has an effect on the amount of acid sites and the acid strength (Corma, 1995) apparently this parallels the catalytic performance in this acylation. To investigate this aspect, a preliminary study of the acidity of some of the BEA and FAU zeolites was conducted by means of TPD-IR. The TPD-IR measurements were performed according to Emeis (1993) at the Shell Research and Technology Centre, Amsterdam. This acidity measurement technique gave a quantitative result for the total amount of Brønsted and Lewis acid sites. The results are presented in figure 10. In this figure the amount of total Brønsted and Lewis site is compared with the activity and selectivity of the catalysts in the standard acylation reaction.

No clear trend could be found when comparing the amount of Brønsted and Lewis acid sites with the activity of the catalysts in the acylation of anisole with octanoic acid. Varying the

![Figure 9. Activity (l. g_{cat}^{-1}.h^{-1}) of the various solid acid catalysts in the acylation of anisole with octanoic acid, measured at standard conditions (428K, 0.2 mol/l octanoic acid in anisole). SAC – Nafion/silica composite, Amb-15 – Amberlyst-15, Zeo – Zeolite from Zeolyst, Süd – zeolite from Südchemie, Mg-sap – Mg-saponite. Si/Al ratio of BEA results in an optimum of the amount of Brønsted acid sites for BEA with a Si/Al of 25, while](image)
the amount of Lewis acid sites decreases when increasing the Si/Al ratio. The highest activity is obtained by BEA with a Si/Al ratio of 50. The results of the TPD-IR measurements of the FAU samples give a slight decrease in the activity, an increase in the amount of Brønsted as well as Lewis sites when increasing the Si/Al ratio from 2.5 to 40. To investigate this acidity aspect a more detailed study of the acidity of the zeolites is required, also because it remains the question whether this technique provides for a correct method for measuring the amount of acid sites. It is assumed that every pyridine molecule will adsorb on a site which is active in the acylation reaction. This might not be the case as the acylation can occur on the outer surface of (for example) a BEA zeolite and as a consequence acid sites are accounted for which are not accessible.

From the zeolites studied, USY had the lowest activity. The MFI zeolites gave no measurable conversion at all. For a different acylation reaction, Corma et al. (1989) also found zeolite MFI to be inactive, which they attributed to steric hindrance. SEM analysis showed that the particle size of the MFI zeolites was rather large (appr. 50 μm) compared to the particle size of the BEA zeolites obtained from Zeolyst, which was very small (< 1 μm). This difference in activity would be expected if acylation were an internally diffusion-limited reaction, with most of the reaction occurring on the external surface. The pore sizes of MFI are relatively small, but not too small for penetration of the aromatic substrate (Freese et al., 1999), the channel size and shape could however limit the formation of the intermediate. In the acylation of anisole with an acylium ion, the size of the intermediate acylium/anisole is 290 Å³, while the size of the intersection of the MFI is 150 Å³ (Freese et al., 1999). So, BEA and FAU type of zeolites are better candidates.
Chapter 2

The nitrogen adsorption isotherms (figure 11) indicate that the BEA zeolite from Südchemie (Si/Al 25) and the Nafion/silica composites contain a large amount of mesopore area whereas the MFI zeolites do not contain mesopore area at all. The pore-size distribution, which can be calculated from the adsorption isotherms of both Nafion/silica composites, shows that the SAC25 mesopores are larger than those of SAC13. So, probably the Nafion nanoparticles in the SAC25 composite are more accessible than in SAC13.

Mg-saponite, a trioctahedral smectite clay, that contains Brønsted acid sites with mild acid strength (Vogels, 1996) showed the lowest activity, indicating that very strong acid sites are necessary for this acylation reaction.

![Figure 11. The nitrogen adsorption/desorption isotherms of SAC13, SAC25, MFI, and BEA.](image)

To investigate the effect of cerium on the activity in the acylation, FAU (Si/Al 2.5) was ion-exchanged in a 1M Ce(NO₃)₃ solution for 16 h (overnight) and calcined at standard conditions (4 h 723K). After testing in the standard acylation of anisole with octanoic acid (428K, 0.2 mol/l) a value of 0.038 l. g⁻¹cat⁻¹.h⁻¹ was found, indicating that no improvement was found compared to the activity of the base FAU material (0.043 l. g⁻¹cat⁻¹.h⁻¹),
Chapter 2

The highest activity, with \( k = 0.19 \, \text{l. g}_{\text{cat}}^{-1}.\text{h}^{-1} \), was exhibited by the Nafion/silica composite SAC25 (B1), this value was also reproducible. In this case 100% conversion was reached after 240 minutes. However, the second batch of SAC25 (B2) showed a lower activity of 0.067 l. \( \text{g}_{\text{cat}}^{-1}.\text{h}^{-1} \). Also with the SAC13 the activity was not the same for the three batches. As the acylation activities are reproducible within one batch, apparently, these materials show a batch-dependency in their performance. The activity of these Nafion/silica composites is expressed by the rate constant \( k \) normalized to the total amount of catalyst, so if the values are corrected for the total amount of Nafion the activity shows a 28-fold increase over the pure Nafion. For the SAC13 a factor of ten is obtained on a Nafion weight basis.

The Nafion/silica composites SAC13 and SAC25 were both tested for possible leaching of the active species by filtering the reaction mixture while hot. After separation of the catalyst the acylation reaction did not proceed, indicating that no leaching of the active species occurred.

![Figure 12. Particle size dependency of the SAC13 and the SAC25 catalyzed acylation of anisole with octanoic acid, measured at standard conditions (428K, 0.2 mol/l octanoic acid/anisole).](image)

To examine whether the acylation in the SAC particles is diffusion-limited, the reaction was performed with different particle sizes of SAC13 and SAC25. The results of these experiments are depicted in figure 12. The apparent activity is clearly influenced by the particle size of the Nafion/silica composite, indicating internal diffusion limitations for the largest particles. Since for the smaller particles the activity hardly changes with particle size, it is possible to determine the reaction kinetics with these small particles. External diffusion limitations can be excluded here in all cases because variation of the stirring speed had no effect on the activity of the reaction.
The selectivities of the various solid-acid catalysts towards the para-substituted aromatic ketone at 50% conversion of the octanoic acid are depicted in figure 13. All selectivities remained constant as a function of the conversion. This indicates the presence of parallel side reactions. The major product formed is the desired para-substituted aromatic ketone. The other products are shown in figure 14.

![Figure 13. Selectivity (%) at 50% conversion of the various solid acid catalysts in the acylation of anisole with octanoic acid, measured at standard conditions (428K, 0.2 mol/l octanoic acid/anisole).](image)

![Figure 14. The side products formed in the acylation of anisole with octanoic acid.](image)

The side products, which are formed in approximately equal amounts, result from reaction of the octanoic acid with the methoxy group of anisole. In the case of Nafion, the demethylation of anisole, has also been demonstrated by Olah et al. (1978) and is attributed to the superacidity of this catalyst (Corma, 1997). In the case of the Nafion composites most likely the acidity is decreasing due to the interaction with the silica matrix leading to a higher selectivity (Botella et al., 1999). The selectivity of the Nafion/silica composites is indeed higher than the selectivity for pure Nafion, but varies from 64% for the first batch of SAC25 (B1) to 93% for the second batch of SAC13 (B2). Again a large batch-dependency, this time in the selectivity, is found for the Nafion/silica composites.

For the zeolites, a very high selectivity is found for FAU, with a value of 97% for a Si/Al of 2.5. This value is larger than the selectivity of BEA. For this latter zeolite no clear relation could be found between the selectivity and the Si/Al ratio. However, when the zeolites are
distinguished according to their supplier a trend can be observed. The BEA samples obtained from Zeolyst (‘Zeo’ in figure 13) all show a similar selectivity of 85% whereas the BEA samples from Südchemie (‘Süd’ in figure 13) showed a much lower selectivity of 58-72%, with a trend towards a higher selectivity with a higher Si/Al ratio. Considering the acidity TPD-IR measurements presented in figure 10, in the case of BEA a lower amount of Brønsted acid sites seems to result in a higher selectivity. The amount of Lewis sites does not seem to influence the selectivity as FAU (Si/Al 40) has a much lower amount of Lewis sites and approximately the same selectivity as FAU (Si/Al 2.5). As was mentioned before in the discussion of the effect of the acidity on the activity in the acylation reaction, to investigate this aspect a more detailed study of the acidity of the zeolites is required. This is because neither the acid strength is accounted for nor the accessibility of the acid sites in the TPD measurement compared to the acylation activity measurement.

The effect of water

To examine whether the water formed could have an effect on the activity some experiments were performed with the in-situ removal of water, so under reaction conditions. To accomplish this, the SAC25 catalyzed acylation of anisole with octanoic acid was performed with and without a drying tube on top of the reflux cooler. Also, dry nitrogen was bubbled through the reaction mixture to establish water removal. The results of these experiments are given in figure 15a. Removal of the drying tube results in a dramatic decrease of the activity. If the nitrogen flow through the reaction mixture is applied, without adding the drying tube, the original activity of approximately 0.19 l/h.g$\text{ catalyst}$ is retrieved. Apparently, the standard

![Figure 15. The effect of water on the SAC25 catalyzed acylation of anisole with octanoic acid. a. Effect on the activity with and without drying tube or nitrogen flush in open reflux. b. Performance of the reaction in an autoclave and in the ‘open’ reflux system, measured at standard conditions (428K, 0.2 mol/l octanoic acid/anisole).](image_url)
experiments were performed under water removal. The standard setup had a drying tube on top, lowering the vapour pressure of water above the liquid and thus removing water from the reaction mixture resulting in a higher activity.

When performing the acylation of anisole with octanoic acid in a closed (micro)autoclave system, see figure 15b, the activity drops significantly, demonstrating the inhibiting effect of water present in the system on the acylation reaction. Since the reactants were not dried prior to use the initial lower activity is most likely caused by the small amount of water in these liquids. In the open system the reactants were heated prior to the catalyst addition, thus removing water present in the reactants before the start of the experiment.

Temperature dependency

The BEA catalyzed acylation of anisole with octanoic acid was performed at various temperatures, namely at 397, 410, 420, 425, and 431K. At 397K no measurable conversion occurred. On the basis of these experiments an apparent activation energy was calculated by substituting the initial first order activity values (normalized for the catalyst concentration) in the Arrhenius equation [3]. The Arrhenius plot is depicted in figure 16.

\[
{k_{\text{app}}} \sim \exp \left( -\frac{E_a}{RT} \right) \quad [3]
\]

The effect of the temperature on the rate is significant. An apparent activation energy of 140 kJ/mol is calculated. Unfortunately, no literature values could be found. This value does not contradict the conclusion that internal mass transfer limitations are absent.

![Arrhenius plot](image)

Figure 16. Arrhenius plot of the BEA (Si/Al 37.5 from Zeolyst) catalyzed acylation of anisole with octanoic acid, measured at standard conditions (428K, 0.2 mol/l octanoic acid/anisole).
Kinetics of the BEA catalyzed acylation of anisole with octanoic acid

The kinetics of the acylation of anisole with octanoic acid was studied by performing the acylation of anisole with octanoic acid at several concentrations of octanoic acid and anisole in cumene. At reflux, the acylation of cumene gives very low conversion. It is assumed that the acylation of cumene is negligible compared to the acylation of anisole. Cumene has a boiling point close to that of anisole. To determine the influence of the reactants separately, experiments were performed by keeping the concentration of one reactant constant and varying the concentration of the other reactant. The initial reaction rate of the octanoic acid is depicted in figure 17. The effect of varying the octanoic acid on the initial reaction rate at a constant anisole concentration of 0.1 mol/l is plotted in figure 17a. The effect of a varying anisole concentration at a constant octanoic acid concentration of 0.1 mol/l on the reaction rate is depicted in figure 17b. The concentration of octanoic acid in pure anisole was also varied and the effect on the initial reaction rate is plotted in figure 18.

Figure 17. The effect of varying the octanoic acid and anisole concentration on the initial reaction rate of the acylation (428K in cumene). a. Varying the acid concentration at an anisole concentration of 0.1 mol/l. b. Varying the anisole concentration at an acid concentration of 0.1 mol/l. Markers – experimental values, line – modelled values.

Figure 18. The effect of varying the octanoic acid concentration in anisole on the reaction rate.

A relatively large experimental error is found for the dependency of the reaction rate on the concentration of octanoic acid. However, it is demonstrated that at a octanoic acid concentration from 0 - 0.4 mol/l, the reaction rate increases linearly with increasing concentration. This
Chapter 2

indicates a first order dependency and confirms the first order assumption made earlier for the definition of the catalyst activities. When increasing the concentration >0.4 mol/l the reaction rate seems not to be affected by the concentration of the reactants anymore. This indicates an adsorption saturation in the kinetics. A single-site Eley-Rideal model appeared to be the best fitting model, since with a dual site Langmuir-Hinshelwood model at some point the reaction rate should decrease while increasing the concentration of one of the components. This is not observed. The elementary steps of the model are given in figure 19.

Anisole (A) + Octanoic Acid (O) → Ketone (K) + Water (W)

**Elementary steps:**

<table>
<thead>
<tr>
<th>Adsorption/desorption</th>
<th>Anisole</th>
<th>A + *</th>
<th>⇄</th>
<th>A*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octanoic acid</td>
<td>O + *</td>
<td>⇄</td>
<td>O*</td>
<td></td>
</tr>
<tr>
<td>Ketone</td>
<td>K + *</td>
<td>⇄</td>
<td>K*</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>W + *</td>
<td>⇄</td>
<td>W*</td>
<td></td>
</tr>
</tbody>
</table>

**Acylation surface reaction (rds)**

\[
\text{A} + \text{O}^{*} \quad \text{or} \quad \text{A}^{*} + \text{O} \\
\text{K} + \text{W}^{*} \quad \text{or} \quad \text{K}^{*} + \text{W}
\]

**Model:**

\[
r = \frac{k_r \cdot C_A \cdot C_O}{(1 + K_A \cdot C_A + K_O \cdot C_O + K_K \cdot C_K + K_W \cdot C_W)}
\]

Figure 19. Elementary steps of the kinetic model proposed for the BEA catalyzed acylation of anisole with octanoic acid.

In this model an adsorbing effect of the reactants and products is included. The assumptions made for this model are that the single-site model applies, that the reaction takes place at the catalyst surface, that the rate-determining step is the reaction of an adsorbed reactant with another not adsorbed reactant, and that inhibition by competitive adsorption occurs. It is not clear which reactant and which product will adsorb on the catalyst surface, so the accompanying adsorption coefficients are lumped into the reaction rate constant. In figures 17 and 18, only initial reaction rates are presented, so the adsorbing effect of the products is not included here. The experimental values as presented in both figures (markers) were fitted to the defined reaction rate expression presented in figure 19 using ‘Micromath Scientist for Windows’ version 2.0. The experimental results for the experiments in cumene and in anisole could not be modelled in a combined fit which is ascribed to different adsorption properties in the different solvents. It seems that the kinetics of the acylation of anisole and octanoic acid in relatively low concentrations in cumene has characteristics different from acylation of
octanoic acid in a high concentration of anisole (pure anisole as solvent). Therefore, the two types of experiments are considered separately when defining the kinetic parameters.

The results of the modelling of the experimental results of the acylation in cumene reveal a similar adsorption for the octanoic acid and the anisole \( (K_a=160 \text{ l/mol} \text{ and } K_o=114 \text{ l/mol}) \). The corresponding fit is presented in figure 17 (line). The adsorption coefficient of cumene was also included in this calculation, and gave a value of 1.88 l/mol, which is much lower than the adsorption coefficients of anisole and octanoic acid. The results of the modelling of the experiments in anisole reveal a much stronger adsorption of octanoic acid compared to the anisole \( (K_a=11 \text{ l/mol} \text{ and } K_o=234 \text{ l/mol}) \). The corresponding fit is presented in figure 19 (line).

The adsorption coefficients of the reactants in the latter case (pure anisole, no cumene) differ significantly from the adsorption coefficients for the measurements in cumene. That explains also that both types of kinetic experiments cannot be modelled simultaneously. In cumene the adsorption coefficients of both anisole and octanoic acid are similar indicating an equal adsorption of these reactants on the surface of the catalyst. In pure anisole, the adsorption of octanoic acid is much stronger than the adsorption of anisole.

*Varying the aromatic substrate in the acylation reaction*

The standard BEA catalyzed acylation reaction with octanoic acid as acylating agent was also performed with cumene and with veratrole (1,2-dimethoxybenzene). See table 3 for the results. Cumene being a a weakly-activated aromatic substrate shows a very low conversion of 6% after 300 min. Veratrole, being a double activated aromatic substrate, was expected to show a much higher activity than anisole, but at the same temperature (428K) only a slightly higher activity was found. At the temperature of 428K, however, this reaction could not be performed under reflux conditions. When this reaction was performed at the reflux temperature of veratrole (481K), the activity was so high that the acid conversion could not be measured properly. For this reason the octanoic acid concentration was doubled and the same reaction was performed at standard temperature (428K) and at the reflux temperature of veratrole (481K). The effect on the activity is clearly demonstrated, as the apparent activity decreases due to the adsorption effect mentioned in the previous section. The effect of temperature is also observable as the activity increases with a factor of 14 when performed at a temperature of 481K instead of 428K. An apparent activation energy of 86 kJ/mol can be calculated from these data, which is much lower than the value presented for the acylation of anisole with octanoic acid, indicating mass transfer limitations.
Chapter 2

Table 3. The results of the acylation of various aromatic substrates with octanoic acid.

<table>
<thead>
<tr>
<th>Aromatic substrate</th>
<th>Concentration octanoic acid (mol/l)</th>
<th>temperature (K)</th>
<th>Activity (l. g_{cat}^{-1}.h^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cumene</td>
<td>0.2</td>
<td>428</td>
<td>0</td>
</tr>
<tr>
<td>Anisole</td>
<td>0.2</td>
<td>428</td>
<td>0.051</td>
</tr>
<tr>
<td>Veratrole</td>
<td>0.2</td>
<td>428</td>
<td>0.091</td>
</tr>
<tr>
<td>Veratrole</td>
<td>0.4</td>
<td>428</td>
<td>0.041</td>
</tr>
<tr>
<td>Veratrole</td>
<td>0.4</td>
<td>481</td>
<td>0.495</td>
</tr>
</tbody>
</table>

Effect of the chain length of the carboxylic acid

The effect of the carbon chain length was studied in the acylation of anisole. The carbon chain length was varied between C4 and C12 and the results are given in figure 20. Unfortunately, the carboxylic acids with lower chain length (acetic acid and propanoic acid) could not be tested in the conventional set-up, since the boiling point of these components is much lower than the applied reaction temperature. The acylation was nevertheless performed and the desired p-acylated aromatic ketone was detected with GC-MS. So, even though the activity could not be determined, acylation took place.

No pronounced effect of the chain length on the acylation activity is observed, in contrast to the findings of Chiche et al. (1986) in the Ce-Y catalyzed acylation of toluene.
Conclusions

- The solid acid catalysts that have sufficient activity for aromatic acylations, are mainly ion-exchange resins such as Nafion and zeolites such as BEA and FAU.
- In the acylation of anisole with octanoic acid, the slurry catalyst screening experiments showed that the Nafion/silica composite SAC25, with 25 wt% of Nafion, exhibited the highest specific activity in the acylation of anisole with octanoic acid compared to zeolites BEA and USY. A particle-size dependency of the Nafion/silica composites indicated that this reaction is internally diffusion-limited in the composite particles.
- The Nafion/silica composites showed a batch-dependency in their performance, indicating that the production is not reproducible. This aspect needs further investigation.
- Water removal during reaction is advantageous for the reaction progress since it inhibits strongly.
- The kinetics of the acylation of anisole with octanoic acid are of an Eley-Rideal type. The adsorption-parameters depend strongly on the solvent used (cumene vs anisole).
- Cumene shows low conversion in the BEA catalyzed acylation with octanoic acid. The acylation conversion rate of veratrole is higher than that of anisole.
- No pronounced effect of the chain length of the carboxylic acids (C4-C12) on the acylation activity of anisole is observed, in contrast to the findings of Chiche et al. (1986) in the Ce-Y catalyzed acylation of toluene.

Acknowledgements

F. Kellendonk and prof. dr. J.A.R. van Veen from Shell Research and Technology Centre Amsterdam are kindly acknowledged for the TPD-IR measurements. Johan Groen and Peter Boeser are gratefully acknowledged for performing the texture analysis measurements. Ingrid Hoek and Hans Vogelaar are gratefully acknowledged for their contribution to this chapter.
Chapter 2

References


Chapter 2


Chapter 2


Kurek, P. R. (1991) Acylation of aromatic compounds by acid anhydrides using solid acid catalysts. US patent US5126489 assigned to UOP, USA.


Chapter 2


Chapter 2


The development of an active catalyst for the acylation of anisole with octanoic acid

The development of an active solid catalyst for the acylation of anisole with octanoic acid is described. From the catalyst screening experiments described in chapter 2 it was shown that zeolite Bea and the Nafion/silica composites exhibited relatively high activities compared to the other solid acid catalysts that were tested.

For this reason, this chapter is divided in two parts:
Part A - Development of Nafion/silica composites
Part B - Modification of BEA by means of steaming and acid leaching.
Development of Nafion/silica composites

Summary

The preparation and performance of Nafion/silica composites are reported. In these materials, the advantage of the high surface area of silica is combined with the high catalytic activity of Nafion (a perfluorinated ion-exchange resin with highly acidic Brønsted sites) for solid acid catalyzed reactions. The sol-gel synthesis method proves to be a relatively simple preparation technique in which composites of any desired Nafion loading between 8 and 40 wt% can be prepared with TMOS or Ludox as a silica source. The micro- and mesoporous samples show surface areas up to 465 m²/g with pore volumes up to 0.95 ml/g, as determined with nitrogen adsorption measurements. The texture can be tuned by various parameters. However, the reproducibility of the synthesis method needs significant improvement. The Nafion/silica composites show a relatively high activity and selectivity in the acylation of anisole with octanoic acid. The high activity is ascribed to the high acidity of the acid sites. The high selectivity is ascribed to an interaction between the Nafion backbone and the silica functional groups, as demonstrated by FT-IR, resulting in a lower acidity of the Nafion active sites. No leaching of the active species is observed during reaction conditions. The composites show strong deactivation in consecutive reactions. However, selectivity is maintained.
Chapter 3A

General introduction

The ion-exchange resin Nafion

Nafion and related polymers were initially developed by DuPont for the commercial application as membranes in electrochemical processes. This is mainly because these materials are relatively inert towards corrosive environments and also due to the high permselectivity, which allows cations to diffuse faster through the membranes than anions (Olah et al., 1986).

The Nafion resin is a perfluorinated ion-exchange polymer. The backbone structure is similar to Teflon, with pendant sulfonic acid groups (Zoppi et al., 1997). The structure of Nafion is shown in figure 1, where $m = 1, 2, \text{ or } 3$ and $n$ has a value of about $6-7$ with $x$ about 1000 (Harmer et al., 1996; Waller and Warren van Scoyoc, 1987), resulting in an equivalent mass of 1200 kg/kmol (0.8 meq H\(^+\)/g). The ionic groups (-SO\(_3\)H) form clusters in the chemically stable Teflon-like matrix (-CF\(_2\)CF\(_2\)-) (Zoppi et al., 1997). These hydrophilic domains form micelles, surrounded by the hydrophobic fluorocarbon backbone and connected by small channels. The Nafion resin is prepared as a copolymer of tetrafluoroethylene and perflouro-2-(fluorosulfonylthoxy)propyl vinyl ether (Hölderich and van Bekkum, 1996; Harmer et al., 1996). Unlike other resinsulfonic acids like sulfonated polystyrenes (Dowex-50, Amberlyst-15, Amberlite IR-112 etc), Nafion and related perfluoroalkanesulfonic acids are stable in corrosive environments and the maximum operating temperature is up to 473K (Waller and Warren van Scoyoc, 1987).

Nafion is commercially available as Nafion NR50 (DuPont) in the form of relatively large (2-3 mm) beads. A disadvantage of these beads is the low surface area (typically 0.02 m\(^2\)/g or less) (Waller and Warren van Scoyoc, 1987). The water selective Perma Pure membranes also consist of the polymer Nafion and are especially developed for the removal of water from gas phase streams (Perma Pure Inc., New Jersey, USA). Nafion is also available as a 5% solution in a mixture of lower aliphatic alcohols and water (Technical Bulletin DuPont, Philadelphia).

What makes Nafion so useful for catalytic purposes is the superacidity of the acidic form. Since the sulfonic acid group is attached to a highly electron withdrawing perfluoroalkyl backbone, a relatively high polarization of the -OH bond results. Because methods of measuring solution acidities cannot directly be applied to solid materials, the determination of
the acidity of Nafion-H is difficult. Nevertheless, studies indicate that Nafion-H resin exhibits acidic character comparable to 100% sulfuric acid, because the estimated Hammett $H_0$ acidity function values of Nafion-H, approximately −12, is comparable to that of 100% sulfuric acid (Olah et al., 1986). The properties of Nafion-H have led to an extensive development of various acid catalyzed reactions, especially by Olah and co-workers. Sharma et al. (1995) describe the use of various ion-exchange resins in catalysis and extensive information about the use of Nafion can be found in the reviews of Olah et al. (1986) and of Waller (1985). Examples of Nafion catalyzed reactions include the alkylation of (substituted) benzene (Olah and Meidar, 1979), the preparation of diacetates from aldehydes (Olah and Mehrotra, 1979), the dehydration of alcohols to ethers (Olah et al., 1997), the esterification of alcohols with carboxylic acids (Olah et al., 1978), the hydration and methanolysis of epoxides (Surya Prakash et al., 1999; Olah et al., 1981), and the transformation of diols (Bucsi et al., 1995).

**Nafion/silica composites**

To overcome the disadvantage of the low surface area (<0.02 m$^2$/g) of the pure Nafion NR50 beads, researchers at DuPont have developed Nafion/silica composites, in which small (20-60 nm) Nafion resin particles are embedded in a porous silica matrix (Harmer et al., 1996). The composites, available under the tradename SAC13 (with 13 wt% of Nafion) are prepared by a sol-gel technique. Due to the increase in surface area and accessibility of the active sites the application of this material as a solid acid catalyst has become attractive. Also the preparation of silica composites with other resins, like Aciplex, has been reported (Okyama et al., 2000).

The way of preparing the Nafion/silica composites is very much analogous to the sol-gel synthesis of pure silica (Brinker et al., 1982). First, a silicon alkoxide, like tetramethyl orthosilicate (TMOS), is prehydrolysed by adding hydrochloric acid. Then, this silicate solution is added to a base solution which contains Nafion. Condensation of the solution is accelerated due to the presence of the base leading to gelation within a few seconds. The resulting composite material is highly porous, with a surface area of around 350 m$^2$/g$^{-1}$. It is also possible to ‘tune’ the microstructure by varying the processing conditions, like the pH (Harmer et al., 1996).

Botella et al. (1999) found that when the surface area of the composites increases, this would result in a stronger interaction between the active phase and the silica support due to the greater number of silanol groups. This strong interaction would result in a decrease in acidity of the sulfonic groups. This was also shown by Pálinkó et al. (1998). By using FT-IR techniques an interaction between the −SO$_3$H groups of the Nafion backbone and the hydroxyl clusters of silica was measured, which causes a decrease in acidity.
The activity of the Nafion/composites with an increased surface area was investigated in various organic reactions, like the Friedel-Crafts alkylation (Harmer et al., 1996; Botella et al., 1999) and acylation (Heidekum et al., 1999a), the Fries rearrangement (Heidekum et al., 1998), the dimerization of α-methylstyrene (Heidekum et al., 1997; Sun et al., 1996b), esterification reactions (Heidekum et al., 1999b), and the 1-butene isomerisation (Sun et al., 1996a).

The Nafion/silica composite is rather expensive, the commercially available catalyst, SAC13 (with 13% of Nafion), costs approximately $1000 per kg (Engelhard De Meern B.V., The Netherlands). Compare this price for instance with a price of about $50 for a kg of a BEA zeolite (Zyolyst International, Great Britain). Perhaps the costs of the composite will decrease in the future when these materials have been fully developed.

The goal of this work is to develop highly active and selective Nafion/silica composites as catalysts for the acylation of anisole with octanoic acid.

Sol-gel process

The most important step in the preparation of the Nafion/silica composite is the formation of the silica network. This is achieved using the sol-gel technique. A ‘sol’ is defined as a dispersion of colloidal particles in a liquid, and a ‘gel’ is defined as an interconnected, rigid network with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micrometer. A silica gel can be formed by gelation of a sol or by hydrolysis and polycondensation of alkoxide precursors (Hench and West, 1990). In the case of colloidal particles, the sol is mixed in water at a pH that prevents precipitation (Iler, 1979). In the case of a liquid alkoxide precursor, such as TMOS or TEOS, hydrolysis reactions result in silica monomers or small oligomers after mixing with water. Subsequently, the hydrated silica tetrahedra interact as a result of (poly)condensation, forming ≡Si-O-Si≡ bonds and eventually the silica network is formed. The corresponding reactions are depicted in figure 2 (Hench and West, 1990).

The gelation rate and the (micro)structure of the the gels are influenced by many variables such as the raw materials, the solvents, the concentrations, the temperature, the presence of salts and the pH (Iler, 1979). Not only the gelation rate is affected, but the (micro)structure is also influenced by these variables (Mackenzie, 1988). Especially the pH is highly relevant, as the gelation time is dependent on the pH of the system. At the ‘point of zero charge (PZC)’ at pH 2, the condensation characteristics change. At lower values the condensation reactions are catalyzed by protons, making the rate of condensation larger than the rate of hydrolysis. After drying, slow hydrolysis results in microporous silica, due to long chains and hardly any crosslinking. Between pH 2 and 7 the condensation reactions are catalyzed by hydroxyl ions,
resulting in a larger rate of hydrolysis compared to the condensation rate. Due to a strong crosslinking network, this results in silica with a higher density. Above pH 7, polymerisation occurs rapidly and silica particles grow in size. Because these particles are charged and repel one another, no aggregation will occur. In this region a colloidal silica solution will remain stable.

\[
\begin{align*}
\text{a. } & \quad \text{H}_2\text{CO} - \text{Si} - \text{OCH}_3 + 4\text{H}_2\text{O} \quad \rightarrow \quad \text{HO} - \text{Si} - \text{HO} + 4\text{CH}_3\text{OH} \\
\text{b. } & \quad \text{HO} - \text{Si} - \text{OH} + \text{HO} - \text{Si} - \text{OH} \quad \rightarrow \quad \text{HO} - \text{Si} - \text{O} - \text{Si} - \text{OH} + \text{H}_2\text{O} \\
\text{c. } & \quad \text{HO} - \text{Si} - \text{O} - \text{Si} - \text{OH} + 6\text{Si(OH)}_4 \quad \rightarrow \quad \text{HO} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{OH} + 6\text{H}_2\text{O}
\end{align*}
\]

Figure 2. Chemical reactions occurring during the silica network formation from a silica alkoxide.


