Stellingen

behorende bij het proefschrift

“Micro- and mesoporous materials as catalysts in organic conversions”

van Michel Verhoeof

1 Het gebruik van NaBr in een door TEMPO gekatalyseerde oxidatie van primaire alcoholen met NaOCl als oxidant is geen vereiste.
Dit proefschrift, Hoofdstuk 6.

2 Gezien het groeimechanisme van zeoliet ZSM-5, kan een vaste stof omkristallisatie van MCM-41 materiaal naar ZSM-5 nooit leiden tot een volledige omzetting.

3 De claim van Aracil et al. dat US-Y katalytisch actief is in de verestering van oliezuur en oleylalcohol is niet gerechtvaardigd daar de reactie zonder katalysator waarschijnlijk even snel verloopt.
Dit proefschrift, Hoofdstuk 2.

4 De door Ardizione et al. geclaimde nauwkeurigheid in de conversie data van ~ 0.5 % lijkt onwaarschijnlijk gezien het verloop van enkele conversie curven.

5 Seri et al. gaan in hun beschouwing over de LaCl₃-gekatalyseerde fructose dehydratatie voorbij aan de rol van het (zure) aan Lanthaan(III) gecoördineerde water.

6 Naast een karakterisering van met cesiumoxide beladen MCM-41 materiaal met IR, XRD en N₂ adsorptie, zou het gebruik van TEM een waardevolle aanvulling zijn geweest gezien de informatie die deze techniek kan geven over de dispersie van de cesiumoxide deeltjes.

7 Anders dan Brown et al. veronderstellen is AlCl₃/ROOH niet een gebruikelijke combinatie voor acylering met vrije carbonzuren.

8 Het is triest om te zien dat in het huidige taalgebruik het woord chemisch synoniem is voor vies.

9 De chemische industrie luidt nu de noodklok vanwege de sterk teruglopende aantallen studenten die scheikunde of scheikundige technologie kiezen, maar heeft dit gezien het personeelsbeleid in het verleden voor een deel aan zichzelf te wijten.

10 Een geslaagd vrijdagmiddagexperiment wordt meestal op een ander tijdstip dan vrijdagmiddag uitgevoerd.
Micro-and mesoporous materials as catalysts in organic conversions

Michel J. Verhoeef
The illustration on the cover shows a TEM picture of MCM-41 looking directly into the channels.
Micro-and mesoporous materials as catalysts in organic conversions

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 maandag 25 september 2000 om 13.30 uur door

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1 Introduction
1.1 Objectives and Justification

Catalysis is an important factor in the chemical industry. Catalytic conversions are involved in more than 80% of the chemical syntheses and in almost all the liquid fuel production. The latter involves bulk processes which mainly apply heterogeneous catalysts. In fine chemistry homogeneous Brønsted acid catalysts like sulfuric acid, p-toluenesulfonic acid and Lewis acid catalysts like AlCl3 are still widely employed. These catalysts have some serious drawbacks, such as the aggressive nature of the catalysts which can cause corrosion. Complete removal of the homogeneous catalysts from the products is sometime difficult, which can cause stability problems, and limits the applications of the products [1]. Moreover, the fact that these catalysts generally cannot be re-used, gives rise to formation of by-products and the necessity to neutralise the acids result in large amounts of waste which have to be discarded. The amount of waste produced in the synthesis of a product can be expressed by the E factor as introduced by Sheldon, which is defined as kg of by-product formed in the synthesis of one kg product (see Table 1). The relatively high E factors in the synthesis of fine chemicals and pharmaceuticals underline the need for cleaner production methods in these segments of the chemical industry.

Table 1 Typical product volumes and E-factors ([2] modified).

<table>
<thead>
<tr>
<th>Industry segment</th>
<th>Order of product tonnage</th>
<th>Kg by-products / Kg product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil refinery</td>
<td>$10^6 - 10^8$</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Bulk chemicals</td>
<td>$10^4 - 10^7$</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>$10^2 - 10^4$</td>
<td>5 - 50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>$10 - 10^3$</td>
<td>25 - &gt; 100</td>
</tr>
</tbody>
</table>

The Dutch Ministry of Economic Affairs promotes research in a number of promising fields in order to improve the competitive position of the industry in the Netherlands. The Innovation Oriented research Programmes (IOP) provide the universities with additional
funding to employ researchers, and are also intended to strengthen the collaboration between universities and industry. In 1989 the IOP on Catalysis was started and over the last ten years this program sponsored some 90 projects in various fields of catalysis (homogeneous, heterogeneous, and biocatalysis) [3]. The IOP on Catalysis is particularly directed towards the fine chemicals industry, because of the low selectivities sometimes encountered there, and especially because of the use of corrosive and toxic reagents involved in the processes in this segment of the chemical industry leading to a high E-factor in this area.

The research described in this thesis was carried out in the framework of the IOP on Catalysis. Main objectives were to develop heterogeneous catalysts which could be employed in the synthesis of oleochemicals, more specifically in the liquid phase process of esterification of fatty acids. New and existing materials have been tested for their catalytic activity and selectivity in the above mentioned reaction. This work was a collaborative project with the University of Amsterdam (Group of Prof. A. Biek), where the research was mainly focused on dimerisation reactions of unsaturated fatty acids, and gas-phase esterifications.

1.2 Esters and esterification

Organic esters are compounds with the general formula as pictured in Figure 1, where $R_1$ and $R_2$ can be either the same or a different aliphatic, aromatic or heterocyclic group.

\[ R_1-\overset{\text{O}}{\text{C}}\overset{\text{O}}{-}R_2 \]

Figure 1 Organic ester.
Organic esters are of considerable economic importance. Esters of glycerol and fatty acids (triglycerides, oils and fats) occur naturally in large quantities and serve predominantly in food applications. They can also be used as a raw material for example in the production of soap, surfactants or bio diesel (transesterification to the methyl esters). Various synthetic esters have been developed for specific uses, e.g. solvents, plasticizers (especially phthalate esters), lubricants and lubricant additives. Numerous volatile esters are used as fragrances in perfumes, cosmetics and foods.

Various synthesis routes for esters are known which are summarised in Figure 4. It should be noted that some routes, especially route H, are not environmentally benign and are applied only on rare occasions.

The most important one is the reaction of a carboxylic acid and an alcohol. If in one molecule both a carboxylic acid group and a hydroxyl group are present, it can form either polyesters or cyclic internal esters (lactones) (see Figure 2). Polyesters formed from terephthalic acid and aliphatic diols, particularly ethylene glycol, are dominating the synthetic fiber market.

![Figure 2](image)

Figure 2  A polyester and a lactone formed from an ω-hydroxycarboxylic acid.

Ingold has classified eight possible mechanisms for the acid and base catalysed ester hydrolysis and formation [4]. The acid-catalysed reactions are all reversible, in contrast to the base catalysed reactions which are reversible only in theory and not in practice.

All the theoretically possible mechanisms except one have been observed. In the case of the acid catalysed ester formation the mechanism classified by Ingold as Aac2 mechanism is the most common (see Figure 3). It may be noted that the alcohol is in general more basic than the carboxylic acid. Operating with an excess of alcohol, which is often recommended, will therefore decrease the rate of reaction. Carboxylic acids are only feebly basic, the
protonated forms having a pKa of approximately -6 whereas the average protonated form of a primary alcohol has a pKa of -4 [5]. Protonation will therefore only take place to a moderate extent, even in the presence of strong acids. It has been shown however, that reasonable rates may be expected despite a low concentration of the protonated acid [6,7]. The other possible mechanisms are rare and found only in cases where the Aac2 mechanism is unfavorable for example, because of the presence of bulky substituents or when tertiary alcohols are involved.

![Chemical Reaction Diagram]

Figure 3 Mechanism, Aac2 in the code of Ingold [4], for ester formation.

Esterification is generally carried out by heating of the reaction mixture. When equimolar amounts of the carboxylic acid and the alcohol are applied the yield normally does not exceed 80%. In order to shift the equilibrium, one of the reaction products has to be selectively removed, for example by distillation. One can also apply an excess of one of the reactants. Although this usually works quite satisfactory, one has the problem of isolating the product after the reaction is completed. In principle carboxylic acids and alcohols react with each other as such, especially at elevated temperatures, though in most cases a catalyst is required in order to achieve an acceptable reaction rate. The contribution of the blank (autocatalytic) esterification depends on the pKa value of the carboxylic acid and the temperature at which the reaction is performed. In the case of the esterification of glycerol with different fatty acids, it has been reported that the blank reaction contributes already significantly at temperatures around 125°C [8].
Figure 4  Ester syntheses, A; Condensation of alcohols and of carboxylic acids, B; Addition of carboxylic acids to olefins, C; Acylation of alcohols with carboxylic anhydrides, D; Acylation of alcohols with ketenes, E; Carbonylation of alcohols, F; Tischtschenko reaction, G; Alcoholysis of nitriles, H; Acylation of alcohols with acyl halides, I; Hydroxy-ethoxylation of carboxylic acids, J; Transesterification methods.
Conventional catalysts that can be used are mineral acids like sulfuric acid, hydrochloric acid, organic sulfonic acids and Lewis acids like boron trifluoride or metal salts. More environmentally friendly alternatives are solid acid catalysts, like acidic ion-exchange resins and zeolites, or enzymes [9]. In the study described in this thesis solid acids have been used to catalyse esterification reactions.

1.3 Oleochemistry

Oleochemicals are chemicals derived from either vegetable or animal oils and fats. The total world production of oils and fats (triglycerides) in 1997 amounted to 100 Mtons, of which 80 Mtons of vegetable and 20 Mtons of animal origin [10]. Over 80% is used for human nutrition and half of the remaining part is used in the animal feed industry. The remaining part of the annual oil and fat production is consumed by the chemical industry. Vegetable oils and fats are obtained from various crops, of which soy beans, oil palm fruits, coconuts, rape seeds may be mentioned as important examples. The triglycerides are isolated by pressing or solvent extraction leaving a meal fraction which may be used as animal feed or further processed to protein fractions.

As valuable side products of oil refining lecithin (emulsifier) and steroids as sitosterol may be mentioned, the latter serving now in the pharmaceutical industry as starting compounds. Glycerol is an important chemical because of two properties. The hydroxyl groups give it a strong affinity for water and as a result it attracts water or retains water in any system where it is incorporated. This is why it is used as a humectant in for example paper, tobacco, cosmetics and similar products. The other distinctive property is the reactivity of the hydroxyl groups which undergo all the reactions of an alcohol group. They can react for example with acids, to yield esters, isocyanates to form urethanes or with nitric acid to form nitro compounds. Monoesters from glycerol and long chain acids can be used as emulsifiers and di- and tri-esters are present in alkyd resins for surface coatings. Polyethers and polyols formed upon reaction of glycerol with ethylene oxide or propylene oxide serve as starting materials for polyurethanes. The polyurethanes formed with isocyanates are used
as surface coatings, insulating materials or foams. Finally, glycerol trinitrate (nitroglycerin) is a well known explosive as well as a pharmaceutical (see Table 2). Presently >90% of the commercial glycerol is of renewable origin although the classical petrochemical route starting with chlorination of propene is still operated by Dow Chemical (USA) and Kashima Chemical (Japan).

Table 2: Uses of glycerol.

<table>
<thead>
<tr>
<th>Industrial Products</th>
<th>Final use</th>
</tr>
</thead>
<tbody>
<tr>
<td>As reactive polyol</td>
<td></td>
</tr>
<tr>
<td>Alkyd resins</td>
<td>Coatings, Paint, Printing inks</td>
</tr>
<tr>
<td>Polyols and</td>
<td>Surface coating, Insulation,</td>
</tr>
<tr>
<td>polyurethanes</td>
<td>Foams</td>
</tr>
<tr>
<td>Mono &amp; diesters</td>
<td>As emulsifiers:</td>
</tr>
<tr>
<td>of various acids</td>
<td>-Food additives</td>
</tr>
<tr>
<td></td>
<td>-Cosmetics</td>
</tr>
<tr>
<td></td>
<td>-Plastics</td>
</tr>
<tr>
<td></td>
<td>-Textiles</td>
</tr>
<tr>
<td></td>
<td>-Antistatic agents</td>
</tr>
<tr>
<td>Nitroglycerin</td>
<td>Explosive, Pharmaceutical</td>
</tr>
<tr>
<td>As hygroscopic agent</td>
<td>Personal care products</td>
</tr>
<tr>
<td></td>
<td>Tobacco</td>
</tr>
<tr>
<td></td>
<td>Paper</td>
</tr>
<tr>
<td></td>
<td>Food products</td>
</tr>
</tbody>
</table>

The fatty acid part of the triglycerides possesses two distinct parts; the hydrophilic carboxylic acid group and the hydrophobic alkyl chain consisting of 11 to 21 carbon atoms (generally 13, 15 or 17), some of which may be linked by a double bond. The carboxylic acid group is the starting function for several important classes of compounds, such as the fatty alcohols, the fatty esters, and the fatty amines and amides. The double bonds when
present are the main reactive sites in the alkyl chain and undergo all usual reactions. Fatty acids bearing a double bond can be converted to dimer or trimers, which find applications in surface coatings, printing inks and lubricants. Epoxidation of the double bond yields epoxy acids which can be used as stabilisers in PVC (see table 3). Metathesis of fatty acid esters e.g. with ethylene, leads to \( \omega \)-functionalised 1-alkenes together with 1-alkenes.