Experimental

Materials

A 5 wt% Nafion solution in a mixture of lower aliphatic alcohols and 10% water was purchased at Aldrich (27470-4), and at DuPont (SE-5012). Tetramethyl orthosilicate (TMOS) was purchased at Aldrich and Fluka. Tetraethyl orthosilicate (TEOS) was obtained from Alfa. Ludox AS40 and Ludox HS30 were purchased at Aldrich. Ludox HS30 (surface area 220 m²/g) has a pH of 9.8 and is stabilized by sodium ions, whereas Ludox AS40 (surface area 135 m²/g) has a pH of 9.1 and is stabilized by ammonium ions. Water glass, a sodium silicate solution, was obtained from Chemproha. MCM-41 (Si/Al ∞) was kindly provided by the Department of Organic Chemistry and Catalysis of the Delft University of Technology. Silica gel with particle size of 35-70 mesh (0.2-0.5 mm) was obtained from Fluka. HCl, HNO₃ and CaCO₃ were obtained from Merck and sodium hydroxide was obtained from Baker.
Characterisation techniques

The Nafion loading was determined by thermal analysis (TGA-DSC). During these measurements the weight of a sample and the energy released or absorbed (in the case of, respectively, exothermic and endothermic reactions) is measured as a function of temperature or time, giving information about the decomposition temperature of the sample and the percentage of decomposing material. The measurements were performed on a STA 1500H thermobalance from Thermal Sciences in a flow of synthetic air (21% O₂ in N₂). Samples of approximately 40 mg were heated at a constant rate of 5K per minute.

Texture analysis of the samples was performed with nitrogen-physisorption and mercury-porosimetry. The nitrogen-physisorption measurements (for micro- and mesopore analysis) were carried out with a Quantachrome Autosorb-6P at 77K. The mercury-porosimetry measurements (for meso- and macropore analysis) were performed on a Carlo Erba Porosimeter 2000.

Surface morphology of the samples was studied using transmission electron microscopy (TEM). This was done on a Philips CM30T electron microscope with a LaB₆ filament as the source of electrons, operated at 300 kV. Samples were mounted on a Quantifoil® microgrid carbon polymer, supported on a copper grid.

FT-IR analysis was performed on a Nicolet Magna 550 FT-IR Spectrometer with a Spectratech Diffuse Reflectance Infrared Fourier Transformed (DRIFT) cell. The samples were powdered, diluted with KBr and dried in-situ at 393K for 10 min. The spectrum of pure KBr was taken as baseline.

The catalytic activity of the Nafion/silica composites was measured batchwise in the acylation of the anisole with octanoic acid in an open reflux glass configuration. The activity measurements were performed under the same reaction conditions as in the catalyst screening measurements (see chapter 2); in a reflux slurry reactor with a drying tube (containing silica gel) on top, an octanoic acid concentration of 0.2 mol/l in anisole, a reaction temperature of 428K (boiling point of anisole), an atmospheric pressure, and a reactor volume of 50 ml. Before measuring the catalytic performance, the Nafion/silica composites were crushed and sieved in a fraction of 53-100 μm and dried for 16 h (overnight) at 383K.

Activity was defined as the initial apparent first order k-value (h⁻¹), normalized for the catalyst concentration, see chapter 2 for the first order derivation. Selectivities were calculated
between the ratio of the acylated aromatic substrate para-octanoyl anisole produced and the converted octanoic acid.

**General preparation technique**

The Nafion/silica composites are prepared by prehydrolysing a silicon alkoxide, like tetramethyl orthosilicate (TMOS), by adding hydrochloric acid. Then, this silicate solution is added to a Nafion-containing base solution. Condensation of the solution is accelerated due to the presence of the base leading to gelation within a few seconds through which the Nafion is fixed in the silica structure.

The silica sources used in this study are TMOS, TEOS, Ludox HS30, Ludox AS40, and water glass. TMOS and TEOS were prehydrolysed with water and 0.04 M HCl in a weight ratio of approximately 70:11:1 (according to Harmer *et al.*, 1996). The pH of Ludox HS30, Ludox AS40 and water glass was modified to a value of 7 with either HCl or NaOH.

The pH of the Nafion solution (2-3) was increased by mixing with a 0.4M NaOH solution in a weight ratio of 2:1. To investigate the effect of the NaOH concentration, the pH of the Nafion solution in some preparations was also modified with a 0.6M, 0.8M, and a 1M NaOH solution.

Because the gelation of the Nafion/silica material occurred very fast (within 10 s), the silicate solution has to be added quickly to the Nafion containing solution, while mixing vigorously. The pH of the silica/Nafion mixture needs to be around 6-7, for gelation to occur (Harmer *et al.*, 1996).

After mixing, the composites were dried at 368K for 3 days. After drying, the material was transformed into its active, protonic form by an acid treatment. This was done by treating the sample in 3.5M HCl for 15 min (10 ml solution/g<sub>sample</sub>) and washing twice in demineralized water. After repeating this treatment 4 times, the sample was treated in 25 wt% nitric acid (20 ml solution/g<sub>sample</sub> was performed for 16h (overnight) and subsequently washed 3 times in demineralized water.

To modify the porosity of the Nafion/silica composite, CaCO<sub>3</sub> can be added to the Nafion solution. Due to the acid treatment, while mixing with the acidic silicate solutions, CaCl<sub>2</sub> and CO<sub>2</sub> are generated leaving relatively large pores in the silica structure. One sample was prepared by adding 15 wt% of CaCO<sub>3</sub> to the Nafion solution prior to mixing with the silicate solution.
Chapter 3A

The catalytic performance of the prepared Nafion/silica composites was compared with the performance of SAC13, a commercial Nafion/silica composite with 13 wt% of Nafion obtained from DuPont (batch 3, see chapter 2). Two catalysts were also prepared by impregnating silica and MCM41 (Si/Al = 1) with the 5 wt% Nafion solution according to the pore volume impregnating method. To investigate possible deactivation of the composites, the catalysts were washed with acetone after performing the reaction, dried at 393K, and tested again (4 times).

Results and discussion

Preparation aspects – variation of the silica source

The preparation of the composites was observed by studying the gelation time. The gelation has to be fast enough to trap the Nafion into the silica matrix, and on the other hand it has to be slow enough for good mixing of the silica with the Nafion. Too slow mixing will result in clustering of the Nafion, resulting in a bad dispersion of the Nafion through the silica. An optimum exists for the gelation time, which was observed visually.

During the preparation of the various Nafion/silica composites, the effect of the various silica sources was directly observable in the gelation step. When a TMOS mixture was added to the Nafion solution, gelation took place within seconds, generating heat. A slightly white gel was formed. Adding the Ludox (either AS40 or HS30) mixture to the Nafion solution, resulted in a very slow gelation; it took a relatively long time (24 h) for the mixture at 368K to gelate. The gelation with TEOS and water glass based mixtures did not proceed at all. Even after heating at 323K, the hydrolysis of TEOS would not occur completely. The addition of the water glass mixture to the Nafion solution resulted in a very slow gelation and an inhomogeneous mixture. For these reasons, only the TMOS and Ludox based preparations were further investigated.

Nafion loadings

During synthesis, the desired Nafion loading in the composite can be tuned by varying the Nafion content in the Nafion solution before mixing with the silica source. After synthesis, the Nafion loadings were determined with TGA-DSC. In figure 3, the results can be found of the measured

![Figure 3. The intended and measured Nafion loadings of the composites (wt%) as measured with TGA-DSC.](image-url)
and the desired Nafion loadings of the catalysts. The loading of a Nafion/silica composite can be tuned from 10 to 40 wt% of Nafion. This is demonstrated for composites based on TMOS and Ludox (HS30).

**Texture analysis**

Texture analysis of the Nafion/silica composites was measured with nitrogen adsorption. The surface area and pore volume calculated according to the BET method are presented in figure 4 (a and b). These values are determined by normalization for the total amount of catalyst (Nafion and silica).

Considering the composites prepared from TMOS, relatively high surface areas are obtained. When increasing the Nafion loading from 8 at 40 wt%, the surface area decreases from 465 m²/g<sub>catalyst</sub> to 90 m²/g<sub>catalyst</sub>. Considering the shapes of the nitrogen adsorption isotherms, all samples reflect the shape of the type IV isotherm, according to the Brunauer classification (Scholten, 1993), revealing the presence of micro- and mesopores. The pore volume decreases with an increasing Nafion content (from 0.95 to 0.4 ml/g<sub>catalyst</sub>). The pore size distributions of the composites are depicted in figure 5.

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![Figure 4](image.png)

**Figure 4.** Surface area of various Nafion/silica composites, as measured with nitrogen adsorption (BET). a. BET (m²/g<sub>catalyst</sub>). b. Pore volume (ml/g<sub>catalyst</sub>).

55
The mean pore diameter of a 13 wt% Nafion/silica (TMOS based) composite has a value of 7.5 nm. Harmer et al. (1996) found higher values for the pore diameters (9.8 nm). Increasing the Nafion loading from 0 to 40 wt%, results in an increased pore diameter. The large decrease in pore volume shows the substantial effect of the increasing Nafion loading on the texture characteristics.

The commercial SAC13 as well as the Ludox based composites show a lower surface area than the TMOS based composites. The SAC13 has a surface area of 148 m$^2$/g$_{\text{catalyst}}$, and both Ludox HS30 based composites show surface areas of 148 and 137 m$^2$/g$_{\text{catalyst}}$ for, respectively.
13 and 20 wt% of Nafion. This decrease in surface area due to an increase in Nafion loading is also observed with the TMOS based composites. Comparing the two types of Ludox, HS30 (surface area 220 m$^2$/g) has a pH of 9.8 and is stabilised by sodium ions, whereas AS40 (surface area 135 m$^2$/g) has a pH of 9.1 and is stabilised by ammonium ions. The composites with 13 wt% of Nafion based on these types of Ludox, show a surface area of 92 m$^2$/g$_{\text{catalyst}}$ for AS40 and 148 m$^2$/g$_{\text{catalyst}}$ for HS30. Various differences between these types of Ludox may have caused the difference in surface area, such as the size of the silica colloidal particles, the type of stabilizing ions (ammonium vs sodium ions) and the silica concentration (40 wt% vs 30 wt%). The Ludox and TMOS based composites have the same pore shape because the isotherms correspond with each other. However, the pore distribution plots of these samples differ, resulting in a lower porosity of the Ludox AS40 sample as the pore diameter increases significantly from 7.5 nm for the TMOS based sample to 19.1 nm for the Ludox based sample, see figure 5b.

Adding CaCO$_3$ to the synthesis mixture before gelation hardly affects the surface area, but results in a higher pore volume (1.25 ml/g$_{\text{catalyst}}$) compared to a composite prepared with the same method but without the addition of the carbonate (0.9 ml/g$_{\text{catalyst}}$). The large pores are ascribed to decomposition of embedded CaCO$_3$ in the silica matrix during treatment of the composites with acid. The carbonate reacts with the acid to form carbon dioxide, leaving large pores in the structure. Considering the shape of the isotherms, the shapes of the pores are similar for the sample with and without CaCO$_3$. The pore diameter can be found in figure 5b. Compared with the sample without CaCO$_3$, a larger pore diameter is obtained (10.2 nm instead of 7.5 nm), and some macropore formation at 110 nm. This corresponds with the results found by Harmer et al. (1996).

Some Nafion/silica composites were prepared with TMOS as a silica source and a varying NaOH concentration (mol/l). Increasing the NaOH concentration from the standard concentration of 0.4 mol/l to 1.0 mol/l results in a decrease of the surface area from 400 m$^2$/g$_{\text{catalyst}}$ to 143 m$^2$/g$_{\text{catalyst}}$. Apparently, by increasing the sodium concentration the surface area characteristics of these materials is affected. The shape of the isotherm of these samples is similar in all cases, indicating that the shape of the pores is not influenced by this modification of the synthesis method. The surface area of the composites prepared from Ludox HS30 (stabilized by sodium ions) is similar (140-150 m$^2$/g$_{\text{catalyst}}$), but this is not only affected by the amount of sodium, but also by other factors like the structure of the silica in the solution.

Two batches of composites were prepared according to exactly the same manner, from TMOS as a silica source and with a NaOH concentration of 0.4 mol/l. Both the surface area and the pore volume of the samples differ significantly; 400 and 333 m$^2$/g for the surface area and
Chapter 3A

0.91 and 0.78 ml/g for the pore volume. This demonstrates that the applied preparation method results in batch dependent samples. This was also observed in chapter 2 with the commercial Nafion/silica composites SAC13 and SAC25.

In general it can be stated that the texture of the composites can be tuned by altering the Nafion loading, selecting the silica source (TMOS or Ludox), addition of CaCO₃, or altering the composition of the synthesis mixture. However, the reproducibility of the synthesis is not satisfactory, as was already noticed in chapter 2 for the commercial Nafion/silica composites. This aspect has to be studied in further detail.

Figure 6. The morphology of the Nafion/silica composites as studied with TEM-EDX. a. TEM micrograph of the Nafion/silica composites. b. EDX analysis of the amorphous structure as shown in the TEM micrograph. c. TEM micrograph of a Nafion particle as shown in one sample (artefact).
Morphology

The morphology of the Nafion/silica composites was studied with TEM-EDX. All composites showed a similar morphology as shown in figure 6a, which resembles the morphology as shown by Harmer et al. (1996). According to the authors, the composites should exist of small Nafion particles entrapped in the silica matrix. However, the Nafion ‘particles’ are not visible in the micrographs. EDX analysis of the Nafion/silica composite also did not reveal any Nafion (C or F signal) in the sample, see figure 6b. Explanations for the fact that the Nafion particles were not detected with this technique are that either the particles are too small or are decomposed under the high energy containing electron beam. It can also be that Nafion is not present as distinct particles, but as a thin film through the silica matrix. This still remains unclear and needs further investigation. Only in one of the TEM micrographs of the sample prepared from TMOS and 13 wt% Nafion, the polymeric structure of the Nafion became visible as a large (8 x 12 μm) particle, see figure 6c. It is possible that this artefact, which was not encountered in further study, originated from a gelation which did not proceed successfully or that the Nafion particle was already present in the solution before the

![Graph showing FT-IR spectra of Nafion, silica and Nafion/silica composites.](image)

Figure 7. FT-IR spectra of Nafion, silica and Nafion/silica composites. a. Pure Nafion. b. Pure silica. c-g. Nafion/silica composites, wt% Nafion varied.

composites were prepared. That this particle consists of the Nafion resin, is concluded from
Chapter 3A

the EDX analysis revealing the presence of C and F in high amounts. The small (175 nm) black dots in this particle consist of silica, as measured by EDX.

Nafion/silica interactions

The interaction between the silica functional groups of the silica matrix and the Nafion resin was studied with FT-IR. The results are presented in figure 7. Pure Nafion (figure 7a) was studied by impregnating KBr with the 5% Nafion/ethanol solution. Pure silica (figure 7b) was prepared analogous to the synthesis of silica/Nafion composite (from TMOS), but without any Nafion added. Nafion/silica composites with varying Nafion contents (8-40 wt%); figures 7c-g) were prepared according to the standard preparation method from TMOS.

The IR spectrum of pure Nafion does not show any bands in the region of 4000 - 1500 cm\(^{-1}\), so only the region of 500-1500 cm\(^{-1}\) will be discussed. Two sharp bands are observed at 1060 and 985 cm\(^{-1}\), which are ascribed to respectively S-O and C-F stretching vibrations. The three overlapping broader bands at 1313, 1234, and 1176 cm\(^{-1}\) are ascribed to CF\(_2\) and CF\(_3\) stretching modes (Xie and Okada, 1998).

The IR spectrum of the pure silica shows broad bands in the regions 3800-2900, 2100-1550, and 1400-700 cm\(^{-1}\). According to Harmer et al. (1996), the Si-O-Si stretching vibrations give a band at 1080 cm\(^{-1}\), which appears to be at 1060 cm\(^{-1}\) in this study. The corresponding bending vibration should give a broad band at 3450 cm\(^{-1}\) (Harmer et al., 1996), which unfortunately is not clearly visible in the current study, due to the broadening effect of physisorbed water in this spectrum.

The Nafion/silica composites with varying Nafion loading show all similar spectra. At 3740 cm\(^{-1}\) a sharp band is observed, which declines at increasing Nafion loadings. The band is assigned to isolated Si-O-H stretching vibrations which interact with the acidic sulfonate groups of the Nafion (Brinker and Scherer, 1990). This corresponds with the study of Palinko et al. (1998). The broad band found at 3550 cm\(^{-1}\) is assigned to Si-O-H stretching vibrations of silanol groups that are interconnected through hydrogen bridges and adsorbed water (Burneau et al., 2000).

The bands at 2990 and 2300 cm\(^{-1}\), with very low intensities, are assigned to, respectively, hydrocarbons and carbon dioxide due to adsorption from the atmosphere. The band at 2990 cm\(^{-1}\) dissipates at higher Nafion loadings, indicating that the pollution by hydrocarbons only occurs at the silica matrix.
In the region of 1500-2000 cm\(^{-1}\), absorbance occurs from the bending vibrations of adsorbed water. Even after drying the samples in-situ, the bands of the adsorbed water did not disappear, indicating that water adsorbs very strongly onto the sample. This was also observed by Harmer et al. (1996) and Palinko et al. (1998).

Comparing the IR spectra of the Nafion/silica composites in the region of 1500-500 cm\(^{-1}\), small shoulders appear at 1425 and 1315 cm\(^{-1}\) at higher loadings. At 1100 and 1000 cm\(^{-1}\) also the intensity decreases. In this study, the FT-IR spectra of the composite cannot be interpreted as a linear combination of the individual silica and Nafion spectra. For example, the small band at 1425 cm\(^{-1}\), cannot be found in either the pure silica or the Nafion spectrum. It could be that this band is from Nafion present in the silica matrix and that all Nafion bands are shifted as a result of interactions between Nafion and silica. The bands correspond then to the bands found in pure Nafion for the CF\(_2\) and CF\(_3\) stretching modes (1425 and 1315 cm\(^{-1}\)), S-O stretching (1100) and C-F stretching vibrations (985 cm\(^{-1}\)).

**Performance of the Nafion/silica composites**

The performance of the Nafion/silica composites was studied in the ‘standard’ acylation of anisole with octanoic acid, as described in chapter 2. The activity of the Nafion composites (l.g\(_{\text{catalyst}}\) \(\cdot\) h\(^{-1}\)) prepared with varying Nafion contents from TMOS and Ludox normalized for the catalyst concentration is compared with the activity of the commercial SAC13 (batch 3) and presented in figure 8a. Also the activity normalized for the amount of Nafion (l.g\(_{\text{Nafion}}\) \(\cdot\) h\(^{-1}\)) is presented in figure 8b, and the selectivity towards the desired p-acylated anisole is presented in figure 8c.

![Figure 8](image_url)

**Figure 8.** Performance of the Nafion/silica composites as function of the Nafion loading (wt%). a. Activity normalized for the total amount of catalyst (l.g\(_{\text{catalyst}}\) \(\cdot\) h\(^{-1}\)). b. Activity normalized for the amount of Nafion (l.g\(_{\text{Nafion}}\) \(\cdot\) h\(^{-1}\)). c. Selectivity (%). Legend: TMOS (♦), SAC13-B3 (■), Ludox AS30 (♦).
Chapter 3A

The activity of the Nafion/silica composites \( (\text{g}_{\text{catalyst}} \cdot \text{h}^{-1}) \) increases linearly when increasing the Nafion loading from 0 to 30 wt%, the activity normalized for the amount of Nafion \( (\text{g}_{\text{Nafion}} \cdot \text{h}^{-1}) \) is consistent with this; at approximately 0.8 \( \text{g}_{\text{Nafion}} \cdot \text{h}^{-1} \) the activity is approximately constant from 8 till 30 wt%. The fact that the activity normalized per unit Nafion is not exactly constant is possibly a reflection of the dispersion. The composite with 40 wt% has a relatively low activity (see also figure 3b), probably due to the formation of Nafion layers and blockage of the pores. The composite with 13 wt% of Nafion and the commercial SAC13 (batch 3) both have a higher activity than the average 0.8 \( \text{g}_{\text{Nafion}} \cdot \text{h}^{-1} \) (1.1 \( \text{g}_{\text{Nafion}} \cdot \text{h}^{-1} \) for the Nafion/silica composite and the 1.25 \( \text{g}_{\text{Nafion}} \cdot \text{h}^{-1} \) for the SAC13 (B3)). The two Ludox based composites show a decrease in activity when increasing the Nafion load, which is also ascribed to the different texture characteristics, see texture analysis.

All Nafion/silica samples show a relatively high selectivity (86-90%), which is constant during the conversion of the octanoic acid. The obtained values for the selectivity are comparable with the selectivity of the third batch of the commercial SAC13 (91%). Compared to the selectivity of pure Nafion in this acylation reaction (46%), see chapter 2, all composites show much higher selectivity. The side reaction, the demethylation of anisole, is attributed to the superacidity of this catalyst (Corma, 1997). The higher selectivity is ascribed to the interaction between the silica functional groups of the silica and the acid groups of the Nafion resulting in a lowering of the acidity of the Nafion active sites. With an increasing Nafion loading, a slight decrease is observed in the selectivity from 90% to 86%. Possible reasons are the lower surface area and pore volume, and a different charge of the Nafion active sites due to the higher Nafion density in the matrix leading to a lower selectivity. Again an optimum is

![Activity and Selectivity graph]

found for the Nafion/silica composite with 13 wt% of Nafion.

Some composites were prepared according to specific methods. The effects of these specific methods on the activity and selectivity can be found in figure 9. Changing the preparation method by varying the materials or by additions, clearly affects the activity, which will be discussed below. Selectivity is in all cases unaffected.
Adding CaCO₃ to the synthesis mixture, results in a lower activity compared to the composite which is prepared similarly. A possible reason could be blocking of the active sites with Ca²⁺ ions that are not removed during the carbonate decomposition. Another reason could be the formation of Nafion clusters due to the decomposition reaction of CaCO₃, which results in a lower activity. Selectivity is not affected by this addition.

Preparation of Nafion/composites with another type of a 5% Nafion solution (SE-5012 from Dupont instead of the ‘standard’ 27470-4 also from DuPont but purchased via Aldrich), results in a lower activity. This indicates the batch dependency of this preparation method, as was already observed in chapter 2, with the varying activities from the separate commercial batches that were obtained.

The performance of the composites being influenced by the nature of the TMOS and the Nafion-solution, might explain the batch dependency of the commercial SAC13 and SAC25 on the activity of the acylation reaction as was demonstrated in chapter 2. Apparently, it is very important for the sol-gel process and therefore also for the performance to consider the nature of the raw materials (TMOS, Nafion) applied for the synthesis. Also the fact that this sol-gel method is very sensitive to various parameters such as pH, locally high concentrations should be avoided. The preparation of the composites on a commercial scale, which is much larger than the laboratory scale used in this study, can therefore result in composites with different characteristics.

The Ludox based composites both show a lower activity than the TMOS based sample, probably due to the lower surface area (see ‘texture analysis’). Also the gelation process of the silica will influence the performance of the catalysts, as the composition and pH of the silica sources differ. Preparation with Ludox HS30 exhibits a higher activity than the composite prepared with Ludox AS40. The difference between the two silica sources is not only the surface area and the amount of silica (respectively 30 and 40%), but also the counterions used to stabilize the mixture. Ludox AS40 is ammonium stabilized and HS30 is sodium stabilized.

Impregnation of silica and MCM41 with Nafion results in a lower activity than the composites. Apparently, the composite preparation method results in highly accessible and active solid acid catalysts for acylation.

The Nafion/silica composites prepared from TMOS with a varying NaOH concentration of 0.4 ('standard') till 1.0 mol/l exhibit a lower activity when increasing the NaOH concentration. This is ascribed to the lower surface area (see ‘texture analysis’) and also the the higher pH during gelation resulting. Selectivity is again not affected by this modification.
Chapter 3A

Leaching considerations

Leaching of the active species was studied by filtering the reaction mixture while hot. This was done for the Nafion/silica samples with 20 wt% of Nafion, and prepared with TMOS and Ludox. After hot filtration, the reaction did not continue. This indicates that no active species leach from the solid catalyst during reaction conditions.

Stability of the composites

Stability of the composites was tested by studying the deactivation of three samples in four subsequent acylation reactions, performed under standard conditions (0.2 mol/l octanoic acid and 428K). The samples that were tested were the composites with 13 wt% of Nafion prepared from TMOS and a NaOH concentration varying from 0.6 – 1.0 mol/l.

![Graph showing deactivation of Nafion/silica composites](image)

Figure 10. Deactivation of Nafion/silica composites. Activity (I_g catalyst \( \cdot h^{-1} \)) after four consecutive reactions. x represents the NaOH concentration during preparation.

Upon re-use, the activity of the Nafion/silica composites decreases, probably due to adsorption of aromatic compounds or oligomers. The rate at which the activity decreases differs for the three samples studied, but after the fourth test, the decrease is similar for all samples (44-49 %). Retesting the composites does not show a pronounced effect on the selectivity towards the p-acylated anisole. In the case of the composite prepared with 0.6 mol/l of NaOH, the selectivity decreases slightly from 89 to 86%, but in the sample prepared from 0.8 mol/l of NaOH the selectivity first decreases from 90 to 87 and in the fourth test a selectivity of 88% is found. The samples prepared from 1 mol/l NaOH, show selectivities of respectively 89, 88, 89 and 84%. The sample prepared from 1 mol/l NaOH seems to show less
strong deactivation than the composites prepared with lower NaOH concentrations. This composite also showed a larger pore volume. Possibly the deactivation was caused by the formation of oligomers which can only be transported out of the pores in this composite, due to its large pores. In the other cases, the pores are too small leading to deactivation.

Conclusions

- The synthesis of a Nafion/silica composite by means of the sol-gel method proves to be a relatively simple and satisfactory technique for the preparation of a solid acid catalyst.
- Composites of any desired Nafion loading between 8 and 40 wt% can be prepared with TMOS or Ludox as a silica source.
- Surface areas up to 465 m$^2$/g with pore volumes up to 0.95 ml/g are obtained with this preparation method. The prepared samples are all micro- and mesoporous.
- The texture can be tuned by altering the Nafion loading, selecting the silica source (TMOS or Ludox), addition of CaCO$_3$, and by altering the pH during the synthesis mixture. However, the reproducibility of the synthesis method needs significant improvement.
- The Nafion/silica composites show a relative high activity and selectivity. The activity and selectivity of the composite with 13 wt% of Nafion matches the activity and selectivity of the commercial SAC13 (batch 3). Some of the composites of the present study proved to have a higher activity and selectivity than the commercial composite SAC13.
- The interaction between the Nafion backbone and the silica functional groups is demonstrated by FT-IR; the high selectivity is ascribed to this interaction resulting in a lower acidity of the Nafion active sites.
- Adding CaCO$_3$ to the synthesis mixture results in a higher pore volume, but the activity in the acylation reaction decreases.
- Increasing the pH of the Nafion mixture prior to gelation results in a decrease of both surface area and activity. Selectivity is not affected.
- The composites show a higher activity than impregnated silica and MCM41 due to a higher accessibility of the active sites. The selectivity is similar.
- The batch dependency, earlier demonstrated in chapter 2 with the commercial SAC13 and SAC25, is ascribed to the difference between the raw materials and their age (TMOS, Nafion) when preparing the composites.
- The Nafion/silica composites do not show any leaching of the active species during reaction conditions, as was demonstrated by hot filtration.
- The composites show strong deactivation upon re-use, but selectivity is maintained.
Chapter 3A

Acknowledgements

Johan Groen and Peter Boeser are gratefully acknowledged for performing the texture analysis measurements. Dr. P.L.J. Kooyman is gratefully acknowledged for performing the electron microscopy investigations. Karen de Lathouder is gratefully acknowledged for her contribution to this chapter.

References


Chapter 3A


Modification of BEA zeolite by means of steaming and acid leaching

Summary

BEA zeolite was modified by steaming and acid leaching in order to increase the catalytic activity in the acylation of anisole with octanoic acid. Steaming the parent BEA (commercial zeolite, Si/Al 12 at 673 K (> 3 h) leads to an increased activity, paralleled with an increase in extraframework aluminum, both tetrahedrally and octahedrally coordinated, as was demonstrated with $^{27}$Al MQ MAS NMR. Leaching the parent BEA in hydrochloric and oxalic acid resulted in high activities compared to the parent material, especially in the case of oxalic acid. Acid treatment leads to removal of mainly the tetrahedrally coordinated extraframework aluminum. Steaming and acid leaching does not affect the texture properties of the zeolite, as was demonstrated with nitrogen adsorption, XRD and TEM measurements. The nature of the (enhanced) activity in the acylation reaction after steaming and acid leaching is probably correlated with the higher accessibility of the active sites.
Chapter 3B

Introduction

Zeo\-lites are microporous, cry\-stalline aluminosilicates based on oxygen-linked SiO_4 tetrahe\-dra. Replacement of some of the Si^{4+} ions in the silica lattice by Al^{3+} ions introduces negative charge which must be compensated by additional positively charged ions, like sodium cations, which are located outside of the Si/Al lattice. In the case of protons as counter-ions, Brønsted acidity is introduced into the zeolite. The various ways in which the SiO_4 and AlO_4 tetrahe\-dra are linked give rise to various systems of internal channels and cages in one, two or three dimensions. These systems of channels and cages lead to uniform pores with 8-, 10- and 12-\membered rings of oxygen atoms, giving rise to small (<0.5 nm), medium (ca 0.55 nm) and large (ca 0.74 nm) pore zeolites.

Zeo\-lite BEA has a highly accessible 3-dimensional structure with two kinds of channels; intersecting elliptical channels with a size of 0.55 x 0.55 nm and 12-ring channels with a size of 0.76 x 0.64 nm (Downing et al., 1997).

The goal of this work is to develop highly active and selective BEA zeolites as catalysts for the acylation of anisole with octanoic acid by means of steaming and acid leaching and to find an explanation for the change in activity, based on the obtained physico-chemical characterisation.

A way to improve the performance of a zeolite is by steaming and acid leaching. This is already done on a large scale for improvement of the performance of other zeolites, like zeolite MFI for the octane boosting in the FCC process, zeolite Y or FAU to create ultrastableY (USY) (Beyerlein et al., 1994), and mordenite for the hydro-isomerisation (Lazaro Munoz et al., 1991; Tromp et al., 2000). Steaming and acid leaching treatments are well-known to cause dealumination of the zeolite structures, that is, removal of aluminum atoms from the framework. Dealumination of a BEA zeolite is reported to occur very easily (Müller et al., 2000).

The explanation for the enhanced performance as a result of steaming and acid leaching is not entirely known yet. Possible reasons are that the accessibility of the active sites is increased due to the treatment or that more active sites are created.

The exact nature of the mechanism of the formation of extra framework aluminum is not known yet. A conceptual model has been proposed by Beyerlein et al. (1997) for the formation of USY from Y; calcination of this zeolite at 773K for 2 h in the presence of steam (1 atm) leads to the expulsion of Al atoms from the framework (tetrahedral) sites. The vacancies created by this Al removal will subsequently be refilled by silicon atoms migrating
from collapsed parts of the crystal. This latter step is often called ‘healing’ in literature, the zeolitic crystal would totally collapse if this step would not occur. In the second step, the vacancies are created by this aluminum expulsion. In the case of the formation of USY from zeolite Y, the resulting structure has a contracted unit cell size and increased hydrothermal stability as the Si/Al ratio of the framework increases (Beyerlein et al., 1997). Severe hydrothermal treatment would eventually lead to collapse of the entire structure, leading to the formation of mesopores in the range of 5-50 nm (Beyerlein et al., 1994).

The role of this extra-framework aluminum on the enhanced activity remains unclear. It is thought that it will block the channels, thereby decreasing the catalytic performance. However, it is also thought to enhance the catalytic performance (Beyerlein et al., 1994). The extra-framework aluminum can be removed from the sample by acid treatment. For FAU it was demonstrated that 24 h of treatment in pH 1.3 is necessary for removal of extraframework aluminum from the lattice (Janssens, 1996).

In bimolecular cracking reactions, it has also been found that creation of mesopores enhance the catalytic performance by reducing (micropore) diffusion limitations (Beyerlein et al., 1997). The explanations given for this phenomenon are derived from the relatively well understood process of introducing mesopores in FAU to create USY (Williams et al., 1999).

Dealumination can be achieved by calcination, steaming, acid leaching or by complexing the aluminum atoms with (for example) oxalic acid. Dealumination during calcination is a kind of ‘in-situ steaming’, due to water produced in the zeolite structure during calcination (Kunkeler et al., 1998). Dealumination during acid treatment is thought to occur due to hydroxyl esters that are formed at the sites where aluminum is expelled from the framework. Dealumination as a result of treatment with oxalic acid, is caused by strong coordination complexation with the aluminum cation. The oxalate ion forms stable complexes with almost any metal ion. The size of oxalic acid (0.29 x 0.54 nm) makes penetration of all zeolite pores possible and can therefore effectively remove aluminum from the lattice by forming a complex of an aluminum ion which is surrounded by one oxalate ion and water ligands. In this way, high Si/Al\textsubscript{bulk} ratios (> 100) are obtained, even with treatment at room temperature (Müller et al., 2000).

In this study, BEA (Si/Al 12) is steamed at temperatures up to 973K, and treated in hydrochloric acid and oxalic acid. The effect of steaming and acid leaching of zeolite BEA on the activity in the acylation of anisole with octanoic acid is studied and compared with characterization data by physico-chemical analytical methods, including $^{27}$Al MAS NMR.
Chapter 3B

Experimental

Materials

BEA (bulk Si/Al 13, see section XRF) was purchased from Zeolyst International (CP 814 E-22), this zeolite is in the NH$_4^+$-form. To convert it to the H$^+$ form, it was calcined for 4 h at 673K (10K/min). Hydrochloric acid was purchased from Merck, and oxalic acid was obtained from Baker.

Steaming and acid treatment procedure

Table 1. Steaming and acid treatment procedures to BEA.

<table>
<thead>
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<th>Name (parent)</th>
<th>Steam temperature K</th>
<th>Steam content Vol%</th>
<th>Steam time h</th>
<th>Acid treatment</th>
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$^*$ Acid treatment after steaming

72
BEA is steamed in a glass fixed-bed configuration with a diameter of either 2 or 5 cm and a bed-height of 4 cm. Water is added by a liquid pump, which evaporates during transport through the tube in the reactor. Before flowing over the BEA sample, the steam is mixed with argon. The amount of water vapour flow in argon was varied from 30 – 72 vol%, and the steaming temperature was varied from 623K-973K for 1 to 24 h. The acid leaching procedure includes treating BEA (5 g) in either 1 M hydrochloric acid or 1 M oxalic acid with a concentration of 20 ml\textsubscript{solution}/g\textsubscript{BEA} by stirring. Table 1 summarises the treatments and sample names.

*Characterisation techniques*

*Texture analysis* of the samples was performed with nitrogen-physisorption and mercury-porosimetry. The nitrogen-physisorption measurements (for micro- and mesopore analysis) were carried out with a Quantachrome Autosorb-6P at 77K. Pore volume and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) model. The mercury-porosimetry measurements (for meso- and macropore analysis) were performed on a Carlo Erba Porosimeter 2000.

*Surface morphology* of the samples was studied using transmission electron microscopy (TEM). This was done on a Philips CM30T electron microscope with a LaB\textsubscript{6} filament as the source of electrons, operated at 300 kV. Samples were mounted on a Quantifoil® microgrid carbon polymer, supported on a copper grid.

*Elemental analysis* (XRF) was performed on a Philips PW1480.

\textsuperscript{27}Al Multiple Quantum Magic Angle Spinning Nuclear Magnetic Resonance (\textsuperscript{27}Al MQ MAS NMR) was used to determine the coordination of the aluminum in the zeolite samples. With this technique pure isotropic spectra with high resolution can be obtained without anisotropic quadrupolar broadening, by making a correlation between the multiple and the single quantum transitions in a two-dimensional mode. The \textsuperscript{27}Al MQ MAS NMR experiments were carried out on a Chemagnetics Infinity 600 (14.1T) operating at 156.3 MHz for aluminum using a Chemagnetics 2.5-mm HX MAS probe. Magic Angle Spinning (MAS) was performed at a speed of > 25 kHz. The samples are measured in wet condition; the conditions during the measurements minimise the chance that any aluminum is escaping detection.

Identification of the crystalline phases by *X-ray diffraction analysis* (XRD) was done on a Philips PW1840 diffractometer, equipped with a PW 1830 generator.
Chapter 3B

The catalytic activity of the BEA samples was measured batchwise in the acylation of the anisole with octanoic acid in an open reflux glass configuration. The activity measurements were performed under the same reaction conditions as in the catalyst screening measurements (see chapter 2); with an octanoic acid concentration of 0.2 mol/l in anisole, 300 mg of catalyst, a reaction temperature of 428K (boiling point of anisole), an atmospheric pressure, and a reactor volume of 50 ml. Before measuring the catalytic performance, the BEA samples were calcined for 16 h at 383K to remove physisorbed water.

Activity was defined as the initial apparent first order rate constant $k$ (h$^{-1}$) normalized for the catalyst concentration (g/l) (see chapter 2). Selectivities were calculated as the ratio of the acylated aromatic substrate para-octanoyl anisole and the converted octanoic acid.

Results

Physico-chemical characteristics

The surface area characteristics of the parent BEA, as determined with nitrogen adsorption, showed a surface area of 640 m$^2$/g, a micropore volume of 0.18 ml/g, and a mesopore volume of 1.1 ml/g. Treating the parent BEA with steam or an acid did not result in any significant changes in the surface area and the pore volume as measured with nitrogen adsorption. All isotherms are identical, showing the same BET surface area as the parent BEA; 640 m$^2$/g within the experimental error of the measurement ($\pm$ 20 m$^2$/g).

A TEM micrograph of the parent BEA is presented in figure 1. Small crystallites are visible with a particle size of 15-20 nm, which are clustered. In figure 1b the TEM micrograph is shown of BEA (#5) that was steamed at 723K for 4 h (#6), and in figure 1c a BEA which is acid leached in 1 M oxalic acid for 1h (#17). As these pictures are representative of all samples, no distinction can be made between any of the samples.
Bulk Si/Al ratios were measured with XRF and the results are depicted in figure 2. The bulk Si/Al ratio of the parent BEA has a value of 13.0. After steaming the bulk Si/Al ratio is not altered; even in the case of 24 h of steaming (#5) the Si/Al ratio is exactly the same as the Si/Al ratio of the parent BEA (13.0). However, after treating the parent or steamed BEA with acid, higher bulk Si/Al ratios are found. For example, an increase in the Si/Al ratio is found from 13 for the parent material to 51 for the oxalic acid treated BEA (#17 and 18).

The $^{27}$Al MQ MAS NMR measurement of the parent BEA is presented in figure 3a. The corresponding $^{27}$Al MAS NMR spectrum are given on top of the MQ MAS spectrum. The spectrum shows two groups of peaks around 55 ppm and around 0 ppm, which are attributed to respectively tetrahedral and octahedral coordinated aluminum. The tetrahedral peak contains the coordinations Al(IV)a and Al(IV)b characteristic of the framework of BEA (van Bokhoven et al., 2000). These peaks are assigned to the crystallographic positions T$_1$-T$_2$ and T$_3$-T$_9$, respectively. The intensity ratio of these two peaks indicates that the sample is strongly dealuminated. Moreover, additional Al(IV)c, Al(V), and Al(VI) are visible, that comprise
about half the intensity of the total spectrum, that may result from a strong dealumination of the sample. It is striking that about half the aluminum present in the spectra of this zeolite can be ascribed to extraframework aluminum. Figure 3b depicts the result after steaming the parent BEA for 24 h at 673K with a steam content of 38 vol% (#5). The $^{27}$Al MQ MAS NMR spectrum of this sample is similar to the spectrum of parent BEA (figure 3a), but reveals increases in intensity of peaks Al (IV)c and Al (VI) that were ascribed to extraframework aluminum (van Bokhoven et al., 2000). No new peaks were observed after the treatment. The spectra of the BEA after 1h, 2h and 10h of steaming (#1, 2, and 4) are not shown but the changes from parent to 24 h are continuous. The $^{27}$Al MQ MAS NMR spectrum of the oxalic acid treated sample is shown in figure 3c. A large loss in intensity of peak (IV)c is clearly observed. The intensity ratio of the (remaining) tetrahedral to the octahedral (VI) peaks has remained constant compared with the parent BEA.

Figure 3a. $^{27}$Al MQ MAS NMR measurement of the parent BEA, the corresponding $^{27}$Al MAS NMR spectrum is given on top.

Figure 3b. $^{27}$Al MQ MAS NMR measurement of the steamed BEA (673K for 24h in 38 vol% steam), the corresponding $^{27}$Al MAS NMR spectrum is given on top. Note the increase in intensity of Al(IV)c and Al(VI).
The effect of steaming and acid treating the parent BEA on the crystallinity was studied with XRD. Steaming of the parent BEA (Si/Al 12) at 673K with a varying time (1-24h) and at various temperatures up to 973K did not result in hardly any loss of crystallinity as measured with XRD, see figure 4. This result indicates the high stability of the material.

Figure 3c. $^{27}$Al MQ MAS NMR measurement of the BEA treated in oxalic acid (#18), the corresponding $^{27}$Al MAS NMR spectrum is given on top.

Note: (IV)c is largely removed.

Figure 4. XRD patterns of parent, steamed and acid leached BEA.
Activity in the acylation reaction

In the acylation of anisole with octanoic acid (0.2 mol/l octanoic acid in anisole at 428K), the parent BEA exhibits an activity of 0.03 l.g\(^{-1}\).h\(^{-1}\), and a selectivity of 80% towards the desired para-acylated anisole.

The effect of steaming the samples on the acylation of anisole with octanoic acid is depicted in figure 5. Steaming the parent zeolite at 673K (38 vol% steam) only leads to a higher activity at steaming times longer than 3 h. After 1-3 h (#1, 2, and 3) the activity is maintained, or even drops slightly, but after 10 h (#4) of steaming the activity increases with 50% and after 24 h (#5) an increase of 140% is observed.

The selectivity drops slightly at steaming times 1-3 h, but increases to 95% after 10 and 24 h of steaming. Increasing the steaming temperature to 723K and the steam content to 72% (#6) results in an increase in the activity of 25%, and a slightly higher selectivity of 88%. At higher temperatures, even up to 973K (#7 and 8), activity is maintained and the selectivity is increased to 98%.

The effect of an acid treatment after steaming on the acylation activity and selectivity is depicted in figure 6. Globally, the acid treatment after steaming does not have a positive effect on the activity, except for the sample that was steamed for 1 h at 673K (#9). Here, an increase in the activity after leaching (HCl) was obtained. For samples steamed in higher steam contents (72%) and high temperatures (923K) the activity even decreased.
Figure 6. The effect of acid leaching after steaming BEA on the activity in the acylation of anisole with octanoic acid, as measured under standard conditions (0.2 mol/l, 428K).

The effect of treating the parent BEA in hydrochloric acid and oxalic acid on the acylation activity and selectivity is depicted in figure 7. Treatment in hydrochloric acid (1M) for 45 or 120 minutes (#15 and 16) results in an increase in the activity with a factor of 2. Treating time does not affect activity between 45 and 120 minutes. Treatment of BEA in 1 M of oxalic acid for 60 min (#17) results in an increase in the activity by a factor of 4. Longer leaching (#18) results in an slightly lower activity compared to the 60 min leached BEA. The selectivity is improved for both acid treatments, especially for oxalic acid where an increase from 80 to 95% is observed.

Figure 7. The effect of acid leaching of BEA on the activity and selectivity in the acylation of anisole with octanoic acid, as measured under standard conditions (0.2 mol/l, 428K).
Chapter 3B

Leaching considerations

It was mentioned in literature (Fang et al., 1995) that enhancement of the performance of zeolites after steaming and acid leaching could be due to migration of the extra framework aluminum into the reaction mixture hereby acting as a homogeneous catalyst. Leaching of the active species was studied by filtering the reaction mixture while hot. This has been done for a steamed BEA (#6), an acid leached sample after steaming (#12, app.1) and a hydrochloric acid leached sample (#15). After hot filtration the reaction did not continue, indicating that no active species had leached from the solid catalyst during reaction conditions. Moreover, a highly charged ion that could possibly act as a homogeneous catalyst, is not expected to leach due to mutual interactions with the negatively charged framework. Besides, in the case of the extraframework species in the pores of the zeolite that could possibly leach under reaction conditions it is more likely that especially these species will be complexed with oxalic acid.

Discussion

In general it can be stated that steaming (longer than 24h, higher temperatures, and higher steam content) and acid treatment lead to an increase in activity and selectivity. For the acid treatment, oxalic acid is the most effective. The BEA structure is not significantly affected as follows from XRD, TEM, BET analysis, and Hg-porosimetry. The only visible changes come from 2D NMR measurements, which give information about the type and coordination of the aluminum in the samples. So any change due to the applied treatment must be one of a very local modification.

The parent BEA used in this study already shows the presence of a significant amount of extraframework aluminum, because the $^{27}$Al MQ MAS spectra of this material are characteristic of strongly dealuminated BEA zeolite (van Bokhoven et al. 2000). This could be explained by an in-situ dealumination process occurring during the calcination step. Especially during the large scale preparation method in industry, this could be the case. It is also possible that not all aluminum is converted to BEA during synthesis.

Steaming the parent BEA at 673K for 1 to 24h does not result in the formation of new aluminum species, but results in an increase in intensity of peaks Al (IV)c, Al(V) and Al(VI) as measured by $^{27}$Al MQ MAS NMR. These peaks are ascribed to extraframework aluminum (van Bokhoven et al., 2000). The decrease in activity at shorter steaming times can be explained by the formation of extraframework aluminum that blocks the active sites. Pores are not blocked, because no change is observed in the surface area characterisation with nitrogen adsorption.
The improvement of both the activity and selectivity after steaming for longer periods than 3 h, cannot be ascribed to the formation of mesopores because TEM and texture analysis did not reveal any changes in surface area, micro- or mesoporosity. Also XRD did not show any significant changes. From the XRF analysis it is demonstrated that the aluminum is not removed from the zeolite after steaming so only the coordination is changed. Indeed, the $^{27}$Al MQ MAS NMR measurements show an increase in intensity of the extraframework aluminum present in all kinds of (4, 5, and 6-) coordinated aluminum species.

The activity is not significantly affected by an acid treatment after steaming. Only in one case an increase in the activity was found. The reason for this increase could be the removal of the extraframework aluminum that was formed on the zeolitic structure by steaming as XRF analysis revealed (figure 2). In this way previously blocked acid sites can become accessible.

Leaching the parent BEA in hydrochloric and oxalic acid resulted in high activities. Especially in the case of oxalic acid, the activity is highly increased while XRF analysis shows an increase in the bulk Si/Al ratio. Apparently aluminum is effectively removed from the zeolite by oxalic acid due to its complexation properties. The $^{27}$Al MQ MAS NMR spectrum reveals a clear decrease of the tetrahedral Al(IV)c peak which was assigned to extraframework aluminum. The intensity of the octahedral peaks seems not to be affected by the acid treatment. There is hardly any pentacoordinated aluminum present, which is completely gone after the oxalic acid treatment. Clearly, not all the octahedrally coordinated aluminum can be removed, and the tetrahedrally coordinated (extraframework) aluminum that is removed is not active in the acylation reaction.

**Origin of the acylation activity**

In literature, it is not very clear whether Brønsted or Lewis sites are responsible for the acylation reaction (see chapter 2). Of course, the ability of strong Brønsted sites to catalyze the acylation reaction is demonstrated by the high performance of the ion-exchange resin Nafion, which does not contain Lewis sites, to catalyze the reaction (see chapter 3, part A). Due to this Brønsted type behaviour, it is easily thought that in zeolite BEA, Brønsted acid sites are responsible for the catalytic activity in the acylation reaction. However, it cannot be ruled out that the aluminum in the zeolite acts as a Lewis type of active site. This type of aluminum either can act as a Lewis acid site or influences the Brønsted acid sites nearby in a positive way.
Chapter 3B

Activity enhancement

The formation of extraframework aluminum results in a higher activity in the acylation of anisole with octanoic acid, because after steaming (>3 h at 673K) the activity is altered and also the intensity of the extraframework aluminum is increased. After acid leaching, the activity is enhanced even more while the amount of tetrahedrally coordinated extraframework aluminum is decreased. It has been suggested by Haouas et al. (2000) that the flexibility of the framework in zeolite BEA is responsible for the activity of the nitration of toluene. According to the authors, a reversible transformation occurs of the tetrahedrally coordinated aluminum into octahedrally coordinated aluminum, which then forms a complex with the reactant. Although no ambiguous assignment of the active species can be made (other than the framework Al(IV)a,b peaks), our results are in agreement with their assignment.

Both steaming and acid leaching lead to the same effect; enhancement of the activity. Two explanations can be given for this enhancement, either additional active sites have been formed or the active sites become more active. Because steaming results in the formation of extraframework aluminum and acid leaching in the removal of extraframework aluminum, it seems more likely that the activity enhancement is due to the formation of additional active sites as a result of a higher accessibility. Probably, some active sites can be blocked by extraframework aluminum. Removal of this ‘site-blocked’ aluminum results in more active sites that are accessible, because by steaming and acid treatment, the aluminum ions become mobile and are transported through the zeolite lattice. The accessibility of the active sites can be increased as a result of clustering of the extraframework aluminum. In this way the local accessibility of the active sites may be enhanced or any negative influence of the tetrahedrally coordinated aluminum on the octahedrally coordinated aluminum is removed. Leaching after steaming, however, does not result in any enhancement because active sites are already made accessible by the steaming procedure.

Selectivity enhancement

The steaming and acid leaching of the parent BEA also results in an enhancement of the selectivity compared to the selectivity of the parent BEA. It is not clear what kind of sites cause the lower selectivity of the parent BEA, but apparently these sites are removed due to these treatments. It is also possible that more selective sites participate or that the selective sites that are already present are more active. Combining these observations with the results from the $^{27}$Al MQ MAS NMR measurements, the selectivity enhancement can possibly be attributed either to the formation of extraframework aluminum or to the removal of extraframework tetrahedral coordinated aluminum.
Conclusions

- The parent BEA, as obtained from Zeolyst International contains large amounts of extraframework aluminum and shows characteristics of strong dealumination.
- Steaming the parent BEA leads to an increase activity at steaming times longer than 3 h (at 673K). This steaming procedure leads to an increase in extraframework aluminum, both tetrahedrally and octahedrally coordinated, as was demonstrated with $^{27}$Al MQ MAS NMR.
- The activity is not significantly affected by an acid treatment after steaming.
- Leaching the parent BEA in hydrochloric and oxalic acid resulted in high activities, especially in the case of oxalic acid. The acid treatment leads to leaching out of the tetrahedrally coordinated extraframework aluminum.
- Steaming and acid leaching do not affect the texture properties of the zeolite, as was demonstrated with nitrogen adsorption and TEM measurements.
- After hot filtration the reaction did not continue, indicating that no active species will leach from the zeolite during reaction conditions.
- It is possible that the nature of the activity in the acylation reaction is correlated with the presence of octahedral coordinated aluminum.
- The nature of the (enhanced) activity in the acylation reaction after steaming and acid leaching is probably correlated with the higher accessibility of the active sites.

Acknowledgements

Dr. J.A. van Bokhoven of the Utrecht University is gratefully acknowledged for fruitful discussions and for performing the $^{27}$Al MQ MAS NMR measurements. Dr. A.P.M. Kentgens of the University of Nijmegen is also acknowledged for the help with the $^{27}$Al MQ MAS NMR measurements. Dr. P.L.J. Kooyman of the National Centre for High Resolution Microscopy, Delft University of Technology, the Netherlands is kindly acknowledged for performing the electron microscopy investigations. J. Groen and P. Boeser from Delft University of Technology are kindly acknowledged for performing the texture analysis measurements. J. Padmos and N. van der Pers, also from Delft University of Technology are kindly acknowledged for performing respectively XRF and XRD measurements. Karen de Lathouder is gratefully acknowledged for her contribution in this chapter.
References


Solid acid coated monoliths – preparation and characterization

Summary

A literature overview is given of the preparation and application of Nafion and zeolite coatings. The main application of Nafion coatings is in electrochemistry. The Nafion membrane is also used as a gas dryer for selective removal of water. Zeolite coatings are mainly applied in membrane applications for gas separations and for the integration of separation and catalysis. The main preparation techniques are dip-coating, *in-situ* synthesis and extrusion of the carrier with the zeolite.

Several methods were developed to apply a solid acid catalyst on a monolith. Dip-coating cordierite and silica monoliths in a Nafion-, Nafion/silica- or BEA-containing dip-mixture proved to be relatively simple and satisfactory coating techniques. The methods result in a homogeneously distributed coated structure with loadings of 2-3 wt% Nafion, 3-15 wt% Nafion/silica composite, or 6-8 wt% BEA. The synthesis of a monolith support with a Nafion/silica composite showed a strong dependence of the loading on the amount of Nafion in the dip-mixture. The *in-situ* synthesis of BEA in the presence of a carrier resulted in blocking of the monolithic channels, and is not under control. In the dip-coating technique, the amount of BEA is good and easily controllable. Furthermore, it is not necessary to adapt the zeolite synthesis formulation for coating applications, so an already optimized zeolite can be applied.
Chapter 4

Introduction

For the application of structured reactors (like monoliths) in heterogeneous catalysis, the catalyst has to be integrated with the reactor. This can be done by coating (fixing) the catalyst on the walls of the structure. In the acylation reaction (chapter 2) and the esterification reaction (chapter 6) two types of catalysts have been studied in their performance as a solid acid catalyst, namely Nafion (as an ion-exchange resin), and BEA zeolite (as a microporous aluminosilicate). With Nafion also composites with silica can be prepared. In chapter 3 an extensive overview is given about the application and preparation of Nafion/silica composites in catalysis.

Literature review

Extensive research has been done in order to develop coatings of solid acid materials on the surface of a support. In this chapter an overview is given of the literature discussing the development of ion-exchange resin- and zeolite coatings on a support. Applications of these solid acid coatings are included, too.

Nafion coatings

In this part the widespread application of Nafion-coatings is reviewed. The preparation of these coatings is in all cases similar, namely by dip-coating the structure in a solution of Nafion in a mixture of lower aliphatic alcohols. This solution is commercially available from DuPont. The preparation of the thin films of perfluorocarbon ionomer dispersion by this evaporative coating technique has been introduced by Grot (1984) and is still being improved, especially by Dow workers (Aikman Jr, 1998; Martin et al., 1988; 1998a; 1998b; Moore and Martin, 1986).

Nafion coated electrodes have been extensively investigated for their application in electrochemistry (for example Weber et al., 1986; Whitely and Martin, 1987; Zen et al., 1998; Kawada et al., 1996; Rubinstein and Bard, 1980; 1981; Moore and Martin, 1986; Martin and Dollard, 1983; Mello and Ticianelli, 1997). Since the discovery of the perfluorinated ionomer membrane as a permselective membrane for the chlorine-alkali process in the late sixties, these membranes have become increasingly important. Coating glassy carbon electrodes with Nafion results in extremely sensitive electrochemical sensors for organic cations in a technique called ion exchange voltammetry. A poly perfluorosulfonate ionomer, like Nafion, is a strong cation exchange polymer, and it prefers to incorporate large hydrophobic cations
rather than inorganic cations, while rejecting anions (Whitely and Martin, 1987). For instance, uric acid can selectively be determined by square-wave voltammetry with pre-anodized Nafion-coated glassy carbon electrodes (Zen et al., 1998). Monitoring the concentration of uric acid is very important as many diseases, like gout, are caused by an inconsistency of the uric acid concentration (the primary product of the human purine metabolism).

Besides for detection purposes, Nafion coated electrodes are also used for regeneration of metal based redox reagents which normally are used only once in the chemical process industry. By regeneration, the redox reagents can be reused for further chemical processes (Fedkiw Jr., 1995).

Another reason to coat electrodes with Nafion, is that the polymer dip-coated graphite electrodes can be made very resistant to chemical attack even by strong oxidants at elevated temperatures. In this case the Nafion itself is not electroactive, but electroactive molecules (like for instance Ru(bipy)$_2^{2+}$) are later attached to the polymer by electrostatic binding (Rubinstein and Bard, 1980). Nafion coatings are also applied to other carrier types than electrodes, like aluminum, for inhibiting corrosion that normally occurs in the presence of chloride ions and dissolved oxygen. This inhibition is believed to result from the unique chloride ion rejection properties of the Nafion film (Kinlen and Silverman, 1983).

Nafion can also be used as a gas dryer, for continuous and selective removal of water from gaseous samples. This application was developed by Perma Pure more than twenty years ago (Perma Pure Inc., 2000), and the principle is that when gas containing water vapor passes through Nafion tubing, the water is absorbed and permeates through the walls of the tubing (figure 1), where it is removed by a sweep gas.

![Figure 1. The principle of the Perma Pure Nafion Dryer.](image)

The main advantages of this system compared to other dryers (like condensors, desiccant and permeation dryers), is that Nafion is highly resistant to chemical attack (only metallic sodium is known to attack it) and it exhibits a highly selective and quick absorption. The gases that are totally retained are atmospheric gases (N$_2$, O$_2$, H$_2$, Ar, He), oxides (CO, CO$_2$, SO$_2$, SO$_3$, NO$_x$), halogens (Cl$_2$, F$_2$, HCl, HF, HBr), sulfur compounds (H$_2$S, COS), organics (aldehydes, THF, cyanides, esters), inorganic acids (HNO$_3$, H$_2$SO$_4$) and the simple hydrocarbons. The compounds that are lost by this membrane are the polar organics (DMSO, alcohols, organic
Chapter 4

acids, ketones), ammonia, and amines. The disadvantage is the limited thermostability (up to 160°C).

In catalysis, Nafion membranes can be used to combine catalytic and separation processes. The use of Nafion as a support material for supporting a metallic catalyst through incorporation of metal ion complexes has also been studied. Reduction of these complexes (like palladium or platinum) results in incorporation of the metal into the Nafion sheets. Due to the high costs of Nafion, a cheaper variant of a support can also be prepared by fabricating a composite membrane of a thin layer of Nafion on a porous PTFE (‘Goretex’, W.R. Gore & Assoc.) support (Hodges et al., 1990). The supported platinum and palladium metal systems prepared in this way were tested in the hydrogenation of cyclohexene, and resulted in higher reaction rates than those of commercially available catalysts (TON of more than 6000). These catalysts could be regenerated many times (Hodges et al., 1990).

Nafion/silica composite coatings

The preparation and application of Nafion/silica composites for slurry reactor configurations has been described in chapter 3. The preparation of a Nafion/silica composite as a coating on a monolith has not been described before in literature. By mixing a silica source with Nafion prior to the (sol-gel) coating, the composites can be prepared on the surface of a monolithic carrier. Advantages of the slurry type composites can in this way be combined with the advantages of a monolith (chapter 1). Also the porosity of the catalyst can be tuned by the addition of CaCO₃. By adding this salt to the synthesis mixture of the slurry catalyst ‘dual porosity’ is introduced according to Harmer et al (1996). After acid treatment with HCl the CaCO₃ will decompose into CaCl and CO₂ leaving large pores in the Nafion/silica network. The size of the pores is influenced by the size of the CaCO₃ clusters, in this way controlling the porosity.

Zeolite coatings in general

The preparation of zeolite coated structures is studied for various purposes. Two main applications are the use of membranes for gas separations and the integration of separation and catalysis. Also the development of a catalytic membrane reactor, in which both applications are combined, is studied extensively (Jansen et al., 1998).
For the development of zeolite coatings mainly three techniques can be considered.

1. The dip-coating technique uses a binder to attach an existing zeolite on the surface of the structure. The support is simply immersed in a suspension of the zeolite crystals in a solvent along with a binder and other additives.

2. In the case of \textit{in-situ} synthesis, the zeolite synthesis is performed in the presence of this support. Also the monolithic structure can be partially transformed into zeolites (Lachman and Patil, 1989).

3. Extrusion of a zeolite into the desired shape (Lachman \textit{et al.}, 1986a; 1990) can result in a high content of catalyst in a support. However, it is likely that active sites of the catalyst are less accessible. Comparing the activity of a silicalite dip-coated monolith with an extruded monolith in the conversion of methanol, a much lower activity is observed for the extruded system, due to blockage of catalyst active sites (Patil and Lachman, 1988). By coating a macroporous carrier with a thin layer of the microporous zeolite these problems are circumvented.

Various types of support can be considered for the preparation of zeolite coatings. Shapes like spheres (van der Pui, 1997), foams (Oudshoorn, 1998), or monoliths (Oudshoorn, 1998; Lachman and Patil, 1989; Patil and Lachman, 1992) have been studied, and different materials like cordierite (Oudshoorn, 1998; Lachman and Patil, 1989; Patil and Lachman, 1992), alumina (van der Pui, 1997), metal (stainless steel) (Oudshoorn, 1998; Clet \textit{et al.}, 1999) and carbon (Vergunst, 1999) were studied. Naturally, the chemical and physical properties of the supports have to be considered. When preparing a zeolite coating a good wetting of the support with the zeolite (synthesis) mixture is necessary, leading to the need for a hydrophilic support (Jansen \textit{et al.}, 1998).