**Table 3**  Fatty acid derivatives and their use.

<table>
<thead>
<tr>
<th>Product</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>I) Modification of the</td>
<td></td>
</tr>
<tr>
<td>carboxylic acid group</td>
<td></td>
</tr>
<tr>
<td>Fatty alcohols</td>
<td>-As such Personal care products,</td>
</tr>
<tr>
<td></td>
<td>-Surfactants Detergent</td>
</tr>
<tr>
<td></td>
<td>formulations</td>
</tr>
<tr>
<td>Fatty amines</td>
<td>-Quats Fabric softeners, Antistatics</td>
</tr>
<tr>
<td></td>
<td>-Ethoxylates</td>
</tr>
<tr>
<td>Methyl esters</td>
<td>Biodegradable diesel fuel</td>
</tr>
<tr>
<td>Metallic soaps</td>
<td>Pharmaceuticals, Cosmetics</td>
</tr>
<tr>
<td>Fatty amides</td>
<td>Plastics</td>
</tr>
<tr>
<td>Esters</td>
<td>Antistatics, Emulsifiers, Lubricants</td>
</tr>
<tr>
<td>Fatty acids as such</td>
<td>Rubber, Soaps, Lubricants</td>
</tr>
<tr>
<td>II) Reactivity of the</td>
<td></td>
</tr>
<tr>
<td>double bonds</td>
<td></td>
</tr>
<tr>
<td>Oligomerisation</td>
<td>Surface coating, Printing ink</td>
</tr>
<tr>
<td>Epoxidation</td>
<td>Plasticisers</td>
</tr>
<tr>
<td>Hydrogenation</td>
<td>Technical hard fatty acids, Candles</td>
</tr>
<tr>
<td>Ozonisation</td>
<td>Lubricant esters</td>
</tr>
<tr>
<td>Metathesis</td>
<td>Terminal olefins Copolymers</td>
</tr>
</tbody>
</table>
An important use of oleochemicals is to improve the performance of the final products in which they are applied. There will only be a demand for products with improved performance when the consumer can afford the higher price of such products. This is why the oleochemical industry is well advanced only in developed countries. Since these markets are more or less saturated, and no major new applications are expected in the near future, the growth of this industry will essentially be parallel to the population growth. If the programmes to create economic growth in developing countries are successful however, these geographic areas may encounter an exponential growth in the consumption of oleochemicals.

1.4 Catalysis

Catalysis has been used by man in fermentation processes already for thousands of years without the insight of how and what. The name catalysis was introduced by Berzelius in 1836. He concluded that besides affinity, which at that time was known as a chemical driving force, another force which accelerates reactions, the catalytic force was operative. The growing need for liquid fuels, starting at the beginning of the 20th century, led to a rapid development in heterogeneous catalysts particularly for the use in oil refineries. The use of heterogeneous catalysts in the synthesis of fine chemicals however, is still rather limited. Fine chemicals differ from oil refinery products not only in the amount in which they are produced but also in composition. Often they contain more than one functional group, making them much more susceptible to unwanted side- or consecutive reactions. Because of that, selectivity becomes an important factor. Three types of selectivity can be distinguished.

- **Chemoselectivity:** The ability to selectively convert one functional group in the presence of other type of functional groups.

- **Regioselectivity:** The ability to selectively convert a functional group in the presence of other groups of the same type.
- **Stereoselectivity**: The ability to direct the reaction towards the formation of only one out of two or more possible stereoisomers. Stereoselectivity can be subdivided in *cis/trans-selectivity*, *diastereoselectivity* and *enantioselectivity*. Especially the latter types of selectivity are of increasing importance in the pharmaceutical industry. Besides selectivity, adsorption characteristics are important when using heterogeneous catalysts. In order to bring two molecules together, which is basically what a catalyst does in a bimolecular reaction, both molecules should be able to adsorb on or in the catalyst. Equally important is a rapid desorption of the reaction product (see Figure 5), with zeolites selected as a class of heterogeneous catalyst, which preferably should be adsorbed more weakly than the reactants.

**Figure 5**

When applying a solvent this can, by its own adsorption characteristics, regulate the inner concentrations of reactants and products, which can be beneficial when side reactions (e.g. polymerisation) can occur.

In the case of equilibrium reactions not only a rapid desorption of the products from the catalyst is important, but in order to shift the equilibrium, removal of at least one of the products is equally important (see Figure 6).

![Zeolite Liquid Phase Diagram](image-url)

**Figure 6**  Zeolite catalysed equilibrium reaction with shifting of the equilibrium.

If these requirements can be fulfilled, solid acid catalysts have many advantages over classical homogeneous acid catalysts. Most obvious advantages are the easy separation of the catalyst from the reaction mixture, and the possibility to run a process in a fixed-bed continuous flow reactor. The fact that solid acids are much easier to handle and in many cases can be regenerated and re-used are important characteristics as well. Materials which might be used as solid acid catalysts for the synthesis of oleochemicals will be discussed later in this chapter.
1.5 Solid acids

1.5.1 General

Acids play an important role in chemical conversions both in industry and in the laboratory. In fact sulfuric acid with a produced volume of 40 million ton each year in the U.S. alone, is probably one of the largest chemicals. The conventional Brønsted- and Lewis acids which are presently in use possess several negative features as has been discussed earlier in this chapter. Several classes of solid acids are known which might be alternatives for the liquid acids. These materials can be divided as follows.

- **Clays**: Materials that consist of layered structures which are built up from tetrahedral and octahedral sheets [12].

- **Silica Aluminas**: Polymorphic form of mixed silica and alumina oxides.

- **Zeolites**: Microporous crystalline aluminosilicates

- **Mesoporous materials**: Mesoporous silicates or aluminosilicates. In contrast to zeolites not crystalline but ordered amorphous materials.

- **Acid resins**: Organic polymers which are functionalised with an acid group (generally a sulfonic acid group).

- **Sulfated oxides**: Metal oxides promoted by sulfate ions.

Several techniques are available for the characterisation of solid acids providing information on the surface, morphology and acidity of the material (see Table 4)
Table 4 Some characterisation techniques of solid acids.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Information on</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$ adsorption</td>
<td>Surface area</td>
<td>Minimum particle size 10 nm</td>
</tr>
<tr>
<td>XRD</td>
<td>Crystallinity</td>
<td></td>
</tr>
<tr>
<td>SEM / TEM</td>
<td>Crystallinity/Morphology</td>
<td>Materials should be sufficiently stable in the electron beam</td>
</tr>
<tr>
<td>MAS NMR</td>
<td>Local order around a specific atom type (Si, Al, H)</td>
<td></td>
</tr>
<tr>
<td>IR</td>
<td>Brønsted and Lewis Acidity</td>
<td></td>
</tr>
<tr>
<td>TPD</td>
<td>Acidity/Side density</td>
<td>Only thermally stable materials</td>
</tr>
<tr>
<td>Hammett Indicators</td>
<td>Acidity/Side density</td>
<td>Not applicable for small pore materials</td>
</tr>
</tbody>
</table>

Though many techniques exist to characterise and quantify the acid sites on a solid material [13,14], an adequate determination of the acidity is still difficult. This is largely influenced by the fact that most techniques are performed in the gas phase on previously degassed or activated samples. This can lead to large differences between the measured acidity and the actual acidity in the liquid phase. Hammett indicators are used in the liquid phase and thus do not have this drawback. When Hammett indicators are used, the acid strength is expressed by the Hammett acidity function [15]. In practice, the acid strength $H_0$ of a solid acid is equal to or lower than the pKa of the weakest base that gives a colour change, and higher than the pKa of the strongest base of which the colour is not changed upon adsorption onto the solid material.

It should be noticed that the indicator molecules are relatively bulky and cannot enter the pores of the small pore zeolites. This implies that in those cases only the acidity of the outer surface can be probed. Despite this drawback Hammett indicators have been applied in this study. Of the different types of solid acids, zeolites, mesoporous materials and to a lesser extend acid resins have been used in the research described in this thesis, and these materials will therefore be discussed in more detail.
Table 5  Hammett indicators suitable for visual measurement of acid strength [16].

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Basic colour</th>
<th>Acid Colour</th>
<th>$H_0$</th>
<th>wt% $H_2SO_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthyl red (1)</td>
<td>Yellow</td>
<td>Red</td>
<td>+4.0</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Butter yellow (2)</td>
<td>Yellow</td>
<td>Red</td>
<td>+3.3</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>4-Benzeneazoaniline (3)</td>
<td>Yellow</td>
<td>Purple</td>
<td>+1.5</td>
<td>0.02</td>
</tr>
<tr>
<td>Dicinnamalacetone (4)</td>
<td>Yellow</td>
<td>Red</td>
<td>-3.0</td>
<td>48</td>
</tr>
<tr>
<td>Benzalacetophenone (5)</td>
<td>Colourless</td>
<td>Yellow</td>
<td>-5.6</td>
<td>71</td>
</tr>
<tr>
<td>Anthraquinone (6)</td>
<td>Colourless</td>
<td>Yellow</td>
<td>-8.2</td>
<td>90</td>
</tr>
</tbody>
</table>

Figure 7  Structures of the Hammett indicators mentioned in Table 5.
1.5.2 Zeolites

1.5.2.1 History

Zeolites were discovered in 1756 by the Swedish mineralogist Cronstedt. He found that the material lost water upon heating and thus called the material a zeolite, which comes from the two Greek words "zeo" and "lithos", meaning "to boil" and "a stone" [17]. In 1840, Damour recognised that zeolite crystals could be reversibly dehydrated without change in morphology [18]. The potential of zeolites was further studied by Eichhorn, who showed the reversibility of ion-exchange [19], and by Weigel and Steinhoff who noticed that dehydrated chabazite preferentially adsorbed water or methanol over acetone or benzene [20]. The name molecular sieve, which is also frequently used for zeolites, originates from this effect. Further studies by McBain on this molecular sieve effect led to the recognition of the potential of separating molecules by zeolites [21]. Work by the group of Barrer (Imperial College, London) and by the industrial research groups of Union Carbide and the Mobil Oil corporation boosted the development of the zeolites science and application. Man succeeded in producing natural zeolites on an industrial scale and found routes to synthesise new structures not found in nature. In total 126 structures have been reported, [22] of which several found practical applications. The first applications were in the separation and purification of gasses (1954) and use as a catalyst (hydrocarbon cracking) followed soon (1959).

1.5.2.2 Current market

Zeolites have found widespread applications in industry, and in some fields the consumption is still growing. Demand for natural zeolites has increased rapidly the last decade, particularly for agricultural applications. It is expected that growth rates remain as
high as 10% per year in the near future. Synthetic zeolites have made dramatic inroads into the detergent builder market over the past 20 years. The markets in the western world however, are nearing saturation and the demand elsewhere is limited due to lack of regulations regarding the use of phosphate. The total demand for zeolites in detergents (mainly zeolite Na-A and also zeolite Na-P) is estimated to be about 800,000 t/y, which is well below the total available capacity of the manufacturers. The use of zeolites as catalysts accounts for about 100,000 t/y, of which 90% are the zeolites H-Y and USY, used in FCC and hydrocracking processes. The market volume of zeolites in catalysis is much smaller than that of zeolites used in detergents but in terms of value, catalysis represents by far the largest market, totally more than $500 \times 10^6$ per year in the USA alone. Other industrial applications of zeolites are as desiccants and in gas purification which in 1991 accounted for 40,000 t/y and 115,000 t/y respectively. It is not expected that these figures changed much since then.

1.5.2.3  Structure and properties

Zeolites are microporous crystalline aluminosilicates with a framework of SiO$_4$- and AlO$_4$-tetrahedra (Al and Si are denoted as T-atoms), which are connected via the oxygen atoms at the cornerpoints of the tetrahedron [23]. Depending on the connection of the T-atoms, different structures can exist. The three most common structure types are, the connected cage, the parallel channel and the crossing channel geometry. The access diameter of the micropores varies between 0.3 and 0.8 nm and mainly depends on the number of T-atoms in the pore openings of the cage, window or channel wall (see Figure 8). The number of T-atoms usually varies between 8 and 12. Recently also 14 ring zeolites have been discovered (UTD-1 [24] and CIT-5 [25]) of which UTD-1 has an elliptical pore with the dimensions of $1.0 \times 0.75$ nm.

Each AlO$_4$ tetrahedron bears a net negative charge which is balanced by a cation (see Figure 9). For different applications, different types of cations are used, e.g. H$^+$ for acid catalysis and Na$^+$ for use in ion-exchange in detergents.
Zeolite pore sizes

8-ring
0.3-0.45 nm
e.g. NaA

12-ring
0.6-0.8 nm
e.g. Y, MOR, BEA

10-ring
0.45-0.6 nm
e.g. MFI, MCM-22

14-ring
0.75-1.0 nm
e.g. UTD-1

Figure 8 Typical zeolite pore sizes.

Figure 9 Schematic presentation of a zeolite.

In 1982 a related class of materials, the microporous crystalline aluminophosphates (AlPO's) was discovered. Because $\text{Al}^{III}$ and $\text{P}^V$ are present in a 1:1 ratio, these systems are
neutral and do not require a counter cation. This class includes very large pore materials, like VPI-5 [26], which has a pore diameter of 1.2 nm. In general these materials are less stable compared to zeolites and therefore they did not find such widespread application. Upon partial substitution of P for Si the so-called SAPO’s are formed, which have a negative lattice charge. Although less than zeolites these materials did find some applications, e.g. in the methanol-to-lower olefins (MTO) process.

As described, the substitution of a SiO₄ tetrahedron by a AlO₄ tetrahedron results in a negatively charged lattice which should be balanced by a counterion. This can be a proton thereby generating Brønsted acid sites. Quantum chemical calculations showed that the proton is not present as a free cation but that it is covalently bonded to an oxygen atom of an aluminate moiety. Depending on the adsorbed species and the type of zeolite, proton transfer will occur or a neutral adsorption complex will be formed [27]. Another factor that contributes to the strong acidity of zeolites (H₀~5.5 ) is the stabilisation of the negative charge left on the lattice with deprotonation. Another important aspect concerning the catalytic activity of zeolites is the adsorption energy of a protonated substrate on the zeolite porewall. Because of the molecular dimensions of their pore systems, zeolites can discriminate between organic molecules. Therefore size restrictions on the reactants, products or transition states may give rise to shape selectivity (see Figure 10).

A good example of transition state selectivity is the MPV reduction of 4-tert-butylcyclohexanone in isopropanol catalysed by zeolite BEA. Because of a less favourable transition state leading to the trans-4-tert-butylcyclohexanol, the selectivity to the thermodynamically less stable, but industrially relevant, cis isomer is more than 95% [28]. When applying an amorphous silica alumina, zeolite H-Y or a homogeneuous Al catalyst the trans isomer is formed in large excess.
1.5.2.4 Zeolites in catalysis

By far the largest applications of zeolites in catalysis are found in the processing of oil feedstocks where, in practically every process zeolites are involved. Most important is FCC cracking where high boiling feedstocks are converted into more valuable lighter fractions.
via cracking. The catalyst used in this process is zeolite USY sometimes accompanied by small amounts of ZSM-5. In fine chemicals industry the use of zeolites and heterogeneous catalysts in general is still in its infancy. In some processes however, zeolites are already applied and in the literature numerous possible applications have been reported, exploiting the many different active sites which can be present in zeolites. Examples of zeolite catalysed reactions are given in Table 6. Each entry illustrates a different type of active site.