\textit{Dip-coated zeolite coatings}

Applying the zeolite crystals by a dip-coating technique results in a coating consisting of randomly oriented zeolite crystal layers useful for adsorption and catalysis purposes (van Bekkum \textit{et al.}, 1994). The dip-coating technique described here is generally the same as described by Lachman \textit{et al.} (1986a; Lachman and Golino, 1987). The support is immersed in a suspension of the zeolite crystals in a solvent containing a binder and other additives followed by evaporation of the solvent by drying and calcination. Because various zeolites are commercially available, this seems to be a relatively simple coating method, as synthesis issues concerning the zeolite itself do not need to be considered. A binder is added to the suspension for better adherence of the zeolite crystals onto the support. Without this binder the deposited crystals will only bind to the surface by van der Waals forces. As a binder, colloidal silica can be used (Patil and Lachman, 1988). In the case of coating a zeolite onto a
cordierite structure, bonding between the zeolite coating and the support can be improved by selectively leaching of the cordierite by an acid treatment leaving a silica rich support. In this case, strong bonds can be formed between the silica rich support and the binder (Patil and Lachman, 1988). In the study of Patil and Lachman (1988) the effect of zeolite and binder content on MFI zeolite coatings was studied. In the case of MFI an optimum was achieved with a dip-coating mixture containing 30-40 wt% of MFI. Higher loadings led to non-uniform and inconsistent loadings, due to a too viscous mixture. The loading of the zeolites with strong adhesion, increased as the (relatively high >10 wt%) binder content in the dip-coating mixture increased. A disadvantage of using a binder is that a risk exists of blocking the active sites of the catalyst. In the study of Patil and Lachman (1988) the activity of the zeolite coating in the conversion of methanol decreased as the amount of binder increased. To overcome this problem, the amount of binder should be minimized. Additionally, a temporary binder can be added for binding the catalyst onto the support before calcination takes place and the zeolite is fixed by the permanent binder (Lachman and Golino, 1987; Patil et al., 1992). As a temporary binder, organic (cellulose) compounds can be used. Also surfactants can be added, to provide a good dispersion of the zeolite in the dip-mixture or reduce apparent viscosities. These components are either burnt or decomposed at a lower temperature than the calcination temperature, but give initially a stability to the coaltlayer before the final fixation takes place. The preparation of a zeolite coating with a dip-coating technique is described in literature mainly for MFI on a conventional ceramic monolith as an application in automotive catalysis (Patil et al., 1992; Beausiseguer et al., 1994). For membrane purposes MFI is best applied by in-situ synthesis (Jansen et al., 1998), but also seeding and further growing has been used to obtain a crack-free, strongly adhering, continuous MFI layered membrane with a thickness of 1-2.5 μm (Vroon, 1995).

**In-situ grown zeolite coatings**

Growing the zeolites directly on the surface of the carrier, is a one-step, binderless method which already has been reviewed in literature (Jansen et al., 1998). Also numerous patents have been published describing the growth of a zeolite on a substrate. In literature, mainly the preparation of directly grown MFI zeolite coatings is reported (Jansen et al., 1993; van der Puil et al., 1999; Antia et al., 1997; Antia and Govind, 1995a; Lai and Gavalas, 1998; Kiricsi et al., 1997; Vroon, 1995). Examples are the synthesis of MFI-type zeolite coatings on cordierite monolithic supports (Grasselli et al., 1994), on stainless steel supports (Geus et al., 1998) and the preparation of a thin layer of zeolite on a substrate by dipping this substrate in the synthesis mixture prior to synthesis (Suzuki, 1987; Patil and Williams, 1993). Also the synthesis of a zeolite membrane from an amorphous dry gel under the vapors of triethylamine, ethylenediamine and water is reported. This technique is called the vapor-phase transport.
(VPT) method (Nishiyama et al., 1996). The advantage of a directly grown zeolite layer compared to the dip-coated support, is that in the former case total coverage of an oriented zeolite crystal layer can be achieved. This can be very relevant in, for example, membrane applications.

The *in-situ* synthesized zeolite coating can be prepared by immersing the support in a zeolite synthesis mixture or in a liquid that only contains template. This latter method can only be applied onto a silica-containing support which acts as a source for the zeolite synthesis. When applying this *in-situ* synthesis method (at least for the MFI synthesis) it has been proven that the composition of the synthesis mixture, the temperature and the duration are of extreme importance for the resulting thickness of the zeolite coating. Also the orientation of the zeolite crystals can be influenced by the composition of the synthesis mixture. This orientation can be important when considering the possible application of the zeolite coating. When oriented zeolite growth is achieved, the crystals can be grown laterally (‘standing’ on the surface) or axially (‘lying’ on the surface) oriented on a surface, resulting in a coating which is most suitable for respectively catalysis or membrane purposes. For MFI type of coatings it has been shown that the concentration of the nutrients influences the orientation of the crystals (Jansen, 1993). To control the zeolite coating by means of synthesizing the zeolite in the presence of a support an understanding of the general theory of heterogeneous nucleation and crystallization is needed (Jansen et al., 1994). However, in spite of all the research that already has been done on this subject, these nucleation and growth processes of the zeolite crystals remain still poorly understood and further research is essential.

For application in catalytic processes, mainly MFI zeolites are grown onto the support (van der Puil et al., 1999; Antia et al., 1997; Antia and Govind, 1995a; Kiricsi et al., 1997). The catalytic applications in which a MFI zeolite is directly grown on a monolithic support can be found in the conversion of methanol and *n*-hexane to gasoline-range hydrocarbons. In these studies, MFI zeolite was grown on a cordierite monolithic structure and catalyst loadings up to 31% were obtained (Antia and Govind, 1995a; 1995b; Antia et al., 1997). Other applications are the development of a MFI and mordenite coated stainless-steel metal gauze support as a NO reduction catalyst for exhaust gas treatment (Ito et al., 1996) and a MFI zeolite disc for the alkylation of toluene with methanol (Kiricsi et al., 1997).

An example of the application of BEA grown onto a support is a reactive distillation column packing for the synthesis of ETBE from ethanol and isobutene. Synthesis of BEA on a support resulted in zeolite coverages of 9-14 g.m⁻² of support. In a monolith with a channel diameter of 2 mm this corresponds to a zeolite loading of ~ 30 kg.m⁻³ of packing. When comparing the performance of this synthesized BEA coating with commercial BEA powder in the synthesis
Chapter 4

of ETBE, it was found that the turn-over numbers of the BEA powder was four times higher than the BEA coating; the selectivity was comparable (Jansen et al., 1998; Oudshoorn et al., 1999).

Apart from catalytic applications, the major emphasis of research in the area of zeolite coating synthesis is on membrane applications. In the separation of gases, zeolites have shown good performance (Vroon, 1995; van de Graaf, 1999), due to their crystalline microporous structure (den Exter et al., 1996; Jansen et al., 1998). Here, the challenge lies in the crystallization of a thin, continuous layer without cracks and pinholes. Also the orientation of the zeolite crystals is important as it might favor the permeability due to the anisotropy of some zeolite pore structures (Jansen and Coker, 1996).

Experimental

Materials

The zeolite coatings were prepared on a ceramic monolithic substrate. The macroporous ceramic monoliths (see chapter 1) studied consisted either of pure silica (SiO₂) or cordierite (2Al₂O₃.5SiO₂.2MgO) and were kindly provided by Corning Inc. The length of the monoliths used for coating experiments, unless otherwise mentioned, is 5 cm. The diameter of the cordierite monoliths is 4.3 cm, and the diameter of the silica monoliths 2.5 cm. The cell density is in both cases 62 cells.cm⁻² (400 cpsi), the dimension of the channels 1.08 x 1.08 mm, and the wall thickness 165 μm.

For the Nafion coating experiments a 5 wt% Nafion solution (SE-5012) in a mixture of lower aliphatic alcohols and 10% water was purchased from DuPont.

The BEA zeolite, with a Si/Al ratio of 37.5, was purchased from Zeolyst (CP 811E-75), the Na₂O content was 0.05wt% and the surface area 650 m²/g₉ₑₒₙₑᵢₑ. The particle size of the zeolite crystals is in the range of 15-20 nm, as measured by TEM. On the TEM picture the BEA crystals are found in large clusters. A particle size distribution of 5-20 μm was measured in a mixture of BEA crystals in water (after ultrasonic treatment) on a Malvern Particle Sizer 2600D by means of laser diffraction. Apparently, the BEA zeolite is agglomerated during the measurement and as a result only the size of the clusters is determined. Whether this agglomeration takes place during or after synthesis, remains unclear.
Other materials used for the preparation of the catalytic coatings are nitric acid (65%), purchased from Merck-Schuchard. Butyl acetate was purchased from Acros, Ludox AS40 (a 40% suspension of colloidal silica in water) and TMOS were purchased from Aldrich, nitrocellulose moistened with 35% ethanol was purchased from Fluka, and Teepol, an alkylaryl sulphonate type of surfactant from Shell was purchased from Chemproha. Ammonium nitrate (\(\text{NH}_4\text{NO}_3\)) was purchased from Baker. Water glass was obtained from Chemproha.

For the in-situ growing of BEA zeolite on the monoliths, Aerosil 200 from Degussa, sodium aluminate (41 wt% Na$_2$O, 54 wt% Al$_2$O$_3$) from Riedel-de Haën, and tetraethylammonium hydroxide (TEAOH) from Aldrich were used.

### Characterisation techniques

The catalyst loading of a monolith was determined by measuring the mass prior to and after each preparation step, using the following formula:

\[
\Delta W_{\text{coat}} = \left\{ \frac{W_{\text{coat}} - W_0}{W_0} \right\} \times 100\% \tag{1}
\]

In the case of the Nafion coatings the catalyst loading on the monolithic substrates was determined by thermal analysis (TGA-DSC). During these measurements the weight of a sample and the energy released or absorbed (in the case of, respectively, exothermic and endothermic reactions) is measured as a function of temperature or time, giving information about the decomposition temperature of the sample and the percentage of decomposing material. In this way the Nafion content of coated monoliths can be calculated, using formula [1]. The measurements were performed on a STA 1500H thermobalance from Thermal Sciences in a flow of synthetic air (21% O$_2$ in N$_2$). Samples of approximately 40 mg were heated at a constant rate of 5K per minute.

**Elemental analysis** (XRF) was performed on a Philips PW1480.

**Texture analysis** of the substrates prior to and after coating was done by nitrogen-physisorption and mercury-porosimetry. The nitrogen-physisorption measurements (for micro- and mesopore analysis) were carried out with a Quantachrome Autosorb-6P at 77K. Pore volume and pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) model. The mercury-porosimetry measurements (for meso- and macropore analysis) were performed on a Carlo Erba Porosimeter 2000.
Chapter 4

Surface morphology of the samples was studied using scanning electron microscopy (SEM). This was done on two types of microscopes. The Nafion coatings were studied on a JEOL JSM-6400 F equipped with a Pioneer EDX, and the zeolite coatings were studied on a Philips XL-20.

Identification of the crystalline phases by X-ray diffraction analysis (XRD) was done on a Philips PW1840 diffractometer, equipped with a PW 1830 generator.

General coating techniques

First, the pre-treatment of the support was studied. Subsequently, the catalytic material was applied in several ways. The monoliths were either dipped into a mixture of a solvent with catalyst particles (dip-coating) or, in case of a zeolite, the catalyst was grown onto the support (in-situ growing). After coating the monolith, this coated substrate was dried and ion-exchanged, and, in the case of a zeolite coating, calcined to convert it into a catalytically active configuration.

Pre-treatment of the monoliths

For the dip-coating of monoliths with Nafion and BEA zeolite, the pre-treatment of the monolith substrates was done by calcining the structures at 1273 K (3 h) to remove any (organic) contaminations from the support. To investigate whether the composition and pore structure could be influenced by an acid treatment, the influence of leaching the bare cordierite monoliths in 1.5M nitric acid for up to 4 h at 368 K was studied. Prior to the coating of the cordierite structures with a Nafion/silica composite layer, the bare structures were dried for 12 h at 383 K.

For the in-situ growing of BEA zeolite on a cordierite monolithic structure, the monoliths were leached in 1.5 M nitric acid at 368 K for 4 h in order to increase the SiO₂-content of the cordierite. Subsequently, the monoliths were washed with millipore water and dried at 383 K for at least 12 h. Then, unless mentioned otherwise, the monoliths were refluxed in a 30 wt% tetraethylammonium hydroxide (template) solution for 4 h to improve the conditions for crystal growth on the monolithic surface (van der Puil, 1997). After this impregnation of the support with the template, the solution was decanted from the monoliths and no additional washing was carried out.
Chapter 4

Nafion dip-coating

Dip-coating the monoliths with Nafion was performed by immersing the monoliths directly in the Nafion solution as received from the supplier. After dipping for approximately 30 min, the monolith is removed from the dip solution, excess liquid is shaken out and the channels are cleared with air. In this study, mainly cordierite monoliths with a cell density of 62 cells.cm$^{-2}$ were coated, unless mentioned otherwise. The Nafion coated monoliths were dried overnight at room temperature, while rotating in a horizontal position to avoid a non uniform distribution of Nafion over the monolith and subsequently dried overnight at 383K.

To convert the Nafion coated monoliths into the active form, the monolithic catalyst has to be exchanged in 25wt% nitric acid. In literature, several procedures for activating Nafion were found (Harmer et al., 1996; Olah et al., 1986), where activation was carried out at different temperatures and times. To investigate the effect of these procedures, the Nafion-coatings were acidified at 293K (room temperature) and at 348K during 4 h or 15 h (overnight). After this activation step, the Nafion coatings were washed with demineralized water (3-5 times until the solution was pH-neutral). After this activation treatment and prior to the catalytic activity test, the monolith is dried at 383K for 15h (overnight).

The effect of a silica layer prior to the Nafion coating, was studied by dip-coating the cordierite monolith sample in Ludox AS40 (colloidal solution of silica in water) and tetra methyl ortho silicate (TMOS) solution. The length and diameter of the monolith samples in this study were both 1 cm. After immersing in the silica solution, the samples were dried at room temperature and calcined for 4 h at 723 K (heating rate 5 K/min).

Nafion/silica composite dip-coating

Synthesis of a Nafion/silica composite layer on a monolith was performed by the same sol-gel method as presented by Harmer et al. (1996) and also as used in chapter 3 for the development of Nafion/silica composites. In both synthesis procedures, gelation is achieved by altering the pH, but the way this pH change is obtained changes; the difference is that in the case of the composites, gelation was achieved by addition of acid or base, and in the case of the coatings gelation is induced by increasing the temperature and hereby removing the solvent. The monolith was dip-coated in a mixture of a silica containing material and the 5 wt% Nafion solution in water and alcohol. As a silica source Ludox AS40 (a 40 wt% colloidal silica solution in water), tetramethyl orthosilicate (TMOS, Si(MeO)$_4$), or water glass (a sodium silicate solution) was chosen. While preparing the dip-mixture (before performing the dip-coating) fast gelation has to be prevented. To achieve this, the pH of the 5 wt% Nafion
solution, which has an acidic character (pH 2) has to be altered before mixing with the Ludox (pH 9) and waterglass (pH 11). The pH of the Nafion solution is increased by adding a 0.4 M NaOH solution in a volume ratio of 2.5 : 1. The TMOS is hydrolysed by mixing with water and 0.04 M HCl in a ratio of 75 : 10 : 1, which resulted in a mixture with a pH of 3. Because this pH is compatible with the pH of the supplied Nafion solution, no additional NaOH is necessary. After mixing, the monolith was immersed for 60 min in the mixture.

After removing the monolith samples (all with length and diameter of 1 cm) from the dip-mixture, excess liquid was removed with air, dried at room temperature for at least 12 h, and subsequently dried at 368 K for at least 48 h (heating rate of 0.1-0.5 K/min). Like the Nafion-coatings, this Nafion/silica composite coating has to be activated with an acid treatment by washing with 3.5 M HCl for four times, and next in 25 wt% HNO₃ for 16 h (overnight). After activation the monolith was dried at 383K for 24 h.

Besides the variation of the silica source, the time of dipping was also varied between 15 and 120 min. The composition of the silica/Nafion dip-mixture was also varied to investigate whether it is possible to control the amount of Nafion in the prepared monolithic catalyst. Finally, a coating was prepared in which (5 wt% or 20 wt%) CaCO₃ was added to the dip-mixture to check the possibility of tuning the coating porosity. Following gelation, the CaCO₃ particles become entrapped in the silica matrix. Acid treatment of the dried gel dissolves out these particles, generating calcium chloride and carbon dioxide. The decomposition of the carbonate introduces large pores (Harmer et al., 1996).

**BEA dip-coating**

Dip-coating the monoliths with BEA zeolite was performed by preparing a mixture of BEA crystals, a solvent, a binder and optionally some extra components such as surfactants. The solvent was either butyl acetate or demineralized water. Dip-solutions with various compositions were prepared. In the case of butyl acetate the amount of BEA zeolite was varied between 5 and 15 wt%, and in water this amount was varied between 5 and 25 wt%. Colloidal silica (Ludox AS-40, a 40 wt% suspension of colloidal silica in water) was added to the dip-mixture as a binder. The standard amount of Ludox added to 100 ml of solvent, was 1 wt% of the total amount of solids for 20 wt% BEA in solvent (which corresponds to 0.6 g of Ludox). To study the effect of the binder, dip mixtures were prepared in water without binder and also with 5 times the standard amount of binder. As a temporary binder, 1.2 g nitrocellulose, moistened with 35% ethanol, was added to the mixtures prepared with butyl acetate for binding of the zeolite crystals before calcination. This amounts to 5 wt% compared to the amount of BEA zeolite. To study the effect of nitrocellulose also a coating was made
without this temporary binder. 1.8 wt% Teepol (0.3 g for the given amount of BEA) was added as a surfactant to disperse the zeolite crystals in water. The effect of this surfactant was studied by varying the amount of Teepol added from 0 till 0.3 g. To obtain a homogeneously dispersed mixture, the slurry was well mixed with a high-shear mixer (UltraTurrax T25 from IKA Labortechnik) for approximately half a minute at 13,000 rpm. Next, the monoliths were dipped into the mixture for three min. Excess liquid was removed with pressurized air. After drying the BEA dip-coated monoliths for one night at room temperature, while rotating in a horizontal position, the monoliths were dried in air by increasing the temperature by 1K/min to 473K and calcined at 673K in air (heating rate 10K/min) for 4 h. To activate the BEA zeolite coated monoliths, ion-exchange was performed in 1M ammonium nitrate (NH₄NO₃) at 323K for 15 h (overnight). After washing the zeolite coatings with demineralized water, calcination was performed at 723K (4 h), with a heating rate of 5K per minute. During this calcination step ammonia is liberated, leaving the protons as active sites on the surface of the zeolite structure. To investigate the adhesion of the BEA zeolite onto the support, the coated monoliths were placed in an ultrasonic water bath, for 15 minutes. After this, the samples were weighed in order to determine any possible weight loss.

*In-situ growing of zeolite BEA on a substrate*

The *in-situ* synthesis of BEA zeolite was based on the study of Van der Puil (1997) and Oudshoorn (1998). The synthesis mixture was aged for 4 h at room temperature while stirring at high speed. As a silica source Aerosil 200 was used as the primary building unit (SiO₂) of the zeolite crystal. The AlO₂⁻-source is an important parameter because it determines the number of catalytic sites (through the Si/Al ratio) of the zeolite. As an AlO₂⁻-source sodium aluminate (41 wt% Na₂O, 54 wt% Al₂O₃) was used. Sodium hydroxide was used to bring the reactants into solution and to achieve a homogeneous mixture by altering the pH. As organic templating agent tetraethylammonium hydroxide (TEAOH) was used. The molar ratio in which the oxides were used was 23.6 SiO₂ : 1.0 Al₂O₃ : 1.87 Na₂O : 3.88 TEAOH : 156 H₂O.

The synthesis procedure was carried out by adding the 35 wt% TEAOH-solution to the Aerosil 200. After stirring this mixture for 20 minutes, the NaOH-solution was added and the mixture was subsequently stirred for 5 minutes. For better mixing conditions a magnetic stirrer is then added to the PE-bottle and after the mixture was placed in a shaking-tray for 3.25 h, the NaAlO₂ solution was added slowly (in about 15 minutes). The mixture was replaced in the shaking-tray for two days. After that the (non-viscous) synthesis mixture was decanted into 35 ml teflon inserts of stainless steel autoclaves in which the pre-treated monoliths were placed. The autoclaves were heated while rotating at 428 K for 25 and 50 h. After synthesis, the autoclaves were cooled to ambient temperature in air. The synthesized batches were washed with demineralized water and subsequently dried at 393 K for 8 h.
(heating rate: 10 K/min). Finally, calcination was performed at 823 K for 12 h (heating rate: 1 K/min).

Results and discussion

In the following sections the results of the preparation and characterization of the coated monoliths will be presented. First, some information will be given about the bare monolithic structures and the pre-treatment of these structures. Next, the dip-coating with Nafton and BEA, and the in-situ synthesis of BEA zeolite will be presented.

Bare monolithic structures

The morphology of the bare monoliths was studied with SEM. The SEM photographs are depicted in figures 2a-c. Figure 2a represents an overview of the bare cordierite structure, in which the walls of the channels are clearly visible. The macroporous structure is also clearly visible (figures 2a and b). The pores that are visible with SEM are approximately 1 to 20 µm in diameter. Figure 2c shows the typical cordierite stacked structure.

The results of the texture analysis (mercury-porosimetry and nitrogen-physisorption) measurements on the bare silica and cordierite monoliths are presented in table 1.
Table 1. Texture analysis measurements of bare monoliths.

<table>
<thead>
<tr>
<th>Material</th>
<th>Nitrogen-physisorption</th>
<th>Mercury-porosimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ml/g)</td>
<td>S$<em>{\text{BET}}$ (m$^2$/g$</em>{\text{monolith}}$)</td>
</tr>
<tr>
<td>Silica</td>
<td>0.12</td>
<td>89</td>
</tr>
<tr>
<td>Cordierite</td>
<td>--</td>
<td>≤ 4</td>
</tr>
</tbody>
</table>

The pore size distribution of both materials obtained by mercury porosimetry are shown in figure 3. In the meso- and macro region (mercury-porosimetry) the silica monolith has slightly smaller pores, and a narrower pore size distribution than cordierite. The pore size values of 0.5-5 μm as determined by mercury-porosimetry are in agreement with the macropores that are visible with SEM. On the micro- and meso scale (nitrogen-physisorption) the silica monolith shows a relatively high surface area (89 m$^2$/g$_{\text{monolith}}$) compared to the cordierite, due to the presence of micropores. The presence of micropores can also be found in the shape of the isotherm of the silica monolith, as this shape represents a combination of the types I and IV according to the Brunauer classification (Scholten, 1993). From the similarity with type IV also mesoporosity is shown.

Figure 3. The pore size distribution of the cordierite and silica monoliths from mercury porosimetry.

Pre-treatment of the monolithic substrates – acid treatment

To examine the influence of leaching the bare cordierite and silica monolithic structures prior to coating, the elemental composition of the treated cordierite and silica monoliths was studied as a function of leaching time. The results of the contents of the major components are depicted in figure 4.
For the cordierite monolith the silica content increases compared to the other major elements. The silica monolith consists mainly of pure SiO₂, from these measurements it seems that the composition of this type of monolith is not influenced by the acid treatment. In the case of the cordierite monolith, the content of alumina (Al₂O₃) and magnesium oxide (MgO) decreases respectively from 34.4 to 27.2 wt% and from 12.9 to 9.8 wt%. From this selective leaching of alumina and magnesium oxide, a silica-rich monolith resulted; the silica content increases from 48.6 to 56.0 wt%. This was also demonstrated by Elmer et al. (1975).

Considering the contents of the minor components of both type of monoliths, see figures 5a and b, it is clear that the silica monolith contains mostly alumina, magnesium oxide, iron oxide and sulphate. Both the alumina and magnesium oxide contents decrease during leaching, but the contents of the other components hardly change. For cordierite, the minor
components are the oxides of the elements titanium, sodium, calcium and iron. Their content hardly changes during leaching. Other elements, if present, have contents of less than 0.06 wt%. The changes in content for all these elements are within the standard error for this analysis technique.

The results of the acid treatment of cordierite as a function of the leaching time did not have any effect on the surface area characteristics, as measured by mercury-porosimetry. All cordierite samples were leached at 293K and at 368K, and leaching time varied between 1 and 7 h, showed a similar pore volume of 0.15-0.17 ml/g and pore radius range of 0.6-6 μm. Compared to the surface area characteristics of the bare cordierite as received, namely a pore volume of 0.15-0.20 ml/g and a pore radius range of 0.5-5 μm, no significant effect was demonstrated on the surface area characteristics.

According to the literature (Shigapov et al., 1999) a surface area up to 255 m²/g_{monolith} can be obtained by acid treatment of the cordierite monoliths. This a value 500 times higher than the surface area of the original cordierite. In this study, however, no increase in surface area was seen at all. Apparently, the type of acid treatment is of importance as the samples in this study were leached in 1.5 M nitric acid at 368 K and the samples from the literature were boiled in 10 M hydrochloric acid.

Pre-treatment of the monolithic substrates – Additional silica layer

A layer of silica was deposited onto the monolithic structure prior to the Nafion coating, as described in the experimental part of this chapter, and subjected to nitrogen-adsorption. The results are presented in table 2.

<table>
<thead>
<tr>
<th>Silica source</th>
<th>Loading (wt%)</th>
<th>total BET surface area (m²/g_{total})</th>
<th>silica BET surface area (m²/g_{Silica})</th>
<th>pore volume (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ludox</td>
<td>16.5</td>
<td>19</td>
<td>115</td>
<td>0.04</td>
</tr>
<tr>
<td>TMOS</td>
<td>8.1</td>
<td>10</td>
<td>123</td>
<td>0.01</td>
</tr>
</tbody>
</table>

By dip-coating the cordierite, which possesses no micropores, with Ludox AS40 and calcination a microporous oxide layer is deposited on the monolithic carrier. In this way the properties, the porosity, and the surface area of a macroporous material can be altered prior to
coating with a catalyst. Dip-coating the cordierite with TMOS leads to a higher surface area compared to the bare cordierite, but with a much lower value than the silica layer obtained from Ludox. The surface area of the silica layer can be calculated using the loading of the monolithic supports, assuming that the cordierite does not contribute to the BET surface area. This results in a surface area of 115 $\text{m}^2/\text{g}_{\text{silica}}$ for the silica layer obtained from Ludox, and a value of 123 $\text{m}^2/\text{g}_{\text{silica}}$ for the silica layer from TMOS.

The isotherm of the silica layer made from Ludox shows mainly mesopores, and no micropores at all. The isotherm of the silica layer made from TMOS shows that the layer consists mainly of micropores and only some mesopores in a very broad range.

**Nafion coating of the monoliths**

After coating a cordierite monolith with a cell density of 62 cells.cm$^{-2}$ with Nafion, the Nafion loading was determined by thermal analysis (TGA-DSC). A typical example of a TGA measurement is shown in figure 6.

At temperatures up to 400 K the weight of the samples decreases due to the desorption of water and other physisorbed compounds. At 550 K the Nafion resin starts to decompose, resulting in a sharp decrease in weight. From this decrease the Nafion loading was calculated. A 2-3 wt% loading was determined for all Nafion coated monoliths that were dipped one time into the Nafion dip-mixture.
Texture analysis

Coating a cordierite and a silica monolith with a Nafion layer results in a lower pore volume than bare monoliths, see figure 7 for the pore volume distribution obtained from mercury-porosimetry. The bare cordierite material shows an average (macro)pore size diameter of ~3000 nm, and the bare silica a (macro)pore size diameter of ~860 nm. Coating the cordierite structure once with Nafion lowers the pore volume by ~20%, and in the case of the silica carrier the pore volume is reduced by ~64%. The diameter of the pores does not change significantly in either case. Apparently, pore-blocking occurs to a larger extent for the silica monolith than for the cordierite. This is obviously due to the texture of the bare monoliths; the silica monolith contains much smaller macropores than the cordierite.

In table 3 the nitrogen adsorption results are presented for these (un)coated samples. The isotherm of the bare silica monolith reveals micro- and (small) mesopores. After coating cordierite once with Nafion, a relatively high surface area of 46 m$^2$/g$_{total}$ is observed, which is mainly ascribed to the presence of micropores. Apparently, due to the coating with Nafion the larger macropores are filled, and micropores are created.

Table 3. Results of texture analysis after coating cordierite and silica samples with a Nafion layer.

<table>
<thead>
<tr>
<th>Material</th>
<th>Number of dips</th>
<th>Nitrogen-physisorption Pore volume (ml/g)</th>
<th>$S_{BET}$ (m$^2$/g$_{total}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>0</td>
<td>0.078</td>
<td>89</td>
</tr>
<tr>
<td>Silica</td>
<td>1</td>
<td>0.076</td>
<td>86</td>
</tr>
<tr>
<td>Silica</td>
<td>5</td>
<td>0.05</td>
<td>35</td>
</tr>
<tr>
<td>Cordierite</td>
<td>0</td>
<td>--</td>
<td>≤ 4</td>
</tr>
<tr>
<td>Cordierite</td>
<td>1</td>
<td>0.02</td>
<td>46</td>
</tr>
<tr>
<td>Cordierite</td>
<td>5</td>
<td>0.02</td>
<td>8</td>
</tr>
</tbody>
</table>
The effect of multiple dip-coating

The effect of dipcoating a Nafion coated monolith more than once, was studied by performing the coating procedure five times. These coatings resulted in a loading of 5-6 wt% Nafion, which is lower than expected. Apparently, there is a higher preference for Nafion to bond to cordierite than to itself. The repeatedly coated structures were also subjected to texture analysis measurements. The results of the nitrogen-physisorption measurements of a silica and a cordierite support are also shown in table 3. The pore size distributions as measured with mercury porosimetry can be found in figure 7. After 5 times of dipping a significant decrease (of approximately 25%) is observed in the pore volume values for the silica and cordierite structures, as determined by mercury-porosimetry. In the case of the silica monolith a drastic decrease is also observed in the $S_{BET}$ and the pore volume, but the specific surface area of the cordierite as determined by nitrogen-physisorption is doubled compared to the bare cordierite. Compared to the once coated monolith a drastic decrease is observed, probably due to blocking of the pores. Multiple dip-coating results in (partial) blockage of meso- and macropores (as indicated by mercury-porosimetry) and micro- and mesopores (as indicated by nitrogen-physisorption) in the case of the silica and cordierite monoliths.
Nafion distribution

The distribution of the Nafion catalyst on the monolith samples was investigated by measuring the Nafion loading of various segments of one Nafion-coated monolith (length 28 cm) by thermal analysis. These TGA measurements show no significant variation for the distribution of Nafion on a monolithic structure, indicating a homogeneously dispersed catalyst layer.

Activation of Nafion after coating – temperature and duration

After applying the Nafion layer and drying, the resin was converted into the active form by an acid treatment in 25 wt% nitric acid. To study the effect of this acidification, the once-coated silica structures were acid-exchanged at 293K (room temperature) and at 348K for 4 h or 16 h (overnight). The effect of the acid treatment was investigated with mercury-porosimetry, the results can be found in table 4.

Table 4. Texture analysis (nitrogen-physisorption and mercury-porosimetry) measurements of Nafion dip-coated monoliths (one time) – effect of acid treatment.

<table>
<thead>
<tr>
<th>Material monolith</th>
<th>Acid treatment duration (h)</th>
<th>Acid treatment temperature (K)</th>
<th>Nitrogen-physisorption</th>
<th>Mercury-porosimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$S_{BET}$ (m²/g&lt;sub&gt;total&lt;/sub&gt;)</td>
<td>Pore volume (ml/g)</td>
</tr>
<tr>
<td>Silica</td>
<td>4</td>
<td>293</td>
<td>88-97</td>
<td>0.07</td>
</tr>
<tr>
<td>Silica</td>
<td>4</td>
<td>350</td>
<td>98</td>
<td>0.08</td>
</tr>
<tr>
<td>Silica</td>
<td>15</td>
<td>293</td>
<td>89-100</td>
<td>0.07</td>
</tr>
<tr>
<td>Silica</td>
<td>15</td>
<td>350</td>
<td>89</td>
<td>0.07</td>
</tr>
</tbody>
</table>

All nitrogen-physisorption measurements show similar pore volumes (0.07-0.08 ml/g) and BET surfaces (88-100 m²/g<sub>total</sub>). The mercury-porosimetry measurements are also comparable. It appeared that the texture of the Nafion silica coated monoliths, as measured by nitrogen-physisorption and mercury-porosimetry, is not influenced by the acid treatment after coating.
Chapter 4

General conclusions of the Nafion coating

Coating cordierite and silica monoliths with Nafion results in a homogeneously distributed coated structure with a low loading of 2-3 wt%. The texture of the carrier material is not affected by this thin layer. Repeating the dip-coating experiments several times does not result in a linear increase of the amount of the loading and, furthermore, introduces (partial) filling of the (macro)-pores. The activation of the Nafion after coating by acid treatment does not affect the texture of the silica monoliths.

Preparation of a monolith support with Nafion/silica composite

Various parameters have been investigated for the preparation of a Nafion/silica composite on a monolithic substrate, including the silica source, the Nafion content, the dipping time, number of dips, and the addition of CaCO$_3$.

After coating with various silica sources and Nafion contents in the dip-mixtures, the loadings of the monoliths are determined by weighing; these results are presented in table 5. During the dip-coating process the pH and the viscosity of the dip-mixture remained constant in all cases. The nitrogen adsorption measurements of all these samples revealed a surface area at the lower detection limit of the technique, namely ≤4 m$^2$/g$_{total}$, no presence of micropores and (from the isotherm) some presence of mesopores. The mercury-porosimetry analysis revealed macropores of 1.4-12 μm. These analyses are very similar to the analysis from the original cordierite, so it can be concluded that the texture is not much affected by the coating. Varying the time of dip-coating the monoliths with a Nafion/silica composite between 15 and 120 min did not result in significant differences in loadings of the structures, as no relation could be found between the monolith loading and the time of dip-coating.

Table 5. Results of the monolith-supported Nafion/silica composite layers prepared with various silica sources.

<table>
<thead>
<tr>
<th>No.</th>
<th>Target % Nafion in coating layer</th>
<th>Silica source</th>
<th>weight increase (%)</th>
<th>% Nafion in coating layer (TGA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>Ludox</td>
<td>14.8</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>Ludox</td>
<td>8.7</td>
<td>10.3</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>Ludox</td>
<td>3.4</td>
<td>24.4</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>Ludox+ Waterglass</td>
<td>1.9</td>
<td>30.5</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>TMOS</td>
<td>5.7</td>
<td>19.6</td>
</tr>
</tbody>
</table>
Silica source
To compare the effect of the silica source, coatings with numbers 3 (Ludox), 4 (Ludox with added waterglass), and 5 (TMOS) in table 5 are compared. The Nafion content of the dip-mixture was adjusted so as to give a coating with 25 wt% Nafion in the coatlayer, and it is seen that the actual Nafion contents obtained were, except for one case, only slightly lower than this. The highest amount of total loading (5.7 wt%) was obtained with TMOS as silica source, while the use of Ludox, with or without waterglass, resulted in relatively low loadings of 3.4 and 1.9 wt%, respectively. This can be explained by the higher silica concentration of the TMOS solution (> 80 wt%) compared with 40 wt% for Ludox. The added waterglass had a negative influence on the amount of loading but gave a remarkably high Nafion percentage in the coating; this will be discussed in the next section.

Also the different sol-gel mechanisms can result in the different catalyst loadings. As mentioned in chapter 3, TMOS starts to gelate with the condensation of silica monomers, followed by the growth and linking of particles into silica chains (Hench and West, 1990). This leads probably to a stronger adherence of the silica to the cordierite structure than the silica from the colloidal silica Ludox, in which the coating is formed by growth and coalescence of the colloidal particles.

Effect of Nafion content
To investigate whether it was possible to tune the Nafion content in the monolith coatings, the results of the wt% of Nafion as determined by TGA are compared with the percentages of Nafion which were aimed for when preparing the dip-mixtures (table 5). The content of Nafion that was aimed for globally matches the content of Nafion measured with TGA, so the Nafion content in the monolith coating can easily be tuned by adjusting the amount of Nafion in the dip-mixture.

Comparing the amount of total coating with the amount of Nafion (table 5), leads to the remarkable observation that the total amount of coating decreases with an increasing Nafion content. A possible reason for this effect is that the Nafion particles disturb the gelation of the silica.

Nafion distribution
The Nafion distribution was studied by thermal analysis of a coating prepared with a mixture of TMOS and Nafion in such a ratio that a 13 wt% Nafion-containing coating should be obtained. The TGA results showed an equal distribution of the Nafion in the Nafion/silica composite coating over the monolith.
Chapter 4

The distribution of the coating was also studied with SEM. In figure 8a-c, the SEM pictures of a Nafion/silica composite coated monolith are presented. The coating that is studied with SEM was prepared from Nafion and TMOS in such a ratio that the theoretical amount of Nafion in the coating should be 25 wt% (sample no. 5 from table 5). Throughout the whole structure the same morphology is seen, and the typical stacked structure of cordierite (figure 2c) is no longer visible. The macropores are also not blocked by the coating, because these are still clearly visible. These results correspond with the texture analyses, indicating that the texture of the original cordierite is not affected by the coating. Unfortunately, Nafion itself is not visible in the TEM pictures, probably due to the particles being too small for detection. It is also possible that decomposition of the small particles occurs under the high energy electron beam.

![SEM pictures of a Nafion/silica coated monolith](image)

**Figure 8a-c. SEM pictures of a Nafion/silica coated monolith**

EDX analysis (figure 9) of the Nafion/silica composite coating showed the presence of Mg and Al in the ratio appropriate to the cordierite composition (2Al₂O₃.5SiO₂.2MgO) but a higher Si ratio as a result of the coating. Carbon from both the Nafion and the sputtered carbon layer applied to render the sample conductance for SEM analysis was also detected, plus F and S in small amounts from the Nafion backbone.
Repeatedly dipping

The effect of repeatedly dip-coating the monoliths on the catalyst loadings is depicted in figure 10. With this coating technique a higher amount of coating can be deposited on a monolithic substrate. In this way also the amount of Nafion in the coating can easily be altered, in the range of 10-50 wt% for a Nafion/silica coating with 13 wt% of Nafion. Whether the active sites remain accessible, will become apparent from the activity measurements. These will be discussed in the next chapter.

Influence of adding CaCO₃

For altering the porosity of the coating, CaCO₃ was added to the dipmixture. This resulted in a thick dip-mixture with a fast gelation, making the coating procedure difficult. It was not possible to perform dip-coating in a dip-mixture with 20 wt% of CaCO₃, as this gelated too fast. The dip-mixture with 5 wt% of CaCO₃ gelated within approximately 1 h, so it was possible to dip-coat the cordierite structures in this mixture. This resulted in a loading of 5 wt%. Texture analysis by nitrogen-adsorption revealed a specific (BET) surface area of 315
Chapter 4

m²/g_{coating} for the coating layer. Compared with the coatings prepared without CaCO₃, a much higher surface area can be obtained in this manner. Nitrogen adsorption analysis reveals a significant change in surface area. The S_{BET} value increases from ≤4 m²/g_{total} (lower detection limit) to 14.6 m²/g_{total}, with the presence of micro- and mesopores.

The coatings prepared with added CaCO₃ resulted in large cracks, as observed with SEM, very likely originating from the drying of the thick gel in which this monolith was dip-coated. It is also possible that the decomposition of the carbonate resulted in the cracks. Consideration of the nitrogen analysis results suggests that addition of a carbonate results also in the formation of micropores. Because all these coatings are treated with acid for activation of the Nafion resin, it is assumed that the coating is firmly attached to the monolithic substrate.

General conclusions Nafion/silica composite coatings

The synthesis of a Nafion/silica composite performed with TMOS and Ludox results in an evenly distributed coating with a monolithic weight increase of 3.5-15 wt%. This weight increase is strongly dependent on the amount of Nafion in the dip-mixture, probably due to gelation problems introduced by the Nafion. The presence of the Nafion is demonstrated by SEM-EDX. The dip-coating time does not affect the loading, and by repeatedly dipping a higher amount of coating can be obtained in the range of 10-50 wt% for a Nafion/silica coating with 13 wt% of Nafion. By adding a carbonate like CaCO₃, the porosity (micro-, meso- and macro-) is altered, as is shown by SEM and nitrogen adsorption. The question whether the Nafion active sites are accessible during reaction is discussed in the next chapter.

BEA dip-coating of monoliths

To study the coating of a monolithic structure with BEA zeolite, various dip-mixtures were prepared to investigate the influence of the various compounds. The loading of the monolith was determined by measuring the weight before and after coating, according to formula [1]. The measured loadings of the various BEA dip-coated monoliths are presented in figure 11. It must be noted that measuring the loading by weighing the samples, implies that the amount of binder is included in the loading.
Figure 11. The loadings of the various BEA dip-coated monoliths. Variation of dip-coat formulation

The effect of the different parameters varied in the dip-mixtures of this preparation method will be discussed in the following sections.

Solvent effect
As solvents, butyl acetate and demineralized water were employed. The butyl acetate was studied since its high evaporation rate, combined with lower surface tension, would be expected to lead to a higher catalyst loading. The solvent choice was found to have a large effect on the maximum BEA content of the dip-mixture; mixtures containing 15 wt% in the case of butyl acetate and 25 wt% in the case of water proved too viscous for use. The amount of BEA zeolite in the dip-mixtures was varied from 5 to 10 wt% in butyl acetate and 5 wt% to 20 wt% in water. It seems that the assumption that butyl acetate would lead to higher catalyst loadings was not correct, since the viscosity of the BEA containing dip-mixtures had a stronger effect on the dip-coating than the evaporation rate and surface tension of the solvents.

Catalyst loading
The measured loading of the monoliths can be found in figure 11. The value of the loading increases with the solids content of the dip-mixture. The dip-mixtures prepared with water lead to very high loadings up to 8 wt% after dip-coating the structures once and calcination. Due to the lower maximum amount of 10 wt% of zeolite in butyl acetate lower loadings of 2.3 wt% are achieved. The dip-mixture with 20 wt% of BEA resulted in a higher average loading (5.9 wt%) compared to the 5 wt% BEA. In the case of the butylacetate dip-mixtures the
highest loading (2.3 wt%) was also obtained with the highest content of BEA zeolites (10 wt%) in the dip-mixture. The silica monolith prepared with a dip-mixture of the 'standard' 20 wt% of BEA in water resulted in a higher loading of the cordierite monolith. This is ascribed to the higher surface area of the carrier and a stronger bonding between the silica monolith and the zeolite coating.

Texture analysis was performed by subjecting the BEA-coated monoliths to mercury-porosimetry and nitrogen-physisorption. For the BEA-coated cordierite a BET surface area of 20-40 m²/g_total was found, so the surface area of the cordierite structure is increased by a factor of 6-10. In this case, the microporous structure of the BEA zeolite enhances the surface area of the cordierite. In the case of the silica structure, however, the surface area decreases from 89 to 62 m²/g_total. Comparing the BET surface area of the zeolite crystals (650 m²/g_zeolite) with the BET surface area of the BEA coated monoliths the loadings of the monoliths can be calculated. The results of four of these calculations can also be found in figure 11. The measured loadings of the zeolite coatings match fairly well with the predicted loadings from the nitrogen-adsorption experiments.

Type of zeolite
The type of zeolite has a large effect on the maximum possible amount of zeolite in the dip-mixture. A 20 wt% BEA dip-mixture in water has an apparent viscosity of 1000 mPa.s. However, when a MFI zeolite (CBV 3024E, Si/Al 15, Zeolyst) is used, dip-mixtures with 30 wt% of zeolite in water can be prepared, having only an apparent viscosity of 6 mPa.s.

Morphology of BEA coatings
In figure 12, SEM micrographs are shown of a monolith coated in a dip-mixture of 20 wt% BEA in water, with 1 wt% of the solids as binder (Ludox), and Teepol as surfactant. The loading of this monolith is 5.9 wt%. The view from above (figure 12a-b) shows the zeolite crystallite. In the cross section of the monolith wall (figure 12c) the BEA zeolite layer is clearly visible (see the arrow). The thickness of the layer, varying from 7 - 15 µm (figure 12c), is of the same magnitude as the particle size of the BEA clusters (see Experimental).
**Influence of the silica binder**

Colloidal silica (Ludox AS-40, a 40 wt% suspension of colloidal silica in water) was used as binder in the dip-mixture. To investigate the influence of the binder on the loading of the monolith, a BEA coating was prepared without the silica binder and a coating in which the amount of binder was 5 wt% of the solids, instead of 1 wt%. This was only investigated with water as solvent. In both cases the loading decreased from 5.9 wt% to, respectively, 5.5 and 3.5 wt%. Apparently, a higher amount of binder has a negative effect on the loading. When measuring the viscosity of the various dip-mixtures, a decrease of viscosity occurred when increasing the amount of binder (from 1000 to 6.8 cP), leading to a lower loading. Coating the monolith with a mixture without binder does not seem to affect the catalyst loading much, but may affect the strength of the carrier-catalyst bonding.

**Influence of temporary binder and surfactant**

In the case of butyl acetate as a solvent, the influence of a ‘temporary’, i.e. decomposable, binder for the zeolite crystals was studied. Nitrocellulose, moistened with 35% ethanol, was added prior to calcination. This gave a loading of 2.3 wt%, compared with the low loading of 0.6 wt% without nitrocellulose, showing the effectiveness of the binding effect to the surface.

The influence of a surfactant to disperse the zeolite crystals in water was studied by adding Teepol to the water-based dip-mixtures. Adding the standard amount of 0.3 g (1.8 wt% based on the BEA content) of Teepol gave a loading 5.9 wt%. With half the amount of surfactant, the loading is lowered to 5.3 wt%, without the surfactant, the loading lowers to 4.9 wt%. It seems that the addition of the surfactant leads to a higher loading.
Chapter 4

Binding of the coating onto support

To investigate the adhesion of the zeolite crystals to the monolithic support, the prepared coatings were subjected to an ultrasonic treatment and the weight loss determined. The weight losses varied from 0.08 till 0.23 wt% of the coated monoliths, compared with 0.11% of the uncoated monolith. This indicates the firm attachment of the zeolite coatings. The highest weight loss was found for the zeolite coating without added silica binder, indicating the function of the silica binder. If the coating prepared with 20 wt% of BEA zeolite in water is considered, this means that 1 wt% of binder (on the basis of the amount of BEA) suffices for a strong adhesion of a BEA zeolite coating on a ceramic support. A low binder content can be favourable for the accessibility of the catalyst in the coating.

General conclusions BEA dip-coated monoliths

The application of a commercial zeolite to a monolithic carrier by means of dip-coating proved to be relatively simple. The maximum amount of BEA (CP811E-75, Zeolyst) that can be applied in water (20 wt%) is higher than in butyl acetate (10 wt%). Coating a monolith in these dip-mixtures resulted in loadings of, respectively, 5.9 wt% (with a layer thickness of approximately 7 μm from SEM) and 2.3 wt%. The texture analysis of a cordierite monolith coated with BEA in water revealed a surface area of 20-40 m²/g_total. For a silica monolith, the S_BET was 62 m²/g_total. Increasing the amount of the silica binder (Ludox) results in a decreased loading, probably due to competition between the binder and the zeolite. In the water-based dip-mixtures, a surfactant is found to be necessary, to stabilize the mixture before coating.

In-situ synthesis of BEA zeolite on a monolith.

Following the in-situ synthesis of BEA on the cordierite supports, according to the preparation method described in the experimental section, the channels of the monolith were completely blocked. XRD analysis of the ceramic material that was synthesized between the channel walls revealed the presence of zeolite BEA besides the presence of the cordierite, see figure 13.

The reflections of cordierite and BEA zeolite (marked by *) are clearly visible in the XRD spectrum of the coated sample. The synthesis method was modified in an attempt to achieve a BEA layer on the monolithic support without blocking the monolith channels. The synthesis mixture was diluted by factors of five and ten, while maintaining the pH of the former synthesis mixture, but none of these synthesis mixtures led to a BEA zeolite coating. Apparently, synthesizing a zeolite BEA layer in-situ on a monolithic support in a controlled way is not a straightforward process and requires further development.
General conclusions in-situ synthetized BEA coated monoliths

Zeolite coatings on monolith walls can be prepared by dip-coating the support in a mixture of available zeolite crystals or by direct synthesis of the zeolite crystals in the presence of the support. The dip-coating technique is a relatively simple technique that can be applied directly for catalytic purposes, but the in-situ synthesis technique still requires further research as the nucleation and growth processes of the zeolite crystals on a support are beyond control.

Final Conclusions

Various methods were developed for the application of a solid acid catalyst on a monolith. Dip-coating cordierite and silica monoliths in a Nafion-, Nafion/silica- or BEA-containing dip-mixture proved to be relatively simple and satisfactory coating techniques. Both methods result in a homogeneously distributed coated structure with loadings of 2-3 wt% Nafion, 3-15 wt% Nafion/silica composite, and 6-8 wt% BEA. The synthesis of a Nafion/silica composite showed a strong dependence of the loading on the amount of Nafion in the dip-mixture. The in-situ synthesis of BEA in the presence of a carrier resulted in blocking of the monolithic channels and is not under control. In the dip-coating technique, the amount of BEA deposited is good and easily controllable. Furthermore, it is not necessary to adapt the synthesis for coating applications, so an already optimized zeolite can be applied.
Chapter 4

Acknowledgements

Corning Inc. (USA) is gratefully acknowledged for supplying the monoliths. Ingrid Hoek and Nynke Aalders are gratefully acknowledged for their contribution to this chapter. J. Groen and P. Boeser are kindly acknowledged for the texture analysis measurements. J. Padmos is kindly acknowledged for the XRF measurements, and E. Fakkeldij is acknowledged for the SEM-EDX contribution.

References


Chapter 4


Chapter 4


Performance of coated monoliths in the acylation of anisole with octanoic acid

Summary

The performance is reported of Nafion and BEA coated monoliths in the acylation of anisole with octanoic acid. The activity and selectivity of the coated systems are comparable with those in slurry. Nafion coated silica monoliths showed a higher activity and selectivity than pure Nafion. Monolith supported Nafion/silica composites do not show any measurable activity, due to an inadequate gelation step in the synthesis. The activity of the BEA coated monolith is slightly lower compared to the original BEA crystals in a slurry operation, which is ascribed to partial loss of surface area owing to the fixation to the support. The selectivity of the BEA coating is maintained compared with the BEA crystals. Nafion coatings are more active than the BEA coatings on a catalyst mass basis, and both catalysts show a comparable selectivity. However, Nafion coatings show low reproducibilities due to poisoning of the active sites. In this respect, the BEA coated structures show to be very promising as structured catalysts for the acylation of anisole with octanoic acid.
Chapter 5

Introduction

Presented is the performance of the various coated monolithic structures in the acylation of aromatics with carboxylic acids. In the preceding chapters the application and preparation of zeolite and Nafion coated substrates are discussed. In this chapter the relation is studied between the preparation of the coated monoliths and the performance in solid acid catalyzed reactions.

Experimental

Materials

Anisole was purchased from Fluka (purity 99.92%) and from Acros (purity 99.34%), octanoic acid was purchased from Fluka, and hexadecane was purchased from Merck. The chemicals were used as received from the supplier.

Testing procedure

The solid acid coated monoliths were prepared by various preparation methods, described in chapter 4. Prior to the activity measurement, the Nafion coated monoliths were dried at 383K for 15h (overnight) in static air. The BEA (dip) coated monoliths were ion-exchanged in 1M ammonium nitrate for 16 h (overnight) at 323K and calcined at 723K for 4 h (heating rate 5 K/min) in static air.

The activity of the coated monoliths was measured batchwise in the acylation of anisole with octanoic acid (figure 1). As a solvent, anisole was used to circumvent optional interactions introduced by an additional component.

\[
\text{H}_2\text{CO} + \begin{array}{c} \text{HO} \\ \text{OH} \end{array} \longrightarrow \text{H}_2\text{CO} + \text{H}_2\text{O}
\]

Figure 1. The acylation of anisole with octanoic acid.

The activity measurements were performed under the same reaction conditions as in the catalyst screening measurements (see chapter 2), with an octanoic acid concentration of 0.2 mol/l in anisole (unless mentioned elsewhere), the reaction temperature was the boiling point
of anisole, 428K, the pressure was atmospheric, the reactor volume was 125 ml, and the internal diameter of the reactor was 45 mm. The liquid reaction mixture was recirculated through the monolith using a nitrogen flow (figure 2). The reaction part is heated by an oil bath. On top of the cooling section a drying tube is placed, which is filled with silica gel.

Activity is defined as the initial apparent first order $k$-value (h$^{-1}$) normalized for the amount of coating (g) per the liquid reactor volume (l), according to the first order derivation presented in chapter 2. As the amount of coating either the amount of Nafion, Nafion/silica or BEA is considered depending on the sample. Selectivities were calculated as the ratio of the acylated aromatic substrate para-octanoyl anisole and total amounts of products at 50% of octanoic acid conversion.

**Analysis**

Samples (~ 250 µl) were taken manually at regular time intervals. Analysis was done by gas chromatography on a Chrompack CP9001 gas chromatograph with FID-detection equipped with a CP9050 autosampler and a CP Sil 8CB column (length 50 m, internal diameter 0.25 mm, film thickness 0.12 µm). $n$-Hexadecane was used as an internal standard.

**Results and discussion**

**Nafion coatings**

**General**

Before discussing the activities of the Nafion coatings, an important remark has to be made about the sensitivity towards contaminations. During the study it became clear that the activity of the Nafion coated structures was very dependent on the type of anisole that was supplied. In some cases, where a different batch of anisole was used the activity dropped significantly, sometimes to zero. After further investigation of these batches, it could be concluded that the impurities in the anisole were mainly chlorine and bromine containing aromatics.
Chapter 5

For a more quantitative approach of this deactivation problem, the amount of active sites in the Nafion can be compared to the amount of poisoning molecules in the anisole. The Nafion capacity is estimated at a value of 1 meq/g (according to the supplier > 0.8 meq/g (Waller and Warren van Scoyoc, 1987). When a loading of 3.5 wt% is obtained, a Nafion coated monolithic sample (dimensions: 5 cm height and 43 mm Ø) with a weight of 30 g contains 1.1 g of Nafion. This corresponds to an amount of 1.1 mmol sites. The amount of anisole is 125 ml (0.865 mol). Considering the claimed purity of the anisole from Fluka (99.92%) and from Acros (99.34%), the ratio of the amount of impurity and the total active sites amounts to a value of 0.9 for Fluka and 7.1 for Acros. This means that in the case of Acros there is a potential excess of contaminating molecules in relation to the amount of active sites. In the case of Fluka there is about the same amount of contaminating molecules as there are active sites. Apparently, poisoning of the acidic active sites occurred, by strong adsorption of the halogenated components. This makes it very difficult to discuss the activities of the coatings properly. For this reason only the main results are given, and only trends are discussed.

Activity

The main results of the various prepared Nafion coated monoliths are presented in figure 3. Some of the Nafion coated cordierite monoliths are tested in an octanoic acid concentration of 0.2 mol/l (white bars) and other in a concentration of 0.04 mol/l (shaded bars). The activity of the silica coated Nafion monoliths is presented as a separate series. Also depicted is the activity of pure Nafion and the commercial Nafion/silica composites (SAC13 and SAC25) in slurry phase. Compared to pure Nafion and SAC13 particles (with an activity of respectively

![Graph showing activity (mol/g h⁻¹) of various Nafion coatings in acylation of anisole with octanoic acid at 428K. Error in multiple reactions is depicted in error bars.]

Figure 3. Activity (mol/g h⁻¹) of the various prepared Nafion coatings in the acylation of anisole with octanoic acid (428K). The error measured in multiple reactions is depicted in the error bars.

124
0.03 \text{l.g}^{-1}.\text{h}^{-1} and 0.04 \text{l.g}^{-1}.\text{h}^{-1})$, a somewhat higher activity is achieved (0.05 \text{l.g}_{\text{coating}}^{-1}.\text{h}^{-1} for the 400 cpsi cordierite coated monolith). Some monoliths are prepared and tested multiple times, the error measured in these results is depicted in the error bars. The presented results without error bars are only measured once. In some cases it can be seen that the error in the activity is relatively large, leading to a low reproducibility (for example in the case of the pre-acidified silica monoliths).

The monoliths measured in a lower acid concentration exhibit a higher activity than the ones prepared in the same way (600 cpsi, and 400 cpsi-pre-acidified) but tested in the ‘standard’ concentration of 0.2 mol/l. This matches the observation described in chapter 2 that the apparent activity in the acylation of anisole with octanoic acid decreases when increasing the octanoic acid concentration, due to an adsorption effect of the carboxylic acid.

**Cell density**

Monoliths with three different cell densities have been coated and tested in the acylation reaction; 200, 400 and 600 cells per square inch (cpsi). Again the large experimental errors make it difficult to make a clear distinction. With these results no relation could be found between the activity and the geometric area. This implies that all catalytic sites are equally accessible to the reactants, leading to the conclusion that mass transfer limitations are absent in these activity measurements.

**Monolith material**

Considering the trend in activities in figure 3, it is clear that the silica monolith exhibits the highest activity. Even when compared to the activity of SAC25 in slurry the activity is somewhat higher. These activities can be compared because both values have been normalized for catalyst concentration (total amount of catalyst divided by the total volume; total amount of catalyst is defined by the amount of Nafion in the case of the Nafion coatings, and by the amount of Nafion/silica composite in the case of the composites). Texture analysis reveals a very high surface area on the micro- and mesoscale (chapter 4) compared to the macroporous cordierite. So, the relatively high activity is probably due to the texture characteristics. It is also possible that the high silica content may result in a high activity. This is further discussed in the following section on ‘pre-treatment’.

**Pre-treatment**

The monoliths have been pre-treated in nitric acid to alter the surface area characteristics of the monolithic material. The effect of pre-treatment on the cordierite monoliths apparently has a contradicting effect on the activity. Considering the monoliths with a cell density of 400 cpsi it is not clear whether an effect is observable of the pre-treatment, due to the extent of the
measuring error. However, when considering the monoliths with a cell density of 600 cpsi the activity increases by a factor of approximately 3. These latter monoliths are measured in a lower octanoic acid concentration of 0.04 mol/l, but comparing both monoliths tested at the lower acid concentration still indicates a rise in activity after pre-acidification. A possible reason for an increased activity is that the silica content of the monoliths has somehow an effect on the activity. In chapter 3, it is observed by FT-IR that an interaction occurs between silica with Nafion in the nafion/silica composites. Evidently, this interaction has an effect on the performance (activity and selectivity) of the Nafion in the acylation reaction. The reason why this effect is not consistent for all types of monoliths remains unclear, but has probably to do with the high sensitivity of the Nafion towards contaminations in the solvent, see also the ‘general’ section of this paragraph.

Additional silica layer

An additional silica layer results in a higher (meso- and microporous) specific surface area compared to the bare cordierite. In figure 3, the activity of the 400 cpsi monolith with an additional silica layer is presented. This coating was made according to the procedure described in chapter 4 from TMOS as a silica source. It is not clear whether the additional silica layer affects the activity of the Nafion coated monolith in the acylation reaction. It seems that the activity of the Nafion coated monolith with an additional silica layer is somewhat higher (0.07 l/g.h) than the ‘bare’ Nafion coated cordierite monolith (0.05 l/g.h), but again the large experimental errors make it difficult to make a clear distinction. Possible reasons for a higher activity are the surface area (micro- and mesopores instead of macropores) and a silica/Nafion interaction.

Multiple dips

The activity decreases when the dip-coating procedure is performed multiple times. Apparently, the amount of active sites does not increase linearly with the amount of catalyst, indicating that the active sites on the ‘first’ applied catalyst layers are blocked by the layers applied afterwards. This is also confirmed by the texture analysis as discussed in chapter 4. Texture analysis revealed a (partial) blockage of meso- and macropores (as indicated by mercury-porosimetry) and of micro- and mesopores (as indicated by N₂-physisorption) in the case of the silica and cordierite monoliths.
Activation after coating

The effect of activating the Nafion coated silica monolithic structures by an acid treatment was also studied (chapter 4). This activation step is necessary to protonate the sulfonic groups of the Nafion. The result presented in figure 3 is the activity of a Nafion coated monolith that was acid-treated for 4 h instead of 15 h (overnight). The shorter exchange time leads to a lower activity, which evidently demonstrates the benefit of the acid treatment. This acid treatment after coating did not have an effect on the texture characteristics, so it is only necessary for the activation of the Nafion.

Selectivity of the Nafion coated monoliths

The selectivity of the Nafion coatings towards the acylated aromatic substrate para-octanoyl anisole is fairly constant in time (figure 4), regardless of the coating procedure (and activity), with a relatively high value of 75 to 80%. The constant selectivity as a function of conversion shows that the non-selective route is a parallel rather than a consecutive reaction.

The selectivity of the Nafion coated monoliths are depicted in figure 5. Compared to the selectivity of pure Nafion and the Nafion/silica composites as measured in slurry, the
monolithic structure appears to have a positive effect on the selectivity, because compared to the Nafion/silica composites the selectivity is 10-15% higher and in the case of the pure Nafion this value is even 30-35% higher. The selectivity of Nafion is associated with the interaction of the resin with the silica matrix in the case of the Nafion/composites (Botella et al., 1999; Pálinko et al., 1998). The interaction between the –SO₃H groups of the Nafion backbone and the hydroxyl clusters of silica of the cordierite (see chapter 4 for the composition of cordierite) and the silica monoliths, leads to a lower acidity of the –SO₃H groups of the Nafion (see also chapter 3) and thereby to a higher selectivity.

Stability of the Nafion coated monoliths

Stability of the catalytic coatings was tested by performing the experiments multiple times with the same sample. In the case of the Nafion resin, the coated monoliths could not be calcined for reactivation due to decomposition of the resin at higher temperature. After washing with acetone, the coated monolith was therefore reactivated with a nitric acid treatment, dried (383 K) and retested.

Three samples coated on a silica monolith, prepared by the standard method, were retested. In all cases the activity dropped from an average of 0.2 till 0.07 l/g.h in the second test and in the third test even to 0.05 l/g.h. This means that these Nafion coated samples are strongly deactivated in the catalytic reaction. This is probably due to irreversible adsorption of halogenated hydrocarbons on the active sites and perhaps also due to some ‘coke’ formation on the strong acid sites. Surprisingly, the activity of the 400 and 600 cpsi cordierite monolith increased when tested the second time. The third time, the activity of the 600 cpsi monolith decreased again. These monoliths were tested in a concentration of 0.04 mol/l instead of the standard 0.2 mol/l of octanoic acid. The reason why the activity increased when tested the second time remains unknown.