Table 6 Zeolite catalysed reactions, some examples.

<table>
<thead>
<tr>
<th>Active site</th>
<th>Reaction</th>
<th>Catalyst</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}^+$</td>
<td>Aromatic acylation</td>
<td>H-BEA</td>
<td>29</td>
</tr>
<tr>
<td>Ti</td>
<td>Epoxidation, Meerwein-Ponndorf-Verley reduction</td>
<td>TS-1, Titanium Beta</td>
<td>30, 31</td>
</tr>
<tr>
<td>Metal cluster</td>
<td>Hydrogenation</td>
<td>Pt/BEA</td>
<td>32</td>
</tr>
<tr>
<td>Metal oxide</td>
<td>Aldol condensation</td>
<td>Cs$_2$O/X</td>
<td>33</td>
</tr>
<tr>
<td>Organometallic</td>
<td>Epoxidation</td>
<td>Entrapped organometallic complex, e.g. Mn Salen</td>
<td>34</td>
</tr>
<tr>
<td>complex</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

More examples of zeolite catalysed reactions in fine chemical synthesis can be found in reviews covering this subject [35, 36, 37, 23].

1.5.3 Mesoporous materials

1.5.3.1 General

As described, zeolites possess several catalytically desirable properties and are therefore applied in a number of processes. Due to the small pore sizes of zeolites ($< 1 \text{ nm}$)
the application in conversions of larger substrates is limited. Some larger pore materials employing Al, P or Ga and P as framework elements have been developed with pore sizes up to 1.25 nm. The use of these materials is limited due to the poor thermal stability and their negligible catalytic activity because of their electronically neutral framework. The first silicate material having uniform pores in the mesopore range, FSM-16, has been reported in 1990 by Yanagisawa et al. [38]. FSM-16 is synthesised starting from a layered crystalline precursor, Kanemite. The sodium ions of Kanemite are exchanged with alkyltrimethylammonium cations after which a partial condensation of the silicate layers occurs forming a three-dimensional SiO₂ network. X-ray diffraction showed that the material consists of a hexagonal arrangement of one-dimensional channels. The first direct synthesis of an ordered mesoporous material was reported by the research group of Mobil Oil corporation in 1992 [39]. The concerning material, MCM-41, consists, like FSM-16 of a hexagonal array of straight channels and has a high surface area. Another comparable material, HMS (Hexagonal Mesoporous Solid), was subsequently reported by Tanev and Pinnavaia and is also a hexagonally ordered material [40]. In contrast to FSM-16 and MCM-41, this material was synthesised using a neutral template (an alkylamine). Since the interaction between this template and silicate is relatively weak, the synthesis of HMS must be performed at room temperature. Probably for the same reason the pore size distribution is not as narrow as for the other materials and long range ordering is almost completely absent. An advantage of HMS is the low price of the template compared to that of the alkyltrimethylammonium template used for the synthesis of FSM-16 and MCM-41 materials. Furthermore, the weak interaction between the template and the silicate, allows removal of the template by extraction with hot ethanol [41]. Various other ordered mesoporous materials have been reported, which mainly differ in silica source and template used (see Table 7).

MCM-41 is a rather expensive material and not easy to prepare. However, MCM-41 is the best ordered mesoporous material and therefore very suitable for research purposes. For this reason MCM-41, in the all silica form as a support and in the Si/Al form as a catalyst was selected for the research described in this thesis. MCM-41 materials will be dealt with in some more detail in the following section.
Table 7 Examples of ordered mesoporous materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Silica source</th>
<th>Template</th>
<th>Dimension</th>
<th>Pore size</th>
<th>Long range order</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FSM-16</td>
<td>Kanemite</td>
<td>ATMAI</td>
<td>1-D</td>
<td>2-4 nm</td>
<td>+</td>
<td>38</td>
</tr>
<tr>
<td>MCM-41</td>
<td>Fumed silica</td>
<td>ATMAI</td>
<td>1-D</td>
<td>2-8 nm</td>
<td>++</td>
<td>39</td>
</tr>
<tr>
<td>MCM-48</td>
<td>Fumed silica</td>
<td>ATMAI</td>
<td>3-D</td>
<td>2-8 nm</td>
<td>++</td>
<td>42</td>
</tr>
<tr>
<td>HMS</td>
<td>TEOS</td>
<td>AA</td>
<td>1-D</td>
<td>2-8 nm</td>
<td>-</td>
<td>40</td>
</tr>
<tr>
<td>MSU-1</td>
<td>TEOS</td>
<td>PEO</td>
<td>3-D</td>
<td>2-6 nm</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>KIT-1</td>
<td>Sodium</td>
<td>ATMAI</td>
<td>3-D</td>
<td>3.4 nm</td>
<td>-</td>
<td>44</td>
</tr>
<tr>
<td>SBA-15</td>
<td>TEOS</td>
<td>co-polymer</td>
<td>1-D</td>
<td>5-30 nm</td>
<td>+</td>
<td>45</td>
</tr>
<tr>
<td>TUD-1</td>
<td>TEOS</td>
<td>TEA</td>
<td>3-D</td>
<td>3-20 nm</td>
<td>-</td>
<td>46</td>
</tr>
</tbody>
</table>

ATMAI  AlkylTriMethylAmmonium Ion  
TEA    TriEthanolAmine  
PEO    Poly Ethylene Oxide  
TEOS   TetraEthyl OrthoSilicate
1.5.3.2 MCM-41

MCM-41 was first reported in 1992 by the research group of Mobil Oil [39]. MCM-41 is one of the members of a complete family of mesoporous materials designated as M4IS. This group of materials consists of a hexagonal phase (MCM-41), a cubic phase (MCM-48), and a lamellar phase (MCM-50). Especially the hexagonal MCM-41 has drawn much attention from research groups all over the world which is reflected by the still growing number of publications on this material (see Figure 11).

![Bar chart showing publications per year for MCM-41][1]

**Figure 11** Publications concerning MCM-41.

MCM-41 is best described as an ordered amorphous material. The material is ordered because of the hexagonal fashion in which the pores are arranged and amorphous because of the lack of crystallinity of the silica forming the porewalls (see Figure 12).

---

[1]: https://example.com/chapter1/figure11.png
Figure 12    Impression of the structure of MCM-41.

MCM-41 is synthesised using cationic surfactant molecules as a template. Depending on temperature and concentration (see Figure 13) the surfactant can form a hexagonal-, cubic- or lamellar liquid crystal phase [47].

The packing parameter (g) has been introduced to describe the tendency of the surfactants to aggregate in a particular morphology [48]. It determines whether spherical micelles, cylindrical micelles or vesicles or bilayers are formed. The packing parameter takes into account the volume of and the number of carbon atoms in the hydrophobic chain of the surfactant and the surface area of the headgroup. The resemblance of the morphology of surfactant-inorganic mesophases and liquid crystal phases and the dependence of the pore size on the surfactant chain length, has led Mobil scientists to postulate the Liquid Crystal Templating (LCT) mechanism [39] (see Figure 14).

This picture was kindly provided by R. Hanssen, Eindhoven University of Technology.
Figure 13  Different liquid crystal phases [47].

Figure 14  Liquid Crystal Templating mechanism [39].
More recently, several observations [49] led to the conclusion that another mechanism should be operative. It appeared that M41S materials could be prepared using template concentrations well below that required for the formation of a liquid crystal phase, and that hexagonal, cubic and lamellar structures may be formed by changing only the silica concentration. Furthermore, hexagonal MCM-41 structures can also be prepared using a short chain surfactant like dodecyltrimethylammonium hydroxide, which does not form rod-like micelles in water and both MCM-41 and MCM-48 can be prepared at temperatures above 70°C where rod-like micelles are not stable. It was concluded that the formation of rod-like micelles prior to the addition of the silica is not required. A new mechanism called the co-operative templating mechanism was proposed by Chmelka et al. [50], which is depicted schematically in Figure 15.

Figure 15  Co-operative templating mechanism [50].
Prior to addition of the silica, the surfactant is in dynamic equilibrium between spherical or cylindrical micelles and single molecules. Upon addition of the silica, the multicharged silicate species ion-exchange with the OH- or Br- anions of the template, to form organic-inorganic ion pairs accompanied by dissociation of the organic micelles and subsequent formation of a new mesophase. The final stage of the MCM-41 synthesis is polymerisation and condensation of the inorganic species. This new mechanism can explain the above mentioned observations and is further supported by a study on a system having a very low surfactant concentration. It was observed that addition of silicate to a 1% solution of surfactant in water led to the formation of an inorganic-organic hexagonal array [51].

1.5.3.3 MCM-41 in catalysis

MCM-41 materials have been tested as catalysts in several reactions in both fine chemistry and in petroleum refining processes. As such, MCM-41 in the proton form is mildly acidic and in the Na or Cs form mildly basic and these forms are able to serve as a catalyst in many organic reactions [52].

A NiMo impregnated Al-MCM-41 catalyst (12 wt% MoO₃, 3 wt% NiO) was found to be more efficient in hydrodesulfurisation and hydrogenation than NiMo loaded on USY or amorphous silica-alumina [53]. This was attributed to its high and easily accessible surface area and to a higher dispersion of the catalytically active ingredients.

The proton form of Al-MCM-41 mixed with Al₂O₃ binder was used for the cracking of naphtha at 540 °C at ~ 3 atm [54]. At the same conversion (45%), the MCM-41 based catalyst produced more C₃-C₅ olefins (74 vs. 54%) and much less light gas and linear hydrocarbons than the medium pore ZSM-5 zeolite. Protonated Al-MCM-41 catalysts were also used for the cracking of olefinic feedstocks such as FCC gasoline. High selectivities towards valuable isobutene and isoamylenes were obtained, components which can be further upgraded into high octane oxygen containing components by etherification with methanol or ethanol [55]. Other patent literature deals with oligomerisation of propene [56], dealkylation of 1,3,5 tri-tert-butylbenzene [57], alkylation of naphthalene with long chain
α-olefins [58] and alkylation of benzene with ethylene [59]. Further applications are in the field of fine chemical synthesis, where reactants with much larger molecular volumes are applied. The combination of large pores and mild acidity has been exploited for example to acetalysations and alkylations [60, 61], Beckmann rearrangements [62] glycosidations [63] and aldol condensations [64]. Though the mildly acidic H-MCM-41 can be useful in several reactions, the potential as a catalyst would be much higher when the acidity would be higher. Therefore, a lot of effort has been put into the enhancement of the acidity. Kozhevnikov et al. impregnated MCM-41 with heteropoly acids (HPAs) [65]. The obtained catalysts were found to be more selective than sulfuric acid or bulk HPA in the liquid phase alkylation of 4-tert-butylphenol by isobutene and styrene. Van Rhijn et al. reported the application of MCM-41 bearing sulfonic acid groups in hydroxyalkylation and esterification reactions [66]. Beside as an acid catalyst, MCM-41 can also be used as a base catalyst. Sodium or cesium exchanged MCM-41 is weakly basic and can be used in reactions requiring only mild basic sites, like the Knoevenagel reaction of [67]. A stronger basic material is obtained by impregnation with cesium oxide, or with a cesium-lanthanum mixed oxide [68]. In the latter case, a slightly less basic material is obtained, but it is reported to be more stable towards water compared to the former. Another approach to obtain basic MCM-41 material has been reported by Brunel et al. [69], who anchored primary and secondary amines to the surface of all silica MCM-41 and by Subba Rao et al. [70] who prepared a strongly basic catalyst by covalently coupling of a guanidine base to an MCM-41 support. Anchoring of catalytically active species is of course not restricted to basic species. The amorphous character of the MCM-41 pore wall results in the presence of a large number of silanol groups which can be used to anchor catalytically active species or precursors of that, to the pore wall.

MCM-41 drew attention as a potential redox catalyst as well. Apart from doubtful activity and leaching problems, redox molecular sieves suffer from the relatively small pore openings of the structures. TS-1 is a good example of a redox molecular sieve which only displays a good activity when small linear molecules are oxidised [71]. Various metals, e.g. Ti [72], V [73], Cr [74] have been incorporated in the MCM-41 framework (see Figure 16), resulting in effective catalysts for the oxidation of bulky substrates. However, in the case of V and Cr the catalytic activity is most likely due to traces of leached metal [75, 76]. In the
case of Ti the catalytic activity is probably heterogeneous when using alkyl hydroperoxides, but that material proved to be unstable under the conditions of catalytic oxidation with aqueous H₂O₂ [77, 78]. This results in the collapse of the MCM-41 framework and thus in titanium leaching. Other possibilities to incorporate metals in MCM-41 are grafting and tethering (see Figure 16).

![Incorporation, Grafting, Tethering](image)

Figure 16 Possible ways to incorporate metals in MCM-41 [79].

Despite the potential of MCM-41 as an acid catalyst or as a catalyst support, there are no industrial applications of MCM-41 at the moment. Especially the template applied for the MCM-41 synthesis makes the material commercially unattractive. The template is relatively expensive and can only completely be removed by calcination which precludes recycling. Another point is that the emissions involved in the removal of the template require scavenging. Other materials mentioned in Table 7, using non-ionic templates, are more likely to see industrial application.

For more information on MCM-41 and its application in catalysis several reviews are available [80, 81, 82].
1.5.4 Acid resins

Although originally developed for cation exchange purposes, acid resins have found widespread application in catalysis [83]. Acid resins are polymers, which are functionalised with an acid group. This group generally is a sulfonic acid group but can also be a carboxylic acid group. The functionality can be introduced either by polymerisation of a functionalised monomer, or by modification of the already formed polymer. A popular acid resin which can be used in various acid catalysed reactions is Amberlyst-15 [76]. This material is comprised of a polystyrene backbone, functionalised with sulfonic acid groups, and cross-linked with 1,4-divinylbenzene.

A more recent development is the resin Nafion [84] (see Figure 17), which has a higher acidity than Amberlyst-15. The acid strength of this material is comparable to 96% sulfuric acid. Also for this material the acidity comes from a sulfonic acid group, which is however significantly stronger compared to the Amberlyst-15 sulfonic acid groups, because of the highly electron withdrawing perfluoroalkyl backbone. Recently nafion incorporated in silica has been reported [85]. The advantage of such systems is that they combine the high surface area of the support with the strong acidic properties of nafion. Because of its high surface area MCM-41 seems to be an interesting candidate as a support for nafion as well. Indeed such a composite material has been prepared and showed a good activity in the acylation of anisole with octanoic acid [86].

\[
\begin{align*}
\left[\begin{array}{c}
\text{CF}_2 & - & \text{CF}_2 \\
\hline
\text{CF} & - & \text{CF}_2 \\
\end{array}\right]_n & \quad \text{CF} & - & \text{CF}_2 \\
\left(\text{OCF}_2 & - \text{CF} & \right)_m & \quad \text{O} & - & \text{CF}_2 & - \text{CF}_2 & - \text{SOH} \\
\text{CF}_3 & & & & & \text{O}
\end{align*}
\]

Figure 17 Structure of Nafion.
Limitations of the sulfonic acid polymeric materials are their low thermal and mechanical stability. The recommended maximum operating temperature for Amberlyst-15 is 120 °C and for Nafion 210 °C. This limits the number of processes in which the materials can be applied and makes a regeneration of the catalyst by calcination impossible. Despite these drawbacks, acid resins are in use for a variety of reactions.

1.6 Scope of the thesis

This thesis describes research on the use of solid acid catalysts, mainly in esterification reactions. The aim is application in oleochemistry and, therefore, the research was focused on mesoporous materials and modifications of mesoporous materials.

Chapter 2 reports the results of a study on the influence of the hydrophobicity of a solid acid on its activity in both gas- and liquid-phase esterification reactions.

Chapter 3 describes the modification of MCM-41 by impregnation with Heteropoly Acids (HPA). Main focus was on the stability of the HPA dispersion during reaction.

Chapter 4 concerns another kind of modification of MCM-41. By increasing the local crystallinity of the material it is attempted to increase the acidity of the material.

Chapter 5 presents some kinetic data on the esterification of dodecanoic acid and 1-octanol catalysed by MCM-41 with sulfonic acid groups covalently bonded to the porewall. In the same chapter, the use of pervaporation using a ceramic membrane in order to remove the water formed during the esterification reaction is described.

Chapter 6 discusses MCM-41 as a support for a catalytically active material. The grafting of the oxidation catalyst TEMPO on MCM-41 is described as well as the use of the resulting material in some oxidation reactions.

Chapter 7 deals with zeolite MCM-22. This material showed a remarkable selectivity in the reductive etherification of substituted cyclohexanones.
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Introduction


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A study on the use of zeolite Beta as solid acid catalyst in liquid and gas phase esterification reactions.
The influence of the hydrophobicity of the catalyst

ABSTRACT

The use of solid acid catalysts rather than homogeneous acids can be beneficial in several reactions because of an easier recovery of the catalyst and their potential of being reused. Zeolitic materials having different Si to Al ratios were tested in esterification reactions. It appears that the hydrophobicity of a solid acid is a key factor for its activity. Hydrophilic materials proved to be inactive in the liquid phase esterification of apolar substrates. This may be ascribed to strong adsorption of water formed during the reaction, which prohibits adsorption of reactants onto the active sites. More polar substrates are able to compete with water for the adsorption sites and thus the influence of the hydrophobicity of the catalyst on its activity becomes less pronounced when such components are used. The influence of the hydrophobicity of the catalysts on their activity in gas phase reactions is negligible. The activity in gas phase reactions is mainly dependent on the amount and the strength of acid sites present in the catalyst.

The gas phase experiments described in this chapter were performed by Drs. R. Koster (group of Prof. A. Bliek, University of Amsterdam).
2.1 Introduction

Currently there is a growing awareness of the environmental impact of chemical processes and consequently of the need of reduction of waste streams [1,2]. To avoid undesirable emissions two solutions can be considered. First option is an end of pipe solution where one converts the pollutant to less harmful compounds before being emitted, in order to minimise its environmental impact. A more elegant approach is to avoid formation of pollutants by using alternative, more efficient processes. Therefore, many studies are focussed on development or improvement of selective catalysts. For the synthesis of fine chemicals and organic intermediates mainly homogeneous acid and base catalysts are applied. These catalysts, however, can not be regenerated, they tend to cause corrosion of reactors and will lead to salt formation due to the neutralisation of the reaction mixture during the isolation of the product. Moreover, a complete removal of these catalysts is not always possible, resulting in limitations in potential applications of the products. Heterogeneous catalysts offer great advantages over homogeneous ones and are therefore an important subject of research [3]. These catalysts can be separated from the reaction mixture more easily and may be suitable for re-use. A potential class of materials which can be used as heterogeneous catalysts are zeolites. Especially zeolite Beta has drawn much attention [4]. Examples of actual or potential successful applications of zeolite Beta include aromatic alkylation [5], aromatic acylation [6], aliphatic alkylation [7], indole synthesis [8] and the highly selective MPV reduction of 4-tert-butylecyclohexanone to the corresponding cis-alcohol [9].

Although zeolites or solid acids in general, and to a lesser extent, solid bases are already used in several bulk chemical processes [10], their use in fine chemical processes is still limited. In esterification reactions, mainly homogeneous catalysts are used. Despite the advantages of solid acids, a simple implementation in existing liquid phase processes is often impossible. In order to obtain sufficient activity, fast adsorption of reactants and desorption of the reaction products is an important factor. One also has to take into account that in a bimolecular reaction, both substrates will be adsorbed on the catalyst. Strong adsorption of one of the reactants may lead to severe inhibition phenomena, or lead to
extensive formation of by-products. Compared to the homogeneously catalysed counterpart, other process conditions, in terms of the reactant ratio, temperature, solvent (if used) etc, may be required. In reactions with water as one of the products, the hydrophobicity of the catalyst can play a dominant role. Especially in equilibrium limited reactions, such as esterifications, a strong adsorption of the produced water will eventually deactivate the catalyst. This has limited the application of solid acids as a catalyst in such reactions.

Both the hydrophobicity and the acidity of zeolites changes with the Si/Al ratio. In this chapter a study is described on esterifications catalysed with zeolites. Since the Si/Al ratio of all zeolites except one was higher than 10, the strength of the acid sites was comparable [11]. Attention was particularly focussed on the relationship between the hydrophobicity and the activity of these materials. Therefore, it was important to have available a good method to quantify the hydrophobicities. Several methods for the determination of the hydrophobicity of solids have been proposed. An example is a method where zeolites are suspended in an aqueous solution of C4 alcohols or butanone. The decrease in alcohol or butanone concentration is then used as a measure of the hydrophobicity [12]. Another method described in the literature uses temperature programmed desorption of a water-loaded zeolite. The decrease in weight between room temperature and 150 °C, divided by the decrease in weight between room temperature and 400 °C is then used as a measure for the hydrophobicity [13]. A more sophisticated method utilises the contact angle of a water droplet on a zeolite surface as a measure of the hydrophobicity [14]. None of these methods proved to be completely satisfactory for the determination of the hydrophobicity of zeolitic materials. In 1991 Weitkamp and co-workers introduced the use of competitive adsorption of water and toluene as a method to probe hydrophobicities [15]. Later, competitive adsorption of water and other hydrocarbons was reported as well [16]. In the study described in this chapter, Weitkamp’s method proved to be a simple and reliable way for hydrophobicity determinations, enabling the comparison of the hydrophobicity of different zeolite samples. The main advantage over the other methods using adsorption of either water or a hydrocarbon as a measure of the hydrophobicity is that in the method introduced by Weitkamp et al. two components are adsorbed and their adsorption ratio is used as a measure of the hydrophobicity. Therefore differences in surface area do not influence the outcome of the measurement. Furthermore, this method does not require large investments
and is easily operated. Therefore, it is now possible to measure activities of a series of catalysts in the esterification reaction and to relate these to their hydrophobicities. For the determination of the acidity of zeolites several methods are available, like the use of model reactions [17], IR spectroscopic methods [18] and microcalorimetry [19]. In the present study NH$_3$-TPD is used for the determination of the acid strength and of the acid site density. Some caution is needed with the interpretation of TPD results because of the interference of diffusion phenomena, the chemical desorption process and because it is difficult to distinguish between chemical and physical adsorption, [20]. In this study, zeolite Beta samples having different Si/Al ratios are used. In the test reactions various substrates differing in polarity, are used, in order to see the influence of the hydrophobicity of the zeolites on their activity in esterification reactions.

Hydrophobicity is expected to be less important in gas phase esterification compared with liquid phase reactions. Clear evidence for this hypothesis cannot be found in literature, since usually small chain carboxylic acids and alcohols are used in gas phase studies, while fatty acids and C6-C8 alcohols are more often encountered in liquid phase studies. Obviously the chain length of the reactant determines its polarity and thus its ability to compete with the reaction water for the adsorption sites in the zeolite. Since the reactants used in gas-phase esterifications are usually rather polar one can expect less influence of the hydrophobicity on the activity of the catalyst in gas phase studies.

The present study involves the determination of the hydrophobicity of various zeolites Beta and their use as catalysts in both liquid and gas phase esterification reactions. For comparison some other zeolites have been used as well.

\section{2.2 Experimental}

\textit{Preparation of zeolites.} Zeolite Beta with Si/Al = 10 and Si/Al = 5 and all Si Beta (further referred to as zeolite H-Beta (10), H-Beta (5) and H-Beta (∞), respectively) were synthesised following a literature procedure [21,22]. Dealumination was performed by stirring zeolite H-Beta (10) (10 g) in a 0.1 M HCl solution (50 ml), or for more severe
dealumination in a 1.0 M HCl solution (50 ml), for 4 h at 80 °C. The zeolite was then recovered by filtration, washed with water and dried at 70°C (0.4 mbar) in a vacuum oven. Zeolite Beta (10) (3 g) was silylated by suspending it in 25 ml of dry toluene. After addition of 0.25 g (2.3 mmol) of trimethylchlorosilane, the suspension was refluxed for 5 h. The modified zeolite was recovered by filtration and was subsequently washed with dry toluene. The zeolites H-Y and H-USY were obtained from Akzo Nobel catalysts b.v. (Amsterdam, The Netherlands) and the zeolite H-MOR was obtained from PQ-zeolites (Delfzijl, The Netherlands). Zeolite H-MCM-22 (Si/Al =15) was synthesised using a literature procedure [23].

Equipment and reactants. ICP analysis was used to determine Si/Al ratios. ICP measurements were conducted on a Perkin-Elmer plasma 2000 by J. Padmos. The zeolites were characterised by XRD using a Philips PW 1840 diffractometer with Cu Kα radiation. MAS-NMR data were recorded on a Varian VXR-400S spectrometer, equipped with a Doty probe. Reactants (p.a.) were obtained from Acros and Aldrich (esterification substrates), Riedel de Haen (sodium aluminate), Fluka (tetracethylammonium hydroxide) and DuPont (Ludox LS-30) and were used without further purification.

Determination of acidities. NH3-TPD measurements were run on a Micromeritics TPD/TPR 2900 equipped with a TCD. The sample (~60 mg) was activated at 600 °C (ramp 10 °C/min) for 30 min in a flow of helium, and then NH3 was adsorbed at 120 °C. Desorption of NH3 was monitored at a temperature ramp of 10 °C/min from 120 °C to 600 °C.

Determination of hydrophobicities. For the determination of the Hydrophobicity Index (HI), a mixture of water and toluene vapours (P_{toluene}=2.92 kPa, P_{water}=2.34 kPa) was passed through a fixed bed adsorber at 35°C. (see Figure 1) [15]. Nitrogen was used as carrier gas with flow rates of 25 ml/min. Every three minutes a sample was taken from the exhaust by means of an automated sampling valve which was subsequently analysed by GC ( HP-17 column, 10 m x 0.53 mm). The final adsorbate loadings were calculated from the breakthrough curves. The HI is defined as HI=X_{toluene}/X_{water}, where X_{toluene} and X_{water} are the weight percentages of toluene and water adsorbed on the sample. All tubes and valves
behind the saturator were heated at 75 °C in order to avoid condensation of water and toluene in the system.

Figure 1  Set-up used for the determination of Hydrophobicity Indices. 1) saturator, 2) valve box, 3) tubular oven, 4) automated sampling valve, 5) GC, 6) flow meter.

Adsorption experiments. Competitive adsorption of the reactants dodecanoic acid and 1-octanol at room temperature was performed by adding a solution of 1-octanol (0.5 mmol), dodecanoic acid (0.5 mmol) and eicosane (0.2 mmol) as an internal standard (assumed not to adsorb), in 30 ml of hexane to 0.50 g of a freshly calcined zeolite (H-Beta, Si/Al 10 and 100). During 10 min samples were taken and analysed by GC in order to follow the adsorption of both reactants.

Esterification reactions. The liquid phase esterification reactions were performed solvent free at 140 °C in a 25-ml glass reaction vessel equipped with a Liebig condenser, which was maintained at 80 °C with the use of a thermostat. In this way water did not
reflux but escaped from the system. In each reaction 5 wt % catalyst and a 1:1 molar ratio
of reactants (each 30 mmol) was used. Eicosane (0.5 g, 1.8 mmol) was used as an internal
standard. The reactions were followed by GC analysis (CP Sil 5 CB, 50 m x 0.53 mm
column).

Steady-state experiments on gas-phase esterification of acetic acid with ethanol, were
performed at the University of Amsterdam using a standard flow set-up having six parallel
reactors. The catalysts were tested in the temperature range 398-473 K. Reactant
concentrations were 0.5 vol. % in nitrogen as carrier gas and the flow through all 6 reactor
tubes was 50 ml/min. The typical catalyst loading was 50 mg. During all experiments one of
the reactors contained no catalyst in order to monitor a possible blank (uncatalysed) reaction.
Side reactions, such as ethanol dehydratation under the formation of diethyl ether or ethene
formation were studied by using ethanol as sole reactant, under the same conditions (0.5 vol% 
ethanol in N₂) as described above. Reactants and products were analysed by means of GC.