Monolith supported Nafion/silica composites

None of the monoliths supported Nafion/silica composites, prepared as described in chapter 4 (table 5), showed any activity in the acylation of anisole with octanoic acid. As Nafion has been detected in the coatlayer by means of TGA (chapter 4), it seems that somehow this resin cannot be converted into the active form by using the applied synthesis procedure. This can either be because the active sites are covered by silica or due to an incorrect synthesis procedure. The Nafion/silica composites that are prepared by practically the same procedure and tested in the slurry reactor configuration, however, do show a high activity (discussed in chapter 3). So, the reason for the lack of activity of the monoliths has to originate from the
difference between the two syntheses (of the monolithic coating and of the slurry catalyst). In both synthesis procedures, gelation is achieved by altering the pH. However, the way this pH change is obtained is different. In the case of the composites, gelation was achieved by addition of acid or base, and in the case of the coatings, gelation is achieved by increasing the temperature and hereby removing the solvent. To investigate this, the Nafion/silica coated monolith was crushed, activated in an acid treatment and tested in the slurry configuration. After crushing, however, still no activity could be measured. It can be concluded that this coating procedure does not result in an active coating for the acylation reaction, due to an inadequate gelation step in the synthesis. Apparently, in the preparation of this Nafion/silica composite, fast fixation of the Nafion in the silica matrix is required.

**BEA coatings**

**General**

The activity of the monoliths coated with BEA, was measured in the standard acylation reaction. The activity of the prepared monoliths is shown in figure 6. Presented are the activities of the monoliths prepared using a mixture of 20 wt% BEA in water. The standard preparation includes the addition of SiO₂ as binder (from Ludox) and a surfactant (Teepol). For more detailed, quantitative, information on the preparation of the BEA coated monoliths, see chapter 4. The effect on the catalytic activity of the cell density, binder, and surfactant was studied. Also the monolithic material was varied by coating a pure silica monolith.

![Figure 6. Activity of the BEA coated monoliths in the acylation of anisole with octanoic acid, measured under standard conditions (0.2 mol/l; 428K).](image-url)
Chapter 5

The BEA coated monolithic structure that was prepared on a 400 cpsi monolith with the standard preparation method of 20 wt% BEA in water, with additional binder and surfactant exhibited an activity of 0.034 l/g.cat.h. in the standard acylation reaction with octanoic acid (0.2 mol/l, 428K). This activity value is the apparent first order rate constant, normalized by the total amount of catalyst (coating) per reactor volume.

The activity is lower than in a slurry configuration (0.055 l/g.h). This can be explained by the fact that the zeolite particles are only partly accessible since the particles are fixated on a support with some binder. However, the remaining activity is quite satisfactory.

Effect of monolith characteristics – cell density and material

The effect of cell density on the activity was studied for three types of monoliths with various cell densities (200, 400 and 600 cpsi). The activities are normalized per amount of BEA catalyst and do not differ much (figure 6). Also the silica monolith does exhibit a similar activity as the cordierite monolith. From these results it is concluded that the performance of the BEA coated monoliths is not influenced by the geometric surface area of the carrier, indicating the absence of mass transport limitations.

Effect of Binder

The effect of the binder was studied by preparing a coating without binder and by increasing the amount of binder with a factor of 5. In both cases the activity drops by about 30%. The lower activity in the case of a higher amount of binder can be due to blocking of the active sites of the zeolite by the silica binder. Apparently, there is an optimum for the amount of binder to be used. The reason for this optimum remains unclear. The coating without binder showed a relatively weak adherence to the monolith (see chapter 4), making this preparation method less suitable for application.

Effect of surfactant

The effect of the alkylarylsulfonate surfactant on the activity was studied by leaving out the surfactant. The activity measured for this coating has a higher value than the standard coating ('400 cpsi'). As the loadings of the monoliths are nearly the same, apparently the surfactant has a negative effect on the activity. Possible reasons could be that calcination was not long enough to decompose and oxidize away all the surfactant or that the surfactants could poison the active sites after calcination. Apparently, no surfactant is needed when preparing a BEA coating.
Stability of the BEA coated monoliths

To investigate the deactivation of BEA coated monoliths, the coatings prepared according the standard method (20 wt% mixture in water, including binder and surfactant) were washed with acetone after reaction, dried at 383K, ion-exchanged with NH4NO3 and recalcined at 723K for 4 h (heating rate 10 K/min). The activity of this regenerated BEA coating was measured in the acylation reaction (of anisole with octanoic acid). The activity dropped with ~65% to 0.012 l.g⁻¹.h⁻¹. Also the coated monoliths prepared from 20 wt% BEA in water without surfactant were regenerated and retested in the same way. The activity of this coating dropped with ~45% to a value of 0.025 l.g⁻¹.h⁻¹. Apparently, it is not possible to restore the original activity by using this regeneration method. Either poisoning molecules cannot be removed from the active sites, longer calcination times and/or higher temperatures should be applied to remove all the deactivating species, or the catalytic activity of the BEA crystals has decreased.

Selectivity of the BEA coated monoliths

The selectivity of the BEA coated monoliths decreases slightly as a function of conversion during the reaction of anisole with octanoic acid performed under standard reactions. This is depicted in figure 7. The selectivities of the various BEA coated monoliths at 50% of conversion are depicted in figure 8. Compared to the original BEA as tested in slurry, the selectivity is maintained. All monoliths give a similar selectivity of about 75-85% towards the main product, the para-substituted octanoyl anisole.

![Selectivity graph](image)

Figure 7. Selectivity (%) of the 400 cpsi BEA coated cordierite and silica BEA coated monolith in the acylation of anisole with octanoic acid as function of conversion, measured under standard conditions (0.2 mol/l; 428K).
Chapter 5

Figure 8. Main selectivities of the various prepared BEA coated monoliths at 50% of conversion in the acylation of anisole with octanoic acid, measured under standard conditions (0.2 mol/l; 428K).

Comparison of Nafion and BEA coated monoliths

The highest activities were obtained with the not pre-acidified Nafion coated silica monoliths, with a value of 0.2 l/g.h. The activity of Nafion coated corderite (0.05 l/g.h) as well as BEA coated corderite (0.03 l/g.h) is much lower. These latter two types of monoliths show comparable activities. Conversions over 90% after 5 h could be obtained with all types of catalytic coated monoliths. The selectivity obtained with the BEA coated monoliths is slightly higher (75-85%) than the selectivity of the Nafion coated monoliths (75-80%). The susceptibility of the Nafion coated monoliths towards contaminations and the resulting strong deactivation leads to large reproducibility errors in the measurements. Considering the deactivation of both types of coatings, the regeneration of the Nafion coatings through a acid treatment and of the BEA coatings by ion-exchange in NH₄NO₃ and subsequent calcination proved not to be successful. The regeneration of BEA can probably be improved by increasing the calcination times and/or temperatures. In these respects, the BEA coated structures are preferred over the Nafion coated monoliths.

132
Chapter 5

Conclusions

Nafion coatings

- The Nafion coatings turned out to be very sensitive for contaminations in the feed stock, leading to a strong poisoning and a bad reproducibility.
- The silica monoliths show a high activity, which is attributed to the texture characteristics of the silica carrier (containing micro- and mesopores).
- Compared to the original Nafion resin particles a much higher activity is achieved.
- Compared to the Nafion/silica composite with 25% of Nafion (SAC25) the activity of the Nafion/silica monolith is also higher.
- The effect of pre-treating the monoliths with an acid is not clearly visible.
- An additional silica layer on the monolithic carrier prior to coating does not seem to improve the performance significantly.
- When the dip-coating procedure is performed multiple times, the activity decreases due to blockage of the active sites by the Nafion.
- The Nafion coatings show a relatively high selectivity of 75 to 80%.
- Compared to Nafion as measured in slurry, the Nafion coated monoliths and the Nafion/silica monoliths show a higher selectivity.
- The higher selectivity is attributed to the interaction between the Nafion backbone and the silica present in the monolithic carrier.
- Re-use is unsatisfactory and needs improvement.

Monolith supported Nafion/silica composites

None of the monoliths coated with Nafion/silica composites showed any activity in the acylation of anisole with octanoic acid. The applied coating procedure does not result in an active catalyst for the acylation reaction, due to an inadequate gelation step in the synthesis.

BEA coatings

- The BEA coated monolith prepared according to the standard method (20 wt% BEA in water, including binder and surfactant) exhibited an activity of 0.034 1/gBEA-h.
- The activity of the BEA coated monolith compared to the original BEA crystals in slurry (in which the catalyst surface is optimally used) is ~38% lower, which is ascribed to the
Chapter 5

reduced accessibility of the zeolite particles by the fixation on a support. However, the remaining activity is quite satisfactory.

• The performance of the monoliths is not influenced by the texture of the carrier material, cell densities and the monolithic material. It can therefore be concluded that mass transfer limitations are absent.

• The amount of binder in the dip-coating mixture has a strong effect on the performance. The lower activity in the case of a higher amount of binder can be due to blocking of the active sites of the zeolite by the silica binder.

• All monoliths give a similar selectivity of about 75-85%, which is comparable to the selectivity of the original BEA zeolite.

General

Good activities and selectivities were obtained by coating a monolithic structure with Nafion and BEA for the acylation of anisole with octanoic acid. The Nafion coatings were more active than the BEA coatings on a catalyst weight basis, and both catalysts show a comparable selectivity. Although the activity of the Nafion coated monoliths is higher, deactivation is very strong due to poisoning of the small number of active sites in Nafion. This leads to large reproducibility problems. In this respect, the BEA coated structures are preferred as structured catalysts for the acylation of anisole with octanoic acid, provided that it is possible that the BEA coating regenerated satisfactorily.

Acknowledgements

Coming Inc. (USA) is gratefully acknowledged for supplying the monoliths. Ingrid Hoek and Nynke Aalders are gratefully acknowledged for their contribution to this chapter.

References


The kinetics of the SAC13 catalyzed esterification of hexanoic acid and 1-octanol

Summary

Esterifications are industrially relevant reactions. The esterification of a carboxylic acid and an alcohol is an acid-catalyzed reversible reaction in which water is formed. The presence of water has two negative effects on the reaction rate; it inhibits the catalyst and limits the maximum obtainable conversion due to the thermodynamic equilibrium.

In the esterification of 1-octanol with hexanoic acid, BEA and the Nafion/silica composite with 13 wt% of Nafion (SAC13) gave the highest activity, being much higher than for the reaction rate without a catalyst. The selectivity towards the formed ester is in all cases >90%, the side reaction being an etherification reaction between two alcohol molecules. The effect of the temperature on the SAC13 catalyzed esterification yielded an apparent activation energy of 58 kJ/mol.

The advantage of water removal is clearly demonstrated: in a closed system equilibrium is not even reached after 400 min, whereas in a system with water removal all the reactants were converted just after 100 minutes under the applied conditions.

No kinetic model was found in literature of the Nafion catalyzed esterification of 1-octanol with hexanoic acid. The kinetic model derived in this study for the mentioned reaction is of an Eley-Rideal type with two reaction steps rate limiting, viz., the adsorption of the carboxylic acid followed by a reaction between an adsorbed carboxylic acid molecule and a ‘free’ alcohol from the solution. A first order dependency in the acid and an inhibiting effect of alcohol ($K_A \approx 5 \, \text{l/mol}$) and a very strong effect of inhibiting water ($K_W \approx 30 \, \text{l/mol}$) were found. The developed kinetic model can be applied in reactor design modelling to predict and optimize this esterification reaction.
Chapter 6

Introduction

Esterifications are industrially relevant reactions e.g. in fragrance manufacture. Especially methyl, ethyl and butyl acetate and dialkyl phthalates are produced on a large scale (Aslam et al., 1994). Polymers such as poly(ethylene terephthalate) (PET) can also be produced by esterification followed by polycondensation. PET is an industrial polymer of great importance, with a worldwide production of 10.2 millions tons in 1990 (Aslam et al., 1994). Another example is the esterification of castor oil (containing 85% of ricinoleic acid and small amounts of palmitic, stearic, oleic, and linoleic acids), which is the feedstock for many industrial products such as nondrying alkyd resins (Erdem-Senatalar et al., 1995). For a review of ester forming methods, see Verhoef (2000).

Catalyzing the reaction with a solid acid, instead of the conventional mineral acids, has the advantages that the solid acids can be recovered and reused after regeneration, and that no corrosive waste streams are produced (Chen et al., 1999). Examples of these solid acids are zeolites, heteropolyacids, and ion-exchange resins. Nafion is an ion-exchange resin, which is widely used in water-separation membranes. In its acidic form Nafion can be used as a highly active catalyst for esterification reactions (Olah et al., 1978; 1986; Doyle and Plummer, 1993; Cho and Yang, 1991). Zeolites are also active catalysts in acid- catalyzed reactions, such as esterifications (Corma et al., 1989; Aracil et al., 1992). In the esterification of acrylic acid with 1-butanol, comparison of the activity of various catalysts showed Nafion to be highly active; Amberlyst and a Nafion/silica composite showed a somewhat lower activity, and FAU zeolite showed a very low activity (Chen et al., 1999). Finally, it has to be mentioned that in the field of biotechnology some (immobilized) enzymes are also studied for their application as esterification catalysts (Garcia et al., 2000; Huang and Chang, 1999).

The esterification of a carboxylic acid and an alcohol is an example of an acid-catalyzed reaction in which water is formed as a second product (figure 1). The presence of the produced water has two negative effects on the reaction rate: it has an inhibiting effect on the activity of the catalyst and it will limit the maximum obtainable conversion, since the reaction is a reversible, equilibrium limited reaction. Generally, water is therefore removed from the reaction mixture.

\[
R'\text{COOH} + R''\text{OH} \rightleftharpoons R'\text{COOR''} + \text{H}_2\text{O}
\]

Figure 1. The esterification of a carboxylic acid and an alcohol.
Chapter 6

For the design of a reactor configuration and simulation purposes, it is essential to describe the reaction rates precisely. Therefore, the objective of the study presented in this chapter is to develop a kinetic model and rate expression which describes an esterification reaction of a carboxylic acid and an alcohol adequately.

The mechanism that is generally accepted for this reaction is depicted in figure 2. In the first step the protonation of the carbonyl oxygen activates the carbonyl group. The second step includes a nucleophilic addition by an alcohol, yielding a tetrahedral intermediate. In the following step a proton is transferred from one oxygen to another yielding a second tetrahedral intermediate, and converts the hydroxyl into a good leaving group. Loss of water leads to a protonated ester, which in turn looses a proton for regeneration of the acid catalyst and giving the free ester product (McMurry, 1988).

![Figure 2. The mechanism of the esterification of a carboxylic acid and an alcohol.](image.png)

For the development of kinetic models in esterification reactions the literature that is available can be divided in homogeneously catalyzed, immobilized enzymatic catalyzed, and solid acid catalyzed reactions. For the homogeneously catalyzed reactions, the study of Nowak (Nowak, 1999) can be considered, in which the kinetics of the esterification of acrylic acid with (iso)octanol, catalyzed by sulfuric acid, is studied. This reaction appeared to be second order. The formed esters, acrylates, are primarily used to prepare emulsions and solution of polymers for coatings, finishes and binders. Also in the study of Keurentjes et al. (1994), the kinetics of the homogeneously catalyzed (methanesulfonic acid) esterification of tartaric acid with ethanol appeared to be second order. In the study of Otton and Ratton (1988), the esterification (and subsequent alkoholysis) catalyzed by carboxylic acids was studied at high temperatures (> 150°C). In that study, Eley-Rideal kinetics was proposed, but with a second order dependency for the carboxylic acid, as this latter reactant also acts as a (homogeneous) catalyst. Eley-Rideal kinetics imply a reaction mechanism in which first the carboxylic acid adsorbs on the catalyst, followed by reaction with the alcohol.
Chapter 6

In biotechnology, mainly lipases are considered. For example, in the esterification of oleic acid (figure 3a) and cetyl alcohol (figure 3b) to form cetyl oleate an extensive kinetic study was performed. The ester formed in this reaction is a sperm whale oil analogue, which has important applications in the cosmetics, lubricants, food and pharmaceutical industries. In that study the reaction was modelled according to Eley-Rideal type of kinetics, combined with competitive inhibition of reactants and products on an immobilized enzyme catalyst. Both alcohol and carboxylic acid were experimentally found to have an inhibiting effect on the performance of this bio-catalyst (Garcia et al., 2000). These results are also found in another study of the same authors (Garcia et al., 1999) in which the esterification of palmitic acid with isopropyl alcohol was studied as a model reaction for the synthesis of fatty esters. Both reactants and products appeared to have an inhibiting effect on the enzymatic catalyst, and the kinetics of the reaction could be described by an Eley-Rideal mechanism (in enzymatic catalysis, having another nomenclature, it is called ‘an ordered bi-bi mechanism’). In the kinetic study on the esterification of geraniol (figure 3c) and acetic acid, a lipase is coated with a surfactant to minimize the inhibition of the lipase by the acid. In this study the water content during reaction decreased the reaction rate, an inhibition was found of the acetic acid on the reaction, and formation of geranyl acetate was relatively insensitive to geraniol concentrations (Huang and Chang, 1999).

A similar mechanism was proposed for the CoCl₂-catalyzed esterification of castor oil and oleic acid, but in this study a fast formation was observed of the catalyst-acid intermediate, followed by a slow formation of the ester and water (Erdem-Senatalar et al., 1995). The only kinetic study found in literature concerning zeolites, is the study of Corma et al. (1989) in which the kinetics of the reaction between phenylacetic acid and ethanol was studied. The FAU zeolite catalyzed reaction was again described according to an Eley-Rideal model. The reaction (performed at a relatively low temperature of 61°C) was modelled with an inhibiting effect of both reactants, with the resulting adsorption constant being 1.6 times larger for the acid than for the alcohol. Another kinetic study in which the activity of various solid acids in the esterification of anthranilic acid and methanol (forming the important perfumery ester – methyl anthranilate) was studied, is the study of Yadav and Krishnan (Yadav and Krishnan, 1998). In this study the esterification was modeled as a second order reaction.
In this chapter the activities of various heterogeneous catalysts in the selected reaction are given with a major emphasis on SAC13 and the absence of internal and external diffusion limitations is discussed. The effect of water is studied, and the kinetics are derived with the aid of various experiments with varying concentrations and ratios of carboxylic acid/alcohol for application in monolithic reactors.

**Experimental**

**Chemicals**

The esterification of 1-octanol and hexanoic acid was chosen as model reaction. Because the esterification reaction also proceeds autocatalytic, without an additional catalyst, the reactions were performed both with and without the presence of a catalyst. The carboxylic acids and alcohols were purchased from Aldrich and used as received.

**Reaction conditions and equipment**

Unless mentioned elsewhere, the molar ratio of the carboxylic acid and the alcohol applied was 1:1, in cumene as solvent. The boiling points of the reactants 1-octanol and hexanoic acid are respectively 469 and 475 K. The reactions were performed batchwise in slurry experiments at 433 K (boiling point of cumene), with the concentrations of both reactants in cumene being 8 wt% (0.45 mol/l). The reactor configurations applied were an open reflux system, at atmospheric pressure with removal of water by the drying tube on top of the condenser, and a closed (micro)-autoclave. In the open reflux system the amount of catalyst was 0.3 g, and the total reaction volume 85 ml. In the micro-autoclave system the amount of catalyst was 0.04 g, the total reaction volume was 12 ml, and the experiments were performed under a nitrogen atmosphere of 10 bar. The stirring speed was 500 rpm and for the analysis of the samples, GC(-MS) was employed with n-hexadecane as internal standard. Samples (~ 250 μl) were taken manually at regular time intervals. Analysis was done by gas chromatography on a Chrompack CP9001 gas chromatograph with FID-detection equipped with a CP9050 autosampler and a CP Sil 8CB column (length 50 m, internal diameter 0.25 mm, film thickness 0.12μm).

**Kinetic measurements**

The effect of various concentrations, carboxylic acid/alcohol ratios and water on the reaction system was studied batchwise in the esterification of 1-octanol and hexanoic acid, using a
Chapter 6

Nafion/silica composite (13% Nafion) as the catalyst. The slurry-phase reaction is performed in two reactor configurations. One reactor setup was an open (reflux) system in which the reaction was performed with removal of water. The other reactor setup was an autoclave in which the reactions were carried out in a closed system. In this closed reactor configuration the effect of water was studied by initially adding a specific amount of water to the esterification mixture prior to an experiment. The activity is defined as the initial reaction rate (slope of the concentration plotted against time) normalized for catalyst concentration.

Catalysts

The activity of various catalysts has been studied. FAU zeolites with a Si/Al ratio of 5 and 80 were kindly provided by Zeolyst (crystal size of 1 μm). BEA zeolite with a Si/Al ratio of 37.5 was purchased from Zeolyst (CP 811E-75) and the BEA zeolites with a Si/Al ratio of 12.5, 25 and 50 were synthesized by Südchemie AG. The BEA zeolites had a crystal size of 15-20 nm and a particle size distribution of 5-20 μm due to the clustering of the crystals. The Nafion/silica composite samples with 13 wt% of Nafion were kindly provided by DuPont and by Engelhard and tested with a particle size of 50-100 μm. All catalysts studied were in the H-form.

Results and discussion

Catalyst screening

The activities of the solid acid catalysts in the esterification of 1-octanol and hexanoic acid are presented in figure 4, expressed as the initial reaction rates normalized for the catalyst concentration. In table 1, the selectivity to ester is presented, the other product being the ether formed from two alcohols.

The BEA zeolites and the Nafion/silica composite with 13 wt% of Nafion (SAC13) display similar activities; compared to the esterification reaction.

Figure 4. Catalyst activities in the esterification of 1-octanol and hexanoic acid, measured at standard reaction conditions (433 K, 1:1 mixture in cumene).
without added catalyst, the reaction rate is increased by a factor of 40. The activities of the faujasites are very low. Apparently, these catalysts are not active enough for catalyzing this esterification reaction. Finally, it must be noted that hardly any effect of the Si/Al ratio on the activity was observed, in contrast to the study of Corma et al. (1989) in which the FAU zeolite catalyzed esterification of phenylacetic acid and ethanol was studied. In contrast to our findings, a high activity was found with FAU zeolites for varying Si/Al ratios; maximum activity was observed with a Si/Al ratio of 15. The Si/Al ratio of the FAU zeolites studied in the phenylacetic acid/ethanol esterification was adjusted by an acid treatment. This probably resulted in a change of characteristics, thereby enhancing the performance of the mentioned catalysts (see chapter 3B). Due to this treatment and also due to the different nature of the reaction, the findings of both studies cannot be compared directly.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Selectivity (%) at 100% conversion of 1-octanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>No catalyst added</td>
<td>99**</td>
</tr>
<tr>
<td>BEA (Si/Al=12.5)</td>
<td>92</td>
</tr>
<tr>
<td>BEA (Si/Al=25)</td>
<td>94</td>
</tr>
<tr>
<td>BEA (Si/Al=37.5)</td>
<td>94</td>
</tr>
<tr>
<td>BEA (Si/Al=50)</td>
<td>93</td>
</tr>
<tr>
<td>FAU (Si/Al=2.5)</td>
<td>88**</td>
</tr>
<tr>
<td>FAU (Si/Al=40)</td>
<td>94**</td>
</tr>
<tr>
<td>SAC13</td>
<td>97</td>
</tr>
</tbody>
</table>

** Selectivity after 300 min (conv. < 100%).

The selectivity of the catalysts towards the formed ester is in all cases high, as a result of adding a catalyst the selectivity decreases due to the formation of ethers over the strongly acidic catalytic sites. The highest selectivity (97%) – for a catalyzed reaction - is obtained by the Nafion/silica composite with 13 wt% of Nafion.

**Reproducibility**

To study the reproducibility of the SAC13 catalyzed esterification reaction of hexanoic acid and 1-octanol, multiple reactions were performed, see figure 5. The rate in which the reactants are converted is in all experiments similar, indicating a good reproducibility.
Diffusion Limitations

To determine whether the esterification reaction over SAC13 is internal or external diffusion limited, the rate dependency on particle size and stirrer speed dependency was investigated. The stirrer speed measurements were conducted in two different configurations; in the reflux reactor (0, 245 and 500 rpm) and in the (micro) autoclave (250, 500 and 1000 rpm). In neither case was any stirrer speed dependency found. In the reflux reactor, the same results were obtained even when no stirring is applied (0 rpm), the boiling of the reaction mixture already ensured sufficiently vigorous mixing. From these results, external diffusion limitations can be excluded. In contrast, varying the particle size of the Nafion/silica composites resulted in a reaction rate dependence (figure 6), indicating internal diffusion limitations.

Figure 6. The particle size dependency measured in the SAC13 catalyzed esterification of hexanoic acid with 1-octanol, measured at standard conditions (433K, 1:1 mixture in cumene). 50-100 μm (+); 100-160 μm (■); 160-210 μm (▲); <50 μm (+); macro (as supplied) - 2 mm (∗).
This does not apply for the measurement with the particles smaller than 50 μm with a lower conversion rate than expected. It was checked whether the reason lies in the Nafion content. TGA revealed that the Nafion content was lower for the particles smaller than 50 μm compared to the other particles. The reason for this remains unclear, but this explains the lower activity in the esterification reactions. To verify the absence of internal diffusion limitations, the Wheeler-Weisz criterion was applied assuming first order rate dependency, equation [1].

\[
\Phi = \eta \phi^2 = \frac{r_{v,\text{obs}} L^2}{D_{\text{eff}} c_s} \left( \frac{n+1}{2} \right) < 0.15
\]  

[1]

In which the observed reaction rate \( r_{v,\text{obs}} \) (mol.s\(^{-1}\).m\(^{-3}\).cat\(^{-1}\)), the characteristic length of the particles \( L \) (m), the effective diffusivity \( D_{\text{eff}} \) (m\(^2\).s\(^{-1}\)) the bulk concentration \( c_s \) (mol.m\(^{-3}\).cat) and the reaction order \( n \) (-) are defined as in equations [2a-e]; the estimation for the effective diffusivity and the accompanying parameters are taken from Coulson et. al. (1983).

\[
r_{v,\text{obs}} = \left( 0.0014 \frac{\text{mol}}{\text{min} \cdot g_{\text{cat}}} \right) = 10.3 \frac{\text{mol}}{m^3 \cdot \text{cat} \cdot s}
\]  

[2a]

\[
L = \frac{V_p}{A_p} = \frac{d_{\text{sphere}}}{6} = \frac{75 \cdot 10^{-6}}{6} = 1.25 \cdot 10^{-5} \text{m};
\]  

[2b]

\[
D_{\text{eff}} = \frac{D_{\text{iq}} \varepsilon}{\tau} ; D_{\text{iq}} = \frac{1.173 \cdot 10^{-13} (\varphi \cdot M)^{0.5} T}{\mu V_m^{0.6}} = \frac{1.173 \cdot 10^{-13} (10 \cdot 120)^{0.5} 433}{0.21 \cdot (0.1572)^{0.6}} = 8.0 \cdot 10^{-9};
\]  

[2c]

\[
D_{\text{eff}} = \frac{8.0 \cdot 10^{-9} \cdot 0.6}{3.5} = 1.4 \cdot 10^{-9} \text{m}^2 \text{s}^{-1};
\]  

[2d]

\[
c_s = 0.45 \cdot 10^3 \frac{\text{mol}}{m^3};
\]  

[2e]

\[
n = 1;
\]  

[2f]

The Wheeler-Weisz criterion (\( \Phi \)) calculated for the reaction (in equation [2f]) performed with a particle size of 50-100 μm has a value of 0.0026 which is much lower than the criterion of 0.15. However, it is surprising that for larger particles still a low Wheeler-Weisz criterion can be calculated. This is because the calculation was done for a first order irreversible reaction, and the esterification is a second order reversible reaction. That is the reason why the equilibrium and the diffusion limited area can be reached earlier. From this it is concluded that no internal diffusion limitations are present in the experiments performed with 50-100 μm. All further experiments were done with a particle size of 50-100 μm.
Chapter 6

Temperature dependency

The esterification reaction, catalyzed by SAC13, was performed at various temperatures, namely at 313, 358, 398, and 433 K. At 313K no conversion was measured. The results are depicted in figure 7a. On the basis of these experiments an apparent activation energy was calculated by substituting the initial reaction rates (normalized for the catalyst concentration) in the Arrhenius equation [3]. The Arrhenius plot is depicted in figure 7b.

![Graph showing conversion and Arrhenius plot](image)

Figure 7. The temperature dependency measurements of the SAC13 catalyzed esterification of hexanoic acid with 1-octanol, measured at standard conditions (433K, 1:1 mixture in cumene). a. Conversion at various temperatures. b. Arrhenius plot of the catalyzed esterification.

\[
t_{\text{app}} = e^{\frac{E_a}{RT}}
\]

[3]

The effect of the temperature on the rate is very significant. An apparent activation energy of 58 kJ/mol is calculated.

Kinetics

To determine the kinetics of this system, various experiments were conducted in both the reflow ('open') configuration and the ('closed') micro autoclave. Because the esterification reaction is a reversible reaction, it is expected that the reaction is limited by the equilibrium in the autoclave and shifts towards full conversion in the reflow setup due to water removal. That water is removed in this latter setup was already demonstrated in the acylation of aromatics (see chapter 2). In figure 8 the conversion of the reactants in these systems is given. Also an experiment with initially added water is depicted for the closed system.
Figure 8. The SAC13 catalyzed esterification of hexanoic acid and 1-octanol measured at standard conditions (0.45 mol/l in cumene) in (a) ‘open’ reflux system, (b) ‘closed’ microautoclave, and (c) ‘closed’ microautoclave system with initially 1.0 g water added.

When performed in the autoclave system, the esterification attains only 30% conversion after 100 min, while the ‘open’ reflux system full conversion is achieved after the same reaction time, as a result of the removal of water. Water removal will also enhance the reaction rate in case water has an inhibiting effect on the catalyst. Additional experiments were conducted in the microautoclave in the presence of initially added water (figure 8c). By adding water the total conversion decreases, probably due to a combination of equilibrium shift and inhibition of the active sites of the catalyst by water.

The effect of this added water on the initial reaction rate is given in figure 9. The initial rates evidently decrease with increasing initial water concentration. If a Langmuir-Hinshelwood type of expression is considered the following equation [4] can be applied to account for this inhibition and subsequently an apparent value for the adsorption term of water can be determined.

\[
r_{\text{obs}} = r_0 \cdot \frac{1}{1 + K_w W}
\]

Figure 9. The effect of initially added water on the apparent initial first order rate constant \( k_{\text{app}} \). Markers – experimental results. Line - Inhibition relation, eq. (4).
Chapter 6

with \( r_{\text{obs}} \) (mol g\(^{-1}\).min\(^{-1}\)) for the initial observed reaction rate, \( r_0 \) (mol g\(^{-1}\).min\(^{-1}\)) for the initial reaction rate in the absence of initially added water, \( K_w \) (l mol\(^{-1}\)) for the apparent adsorption constant of water, and \( W \) (mol l\(^{-1}\)) for the initial concentration of water. This reaction rate dependency on the adsorption of water is depicted in figure 9, evidencing the rate inhibition by water adsorption.