2.3 Results and Discussion

2.3.1 Catalyst characterisation

Zeolite Beta samples containing two different Si/Al ratios (5 and 10) were synthesised
using a literature procedure [21, 22]. XRD showed both materials to have a good
crystallinity. In order to obtain materials with higher Si/Al ratios, zeolite Beta with Si/Al
ratio 10 was subjected to a dealumination procedure. Dealumination in 0.25 M aqueous
HCl at 80 °C resulted in a change in the Si/Al ratio from 10 to 20. Application of 1.0 M 
HCl at 80 °C yielded a material with a Si/Al ratio of 100 (further referred to as H-Beta
(100)). NH₃-TPD experiments yielded information on the relative amount of weak and
strong acid sites present in the zeolites H-Beta (5), H-Beta (10) and H-Beta (45) (see Figure
2). All three samples showed a desorption peak in the temperature range of 150-320° C.
Desorption at these temperatures should be ascribed to both physically adsorbed ammonia
and to adsorption on weak acid sites. The desorption peak with its maximum at 420 °C originates from ammonia adsorbed on strong acid sites. Note that such a maximum is absent in the desorption curve of zeolites H-Beta (5) indicating that no strong acid sites are present in this material. This observation is consistent with the theory that the acid strength of a zeolite site is reduced if another aluminium is present as next nearest neighbour of an aluminium, which is likely to be the case with a Si/Al ratio of 5 [24].

![Ammonia TPD curves](image)

**Figure 2** Ammonia TPD of; a) H-Beta (Si/Al = 10), b) H-Beta (Si/Al = 5) and c) H-Beta (Si/Al = 45).

Competitive adsorption of water and toluene from the vapour phase was used for the determination of the Hydrophobicity Indices (HI) of all H-Beta samples applied in this study.

Figure 3 gives two typical examples of the breakthrough curves obtained by competitive adsorption of water and toluene. Figure 3a shows the curve for zeolite Beta with Si/Al=10. Toluene starts breaking through already after 50 min whereas water is still fully adsorbed for another 60 min while expelling toluene. In Figure 3b it can be seen that in the case of zeolite Beta with an Si/Al of 100 both adsorbates break through after ~ 45 min, indicating that this material has a much lower hydrophilicity than the former. In general, the Hydrophobicity Index (HI) of the H-Beta materials follows the trend of an increasing hydrophobicity with increasing Si/Al ratio, although the absolute numbers (see Table 1)
differ from the hydrophobicity data presented on zeolite Beta by Stelzer et al. [25]. Most likely this difference is caused by a difference in crystallinity between the zeolite Beta samples.

![H-Beta (Si/Al=100)](image1)

![H-Beta (Si/Al=10)](image2)

Figure 3 Breakthrough curves of water (○) and toluene (■) used for the determination of the HI of H-Beta (Si/Al=10) and H-Beta (Si/Al=100).

For comparison, the HIs of some other zeolites were determined as well. The obtained values correspond well with what could be expected from their Si/Al values (see Table 1).
Table 1  Some zeolites with their HI.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Si/Al</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-MCM-22</td>
<td>15</td>
<td>2.5</td>
</tr>
<tr>
<td>H-MOR</td>
<td>6</td>
<td>1.2</td>
</tr>
<tr>
<td>H-USY</td>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>H-Y</td>
<td>2</td>
<td>0.3</td>
</tr>
<tr>
<td>H-Beta</td>
<td>5</td>
<td>0.8</td>
</tr>
<tr>
<td>H-Beta</td>
<td>10</td>
<td>2.3</td>
</tr>
<tr>
<td>H-Beta</td>
<td>45</td>
<td>4.8</td>
</tr>
<tr>
<td>H-Beta</td>
<td>100</td>
<td>5.4</td>
</tr>
<tr>
<td>H-Beta</td>
<td>$\infty$</td>
<td>10.8</td>
</tr>
</tbody>
</table>

The influence of the hydrophobicity of the materials on their catalytic activity in esterification was determined by using substrates with different polarities.

2.3.2 Liquid phase esterification reactions

Esterification rates of dodecanoic acid and 1-octanol are remarkably different between zeolite Beta (10) and zeolite Beta (100) (see Figure 5). Due to evaporation of reactants during the reaction a maximum yield of 80% was obtained. The more hydrophobic zeolite Beta (100) showed a good catalytic activity whereas the rate of the zeolite Beta (10) catalysed reaction hardly exceeded the blank (uncatalysed) reaction. The difference is even more pronounced when one considers the initial Turn Over Frequency (TOF) (during the first hour) of both catalysts (see Figure 6). The TOF values are calculated by assuming all aluminium sites to be equally active and are given as mol of product mol Al\(^{1}\) h\(^{-1}\).

H-Beta (5) appears to be completely inactive, as the conversion curve was the same as that of the blank reaction. This was also the case for various other zeolites, as H-MOR, H-
MCM-22, H-Y and H-USY. Considering the amount of acid sites one would expect the zeolites with low Si/Al ratio to be more active. Although for H-Beta (5), H-Y, H-USY and H-MOR one could argue that the acid strength per site is less than that of H-Beta (100) [24], this is certainly not the case for H-Beta (10).

Figure 5  Comparison of H-Beta (10) with H-Beta (100) in the solvent-free liquid phase esterification at 140 °C of dodecanoic acid and 1-octanol. H-Beta (10) ■, H-Beta (100) ○, Blank (uncatalysed ) reaction ▲.

Figure 6  Performance of two H-Beta catalysts with different Si/Al ratio in the esterification of dodecanoic acid and 1-octanol.
Competitive adsorption of dodecanoic acid and 1-octanol showed that the two reactants were adsorbed on H-Beta (100) in a 1:3 ratio (see Figure 7). This adsorption ratio is the same for H-Beta (10) indicating that a difference in the adsorption of the reactants on the catalysts does not account for the difference in the catalytic activity in the esterification reaction.

![Graph showing competitive adsorption](image)

**Figure 7** Competitive adsorption of dodecanoic acid (■) and 1-octanol (●) from a solution on zeolite H-Beta (100) at room temperature.

A more likely explanation is that early during the reaction the H-Beta (5) and H-Beta (10) catalysts accumulate water formed during the esterification reaction. The reactions were performed using 30 mmol of reactants and 0.50 g of catalyst. Considering the pore volume of zeolite Beta (~0.17 ml/g [26]), this means that already at 15% conversion the zeolite can be completely filled with water, and even earlier the catalytic sites can all be occupied. As a result, fresh substrate can no longer reach the active sites resulting in deactivation of the catalyst. This hypothesis is supported by a $^1$H NMR spectrum of a spent H-Beta (10) catalyst, which showed considerable amounts of water to be present in the catalyst compared to the amount of reactants. Therefore, in order for H-Beta to be an active catalyst in the esterification of apolar substrates the material should have a hydrophobic character. This implies that a high Si/Al ratio is required. This means, however, that also the amount of active sites is limited. In order to overcome the hydrophilic nature of the H-Beta (10) catalyst without decreasing the amount of acid sites, the catalyst was silylated using
trimethylchlorosilane (see Figure 8). The idea was to randomly anchor trimethylsilyl groups to silanol groups on and in the zeolite Beta, thereby giving the material a more hydrophobic character and thus facilitating removal of water formed during the reaction.

\[
\text{Si} - \text{OH} + \text{ClSi(Me)}_3 \rightarrow \text{Si} - \text{OSi(Me)}_3
\]

Figure 8  Silylation of silanol groups of zeolite Beta.

In this way a highly active catalyst was obtained. Unfortunately, the stability of this catalyst was rather poor. Upon re-use all additional activity gained by the silylation was lost. The trimethylsilyl groups appeared to be readily hydrolysed from the catalyst, resulting in an increase in hydrophilicity. This loss of the trimethylsilyl groups can well be observed during the HI determination of this material (see Figure 9). The initial breakthrough of water starts almost immediately, but after 45 min the slope of the breakthrough curve decreases, most likely due to a decrease of hydrophobic character. Solid state NMR measurements confirmed the loss of the trimethylsilyl groups.

Figure 9  Hydrophobicity determination of trimethylsilylated H-Beta (10).
Chapter 2

Upon increasing the polarity of the substrates, the influence of the hydrophobicity is decreased (see Figure 10). Due to their higher polarity, these substrates are able to compete with the reaction water for the available adsorption sites. Water formed inside the zeolite during the reaction is easily replaced by fresh substrate allowing the reaction to continue. One has to keep in mind that although the activity per gram of catalyst is virtually the same, the activity for each active site (TOF) is still much higher in the case of the hydrophobic catalyst.

![Graph showing ester yield over time]

Figure 10  Comparison of H-Beta (10) with H-Beta (100) in the liquid phase, solvent free esterification of butyric acid and 1-hexanol at 140 °C. H-Beta (10) ■, H-Beta (100) ◆, Blank (uncatalysed) reaction ▲.

2.3.3 Gas phase reactions

Activity experiments in the gas phase esterification of acetic acid and ethanol using different zeolite H-Beta catalysts showed that the catalytic activity of the zeolite increased with increasing amount of aluminium in the framework. Only zeolite Beta having a Si/Al ratio of 5 did not follow this trend. (see Figure 11). This is not surprising however, since the activity of a solid acid in esterification reactions is known to depend not only on the amount
but on the strength of the acid sites as well [27]. A blank reaction was not observed in the
gas phase esterifications. Presumably in the autocatalysis in the liquid phase, clusters of
several carboxylic acid and alcohol molecules are involved, which are not present in the gas
phase, due to the low concentrations of reactants. For all catalysts a high selectivity towards
the ester (>99%) was observed.

![Graph showing ethanol conversion for different H-Beta catalysts at various temperatures.]

Figure 11   Activity of different H-Beta catalysts in the gas phase esterification of acetic
acid and ethanol at 125 °C, 150 °C, 175 °C and 200 °C.

Ethanol dehydration towards diethyl ether showed that the etherification reaction depends
to a smaller degree on the strength of the acid site and is much more influenced by the
amount of acid sites present. In this reaction the activity of the catalysts increased with an
increasing aluminium content (see Figure 12).

Based on the experimental data presented in Figure 11 it may be concluded that in this gas-
phase esterification example the influence of the hydrophobicity of Beta can be neglected.
The polar substrates are capable to competitively adsorb with the water which is formed
during reaction and thus no inhibition occurs by preferential adsorption of water. Furthermore, the reactions in the gas-phase are performed in a stream of nitrogen which probably also enables the gradual desorption of water from the catalyst at the applied temperatures.

![Diagram showing ethanol conversion over different zeolite H-Beta catalysts at 125 °C, 150 °C, 175 °C and 200 °C.](image)

Figure 12 Ethanol dehydratation over different zeolite H-Beta catalysts at 125 °C, 150 °C, 175 °C and 200 °C.

2.4 Conclusions

The catalytic activity of zeolite Beta samples in liquid and gas phase esterification reactions has been correlated to their Hydrophobicity Indices. It has been shown that these solid acid materials can be useful replacements for homogeneous liquid acid catalysts. One should bear in mind however, that a good adsorption/desorption rate of reactants and products (especially water) is required in order to obtain a fair catalytic activity. Therefore,
for the selection of a liquid phase esterification catalyst one must take into account the polarity of both the reactants and products, and that of the potential catalyst. In gas phase esterification of short chain carboxylic acids and alcohols the polarity of the zeolite Beta samples seems to be less important, probably because of the higher polarity of the reactants employed in the gas phase reactions.
References

A study on the stability of MCM-41-supported heteropoly acids under liquid- and gas-phase esterification conditions

Abstract

MCM-41 supported heteropoly acids (HPAs, H$_3$PW$_{12}$O$_{40}$ or H$_4$SiW$_{12}$O$_{40}$) are used as catalysts in the liquid-phase esterification of 1-propanol and hexanoic acid and in the gas-phase esterification of acetic acid and 1-butanol. For both reactions MCM-41-supported HPAs proved to be active catalysts. In the liquid phase esterification of 1-propanol and hexanoic acid performed in refluxing toluene an initial conversion of 0.33 mmol min$^{-1}$ g$^{-1}$ was obtained for MCM-41 containing 33 wt% HPA, which corresponds to a TOF of 60 h$^{-1}$. In the gas-phase esterification of 1-butanol and acetic acid at 110 °C a TOF of 40 h$^{-1}$ was obtained for the MCM-41 loaded with 33 wt% HPA.

XRD and TEM studies on spent catalysts show that the initially high dispersion of HPA units is lost during reaction both in the liquid- and in the gas-phase esterifications. Large clusters (~10 nm) of HPA are formed on the outer surface of the MCM-41 support. This clustering also occurred when less polar substrates were applied. The polarity of the substrates is not the only factor responsible for the cluster formation. It is expected that water, formed in esterification, plays a major role in the transport of the HPA from the MCM-41 pores to the outer surface, leading to formation of HPA clusters on the outer surface.

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3.1 Introduction

In 1992, researchers at the Mobil Central Research Laboratory discovered the mesoporous ordered material of the MCM-41 type [1]. Since then, a growing interest has been manifested in testing these materials as catalyst, as catalyst-precursor and as catalyst support. Though related to zeolites, MCM-41 materials are not crystalline, but rather materials that consist of ordered channels surrounded by amorphous walls. This long-range order generates an apparent X-ray diffraction pattern at low angles. The intensity of the peaks is a measure for the degree of ordering of the channels and usually referred to as the crystallinity of the material. Ideally, the material consist of a hexagonal array of straight channels with a uniform pore size which can be engineered in the range from 2 to 8 nm. In practice, every sample contains some disordered material (see Figure 1). The disordered phase consists of tortuous and not hexagonally packed channels. Since the disordered phase also exhibits mesoporosity and has a high surface area, it is not clear whether this affects the feasibility of the material as a catalyst or as a support.

![Figure 1](image.png)

TEM micrographs of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loaded MCM-41 (33 wt%) a) ordered phase  b) disordered phase.
The MCM-41 materials have a high thermal stability (up to 900 °C), a large surface area (up to 1000 m²g⁻¹) and a large adsorption capacity for organic molecules. Acid sites can be generated by incorporation of aluminium in the MCM-41 framework. These sites in H-MCM-41 are weakly acidic and can certainly not be compared with the strong acid sites present in zeolites in their protonic form. They rather correspond with the acid sites found in amorphous silica-aluminas. There are, however, several examples of reactions requiring a mildly acidic catalyst for which MCM-41 is the catalyst of choice [2-7]. Recently, it has been reported that MCM-41 in the Na or Cs form exhibits weak base catalytic activity [8].

Besides the use of aluminium-containing MCM-41 as a solid acid catalyst, the all-silica form is used as a support for catalytically active materials such as metal complexes, heteropoly acids, noble metal particles or even enzymes [9-13]. Our interest is in the HPA loaded MCM-41 since these materials have acid strength comparable or stronger than zeolites. Reactions catalysed by supported heteropoly acids include alkylation of isobutane, Diels-Alder reactions and phenol alkylation [14,15].

Here we wish to report the results of a study on the use of MCM-41 supported HPAs in esterification reactions. Previously our group studied the potential of HPA and HPA on carbon in various esterification reactions [16]. In the present work HPAs (H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ ) were impregnated from aqueous solution on an all-silica MCM-41 material with a pore diameter of 3.5 nm. Both liquid-phase and vapour-phase esterification were investigated and the HPA systems were compared with zeolite H-Beta and H-MCM-22. Special attention was paid to the stability, in particular to the dispersion of the HPA particles on both the fresh and the spent catalysts. The dispersion of the HPA was determined by means of XRD and TEM measurements. In the previous publications regarding HPA on MCM-41 such a comparison was not included [10,17].

Liquid-phase reactions (1-propanol/hexanoic acid) were carried out in a batch reactor using toluene as the solvent. The gas-phase reactions (1-butanol/acetic acid) were performed in a continuous down-flow fixed-bed reactor under plug-flow conditions.
3.2 Experimental

The all silica MCM-41 material used in this study was synthesised following the procedure of Beck et al. [1c]. Silica sources used were Cab-osil M-5 (fumed silica, Fluka) and sodium silicate solution (Aldrich). The template cetyltrimethylammonium bromide and trimethylammonium hydroxide (TMA) were obtained from Aldrich. MCM-41 was synthesised by heating the synthesis gel (composition: 1 SiO₂, 63.3 H₂O, 0.04 (TMA)₂O, 0.016 (C₁₈NMe₃)₂O) in a polypropylene bottle at 100 °C for two days. The resulting solid was filtered, washed with deionized water and dried in a vacuum oven at 50 °C /0.3 mm Hg. The template was removed by calcination at 540 °C for 10 h. Both X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) data correspond with data of well-defined MCM-41 material as described in the literature [1].

The HPAs were obtained commercially (H₃PW₁₂O₄₀, Acros and H₃SiW₁₂O₄₀, Aldrich), and were used without further purification. The supported catalysts were prepared by impregnation of the HPAs onto all-silica MCM-41 following the procedure of Kozhevenikov et al. [18]. Typically 1 g of MCM-41 was suspended in 30 ml of an aqueous solution of H₃PW₁₂O₄₀ or H₃SiW₁₂O₄₀ so as to obtain loadings of 10 to 33 wt%. After stirring the suspension overnight at room temperature, the solvent was evaporated, yielding the MCM-41 supported heteropoly acid. The materials were dried and mildly calcined at 130 °C and stored in a desiccator over P₂O₅ until use. Zeolites MCM-22 (Si/Al 15) and H-Beta (Si/Al 12) were prepared following literature procedures [19,20].

X-ray diffractograms were recorded on a Philips PW 1840 diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) was performed using a Philips CM 30 ST or CM 30 T electron microscope operated at 300 kV. Samples for TEM were prepared by placing droplets of a suspension of the sample in ethanol on a polymer microgrid supported on a Cu grid. EDX elemental analysis was performed using a LINK system attached to the TEM equipment. Hydrophobicity Indices were determined using a set-up as described by Berke et al. [21]. For determination of the HI, a mixture of water and toluene vapours (P₉₅₆=2.92 kPa, P₉₅₆=2.34 kPa) was passed through a fixed bed adsorber at 35
C. Nitrogen was used as carrier gas with flow rates of 25 ml/min. The final adsorbate loadings were calculated from the breakthrough curves. The HI is defined as $HI = X_{toluene}/X_{water}$, where $X_{toluene}$ and $X_{water}$ are the weight percentages of that component adsorbed on the sample. More detailed information on the HI determination is provided in chapter 2. The liquid-phase esterification of 1-propanol with hexanoic acid was carried out in a 250 ml glass reaction vessel equipped with a magnetic stirrer, a Dean-Stark trap for water removal and a reflux condenser. The reactor was charged with 3.1 g (25 mmol) of hexanoic acid, 3.1 g (50 mmol) of 1-propanol, and 0.5 g of catalyst. Toluene (150 ml) was used as the solvent. The reaction was conducted at reflux temperature (110 °C). The reactions were followed by GC analysis (CP Sil 5 CB, 50 m x 0.53 mm column).

Vapour-phase experiments were performed using a fixed-bed continuous down-flow reactor consisting of a vertically mounted borosilicate glass tube (7 mm i.d.) heated by a fluidised bed oven. To obtain plug-flow conditions catalyst particles in the range of 0.7 - 1.0 mm were used which were obtained by repeatedly pressing, crushing and sieving of the catalysts powder. The reactant mixture was pumped into a stream of preheated carrier gas (N2) by means of a motor-driven syringe pump. Samples were taken on-line and analysed by GC (CP Sil 19 column). The test reaction for the gas-phase esterification was the conversion of 1-butanol with acetic acid. Typical reaction conditions were 50 ml min⁻¹ total gas flow, a substrate concentration of 5 vol% of each reactant in nitrogen, a temperature of 110 °C and 1 g catalyst bed.

3.3 Results and Discussion

3.3.1 Liquid phase experiments

MCM-41 materials impregnated with HPAs appeared to be very active catalysts for the liquid phase esterification of 1-propanol with hexanoic acid. An initial conversion of
0.33 mmol/min/g catalyst was obtained (TOF of 60 h\(^{-1}\)) for the highest HPA loaded MCM-41 (33 wt% HPA). The activity of purc HPA is lower than that of the HPA supported on MCM-41. Since the solubility of HPA in the reaction mixture is low under the reaction conditions (0.04 g HPA in 150 ml toluene containing 50 mmol 1-propanol and 25 mmol hexanoic acid), the enhanced activity may be ascribed to a high dispersion of the HPA on MCM-41, providing more exposed surface proton sites than pure HPA. This is consistent with the observed lower reactivity of the catalyst upon sintering of the HPA (see below). A higher intra-porous concentration of both alcohol and acid than the concentration in solution, due to sorption by MCM-41, could also contribute to the higher activity of the composite catalyst. This assumption is supported by the relatively large amounts of substrates adsorbed by the composite system (0.18 g g\(^{-1}\) 1-propanol and 0.20 g g\(^{-1}\) hexanoic acid) when a solution with the same composition as the reaction mixture is added to fresh evacuated catalyst at room temperature. The activity of MCM-41-supported HPA varied slightly with different batches. The HPA-on-MCM-41 systems are more active on a weight basis than the zeolites H-Beta and H-MCM-22 (see Figure 2). Moreover MCM-41 (Si/Al=16) itself displayed a very low activity which can be ascribed to its low acid strength. The activity is hardly higher than that of the blank (uncatalysed) reaction.

![Figure 2](image)

Initial activities of various solid acid catalysts in the liquid phase esterification (standard formulation, 0.5 g catalyst) of 1-propanol and hexanoic acid in toluene (HPA used is PW\(_{12}\)). H-BEA (A); H-MCM-41 (B); H-MCM-22 (C); MCM-41 20 wt% HPA (D); MCM-41 33 wt% HPA (E); Pure HPA (F).
Two supported HPAs (33 wt% on MCM-41) were tested, H₃PW₁₂O₄₀ and H₃SiW₁₂O₄₀, of which the former was less active than the latter (see Figure 3). Since the strength of all Keggin HPAs is very high (Hₒ = -13) and depends only weakly on their composition [22], it is not likely that the difference in activity is caused by a difference in acid strength. Moreover H₃PW₁₂O₄₀ is generally considered to be slightly stronger acidic than H₄SiW₁₂O₄₀. On the other hand H₄SiW₁₂O₄₀ contains 4 protons per Keggin unit compared to H₃PW₁₂O₄₀ only 3. Also small deviations in dispersion or loading might cause the difference in activity. When re-used after one reaction cycle the activity of both catalysts decreased significantly (see Figure 3).

![Conversion plot of fresh and of re-used catalysts in the liquid phase esterification of 1-propanol and hexanoic acid: ◊ SiW₁₂ fresh, □ PW₁₂ fresh, Δ SiW₁₂ re-used, × PW₁₂ re-used. The curve of PW₁₂ slightly deviates in the first half hour probably because of a slower heating of the reaction mixture.](image)

Figure 3

Figure 4 shows the XRD patterns of the initial MCM-41, pure HPA (H₃PW₁₂O₄₀), a HPA (H₃PW₁₂O₄₀)-loaded-MCM-41 catalyst (33 wt%) and the used HPA-on-MCM-41 catalyst. Loading of HPA gives rise to a decrease in intensity of the peak at 2.3 °(2 θ) and a broad signal appears around 7.5 °(2 θ). It should be noticed that no patterns of any bulk HPA crystal phase are observed for the fresh composite catalyst, indicating that the HPA is finely
dispersed on the MCM-41 support. TEM did not show any loss in crystallinity leading to the conclusion that the loss in intensity in the X-ray spectrum is caused completely by the filling of the pores with HPA particles. After one reaction cycle in the esterification of 1-propanol and hexanoic acid, the XRD of the spent catalysts showed new signals corresponding to those observed for the pure HPAs. This indicates substantial sintering of the catalyst.

Figure 4  XRD’s of from top to bottom: pure $\text{H}_3\text{PW}_{12}\text{O}_{40}$, all-silica MCM-41, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loaded (33 wt%) MCM-41, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ loaded (33 wt%) MCM-41 after reaction (liquid phase esterification of 1-propanol and hexanoic acid for 7 h.

Keeping in mind the minimum particle size necessary for a complete X-ray spectrum, it can be concluded that the size of the HPA crystals is at least 10 nm. Considering the pore size of the MCM-41 (3.5 nm) used, these HPA crystals should be located on the external surface of the support. The existence of large HPA crystals on the MCM-41 external surface was confirmed by TEM. (see Figure 5 compared to Figure 1)
Figure 5 Two TEM micrographs of the spent catalyst (PW₁₂ loaded (33 wt%) MCM-41).

3.3.2 Gas phase experiments

Both H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀ supported on MCM-41 (33 wt% HPA on MCM-41) were active catalysts in the vapour phase esterification of acetic acid with 1-butanol. Both systems resulted in 95 % conversion of 1-butanol. The selectivities of ester formation based on 1-butanol conversion were 85 % and 80 % for the H₃PW₁₂O₄₀ and the H₄SiW₁₂O₄₀ catalyst, respectively, and remained constant over 20 h. Apart from esterification, also the formation of light components, 1- and 2-butene and of dibutyl ether occurred. The formation of by-products was somewhat more pronounced for the H₄SiW₁₂O₄₀ catalyst. A conversion of 95 % corresponds to a Turn-Over-Frequency (TOF) of about 40 h⁻¹ per HPA for both catalysts. For the TOF per proton site one should divide by 4 for SiW₁₂ and by 3 for PW₁₂. Although no decrease in activity and selectivity with time on stream was observed over 20 h, the catalysts became dark-coloured already after 4
h. In the absence of a catalyst, a conversion of 10% was obtained under similar conditions. In this reaction no side products were detected.

The clustering of HPA onto the external MCM-41 surface, found in liquid-phase esterification, appeared also to occur in gas-phase esterification. The clustering, as observed by TEM after 20 h on stream for the 33 wt% PW12 and 33 wt% SiW12 on MCM-41 catalyst was, however, much less severe than the clustering observed for the same catalysts after 6 h service in the liquid phase at the same temperature (110 °C).

The clustering can be explained by increased mobility of the HPA units due to dissolution in the adsorbed mixture of reactants and ester product and especially in the water formed. It may be assumed that the internal concentrations of these compounds are much higher than the bulk liquid concentrations. Upon arrival at the pore mouth the HPA is confronted with the apolar toluene and "reprecipitates" by forming clusters at the outer MCM-41 surface.

If the reactants used are an important factor for the sintering of the HPA, one would expect the migration to be slower when less-polar long-chain reactants are used. However, in the esterification of 1-octanol (6.5 g, 50 mmol) with dodecanolic acid (5.0 g, 25 mmol) in the presence of 33 wt% H3PW12O40 on MCM-41 (0.5 g) in 150 ml toluene also outer surface cluster formation was observed indicating that especially the reaction water is a HPA mobilizer. Determination of the Hydrophobicity Index (HI) of all-silica MCM-41 and MCM-41 supported HPA further supported this assumption, since the composite material was considerably more hydrophilic than the original material (see Figure 6). Considering the HPA mobility in the gas phase experiments, the relatively low reaction temperature (110 °C) will lead to a substantial and liquid-like steady state pore filling. The reactant acetic acid and particularly the product water will act as HPA solvating molecules and can enhance the mobility of the HPA units. Recently, Chu et al. applied a comparable catalyst system in the gas-phase esterification of acetic acid and 1-butanol [17]. Small amounts of leaching from the support were reported. Although no further data considering the characterisation of the spent catalyst were given by the authors, it is very likely that in their work sintering of the HPA units occurred as well.

In liquid-phase esterifications the sintering of the HPA leads to formation of large HPA clusters. As a consequence the available HPA surface area drops, and so does the activity of
the catalyst. In gas-phase esterifications the sintering phenomenon is less severe and did not lead to loss of activity. It can be expected however, that upon longer times on stream larger clusters will be formed and consequently the activity will decrease.