To determine the influence of the reactant concentrations separately, experiments were performed by keeping the concentration of one reactant constant and varying the concentration of the other reactant. The reaction rate of the carboxylic acid in these reactions is depicted in figure 10. The effect of varying the acid concentration on the reaction rate at a constant alcohol concentration of 0.45 mol/l, is plotted in figure 10a. Figure 10b gives the effect of a varying alcohol concentration on the initial reaction rate at a constant acid concentration of 0.45 mol/l.

![Figure 10](image-url)  
*Figure 10. The effect of varying the carboxylic acid/alcohol concentration on the initial reaction rate of the esterification (433K). a. Varying the acid concentration at an alcohol concentration of 0.45 mol/l. b. Varying the alcohol concentration at an acid concentration of 0.45 mol/l.*

When increasing the acid concentration relative to the alcohol concentration, a linear relationship is found, indicating a first order dependency of the initial reaction rate on the acid concentration. However, when the concentration of alcohol is increased the reaction rate decreases, indicating an inhibiting effect of the alcohol on the reaction rate. This indicates a negative order dependency of the reaction rate on the alcohol concentration.

Also, a side reaction is observed in which an ether is formed from two alcohol molecules. To investigate this side reaction, some etherification experiments were performed in which the concentration of alcohol was varied between 0.2 and 0.9 mol/l. Also an etherification reaction was performed without any catalyst, but this reaction did not give any conversion of the alcohol. The initial reaction rates of these etherifications did not depend on the alcohol concentration, indicating a zero order dependency. The rate at which the etherification proceeds, is of the order of \( 1.25 \times 10^{-4} \) mol/g.min, a factor of 12 lower than the esterification reaction rate (0.0014 mol/g.min) at the standard conditions.
Chapter 6

Kinetic model of the esterification

The kinetic models found in literature for esterification reactions imply often a first order in both reactants (see introduction). Apart from the biocatalyzed reactions, only in one study (the study of Corma et al., 1989) of a heterogeneously catalyzed reaction an inhibiting effect of both reactants was modelled. From the data presented in that article, an increase is observed in the initial rates when increasing the concentration of the carboxylic acid while keeping the alcohol concentration constant and vice versa. Those results are not comparable with our results, probably because the catalyst, the reactants and the reaction conditions are different. Because no model was found in literature of a Nafion catalyzed esterification reaction including an inhibiting effect of the alcohol, a new kinetic model is derived in this study.

For the formulation of the kinetic model, a model is considered in which one or more reactants adsorb at the surface of a solid acid catalyst. Because the reaction order in the acid appears to be 1 and the apparent order for the initial reaction rate in the alcohol negative, an Eley-Rideal type of model is proposed.

In the kinetic model the acid adsorbs on the catalyst surface first. After adsorption, the adsorbed acid reacts with a ‘free’ alcohol from the solution. After reaction an ester and a water molecule is formed. This one-site model implies that only one of the products will remain adsorbed after reaction. In the reaction mechanism of the esterification, the ester is protonated, after which water will be released (McMurry, 1988). Therefore, the adsorption of the ester will be considered in this model. The elementary steps of the proposed model are depicted in figure 11. In this model the reaction occurs through a two-step mechanism. First, the acid is adsorbed on the active sites of the catalyst in step 1, and secondly the adsorbed acid (C*) reacts with alcohol (A) in step 3. These two reaction steps are considered the rate determining steps.

Also a side reaction is observed in which an ether is formed between two adsorbed alcohols (step 4). Besides the reaction, the reactants and products also adsorb and desorb on the active sites of the catalyst. The adsorption and desorption of alcohol, water, ester, and ether are elementary steps 2, 5, 6, 7 respectively. These steps are considered to be in quasi-equilibrium.
Summarizing, the assumptions made are;

- Single site reaction
- Reaction takes place at the catalyst surface
- Two rate determining steps
  - adsorption of the acid
  - reaction of adsorbed acid with alcohol from the solution
- Inhibition of the alcohol, water, ester, and ether through competitive adsorption

For the derivation of the kinetic model the reaction rate is defined from the two rate determining steps, 1 and 3. This results in equation [5] and [6].

\[ r_1 = k_1 C^* - k_{-1} C^* \]  \hspace{1cm} [5]

\[ r_3 = k_3 A(C^*) - k_{-3}(E^*) W \]  \hspace{1cm} [6]

The amount of adsorbed carboxylic acid is defined in equation [7] by considering reactions (1) and (3) are in series, and thus equal:

\[ k_3 A(C^*) - k_{-3}(E^*) W = k_1 C^* - k_{-1} C^* \]  \hspace{1cm} [7]

Because the elementary steps 2, 5, 6, and 7 are considered to be in quasi-equilibrium the alcohol and product surface concentrations are related to their concentrations in the liquid phase:

\[ K_A = \frac{(A^*)}{A(*)}; \quad K_W = \frac{(W^*)}{W(*)}; \quad K_E = \frac{(E^*)}{E(*)}; \quad K_T = \frac{(T^*)}{T(*)} \]  \hspace{1cm} [8a-d]
Combining the amount of adsorbed ester in [8c] with equation [7] the amount of adsorbed carboxylic acid follows in equation [9a and b]

\[(k_4C + k_{-3}K_E EW)(*) = (k_A + k_{-1})(C*)\;\quad [9a]\]

\[C(*) = \frac{k_4C + k_{-3}K_E EW}{k_A + k_{-1}}\;\quad [9b]\]

The total amount of sites is defined in the site balance:

\[N_T = (*) + (C*) + (A*) + (W*) + (E*) + (T*)\;\quad [10]\]

Combining equations [8a-d] and [9] in the site balance equation [10]:

\[N_T = (*) + \frac{k_4C + k_{-3}K_E EW}{k_A + k_{-1}}(w*) + K_A A(*) + K_w W(*) + K_E E(*) + K_T T(*)\;\quad [11]\]

Reformulating [11] gives an expression for the amount of available free active sites:

\[(*) = \frac{N_T}{1 + \frac{k_4C + k_{-3}K_E EW}{k_A + k_{-1}} + K_A A + K_w W + K_E E + K_T T}\;\quad [12]\]

The expression for the amount of carboxylic acid adsorbed on the catalyst [9] and the amount of adsorbed ester [8c] is combined with rate expression from elementary step 3 [6], and after including the obtained expression for the amount of available free active sites, equation [13] is obtained for the reaction rate.

\[r = \frac{k_3N_T \left( \frac{k_A A + k_{-1}K_E EW}{k_A + k_{-1}} - \frac{k_{-3}K_E EW}{k_3} \right)}{1 + \frac{k_4C + k_{-3}K_E EW}{k_A + k_{-1}} + K_A A + K_w W + K_E E + K_T T}\;\quad [13]\]

Which can be reformulated into equation [14]:

\[r = \frac{k_3N_T \left( \frac{k_A k_3A - K_E k_{-3}k_{-1}EW}{k_3(k_A + k_{-1})} \right)}{1 + \frac{k_4C + k_{-3}K_E EW}{k_A + k_{-1}} + K_A A + K_w W + K_E E + K_T T}\;\quad [14]\]
Chapter 6

After including the overall reaction equilibrium constant, equation [15], the final model for the reaction rate of the esterification reaction is obtained in equation [16].

\[ K_{eq} = \frac{K_1 K_3}{K_E} \]  \hspace{1cm} [15]

\[ r = \left( \frac{k_1k_3N_T}{(k_3A + k_{-1})} \right) \left( \frac{AC - \frac{EW}{K_{eq}}}{1 + \left( \frac{k_1C + k_{-1}K_E EW}{k_3A + k_{-1}} \right) + K_E E + K_A A + K_W W + K_T T} \right) \] \hspace{1cm} [16]

The obtained kinetic model for the reaction rate of the esterification can be simplified into expression [4] for the inhibition of water, when the initial reaction is considered. The concentration of the produced ester and ether is initially zero, while both alcohol and acid concentrations are known, leading to the initial rate expression [17]

\[ r_o = \frac{k_1k_3N_T AC}{(k_3A + k_{-1}) \left( 1 + \frac{K_1C}{k_3A + k_{-1}} + K_A A \right)} \cdot \frac{1}{\left( 1 + \left[ \frac{K_W}{1 + \left( \frac{k_1C}{k_3A + k_{-1}} + K_A A \right)} W \right] \right)} \] \hspace{1cm} [17]

In equation [17], the first part between round brackets represents \( r_o \) in equation [4]. Similarly, the part between the straight brackets represents \( K_W \) in equation [4].

Parallel to the esterification also an etherification occurs. In literature, a kinetic model for the Nafion catalyzed etherification of methanol and isobutanol is based on a dual-site mechanism with second order kinetics and an inhibition of the alcohol (Nunan et al., 1993). For the SAC13 catalyzed etherification of 1-octanol the same model is proposed, see equation [18] for the reaction rate definition. For the elementary step of this reaction see figure 11 ('etherification reaction').

\[ r_e = k_e (A^*)^2 \] \hspace{1cm} [18]

Here only the forward rate is considered since the extent of this reaction is much smaller compared to the esterification. Substituting the definition for \( A^* \) [8a] in formula [18] and combining with the obtained expression for the amount of available active sites [12] leads to
\[ r_d = \frac{k_4 K_A^2 A'(sN_T)}{\left(1 + \frac{k_j C + k_{-j} K_E EW}{k_j A + k_{-j}}\right)^2 + K_A A + K_W W + K_E E + K_T T} \]  

[19]

The concentration profiles of all experiments (the experiments performed in the ‘open’ reactor system with varied acid/alcohol ratio, and the experiments performed in the ‘closed’ system with initially added water discussed earlier) are fitted simultaneously to the defined reaction rate expressions using ‘Micromath Scientist for Windows’ version 2.0. During the fitting of the parameters it was directly clear that the values for \(k_j\), \(K_T\), and \(K_E\) were that low that they can be assumed zero. This information was applied to simplify equations [16] and [19], leading to equation [20] and [21]:

\[ r = \left(\frac{k_j N_T}{A}\right) \frac{\left\{\frac{AC - EW}{K_{eq}}\right\}}{\left(1 + \frac{k_j C}{k_j A}\right) + K_A A + K_W W} \]  

[20]

\[ r_d = \frac{k_4 K_A^2 A'(sN_T)}{(1 + \frac{k_j C}{k_j A} + K_A A + K_W W)^2} \]  

[21]

Physically, this implies a weak adsorption of the ester and ether product, and a low desorption rate (at least indeterminable on the basis of the current data) of the carboxylic acid. From equation [20] the negative order in the alcohol can be deduced and an approximate first order in the carboxylic acid.

Some of the resulting fits (including the experimental data) are plotted in figure 12. The values of the kinetic parameters, the reaction rate constants and the adsorption constants of reactants and products are given in table 2, including their error margin.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>95% confidence limit</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>0.014</td>
<td>0.003</td>
<td>(l\cdot\text{cat}^{-1}\cdot\text{min}^{-1})</td>
</tr>
<tr>
<td>(K_A)</td>
<td>5.3</td>
<td>1.5</td>
<td>(l\cdot\text{mol}^{-1})</td>
</tr>
<tr>
<td>(K_W)</td>
<td>29.4</td>
<td>4.0</td>
<td>(l\cdot\text{mol}^{-1})</td>
</tr>
<tr>
<td>(k_3)</td>
<td>0.017</td>
<td>0.002</td>
<td>(l\cdot\text{cat}^{-1}\cdot\text{min}^{-1})</td>
</tr>
<tr>
<td>(k_4)</td>
<td>0.00013</td>
<td>2\times10^{-5}</td>
<td>(l\cdot\text{cat}^{-1}\cdot\text{min}^{-1})</td>
</tr>
<tr>
<td>(K_{eq})</td>
<td>1.6</td>
<td>0.4</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2. The values of the estimated parameters in the kinetic model.
From figures 12a-d it can be concluded that the kinetic model fits the experimental data fairly well, as the fitted lines follow the measured experimental points. From table 2, the values for the kinetic parameters, a very strong water adsorption is found, with a $K_W$ of 29.4 l/mol. The adsorption of the alcohol is also relatively strong, although lower than for water, with a $K_A$ of 5.3. The values for the $k_i$, $K_T$, $K_E$ are so low that they were assumed zero. This means that the desorption of the carboxylic acid ($k_i$), and the inhibiting effect of the ether and the ester ($K_T$, $K_E$) can be assumed negligible, confirming the choice for neglecting these parameters in the etherification (equation [19]). Finally, the rate constant for the adsorption of the carboxylic acid has a value of 0.014 $l/g_{cat}.min$, and the esterification rate constant a value of (0.017 $l/g_{cat}.min$), both of a similar magnitude.

Figure 12. The concentration profiles of some of the esterification reactions. Line – Fitted according to the model. Markers – Experimental data. a. ‘open’ slurry system, initial ratio Alcohol/Acid=4:1; b. ‘open’ slurry system, initial ratio Alcohol/Acid=1:2; c. ‘closed’ slurry system, initial ratio Alcohol/Acid 1/1; d. ‘closed’ slurry system, initial ratio Alcohol/Acid 1/1; initial water concentration 0.85 mol/l.

The kinetics of esterification reactions of other substrates found in literature corresponds well with the Eley-Rideal type of kinetics found in this study (Garcia et al., 2000; Otton and Ratton, 1988; Erdem-Senatalar et al., 1995; Corma et al., 1989). However, the inhibiting effect of the alcohol was not described earlier in literature. In the study of Corma et al.(1989),
an inhibiting effect was found of both carboxylic acid and alcohol, with the adsorption constant being 1.6 higher than the adsorption constant of the alcohol. The reason for this, is that system studied here is obviously very different, especially when considering the Nafion catalyst, the reaction conditions, and the reactants. Comparing the results with the Lewis acid catalyzed system (the CoCl₂ catalyzed esterification of castor oil and oleic acid (Erdem-Senatalar et al., 1995) found in literature, it seems that the adsorption of a carboxylic acid is weaker on Nafion than on a Lewis acid. In the latter study a fast formation was found of the catalyst-acid intermediate followed by a slow formation of the ester and water. However, no inhibiting effect was found of only the alcohol.

The kinetic model developed in this study enables the prediction and optimization of the performance of the esterification reaction by choosing the right process conditions. The inhibiting effect of the alcohol and water should be considered. A possibility to achieve a low water concentration, is to remove the water in-situ, for example by stripping the water out of the mixture during reaction. To keep the alcohol concentration low, a plug-flow reactor can be used in which low amounts of alcohol are added to the reaction mixture in stages ('staged feeding'). These reactor configuration options are discussed in more detail in the next chapter.

Conclusions

In the esterification reaction of hexanoic acid and 1-octanol, zeolite BEA and the Nafion/silica composite with 13 wt% of Nafion (SAC13) gave the highest activity, being much higher than for the reaction rate without a catalyst. The performance of this reaction proved to be reproducible. The selectivity towards the formed ester is in all cases >90%, the side reaction being an etherification reaction between two alcohol molecules. The effect of the temperature on the SAC13 catalyzed esterification yielded an apparent activation energy of 58 kJ/mol.

The advantage of water removal is clearly demonstrated, in a closed system equilibrium is not even reached after 400 min, whereas in a system with water removal all the reactants were converted just after 100 minutes under the applied conditions. Water is a strong inhibitor in the reaction.

No kinetic model was found in literature of the Nafion catalyzed esterification of 1-octanol with hexanoic acid. The kinetic model derived in this study for the mentioned esterification reaction is of an Eley-Rideal type with two reaction steps rate limiting, viz., the adsorption of the carboxylic acid followed by a reaction between an adsorbed carboxylic acid molecule and a 'free' alcohol from the solution. A first order dependency in the acid and an inhibiting effect of alcohol (\( K_A = 5 \) l/mol) and a very strong effect of inhibiting water (\( K_W = 30 \) l/mol) were found. The developed kinetic model can be applied in reactor design modelling to predict and optimize this esterification reaction by choosing the right process conditions.
Chapter 6

Nomenclature

* Active site
A Alcohol concentration [mol.l⁻¹]
cₛ Bulk concentration [mol.mₑₜ⁻³]
C Carboxylic acid concentration [mol.l⁻¹]
Dₑₜ Effective diffusivity [m².s⁻²]
E Ester concentration [mol.l⁻¹]
k Rate constant [l.gₑₜ⁻¹.min⁻¹]
K Adsorption constant [l.mol⁻¹]
Kₐ Apparent adsorption constant of water [l.mol⁻¹]
L Characteristic length of the particles [m]
n Reaction order [-]
Nₑₜ Catalyst concentration [g.l⁻¹]
r Reaction rate [mol.l⁻¹.min⁻¹]
rᵥₐₜ Observed reaction rate - Wheeler-Weisz calculation [mol.s⁻¹.mₑₜ⁻³]
rₒₜ Initial observed reaction rate - water effects [mol.gₑₜ⁻¹.min⁻¹]
rₒ Initial observed reaction rate (no initially added water) [mol.gₑₜ⁻¹.min⁻¹]
T Ether concentration [mol.l⁻¹]
W Water concentration [mol.l⁻¹]

Greek letters

Φ Wheeler-Weisz criterion [-]

Acknowledgements

Remko Spruijt, Susan van Bokhorst and Xander Nijhuis are gratefully acknowledged for their contribution to this chapter.

References

Chapter 6


Reactor configurations in esterification

Summary

Reactor configuration options are discussed for the optimal performance of the solid acid catalyzed esterification of 1-octanol and hexanoic acid. Simulating the esterification of 1-octanol and hexanoic acid results in a higher performance of the reaction in a fed-batch reactor, in which alcohol is continuously fed to the system compared to a batch reactor. In this way, the inhibiting alcohol concentration can be kept as low as possible during the esterification reaction.

Applying co-and countercurrent reactive stripping in a finned monolithic reactor removes the inhibiting water that is produced and enhances the performance of the esterification of 1-octanol and hexanoic acid when compared to a system without any additional stripping (conversion 62%). Counter-current stripping results in a higher conversion (98%) than co-current stripping (84%).

Performing the esterification of 1-octanol and hexanoic acid in a BEA coated finned monolith results in only a slightly lower activity when compared to the slurry phase. Regenerating BEA coated monoliths between consecutive reactions by calcination in static air at 723K suffices for maintaining the performance. The activity of these BEA coated structures also gave high conversions on a pilot scale. On this latter scale the enhancement was shown of the countercurrent water stripping on the performance of the structured catalysts.
Chapter 7

Introduction

In this concluding chapter, the reactor configurations for an optimal performance of the solid acid catalyzed esterification will be described. From the kinetic study on the esterification reaction it was demonstrated that the reaction is inhibited by the alcohol, used as a reactant, and by the water that is produced. Two reactor types are considered, a batch and a continuous reactor.

The inhibition of alcohol can be minimized by keeping the alcohol concentration during reaction conditions low, for example in a fed-batch configuration with continuous feeding of the alcohol. The effect of performing the reaction in a fed-batch is studied by simulating the reaction in this reactor using the kinetic data obtained in chapter 6, and comparing the results with a batch reactor. In a continuous reactor this could be achieved by segregated feeding of the alcohol at several locations in the reactor or even through a membrane. Numerically this corresponds to a fed-batch system and similar results can be observed.

The inhibition of water can be minimized by removal of this product during reaction. This can be achieved by reactive stripping or with a membrane which is selective for water (Bakker et al., 1998). This latter option has not been investigated in this study. The reactive stripping operation in the monolithic reactor is studied by simulating the esterification in this reactor, in co- and countercurrent mode and compared with no stripping. These stripping operations are described in chapter 1.

The effect of reactive stripping on the performance was studied experimentally by performing the esterification reaction of 1-octanol and hexanoic acid using a BEA coated finned monolith that was developed in chapter 4 and 5 (chapter 5) with and without stripping.

Simulation of the esterification reaction in a fed-batch and batch mode.

To predict the performance of the SAC13 catalyzed esterification of 1-octanol and hexanoic acid in a batch- and a fed-batch reactor, the following assumptions were made:

- The reaction follows the kinetic model as presented in chapter 6 (eq [16]), including the etherification reaction.
- The amount catalyst used is 10 g of SAC13.
- The total amount of hexanoic acid is 3.9 mol.
- The total amount of 1-octanol is 3.9 mol.
Chapter 7

- Total reaction volume is 1 l (i.e. 3.9 mol 1-octanol and 3.9 mol hexanoic acid).
- Only pure components are applied (no solvent).
- A reaction temperature of 427K.
- Water is removed during reaction conditions by means of, for example, stripping or membrane application.

For the batch operation, initially, the total amount of reactants (3.9 mol 1-octanol and 3.9 mol hexanoic acid) are mixed. The conversion is calculated according to the kinetic model shown in chapter 6 (equation [16]). The amount of reactants and products can be calculated with this conversion and the reactor volume, which changes in time due to the differences in density of alcohol, acid, ester, and ether. See figure 1 for the equations used for calculating the concentration evolution. The results, calculated for a reaction time of 200 min, can be found in figure 2a.

For the fed-batch operation, initially, 3.9 mol hexanoic acid and 0 mol 1-octanol are mixed. Next, the alcohol is fed with a feed rate of 0.039 mol/min. The amount of reactants and products are calculated similarly as above, with the defined kinetic model in chapter 6 (eq. [16]) and the reactor volume which changes in time due to feed stream of the alcohol and the differences in density between the alcohol, acid, ester, and ether; see figure 1 for the used equations. This was calculated for a reaction time of 100 min. After 100 min, the feeding of alcohol was ended (total of 3.9 mol alcohol added) and the reaction mixture was kept as a batch reactor for another 100 min to convert all the alcohol left after the first 100 min. The results can be found in figure 2b.

The batch reactor shows 99% conversion of the alcohol after 165 min, while the same conversion is obtained after 145 min in the fed-batch configuration. In this process, where the alcohol inhibits the reaction, the benefit of using a fed-batch configuration is clearly demonstrated. The selectivity of the batch configuration at full conversion is lower (96.8%) than the selectivity of the fed-batch configuration (99.6%). The selectivity is influenced by the rate of the etherification (as a side reaction) which is dependent on the alcohol concentration. A higher selectivity will result for the fed-batch configuration due to the lower alcohol concentration during the process. Since the water is removed continuously during the process all ether formed represents a permanent loss of the alcohol reactant.
For both Batch and Fed-batch:

\[ r_{\text{ester}} = \left( \frac{k_1 k_s N_T}{(k_j A + k_{-j})} \right) \left( \frac{AC - EW}{K_{eq}} \right) \]

\[ r_{\text{ether}} = \frac{k_3 K_A^2 A^3 (s N_T)}{\left(1 + \left( \frac{k_j C + k_{-j} K_E EW}{k_j A + k_{-j}} \right) + K_A A + K_W W + K_E E + K_T T \right)^2} \]

\[ V = \frac{N_{al}}{M_{al} \cdot \rho_{al}} + \frac{N_{ac}}{M_{ac} \cdot \rho_{ac}} + \frac{N_{es}}{M_{es} \cdot \rho_{es}} + \frac{N_{et}}{M_{et} \cdot \rho_{et}} \]

\[ \frac{dN_{al}}{dt} = -r_{\text{ester}} \cdot V; \quad \frac{dN_{ac}}{dt} = -r_{\text{ester}} \cdot V; \quad \frac{dN_{es}}{dt} = r_{\text{ester}} \cdot V; \quad \frac{dN_{et}}{dt} = -r_{\text{ether}} \cdot V \]

Initial conditions \( t=0; \ N_{ac}=3.9 \ \text{mol} ; \ N_{es}, N_{et}=0 \)

For Batch:

\[ \frac{dN_{al}}{dt} = -r_{\text{ester}} \cdot V - 2 \cdot r_{\text{ether}} \cdot V \]

Initial conditions \( t=0; \ N_{al}=3.9 \ \text{mol} \)

For Fed-batch:

\[ \frac{dN_{al}}{dt} = -r_{\text{ester}} \cdot V - 2 \cdot r_{\text{ether}} \cdot V + \varphi_{N_{al}} \]

Initial conditions \( t=0; \ N_{al}=0 \ \text{mol} \)

Figure 1. The equations used for calculating the concentration profiles of the SAC13 catalyzed esterification of 1-octanol and hexanoic acid in a batch and fed-batch reactor.
Figure 2. Simulation of the SAC13 catalyzed esterification of 1-octanol and hexanoic acid in a batch and a fed-batch reactor. a. Batch. b. Fed-batch.
Chapter 7

Simulation of reactive stripping during esterification in a monolithic reactor

To predict the performance of a catalyst coated monolith in the esterification reaction in a monolithic reactor with and without co- and countercurrent reactive stripping the ‘falling laminar film flow model’ was used (Skelland, 1974). In this model, the gas and liquid are both considered as a laminar flow. The assumptions made in this model are:

- A laminar flow of gas and liquid
- The water partition over gas and liquid follows Henry’s law
- Mass transfer from liquid to solid is neglected
- Gas to liquid mass transfer is calculated by the penetration theory
- As water is the most volatile component, only the evaporation of water is considered.
- The kinetics of the SAC13 catalyzed esterification reaction is the model as developed in chapter 6.
- Total wetting of the monolith.

The concentration profiles over the length of the monolith reactor are modelled using 'Pdesol' v. 2.0 by Numerica. The relations of which the model consist are described in table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass transfer coefficient (gas) (k_g)</td>
<td>(k_g = Sh \cdot \frac{D_x}{d_{channel}}); (Sh = 3.66)</td>
</tr>
<tr>
<td>Mass transfer coefficient (liquid) (k_l)</td>
<td>(k_l = Sh \cdot \frac{D_l}{d_{film}}); (Sh = 2)</td>
</tr>
<tr>
<td>Partition coefficient for water over gas and liquid (m)</td>
<td>(m = \frac{H_{water}}{R \cdot T})</td>
</tr>
<tr>
<td>Overall mass transfer resistance for gas phase (k_{og})</td>
<td>(k_{og} = \frac{1}{\frac{1}{k_g} + \frac{m}{k_l}})</td>
</tr>
<tr>
<td>Overall mass transfer resistance for liquid phase (k_{ol})</td>
<td>(k_{ol} = m \cdot k_{og})</td>
</tr>
</tbody>
</table>
Re = \frac{\rho v d}{\eta} \quad [1]

The Reynolds number, eq. [1], was calculated by using the variables as presented in table 2. For the gas phase a Reynolds number of 210 was calculated and for the liquid phase a Reynolds number of 40 was calculated. These values are both much lower than 2000, indicating that the application of the correlations for the laminar flow is permitted.

Table 2. The variables used for the calculation of the Reynolds number for validating the laminar flow.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Gas phase</th>
<th>Liquid phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ( \rho (kg/m^3) )</td>
<td>30</td>
<td>800</td>
</tr>
<tr>
<td>Superficial velocity ( v (m/s) )</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>'diameter' ( d (m) )</td>
<td>3.5.10^{-3} (channel diameter ( d_{ch} ))</td>
<td>5.10^{-4} (film thickness ( d_{film} ))</td>
</tr>
<tr>
<td>Viscosity ( \eta (Pa.s) )</td>
<td>2.5.10^{-5}</td>
<td>1.10^{-4}</td>
</tr>
<tr>
<td>Diffusivity ( D (m^2/s) )</td>
<td>5.6.10^{-5}</td>
<td>3.10^{-8}</td>
</tr>
</tbody>
</table>

The mass transfer coefficients \( k_g \) and \( k_l \) follow from the penetration theory for respectively radial diffusion with laminar flow in a tube and radial diffusion with laminar flow between two coaxial cylinders. In the case of the laminar gas flow, the Sherwood number of 3.66 is applied (Perry et al., 1997) and for laminar liquid flow the Sherwood number of 2 (Perry et al., 1997). For the gas phase, the validity of the penetration theory for radial diffusion with laminar flow (Sh=3.66) is verified using equation 7.2a. For the liquid phase, the validity of the penetration theory for the radial diffusion with laminar flow between two coaxial cylinders is verified using equation 7.2b.

\[
x > \frac{v \cdot d_{channel}^2}{D_g} \cdot 0.1 \quad [2a]
\]

\[
x > \frac{v \cdot d_{film}^2}{D_l} \cdot 0.1 \quad [2b]
\]

In equations [2a] and [2b], \( x \) represents the length of the reactor (m) after which the penetration theory approximation is allowed. \( D_g \) and \( D_l \) represent the diffusivity for respectively gas and liquid. For the gas phase a value of \( x > 0.01 \) m is calculated from equation [2a], with \( v = 0.05 \) m/s, \( d_{ch} = 3.5.10^{-3} \) m, \( D_g = 5.6.10^{-5} \). For the liquid phase, the value for \( x \) that is calculated is \( x > 0.08 \) from equation [2b], with \( v = 0.01 \) m/s, \( d_{film} = 5.10^{-4} \) m, \( D_l = 3.10^{-8} \). So, in the case of a monolith longer than 0.08 m, these correlations are allowed.
Chapter 7

The collected kinetic parameters from chapter 6 were used in the model. For the simulation the esterification reaction performed in a monolithic reactor with and without stripping, the following parameters are considered: a total reactor length of 12 m, a catalyst loading of 10 wt%, a superficial velocity of the gas of 0.05 cm/s, and a superficial velocity of the liquid of 0.01 cm/s. The results of the simulation are depicted in figure 3. In this figure, the concentration profiles of both esterification products (water and ester) are plotted vs the reactor length without stripping (only liquid flow with stagnant gas phase) and with co- and countercurrent stripping.

![Graph showing concentration profiles of water and ester](image)

Figure 3. Simulation of the effect of co- and counter-current stripping on the esterification reaction over SAC13, as modelled with the falling film model.

From figure 3 it is clear that the reactive stripping operation is highly beneficial for the advancement of the reaction. This is due to the removal of the inhibiting water product. For the operation without stripping, the same concentration profiles are obtained for both products (water and ester). However, applying co- or counter-current stripping the yield of ester at the end of the reactor is much higher compared to the operation without stripping. The concentration of water will increase towards the end of the reactor in the case of co-current stripping. However, in the case of counter-current stripping the water concentration will only increase initially. After approximately 1.5 m the water concentration will decrease due to the counter-current stripping mode.

The conversion of the alcohol (%) and the yield of the ester (%) at the end of the reactor are presented in table 3.
Table 3. The effect of co- and counter-current stripping on performance of the esterification reaction in a monolith of 12 m.

<table>
<thead>
<tr>
<th></th>
<th>Conversion of the alcohol at the end of the reactor (%)</th>
<th>Ester yield at the end of the reactor (%)</th>
<th>Selectivity at the end of the reactor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counter-current stripping</td>
<td>98.6</td>
<td>95.6</td>
<td>97.0</td>
</tr>
<tr>
<td>Co-current stripping</td>
<td>84.3</td>
<td>82.1</td>
<td>97.5</td>
</tr>
<tr>
<td>Without stripping</td>
<td>62.0</td>
<td>61.2</td>
<td>98.6</td>
</tr>
</tbody>
</table>

The conversion of the alcohol and the ester yield are higher in the case of both co- and counter-current stripping compared to the operation without stripping, due to the removal of the inhibiting water.

The selectivity is higher in the configuration where no stripping is applied, but the ester yield is lower. This is due to the dependency of the esterification and the etherification rate on the water concentration. In the kinetic model (see chapter 6), the water inhibition on the etherification rate is stronger than on the esterification rate. Because the water concentration is higher than in the case of the stripping operations, the selectivity will be lower.