Figure 6 Breakthrough curves of water (●) and toluene (■) in competitive adsorption [21] and derived the Hydrophobicity Index (HI) for all-silica MCM-41 (top) and of MCM-41 loaded with 33 wt% HPA (bottom).
3.5 Conclusions

Composite solid acid catalysts comprising all-silica MCM-41 and Keggin type heteropoly acid HPA (H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀) are very active in the liquid-phase esterification of 1-propanol with hexanoic acid and in the vapour-phase esterification of 1-butanol with acetic acid. Probably because of the high dispersion, offering a large surface area of HPA, the supported HPA is more active than pure HPA. It should be noted however, that these catalysts when subjected to the esterification conditions have a tendency to form large HPA clusters on the external surface of the supporting material. This is observed both in liquid-phase reactions and to a lesser extent in gas-phase reactions. Since the cluster formation occurred in the liquid-phase both when polar and when apolar substrates are applied, water formed during the reaction can be considered as the main HPA mobilizer. Therefore this composite MCM-41/HPA catalyst should preferably be applied in reactions where no water is involved.
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4 On the Partial transformation of MCM-41 material into zeolites: the formation of nano-sized MFI type crystallites

ABSTRACT

A new potentially catalytic material has been developed by partial recrystallisation of the porewall of MCM-41. Recrystallisation is induced by impregnation of MCM-41 with tetrapropylammonium hydroxide followed by a hydrothermal treatment. This procedure resulted in the formation of small particles of approximately 3 nm which can be observed with TEM. The fact that the formation of these particles resembles the first stages of ZSM-5 formation and the fact that a templating material is used which is also frequently applied in the synthesis of ZSM-5 suggests that the 3 nm particles have a ZSM-5 structure. Furthermore, $^{13}$C NMR on recrystallised MCM-41 shows a split-up of the methyl signal of TPA, which is also known to be present in as-synthesised ZSM-5. After calcination of the recrystallised material the small crystallites could no longer be observed, although IR measurements still show some ZSM-5 like acidity to be present. Other, milder calcination routes should be developed in order to preserve the ZSM-5 crystallites. Another stability problem encountered concerns the stability of the MCM-41 since the hydrothermal treatment severely damaged the framework. It was found that the use of a template molecule, hexadecylamine, to support the framework during the recrystallisation was beneficial.
4.1 Introduction

Due to environmental concern, the interest in solid acid catalysts as replacements of liquid acids is growing [1]. The problems associated with the currently used catalysts such as mineral acids or metal halide Lewis acid catalysts are their toxicity, corrosivity and effluent disposal. Furthermore, a complete separation of the product and the catalyst is sometimes difficult. Zeolites possess several catalytically desirable properties: a high surface area, tuneable pore size, hydrophilicity and acidity and a high thermal and chemical stability. Therefore, they are gaining importance in the quest for cleaner processes. Industrial examples [2] include aromatic alkylation [3], the synthesis of tert-butylamine from ammonia and isobutene over zeolite MFI [4], the conversion of methanol and ammonia to mono- and dimethylamine over modified mordenites [5] or zeolite Rho [6], and the hydration of cyclohexene to cyclohexanol over H-ZSM-5. Furthermore, zeolites have found widespread applications in the oil refining [7]. A disadvantage of zeolitic catalysts is their limited pore size (up to 1.0 nm), which renders them useless with larger sized reactants.

The discovery of the mesoporous material, MCM-41 [8] has greatly enlarged the window of porous materials applicable as catalyst for organic reactions. Unfortunately the acid strength of MCM-41 resembles that of the amorphous silica aluminas, rather than that of the more strongly acidic zeolites [9]. Although the material is valuable for many organic conversions [10,11], an enhancement of its acidity is desirable for an extension of its applicability.

Several approaches aimed at increasing the acid strength of the material. Independently three groups showed that heteropoly acids (HPA) supported on MCM-41 are excellent catalysts in several reactions [12, 13, 14]. However, the lack of stability of this catalyst system in case polar reactants or products are involved [15], prevents its introduction in many industrial applications. Another possibility is the use of sulfonic acid groups covalently attached to the MCM-41 pore wall via an organic spacer [16]. There, leaching seems not to be a problem, but the organic spacer limits the thermal stability of the system and, consequently, the possibilities of thermal reactivation of the catalyst. Another
approach is the simultaneous synthesis of a micro- and mesoporous composite material using *in situ* formation of MFI and MCM-41 material [17]. Complex aggregates of MCM-41 and MFI were obtained of which the relative amounts of MCM-41 and MFI can be tuned by varying the synthesis conditions. However, it is not quite clear whether these materials offer more possibilities than a physical mixture of both phases would do.

The present paper deals with the partial recrystallisation of the MCM-41 pore wall to ZSM-5 crystallites, a concept illustrated in Figure 1.

![Diagram](image)

**Figure 1** Partial recrystallisation of the MCM-41 pore wall.

Recrystallisation is induced by introducing the template for ZSM-5 crystallisation: tetrpropylammonium (TPA), by impregnation or ion exchange. An increase of the local crystallinity around the aluminium atoms is expected to give MCM-41 a more zeolite-comparable acid strength. Ostwald's rule of successive transformations states that a metastable silicate phase will successively transform to more stable (denser) phases until it reaches the most stable phase (quartz)[18]. This implies that, in principle, recrystallisation of MCM-41 to ZSM-5 is possible. It may be noted that if an amorphous phase exists between MCM-41 and ZSM-5, this may be formed first, after which ZSM-5 will be formed. Attempts to reproduce a former procedure [19] resulted in amorphised MCM-41 before the formation of any ZSM-5.
It will be shown that the formation of nano-sized particles, resembling ZSM-5, homogeneously dispersed over the MCM-41 framework is possible.

4.2 Experimental

MCM-41 material with a Si/Al ratio of 32, was synthesised following the procedure of Beck et al.[8°]. Silica sources used were Cab-osil M-5 (fumed silica, Fluka) and sodium silicate solution (Aldrich). The template cetyltrimethylammonium bromide and tetramethylammonium hydroxide (TMA) as well as aluminum isopropoxide were obtained from Aldrich. MCM-41 was synthesised by heating the synthesis gel (molar composition: 1 SiO₂, 63.3 H₂O, 0.04 (TMA)₂O, 0.016 (C₁₆NMe₃)₂O, 0.016 Al₂O₃) in a polypropylene bottle at 100 °C for two days. The resulting solid was filtered, washed with deionized water and dried in a vacuum oven at 50 °C/0.3 mmHg. The template was removed by calcination at 540 °C for 10 h in air, yielding H-MCM-41 with a Si/Al ratio of 30.

Recrystallisation experiments were carried out in four ways.
Procedure 1: MCM-41 was ion-exchanged to TPA-MCM-41 by shaking a suspension of 2.00 g H-MCM-41 in 1.22 g 25 wt% TPA-OH solution in 1 l water overnight at room temperature. The solid was recovered by centrifugation, washed with 100 ml of water, re-dispersed into 30 ml of water and subjected to a hydrothermal treatment at 170 °C in a 15 ml teflon-lined autoclave using different synthesis times. The recrystallised MCM-41 was recovered by centrifugation, washed with deionized water, centrifuged again and subsequently dried in a vacuum oven at 60 °C. The TPA template was removed by calcination in air at 500 °C for 6 h.

The other three methods used MCM-41 in its Na form as the starting compound. Na-MCM-41 was obtained by a three times repeated ion exchange in 1 M aqueous NaCl at room temperature.

Procedure 2: Impregnation with TPA-OH was performed by suspending Na-MCM-41 in a solution containing the appropriate amount of TPA-OH (Al to TPA ratio =1, 1 g MCM-41/50 ml). The suspension was then shaken for 2 h at room temperature, followed by
evaporation of the water in a rotary evaporator. The recrystallisation synthesis mixture was obtained by suspending TPA/MCM-41 in water (1 g/10 ml) which was aged overnight prior to recrystallisation at 170 °C. Work-up was as described above.

Procedure 3: The impregnation of MCM-41 with TPA-Br was similar to that with TPA-OH. For the actual recrystallisation the TPA/MCM-41 was suspended into water (1 g MCM-41 /10 ml) after which the pH was adjusted to 9 using a 0.1 M NaOH solution. Again the same hydrothermal treatment was applied.

Procedure 4: As procedure 2 with the exception that prior to the hydrothermal treatment, hexadecylamine was added in order to support the MCM-41 structure during the recrystallisation. Impregnation with hexadecylamine was achieved by dissolution of 3.41 g (14 mmol) hexadecylamine in 60 ml ethanol followed by addition of 3 g TPA-Na/MCM-41. This suspension was shaken overnight at room temperature followed by evaporation of the ethanol. The hydrothermal treatment is the same as that of the other procedures.

X-ray diffractograms were recorded on a Philips PW 1840 diffractometer using Cu Kα radiation. Transmission Electron Microscopy (TEM) was performed using a Philips CM 30 ST or a CM 30 T electron microscope operated at 300 kV. Samples were prepared for TEM by placing droplets of a suspension of the sample in ethanol on a polymer microgrid supported on a Cu grid. CP-MAS 13C NMR spectra were recorded on a Varian VXR-400S spectrometer, equipped with a 5 mm Doty probe. Contact times of 2 ms and sine-bell resolution enhancement were applied. N2 adsorption isotherms were measured on a Quantachrome Autosorp-6B at 77 K. The samples were pre-treated in vacuum at 350 °C for 16 h. Infrared spectra of acidic OD groups in calcined materials were obtained by selective deuteration of calcined samples at 323 K with hexadeuterobenzene, in a standard infrared set-up (Biorad FTS-175 and vacuum cell), after activation at 673 K in vacuo. Details of the procedure are described elsewhere [20]. The hydro-isomerisation tests were carried out in a fixed bed reactor at a total pressure of 30 bar. The feed consisted of n-heptane and hydrogen in a 1/4 molar ratio. The temperature at which a conversion of 40% was reached was used as an indication of the acidity of the catalytic material.
4.3 Results

The ion-exchange of MCM-41 to TPA-MCM-41 (procedure 1) was performed in a diluted TPA-OH solution at room temperature. Nevertheless, TEM showed the MCM-41 framework to be significantly damaged by this procedure. XRD showed a strong decrease of the intensity of the d_{100} signal and an almost complete disappearance of the long range ordering. At very low angle (0.62° 2θ) a new signal appeared. Though very speculative, this signal might be ascribed to the formation of larger pores due to the partial collapse of the MCM-41 framework. N₂ adsorption experiments show macropores to be present, though these N₂ condensations can be caused by inter particle void spaces as well. The hydrothermal treatment caused a further decrease in crystallinity up to a point were no MCM-41 was present anymore. Neither XRD nor TEM showed indications of ZSM-5 formation.

In the second recrystallisation method, TPA was offered by means of impregnation instead of ion-exchange. Once again the alkaline character of TPA-OH caused severe damage to the MCM-41 structure, as witnessed by the XRD spectrum. Na-MCM-41 impregnated with TPA-OH showed a sharp decrease of the d_{100} signal in the XRD spectrum of MCM-41 and a complete disappearance of all higher-order signals (see Figure 2). During the hydrothermal treatment, the d_{106} signal decreased further until no crystallinity could be detected anymore. N₂ adsorption shows a dramatic collapse of the MCM-41 structure. After 1 h of hydrothermal treatment the MCM-41 structure was found to be severely damaged and the surface area dropped from 855 m²/g for the parent material to 74 m²/g. Upon hydrothermal treatment, a very small XRD signal, at 2θ= 23°, became visible, indicating the formation of ZSM-5.
Figure 2  XRD of from top to bottom Na-MCM-41, TPA-OH impregnated MCM-41 and TPA-MCM-41 after one h hydrothermal treatment at 170°C.

TEM confirms the MCM-41 framework to be increasingly damaged upon longer recrystallisation times, up to a point where no MCM-41 is present anymore. Already after one hour of hydrothermal treatment some dark spots, caused by a denser crystal phase, become visible. Both the amount and the size of these spots appeared to be independent on the recrystallisation time. These dark spots all were 3 nm in size and were homogeneously distributed over the sample (see Figure 3).
Figure 3  TEM photographs with different magnification of recrystallised material (Procedure 2). A; magnification of $4.0 \times 10^5$, B; Magnification of $1.3 \times 10^6$. The dark spots are small crystalline areas probably with a ZSM-5 like structure.
Support for formation of ZSM-5 structures was obtained from $^{13}$C NMR. TPA confined in a ZSM-5 structure shows a characteristic splitting of the methyl $^{13}$C NMR signal at 11 ppm. This is ascribed to the different surroundings of the propyl chains extending in the two different channels of the ZSM-5 crystallite. $^{13}$C NMR performed on as-synthesised recrystallised MCM-41 showed a small splitting of the signal at 11 ppm as well (see Figure 4, see arrow).

Figure 4 $^{13}$C NMR of recrystallised MCM-41.

In MCM-41 impregnated with TPA (before hydrothermal treatment) this splitting of the methyl signals was absent. After removal of the TPA by calcination neither the dark spots in TEM nor the signal at 23° 2θ in the XRD spectrum could be detected any longer. IR measurements (see Figure 5) on the calcined material show a weak signal of ZSM-5 like acid sites suggesting some of the crystallites are still present. Figure 5 shows infrared spectra of calcined, selectively deuterated MCM-41, of MCM-41/ZSM-5 materials and of a ZSM-5 material for comparison. The spectrum of acidic deuteroxy (or hydroxyl) groups in MCM-41 is not fully understood [20]. It displays two peaks at 2738 and 2625 cm$^{-1}$ (corresponding OH stretching mode frequencies are 3710 and 3560 cm$^{-1}$) which have been tentatively assigned to silanol groups and hydrogen-bonded bridging, zeolite-like deuteroxy groups. (Exchange of silanol groups with C$_6$D$_6$ is much more pronounced in
MCM-41 than in other materials, an observation which is discussed in more detail in ref. [20]). In the spectrum of the recrystallised material after treatment with C₆D₆, a weak additional feature is present at approximately 2667 cm⁻¹. Bridging deuteroxy groups in ZSM-5 display a peak at 2664 cm⁻¹.