Comparing the selectivity of the co-current stripping with counter-current stripping, a slightly lower selectivity is obtained by the counter-current operation for the same reasons. The water concentration over the reactor differs in both stripping operations, see figure 3. The water concentration decreases from top to bottom of reactor in the case of co-current stripping, while the water concentration initially increases in the case of counter-current stripping. Because the rate of the reversible esterification is influenced by the water concentration, and the etherification is modelled as a non-equilibrium reaction, the selectivity will be lower for the case with the highest water concentration, i.e. the counter-current operation.

In practice, the reactor length of 12 m can easily be achieved by stacking shorter fragments of monoliths (for example with a length of 0.5 m). Due to the parallel channels and the equal gas–liquid radial distribution from top to bottom, a stacked monolith will give an equal performance as a monolith which is not stacked.

By increasing the monolith length of 12 m to, for example, 20 m the conversion can be increased even more, see table 4, but for a small increase in conversion a much longer monolith is necessary. Increasing the length of the monolith with 8 m results in an increase of
conversion of 1.1%, but in this case the etherification reaction is favoured leading to a reduced yield.

Table 4. The effect of co- and counter-current stripping on performance of the SAC13 catalyzed esterification reaction in a monolith of 20 m.

<table>
<thead>
<tr>
<th></th>
<th>Conversion of the alcohol at the end of the reactor (%)</th>
<th>Ester yield at the end of the reactor (%)</th>
<th>Selectivity at the end of the reactor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counter-current stripping</td>
<td>99.7</td>
<td>94.7</td>
<td>95.0</td>
</tr>
<tr>
<td>Co-current stripping</td>
<td>84.4</td>
<td>82.0</td>
<td>97.2</td>
</tr>
<tr>
<td>Without stripping</td>
<td>70.9</td>
<td>70.0</td>
<td>98.7</td>
</tr>
</tbody>
</table>

Reactive stripping using BEA coated monoliths in the esterification of 1-octanol and hexanoic acid.

For the application of monolithic structures in the esterification reaction cordierite monoliths were coated with zeolite BEA. Unfortunately, the Nafion coated monolithic structures gave no activity in the described pilot scale set-up. The reason for this lack of activity remains unclear, but, as noted in chapter 5, the Nafion is highly susceptible to poisoning due to the low number of active sites. Using larger amounts of reactants this problem will only become stronger. For this reason the study was limited to BEA coated finned monoliths.

The cordierite structures were kindly provided by Corning. The monoliths were coated using the coating procedure described in chapter 4 by dipping the cordierite monolithic structures in a mixture of 2 l of water containing 20 wt% BEA zeolite crystals, 1 wt% of colloidal silica (Ludox AS40, Aldrich) as a binder and 1 wt% of Teepol as a surfactant (to stabilize the suspension). The BEA zeolite used for this coating procedure had a Si/Al ratio of 37.5 (CP 811E-75) and was obtained from Zeolyst International. After dip-coating the structures, a calcination step was executed at 723K for 4 hours. After calcination, the structures were ion-exchanged with a 1 M ammonium nitrate solution at 298K for 16 h (overnight) and calcined for a second time at 723K for 4 hours. A 10 wt% loading of BEA was obtained. The specific activity of this BEA coated monolith was tested on a labscale (monolith dimensions: diameter 43 mm, length 50 mm) in a reflux reactor with internal recirculation at atmospheric pressure
with water removal, see figure 2 from chapter 5 for a schematic view of the set-up. The reaction conditions were the same as for the slurry experiments described in chapter 6, the only difference being the reactor volume (125 ml). Reaction temperature was 427K, concentration of both hexanoic acid and 1-octanol was 0.5 mol/l in cumene. In all cases, the activity was defined as the initial first order rate constant \( k (m_{\text{liq}}^3 \cdot \text{min}^{-1} \cdot g_{\text{cat}}^{-1}) \) normalized for the catalyst concentration.

The activity of the BEA coated internally finned monolith with a length of 2 m and a diameter of 4.3 cm was tested on a pilot scale with recirculation (figure 4) in the esterification reaction of hexanoic acid and 1-octanol. In this setup also counter-current water stripping was performed. The reaction temperature was the same as in the slurry experiments, 427 K. This was achieved by controlling the entire set-up at this temperature, including the vessels and the tubings. Total pressure in the system was 10 bar and total liquid volume was 0.01 m³. The molar ratio in which the reactants were applied was 1:1 and the concentration was 500 mol.m⁻³ in toluene. Toluene was chosen as solvent due to practical reasons. It is assumed that the performance of the esterification reaction in toluene is comparable to the performance in cumene. To investigate this aspect in more detail, further study is necessary. The feed rate of the liquid was 25 kg/h and of the gas 500 NI/h. With these conditions a liquid hold-up of ~1.62% in the reactor (the part of the total volume in the monolith) was calculated with the correlations given by Lebans (1999).

For the counter-current stripping application, the water produced can be removed very conveniently. The water stripping is achieved in the gas phase by an inert gas (nitrogen). After reaction, evaporated product, reactants and solvent can be easily separated from the water, since after condensation (288 K) a phase separation will occur. Solvent and reactants are recycled into the system. A residual water concentration will remain, corresponding to the saturation concentration of water in toluene at 288K.

The activity of the BEA-coated monolith was tested in the above-mentioned esterification reaction in the labscale reflux reactor. From these experiments a first order rate constant \( k \) of \( 1.5 \times 10^{-3} m^3 \cdot \text{min}^{-1} \cdot g^{-1} \) in cumene could be derived for a coated monolith, which is ~25% lower than the \( k \) obtained in the slurry phase for the same catalyst (\( 4.6 \times 10^{-3} m^3 . \text{min}^{-1} . g^{-1} \)) in cumene.
Since the stability of a solid acid catalyst is a very important aspect for industrial application, also deactivation was studied. The BEA coated monoliths were regenerated after performing the reaction by calcination in static air for 4 h at 723 K (heating rate of 10 K/min). The conversion of the alcohol after performing the reaction in four consecutive reactions and regenerations is depicted in figure 5. Apparently, regenerating the BEA coated monoliths between consecutive reactions by calcination in static air at 723K suffices for maintaining the activity in the esterification reaction.

The conversion of the reactants in the pilot reactor system as a function of time is depicted in figure 6. In this figure the activity in the esterification with counter-current stripping is compared with the performance without stripping with nitrogen. Also the reaction without any catalyst was measured as well as the reaction in the presence of a bare cordierite monolith. An efficient active zeolite coated monolith has been prepared, because in the presence of the zeolite coated structures higher activities are observed than the esterification reaction without or with a bare cordierite monolith. The latter two experiments exhibited similar conversion rates as the slurry experiments in which no catalyst was added. For comparison between stripping and no-stripping the conversion at 130 min is considered. At this point the conversion is about 87% in the stripping configuration compared to 75% in the no-stripping configuration.

The high conversion levels reached even without stripping in the pilot scale reactor can be easily explained. In the pilot scale experiments the gashphase volume was about 90% of the total reactor volume. Since the amount of water in the liquid phase is proportional to the vapour pressure of water (being 6.2 bar at the temperature of 427 K), it can be calculated that nearly all the water formed is present in the gas phase, moving the equilibrium reaction towards the right.
Figure 6. The effect of counter-current stripping in the esterification reaction performed on a pilot-scale with BEA coated monolith. (■) Without any catalyst added. (♦) Catalysed by a BEA coated internally finned monolith. (▲) Catalysed by a BEA coated internally finned monolith, with counter-current water stripping.

In these pilot scale experiments, selectivities of 85 and 87% were obtained at 100% of conversion, respectively for the stripping and the no-stripping configuration. The reference experiments (no catalyst, with and without bare cordierite monolith) gave 100% of selectivity, analogous to the slurry experiments without an additional catalyst. This is because the etherification reaction, determining the selectivity, does not occur without the presence of a solid acid catalyst like BEA or Nafion.

Evaluation

The esterification reaction of 1-octanol and hexanoic acid to form an ester and water is a thermodynamically limited reaction. Moreover, water inhibits the reaction. Removal of water is therefore essential to enhance the performance of this reaction. This can be accomplished by (co- or counter-current) reactive stripping in a monolith. At high conversions the counter-current application is preferred over co-current. Additionally the alcohol is also shown to inhibit the reaction. This inhibition can be minimised by feeding this reactant to the reaction mixture in a fed-batch configuration. This has a higher performance than the batch configuration in which all reactants are mixed at once. Because the selectivity depends on the alcohol concentration, also the selectivity is increased in this way. Both aspects, water stripping and staged feeding of alcohol, can very well be applied by using a membrane or performing the reaction in a monolith.
Chapter 7

Conclusions

Simulation of the esterification reaction in batch operation
The simulation of the esterification of 1-octanol and hexanoic acid shows a higher performance in a fed-batch reactor, in which alcohol is continuously fed to the system compared to a batch reactor. In this way, the inhibiting alcohol concentration can be kept as low as possible during the esterification reaction.

Simulation of the esterification reaction in continuous operation
Applying co-and countercurrent reactive stripping in a monolithic reactor enhances the performance of the esterification of 1-octanol and hexanoic acid when compared to a system without any additional stripping (conversion 62%). At a reactor length of 12 m, countercurrent stripping results in a higher conversion (98%) than co-current stripping (84%).

Performance of the esterification reaction in a solid acid coated monolith
Performing the esterification of 1-octanol and hexanoic acid in a BEA coated monolith on lab-scale results in a lower activity (~ 25%) when compared to the slurry phase. Regenerating BEA coated monoliths between consecutive reactions by calcination in static air at 723K suffices for maintaining the activity. The activity of these BEA coated structures gave also high conversions on a pilot scale. On this latter scale, the counter-current water stripping results in an improved performance of the structured catalysts.

Nomenclature

\[ A \text{ Alcohol concentration} \quad [\text{mol}.l^{-1}] \]
\[ C \text{ Carboxylic acid concentration} \quad [\text{mol}.l^{-1}] \]
\[ d_{ch} \text{ Channel diameter} \quad [\text{m}] \]
\[ d_{film} \text{ Film thickness} \quad [\text{m}] \]
\[ D \text{ Diffusivity} \quad [\text{m}^2.s^{-1}] \]
\[ D_g \text{ Diffusivity for gas} \quad [\text{m}^2.s^{-1}] \]
\[ D_l \text{ Diffusivity for liquid} \quad [\text{m}^2.s^{-1}] \]
\[ E \text{ Ester concentration} \quad [\text{mol}.l^{-1}] \]
\[ k \text{ Rate constant} \quad [\text{l.g}.cat^{-1}.\text{min}^{-1}] \]
\[ k_g \text{ Mass transfer coefficient (gas)} \quad [\text{m}.s^{-1}] \]
\[ k_l \text{ Mass transfer coefficient (liquid)} \quad [\text{m}.s^{-1}] \]
Greek letters

η  
Viscosity  
\text{[Pa.s]}

ρ  
Density  
\text{[g.l^{-1}]}

Acknowledgements

Corning Inc. (USA) is gratefully acknowledged for supplying the monoliths. Susan van Bokhorst and Xander Nijhuis are gratefully acknowledged for their contribution to this chapter.

References


Summary

Acylation and esterification are examples of acid catalyzed reactions, which are abound in the fine chemical (pharmaceutical, fragrance and agrochemical) industry. The conventional 'catalysts' for these reactions (metal halides, like AlCl₃, or strong mineral acids, like HF and H₂SO₄) cannot be regenerated and lead to very corrosive waste streams. The use of solid acid catalysts can overcome these disadvantages, because these catalysts can be separated from the reaction mixture and reused. Examples of solid acids are the zeolites and ion-exchange resins. The main disadvantage of using solid catalysts in liquid phase reactions, is the laborious and expensive separation of the catalyst particles from the reaction mixture. Also due to the high stirring speed for mixing attrition of the particles occurs. By integration of the catalyst with the reactor using a structured support, separation and attrition problems are circumvented, so the catalyst can be used for a longer period. An example of a structured reactor is a monolith or honeycomb in which the catalyst can be applied as a thin layer on the walls. A monolithic support consists of a macroporous material, often cordierite, that is structured in straight parallel channels. Another advantage of the structured packing is the fact that the reactants can be mixed before contacting the catalyst to prevent strong adsorption problems. In this way also the undesired side-reactions do not occur, because local high concentrations of reactants and products are prevented.

The aim of this study is to develop a structured reactor configuration with an improved performance for a solid acid catalyzed process, i.e. in which optimal activity and selectivity is achieved and catalyst filtration is eliminated. To achieve this goal chemistry and technology are combined.

The acylation of aromatics was studied in this thesis (chapter 2). In the acylation of anisole with octanoic acid, slurry catalyst screening experiments showed a high activity for the Nafion/silica composite SAC25, with 25 wt% of Nafion, and for the zeolites BEA and USY. However, the Nafion/silica composites showed a batch-dependency in their performance, indicating that their production is not reproducible. In the same reaction, it was demonstrated that water removal during reaction is advantageous for the reaction progress since it inhibits strongly. The kinetics of the BEA catalyzed acylation of anisole with octanoic acid are of an Eley-Rideal type. Cumene shows low activity in the acylation with octanoic acid. The
Summary

The acylation activity of veratrole is higher than that of anisole. No pronounced effect of the chain length of the carboxylic acids (C4-C12) is observed on the acylation activity of anisole.

Further development was focussed on the further enhancement of the activity of the two most active catalysts in the acylation reaction, the Nafion/silica composite and BEA zeolite.

In the preparation of a Nafion/silica composite (chapter 3A), the advantage of the high surface area of silica is combined with the high catalytic activity of Nafion (a perfluorinated ion-exchange resin with highly acidic Brønsted sites). The sol-gel synthesis method proved to be a relatively simple preparation technique in which composites of any desired Nafion loading between 8 and 40 wt% could be prepared with TMOS or Ludox as a silica source. The micro- and mesoporous samples showed surface areas up to 465 m²/g with pore volumes up to 0.95 ml/g, as determined with nitrogen adsorption measurements. The texture could be tuned by various parameters. The Nafion/silica composites show a relative high activity and selectivity, although the reproducibility of the synthesis method needs significant improvement, mainly due to the quality of the synthesis chemicals. The high activity is ascribed to the high acidity of the acid sites. The high selectivity is ascribed to an interaction between the Nafion backbone and the silica functional groups, as demonstrated by FT-IR, resulting in a lower acidity of the Nafion active sites. No leaching of the active species is observed during reaction conditions. The composites show strong deactivation in consecutive experiments.

BEA zeolite was modified by steaming and acid leaching in order to increase the catalytic activity in the acylation of anisole with octanoic acid (chapter 3B). Steaming the parent BEA (commercial zeolite, Si/Al 12 at 673 K (> 3 h) led to an increased activity, paralleled with an increase in extraframework aluminum, both tetrahedrally and octahedrally coordinated, as was demonstrated with 27Al MQ MAS NMR. Leaching the parent BEA in hydrochloric and oxalic acid resulted in high activities, especially in the case of oxalic acid. Acid treatment led to removal of mainly the tetrahedrally coordinated extraframework aluminum. Steaming and acid leaching do not affect the texture properties of the zeolite, as was demonstrated with nitrogen adsorption, XRD and TEM measurements. The nature of the (enhanced) activity in the acylation reaction after steaming and acid leaching is probably correlated with the higher accessibility of the active sites.

To integrate the catalyst into a structured reactor, the catalysts have to be coated onto the walls of the monolith. Therefore, the preparation and characterization of a solid acid coated monolith was studied (chapter 4). The two catalysts that were investigated are Nafion and BEA. A literature overview is given of the preparation and application of Nafion and BEA coatings. The main application of Nafion coatings is in electrochemistry. The Nafion membrane is also used as a gas dryer for selective removal of water. Zeolite coatings are
Summary

mainly applied in membrane applications for gas separations and for the integration of separation and catalysis. The main preparation techniques are dip-coating, in-situ synthesis and extrusion of the carrier with the zeolite. In this thesis, several methods were developed to apply a solid acid catalyst on a monolith. Dip-coating cordierite and silica monoliths in a Nafion-, Nafion/silica- or BEA-containing dip-mixture proved to be a relatively simple and satisfactory coating technique which results in a homogeneously distributed coated structure with loadings of 2-3 wt% Nafion, 3-15 wt% Nafion/silica composite, or 6-8 wt% BEA. The synthesis of a monolith support with a Nafion/silica composite showed a strong dependence of the loading on the amount of Nafion in the dip-mixture. The in-situ synthesis of BEA in the presence of a carrier resulted in blocking of the monolithic channels, and is not under control. In the dip-coating technique, the amount of BEA is well and easily controllable. Furthermore, it is not necessary to adapt the zeolite synthesis formulation for coating applications, so an already optimized zeolite can be applied.

The performance of the Nafion and BEA coated monoliths in the acylation of anisole with octanoic acid is also reported in this thesis (chapter 5). Compared with the activity of the catalysts in slurry configuration, good activities and selectivities were obtained for the coated systems. Nafion coated silica monoliths showed a higher activity and selectivity than pure Nafion. Monolith supported Nafion/silica composites do not show any measurable activity, due to an inadequate gelation step in the synthesis. The activity of the BEA coated monolith is slightly lower compared to the original BEA crystals in a slurry operation, which is ascribed to the zeolite particles being only partly accessible due to the fixation on the support. The selectivity of the BEA coating is maintained compared with the BEA crystals. Nafion coatings are more active than the BEA coatings on a catalyst mass basis, and both catalysts show a comparable selectivity. However, Nafion coatings show low reproducibilities due to poisoning of the (low amount of) active sites. In this respect, the BEA coated structures show to be very promising as structured catalysts for the acylation of anisole with octanoic acid. Stability of the system still needs improvement as shown by repeated re-use.

The esterification of 1-octanol with hexanoic acid (chapter 6), producing ester and water, was also studied. BEA and the Nafion/silica composite with 13 wt% of Nafion (SAC13) gave the highest activity, being much higher than for the reaction rate without a catalyst. The selectivity towards the formed ester is in all cases >90%, the side reaction being an etherification reaction between two alcohol molecules. The effect of the temperature on the SAC13 catalyzed esterification yielded an apparent activation energy of 58 kJ/mol. The presence of water has two negative effects on the reaction rate; inhibition of the catalyst and limitation of the maximum obtainable conversion due to the thermodynamic equilibrium. This was demonstrated by performing the same SAC13 catalyzed esterification reaction in a closed system. Equilibrium was not even reached after 400 min, whereas in a system with water removal all the reactants were converted just after 100 min under the applied conditions.
Summary

The kinetics of the reaction of 1-octanol and hexanoic acid was studied, and a kinetic model was derived which could describe the reaction rate. The kinetic model for this reaction appeared to be of an Eley-Rideal type with two reaction steps rate limiting, viz., the adsorption of the carboxylic acid followed by a reaction between an adsorbed carboxylic acid molecule and a ‘free’ alcohol from the solution. A first order dependency in the acid, a moderate inhibiting effect of alcohol, and a strong inhibiting effect of water were found.

The developed kinetic model for the esterification reaction was applied for prediction and improvement of the performance of two reactor types in the esterification reaction (chapter 7). The kinetics showed an inhibiting effect of the alcohol and of water on the reaction rate. Simulating the esterification of 1-octanol and hexanoic acid in a fed-batch reactor, in which alcohol is continuously fed to the system results in a better performance of the reaction compared to a batch reactor. In this way, the alcohol concentration can be kept as low as possible during the esterification reaction, so less of the byproduct dioctyl ether is formed. To suppress the inhibition of water, it has to be removed from the surface of the catalyst, for example with a dry inert gas by means of stripping. Simulating the application of co-and countercurrent reactive stripping in a continuous finned monolithic reactor for the removal of the inhibiting water resulted in an enhancement of the performance of the esterification of 1-octanol and hexanoic acid when compared to a system without any additional stripping (conversion 62%). Counter-current stripping resulted in a higher conversion (98%) than co-current stripping (84%).

Experimentally, the esterification of 1-octanol and hexanoic acid was performed using a BEA coated finned monolith. These BEA coated structures also gave high conversions on a pilot scale. On this latter scale the enhancement was shown of the counter-current water stripping on the performance of the structured catalysts. Regeneration of the BEA coated monoliths between consecutive reactions by calcination in static air at 723K was sufficient for maintaining the performance.

Concluding, in this thesis a contribution has been made to improve the performance of two acid catalyzed reactions, acylation and esterification. Firstly, in a chemical way, by increasing the activity of the most active catalysts for these reactions even further by means of modification and, secondly, in a technological way, by studying the kinetics and applying the developed kinetic model to select two reactor types of which the performance is predicted and optimized. The approach in this thesis also serves as a tool for the enhancement of other systems in other studies. Finally, viewed from an industrial point of view, a structured reactor is developed in which reactor and catalyst are integrated, thereby circumventing the difficult filtration and reactant contacting problems often encountered when using slurry catalysts in acid catalyzed liquid phase reactions. To achieve this goal a solid acid coated monolith was developed.
Samenvatting

Zuur gekatalyseerde reacties zijn veelvoorkomende reacties in de fijnchemische industrie voor de synthese van onder andere geneesmiddelen en geurstoffen. Voorbeelden van de conventionele ‘katalysator’ voor deze reacties zijn metaal haliden (zoals AlCl₃) en sterke zuren (zoals HF en H₂SO₄). Deze zijn niet herbruikbaar en leiden tot sterk corrosieve afvalstromen. Vaste zuren, zoals zeolieten en ion-uitwisselings-harsen, zijn daarentegen wel herbruikbaar omdat het mogelijk is ze af te scheiden en te regenereren. Echter, het scheiden van de vaste (poedervormige) katalysator deeltjes van het reactiemengsel is een zeer arbeidsintensief en duur proces. Filtratie (en attritie) problemen kunnen worden voorkomen door integratie van de katalysator met een gestructureerde reactor, waarin de katalysator als een dun laagje wordt aangebracht op de wand van de reactor. Een monoliet is een voorbeeld van een gestructureerde reactor dat bestaat uit rechte parallele kanalen. Het doel van dit onderzoek is een gestructureerde reactor te ontwikkelen voor een vaste zuur gekatalyseerd proces met een optimale activiteit en selectiviteit.

Het onderzoek dat in dit proefschrift beschreven staat omvat de studie naar twee zuur-gekatalyseerde reacties, de acylering van aromaten (hoofdstuk 2) en de verstering van carbonzuren met alcoholen (hoofdstuk 6). In beide reacties is de activiteit en selectiviteit van diverse vaste zure katalysaten onderzocht. Zowel in de acylering van anisool met octaanzuur als in de verstering van hexaanzuur met 1-octanol blijken de Nafion/silica composiet en zeoliet BEA een hoge activiteit en selectiviteit te geven. Beide reacties vertonen een kinetiek met een Eley-Rideal karakter. Bij de acylering blijkt het verwijderen van water de activiteit sterk te stimuleren. In de verstering heeft het water twee negatieve effecten op de reactiesnelheid; het remt de katalytische reactie en het limiteert de maximum haalbare conversie door de ligging van het thermodynamisch evenwicht. Bij de verstering is er tevens een eerste orde afhankelijkheid in het carbonzuur gevonden en een remmende werking van het alcohol. Voor de verstering is een kinetisch model opgesteld die de reactiesnelheid nauwkeurig beschreven kan worden.

Verdere verbetering van de twee meest actieve katalysatoren, de Nafion/silica composiet en zeoliet BEA, staat beschreven in hoofdstuk 3. Tijdens de bereiding van een Nafion/silica composiet wordt het voordeel van het hoge oppervlak van silica gecombineerd met de hoge katalytische activiteit van Nafion (een ion-uitwisselingshars met sterk Brønsted zure plaatsen). De sol-gel synthese is een relatief eenvoudige methode waarbij micro- en mesoporeuze composieten (tot 465 m²/g met iedere gewenste belading (tussen de 8 en de 40 gewichts%) kunnen worden bereid. BEA zeoliet kan gemondificeerd worden door het te stomen en te behandelen in zuur. Deze modificaties leiden niet tot verandering in de
Samenvatting

Poriestructuur van de zeoliet. Met $^{27}$Al MQ MAS NMR wordt er een grotere hoeveelheid aan tetraëdrisch en oktaëdrisch ‘extraframework’ aluminium gevonden als gevolg van stomen bij 673K (> 3 uur). Het behandelen van BEA in sterke zuren (zoals zoutzuur en oxaalzuur) leidt juist tot verwijdering van voornamelijk tetraëdrisch aluminium. Zowel de gesynthetiseerde Nafion/silica composieten als de gemodificeerde BEA vertonen een verhoogde katalytische activiteit in de acylering van anisool met octaanzuur.

De ontwikkeling van een geïntegreerd katalysator/reactor systeem is onderzocht door een keramische monoliet te coaten met de twee meest actieve zure katalysatoren, BEA and Nafion. De bereiding van een gecoate monoliet met behulp van een dip-coatingstechniek blijkt een relatief eenvoudig uitvoerbare methode die resulteert in een belading van 2-3 gewichts% Nafion en 6-8 gewichts% BEA (hoofdstuk 4). De BEA- en Nafion-gecoate monolieten geven een redelijk goede activiteit in de acylering van anisool met octaanzuur vergeleken met de activiteit van dezelfde katalysator in een slurry configuratie (hoofdstuk 5). De Nafion-coatings blijken echter zeer gevoelig te zijn voor verontreinigingen in het reactiemengsel.

Voor de veresteringsreactie is een kinetisch model opgesteld waarmee de reactiesnelheid nauwkeurig beschreven kan worden (hoofdstuk 6). Met behulp van dit model is de reactiesnelheid in een bepaalde reactorconfiguratie te voorspellen (hoofdstuk 7). Op deze manier is het mogelijk een reactorconfiguratie te selecteren met een zo optimaal mogelijk resultaat. Zowel alcohol als water hebben een remmende werking op de veresteringsreactie.

Simulatie van de reactie in een zogenaamde ‘fed-batch’ reactor waarin de alcoholconcentratie zo laag mogelijk gehouden wordt door het langzaam toe te voeren aan het reactiemengsel, resulteert in een verhoogde activiteit ten opzichte van de activiteit in een gesloten systeem. De remming van water kan voorkomen worden water te verwijderen tijdens de reactie. Dit kan bijvoorbeeld met behulp van een inert gas, het zogenaamde ‘stripen’. Simulatie van de reactie met mee- en tegenstrooms reactief stripen resulteert in een verhoogde activiteit ten opzichte van de configuratie zonder stripen; het tegenstroomse stripen resulteert in een hogere conversie dan het meestrooms stripen.

Het in dit proefschrift beschreven onderzoek laat zien hoe een gekatalyseerd reactiesysteem verbeterd kan worden door middel van de chemie en door toepassen van de juiste technologie; met behulp van de chemie zijn er katalysatoren ontwikkeld met een verbeterde activiteit. Met behulp van de (reactor)technologie is aangetoond dat indien de juiste reactiecondities en de juiste reactorconfiguraties gekozen worden, optimale resultaten behaald kunnen worden. Vanuit een industriële oogpunt is er bovendien een geïntegreerd katalysator- en reactor-systeem ontwikkeld door een monoliet te coaten met een katalysator. Met zo’n systeem kunnen filtratie- en attrtieproblemen voorkomen worden.
Dankwoord

Hierbij wil ik graag de mensen bedanken die hebben bijgedragen aan dit proefschrift. Allereerst natuurlijk mijn promotoren, Jacob Moulijn en Freek Kapteijn, die mij de kans hebben gegeven dit onderzoek uit te voeren. Jacob, bedankt voor de vrijheid die ik van je kreeg en vooral ook omdat je altijd achter mijn keuzes stond. Freek, bedankt voor de prettige begeleiding. Ik heb onze samenwerking altijd erg gewaardeerd en heb veel van je geleerd. Ik heb ook veel gehad aan de motiverende inbreng van Roger Downing die ik daarvoor graag van harte wil bedanken. Xander Nijhuis, bedankt voor de (soms iets te) enthousiaste samenwerking en voor het mij bijbrengen van zowel techniek als technologie.

Het IOP (Innovative Oriented Programme) wil ik graag bedanken voor de financiering van dit project. Ik ben altijd met veel plezier naar de halfjaarlijkse bijeenkomsten geweest en de leden van de begeleidingscommissie wil ik graag bedanken voor hun stimulerende inbreng.

Grote dank aan Nynke Aalders, Susan van Bokhorst, Ingrid Hock, Karen de Lathouder, Remko Spruijt en Hans Vogelaar die hebben bijgedragen aan een groot deel van het werk. Daarbij wil ik ook graag de vele research practicanten niet vergeten. Ook de mensen die de talloze analyses hebben uitgevoerd wil ik graag bedanken. Peter Boeser en Johan Groen voor de textuur analyses, Patricia Kooymans voor de TEM-EDX, Elke Fakkeldij voor de SEM-EDX, Joop Padmos voor de XRF en Nick van der Pers voor de XRD metingen. Daarbij wil ik ook graag Jeroen van Bokhoven noemen voor het NMR werk en het meedenken.

Tevens dank aan de heren van de technische afdeling die mij altijd goed bijstonden als er weer iets gemaakt moest worden, Gerard Ruigrok, Bas Vogelaar, Harrie Jansen en Bart van der Linden. Onze topfotograaf Fred Hammers, de glasblazerij en het chemicaliën magazijn natuurlijk niet te vergeten… Grote dank aan Sandra Meester voor de secretariële ondersteuning en al die keren dat er weer iets geregeld moest worden, met name in het laatste jaar.

Alle collega’s van de sectie Industriële Katalyse, bedankt voor de prettige werksfeer! Jullie waren fijne collega’s en ik wens jullie allemaal veel succes met de promotie of andere werkzaamheden. In het bijzonder wil ik hierbij mijn kamergenoten, Hank Reinhoudt en Peter Waller, bedanken voor de gezelligheid op de kamer. Hank (en Stephanie) bedankt voor de goede vriendschap, we houden de lekkere etentjes nog lang vol.
Dankwoord

Ik vind het een eer dat Jeroen van Bokhoven en Roland Vogels mijn paranimfen willen zijn. Zij hebben mij laten zien (en laten mij nog steeds zien) hoe leuk de wetenschap kan zijn, en daarom wil ik ze bedanken voor alles wat ik van hun heb geleerd en nog steeds mag leren!

Verder wil ik graag al mijn goede vrienden en lieve familie bedanken. Het is fijn om tijdens zo’n promotie zulke lieve mensen om je heen te hebben. In het bijzonder wil ik graag mijn ouders bedanken die altijd voor me klaar staan. Paps en mams, bedankt voor alle steun! Tenslotte wil ik mijn lieve maatje Bas bedanken, eigenlijk voor alles. Ik hoop dat we samen heel oud worden en altijd zo gelukkig blijven.
List of publications and presentations

Publications


Oral presentations


List of publications and presentations


Curriculum Vitae


Aansluitend aan het promotieonderzoek werkte zij korte tijd als post-doc bij de sectie Industriële Katalyse van de Technische Universiteit Delft. Sinds 1 januari 2001 werkt Annemarie bij Engelhard De Meern aan de ontwikkeling van katalysatoren voor de chemische industrie.