Figure 5  Infrared spectra of (a) MCM-41, (b) MCM-41/ZSM-5 and (c) ZSM-5, after activation in vacuo and selective deuteration with deuterobenzene at 323 K (see text).

Heptane hydroconversion experiments with MCM-41/ZSM-5 did not show any increased acidity as compared to the parent MCM-41.

In procedure 3 TPA-Br was used as a template in an effort to decrease the damage on the MCM-41 structure, caused by the impregnation with TPA-OH. In order to obtain the same alkaline conditions as in procedure 2, the pH was adjusted to pH 9 by addition of NaOH prior to the hydrothermal treatment. Formation of ZSM-5 crystallites did not occur after one hour, but in the samples which were subjected to 2 and 3 h hydrothermal treatment some ZSM-5 crystallites were formed. As expected, the impregnation with TPA-Br did not
affect the MCM-41 framework. The effect of the hydrothermal treatment however, was the same as when TPA-OH was used as a template.

To avoid rapid collapse of the framework during hydrothermal treatment it was investigated (procedure 4) whether supporting the framework with a template molecule was of benefit. After the impregnation with TPA-OH, MCM-41 was impregnated with hexadecylamine, a molecule frequently used for the synthesis of mesoporous materials of the HMS type [21]. XRD indicates the MCM-41 structure to be retained longer compared to the other experiments. N₂ adsorption experiments showed that mesopores were still present after one h hydrothermal treatment. The surface area decreased to 530 m²/g compared to 74 m²/g in the experiment where the MCM-41 structure was not supported (see Table 1). However, the MCM-41 structure also collapsed ultimately: after 2 h of hydrothermal treatment, N₂ adsorption showed no sign of mesopores anymore and only a small d₁₀₀ signal was still present in the XRD spectrum. Here too, small signals at 23 2θ appeared after 1 h in the XRD spectrum once again, indicating formation of small ZSM-5 crystals.

<table>
<thead>
<tr>
<th>Procedure 2 (m²/g)</th>
<th>C₁₆H₃₃NH₂ added (m²/g)</th>
</tr>
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<tbody>
<tr>
<td>Parent MCM-41</td>
<td>855</td>
</tr>
<tr>
<td>TPA/ MCM-41</td>
<td>822</td>
</tr>
<tr>
<td>1 h 170 ºC</td>
<td>74</td>
</tr>
<tr>
<td>2 h 170 ºC</td>
<td>40</td>
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4.4 Discussion

Of the four recrystallisation methods, the methods using impregnation with TPA as a way of offering the template, were successful in generating small zeolite crystallites. By impregnation of Na-MCM-41 with TPA-OH a substantial amount of OH⁻ ions is occluded in the MCM-41 pores. Due to their strong mineralising ability, these OH⁻ ions can give the
Si and Al species the mobility necessary for recrystallisation. When TPA is offered to the MCM-41 by ion-exchange, no basicity is generated in the MCM-41 pores, and as a consequence no recrystallisation occurs. The high basicity required for recrystallisation also causes serious damage to the MCM-41 material and ultimately leads to a complete collapse of the framework. By contrast the MCM-41 framework was not affected by impregnation with TPA-Br. In order to generate the required basicity, the pH of the synthesis mixture was adjusted to 9 with NaOH. This resulted in the same rapid collapse of the material as observed when TPA-OH was applied as a template.

ZSM-5 crystallites in the recrystallised samples could best be detected using TEM. Due to the higher density of the zeolite particles compared to the amorphous MCM-41 pore walls (1.9 g/cm³ vs. 1.1 g/cm³) these zeolite crystallites can be seen as dark spots in the TEM micrographs. Due to the small size of the particles XRD was of limited use and a complete XRD pattern could not be obtained. However, some reflections could be observed though with considerable line broadening and with low intensities. The signal at 23 ° 2θ is ascribed to small ZSM-5 particles. 13C NMR gave further support: although considerable resolution enhancement was necessary to visualise it, a small split-up of the methyl signal of TPA, characteristic for TPA in a ZSM-5 environment, could be observed. Burkett and Davis [22] in their study on ZSM-5 crystal growth reported a strong interaction between TPA and silica species long before any long range ordering is found. In an early stage of crystal growth, TPA is enclathrated into a silica structure resembling the channel intersections.

The formation of 3 nm particles as shown by TEM is in agreement with the initial stage of the ZSM-5 crystal growth mechanism proposed by Dokter et al. [23]. This mechanism starts with the formation of silicate-TPA clusters of ~3 nm and is followed by an aggregation of these particles. Formation of the 3 nm particles has later been confirmed by Schoeman [24] and De Moor et al. [25]. Further densification ultimately leads to the formation of ZSM-5 crystals. In our recrystallisation experiments the crystal growth stops at the 3 nm silicate-TPA cluster stage. Apparently these particles are not sufficiently mobile to allow the aggregation process. This suggests that the ZSM-5 crystallites are growing from the MCM-41 pore wall, following a semi-solid state transformation, and not from
dissolved silicate species. This idea is further supported by the homogeneous distribution of the dark spots observed in TEM.

The recrystallisation procedure involves two processes: the formation of 3 nm ZSM-5 crystallites and the amorphisation of the MCM-41. The latter is caused by the alkaline conditions required for the partial transformation to ZSM-5. To slow down the collapse of the MCM-41 framework Kloetstra et al. [19] applied glycerol as the medium for recrystallisation. Because of the low solubility of silica in this medium, the framework was better retained as compared with recrystallisation in water. Glycerol however, also inhibited the formation of ZSM-5 crystallites. Filling the MCM-41 pores with a “template” molecule, i.e. hexadecylamine, in order to support the MCM-41 framework, allows the use of water as the reaction medium. In this way, formation of ZSM-5 crystallites is possible and the collapse of the MCM-41 structure is slowed down, though not prevented. An alternative way to maintain a mesoporous structure is by using a parent material with a thicker pore wall. Then, more pore wall silica can be “consumed”, without a collapse of the mesoporous structure.

Calcination of recrystallised MCM-41 samples led to a disappearance of the dark spots in TEM and of the XRD signal at 23° 2 θ, indicating a collapse of the ZSM-5 crystallites. The infrared spectra (Figure 3) however, indicate that a small amount of ZSM-5 like material is still present after calcination and is still retaining some acidity, albeit too little to detect in a catalytic n-heptane hydroconversion experiment. It should be noted that alternative interpretations for such small changes in infrared spectra are possible, and more definite statements can only be made after a treatment has been found to remove organic template material without damaging ZSM-5 crystallinity.

4.5 Conclusions

In conclusion, it is possible to partially recrystallise MCM-41 yielding homogeneously distributed 3 nm particles. Both 13C NMR and small signals on XRD suggest that these particles are ZSM-5 crystals. Alkaline conditions are required but these inevitably also lead
to the collapse of the MCM-41 framework. Supporting the MCM-41 framework by means of a long chain template molecule increased the stability of the mesoporous material. It appeared to be possible to maintain a large surface area when the material was subjected to one hour of hydrothermal treatment, which is sufficient to achieve crystallisation of small ZSM-5 crystallites. It is expected that the present method of creating small ZSM-5 particles can be applied not only to MCM-41 but also to other mesoporous aluminosilicates.
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5 Application of a ceramic pervaporation membrane in esterification using a heterogeneous hybrid catalyst*

ABSTRACT

In this chapter the use of a mesoporous heterogeneous catalyst in combination with a ceramic pervaporation membrane in the esterification of dodecanoic acid and 1-octanol is reported. The uniform pores of the mesoporous catalyst offer the possibility to induce shape selectivity, e.g. when bifunctional reactants are applied. To achieve this, the contribution of the blank (uncatalysed) reaction has to be minimised. Kinetic experiments have been performed to determine the temperature dependence of both the blank and the catalysed reaction. It appeared that at reaction temperatures below 120°C the blank reaction was negligible. By pumping the reaction mixture continuously along a ceramic pervaporation membrane unit, it was possible to remove water from the reaction mixture and to shift the equilibrium to the product side. Although some attrition occurred in the pervaporation unit, the catalyst appeared to be stable.

* The experiments using a pervaporation membrane for water removal were executed at the Akzo Nobel Central Research in Arnhem, The Netherlands. The results will be published in a joint publication. Dr.ir. W.J.W. Bakker and Ms I.A.A.C.M Bos are gratefully acknowledged for their help and hospitality.
5.1 Introduction

Esters form an important part of the products and intermediates in oleochemistry. Although many esters occur in nature, most commercially available esters are from synthetic or semi-synthetic origin. Because of their pleasant and often characteristic smell volatile esters of short chain and medium chain alcohols and carboxylic acids are applied in beverages, cosmetics, perfumes and soaps. Low-boiling esters are also used as solvents, coatings and in printing ink. Higher boiling esters e.g. dialkyl phthalates are applied on a large scale as plasticisers [1].

At present, mainly homogeneous catalysts are used for esterifications in the oleochemicals industry. Those catalysts, like p-toluenesulfonic acid or sulfuric acid cause problems, like corrosion of the reactor, dehydration of the alcohol or colouring of the product making a decolouration step necessary. Lewis acid catalysts as Sn(II), Sn(IV) and Fe(III) chlorides and tetra-alkoxy titanates and zirconates can be very effective catalysts [2,3], but usually require higher reaction temperatures and may be oxygen sensitive [1]. Because of this, the use of heterogeneous catalysts can be beneficial in esterification processes. As heterogeneous replacements for the present day catalysts, zeolites might be interesting candidates. Because of steric constrains, however, the use of zeolites in oleochemical conversions is restricted to the short chain, unbranched compounds.

The ordered mesoporous material MCM-41 might be a potential catalyst for the conversion of the larger substrates [4,5]. However, because of its weak acidity, modification of this material is required before it can be employed in esterification reactions. The amorphous character of the MCM-41 pore wall results in a large amount of silanol groups. These can be used to covalently anchor catalytically active species, or precursors of that, onto the MCM-41 material [6]. Here MCM-41 is functionalised with sulfonic acid groups, covalently anchored to the MCM-41 pore wall, leading to a hybrid mesoporous material possessing strong acid sites [7,8]. The adjustable pore size of MCM-41 might offer the possibility to induce selectivity. This can be useful for the synthesis of monoglycerides and derivatives, which have a wide application as emulsifiers in food, pharmaceuticals and cosmetics [9]. To achieve optimal selectivity, interference of an autocatalytic blank
reaction should be minimised [10]. This might be possible by tuning the reaction temperature.

The esterification reaction is limited by its thermodynamic equilibrium. Currently, in many esterification processes the equilibrium is shifted to the ester side by using an excess of one of the reactants or by direct removal of one of the products by distillation. When using the first method a separation/recycle step is required, whereas the latter method limits the degrees of freedom with respect to temperature, pressure and reactants. Moreover, in general this method is relatively energy intensive. Selective removal of water by means of a pervaporation membrane offers the opportunity to shift the reaction equilibrium to the desired direction in an efficient way as shown by Bakker et al.[11]. Consequently, equimolar amounts of reactants can be used and the choice of reactants is not limited by vapour-liquid equilibria. Furthermore, no energy intensive distillation step is required and the reaction can be performed in small continuously operated flexible multipurpose reactors with integrated membranes [12]. During the past two decades membrane separation processes have been improved and optimised for large scale industrial applications [13]. Some examples of esterification reactions applying water pervaporation with polymeric membranes have been reported [14,15,16]. In most cases the current commercially available membranes are based on organic polymers [17]. They are however marked by a low thermostability and are not always resistant to the applied reactants. Furthermore, they can not withstand severe operating and cleaning conditions. Because of this the use of inorganic membranes is growing. Although ceramic membranes have some disadvantages over polymeric membranes (e.g. brittleness and higher cost), they are stable at much higher temperatures and are stable towards thermal cycles as well. This allows a thermal regeneration which implies that much longer life-times are possible as compared to their polymeric counterparts.

During the last decade, particularly the development of microporous inorganic membranes for gas purification showed considerable progress [18,19]. Especially preparation under clean room conditions seems to decrease the amount of defects in the membranes and to improve the reproducibility of the membrane synthesis. Application of inorganic membranes in catalytic processes is becoming increasingly important [20,21,22]. For selective removal of water from organic mixtures, zeolite A membranes [23,24,25] as well
as microporous amorphous membranes can be applied. Very recently zeolite membrane modules entered the market for dehydration of solvents [24,26].

In this chapter a heterogeneously catalysed esterification reaction performed in a pervaporation unit equipped with a microporous amorphous ceramic membrane is reported.

### 5.2 Experimental

All chemicals were obtained from Aldrich unless stated otherwise and were used as such. The MCM-41 material was synthesised following the procedure of Beck et al. [5]. Silica sources used were Cab-osil M-5 (fumed silica, Fluka) and a solution of sodium silicate. MCM-41 was synthesised by heating the synthesis gel (Molar composition: 1 SiO$_2$, 63.3 H$_2$O, 0.04 (TMA)$_3$O, 0.016 (C$_{16}$NMe$_3$)$_2$O) in a polypropylene bottle at 100°C for two days. The resulting material was thoroughly washed with water, dried and subsequently calcined in a stream of air at 540 °C for 12 h.

Modification of the MCM-41 material with sulfonic acid groups [7] was performed by suspending 32 g MCM-41 in 50 ml of toluene after which 19.30 g (98 mmol) of (3-mercaptopropyl)trimethoxysilane (MPTS) was added. The reaction mixture was refluxed overnight after which the solid was recovered by filtration. The excess of MPTS was removed by extraction with diethyl ether (10 h) and dichloromethane (4 h) using a soxhlet apparatus. The solid was suspended in a mixture of 200 ml of water and 50 ml of 35 wt% aqueous hydrogen peroxide of which the pH was adjusted to 7 and stirred for 5 h. Then the solid was filtered off and resuspended in 0.2 M aqueous sulfuric acid. This suspension was stirred for another 2 h after which the solid was recovered by filtration and dried at 60 °C under vacuum. $^{13}$C NMR data (see Table 1) are in harmony with literature data.
Table 1  NMR data of functionalised MCM-41.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1 (ppm)</th>
<th>C2 (ppm)</th>
<th>C3 (ppm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41 -SH</td>
<td>27</td>
<td>27</td>
<td>11</td>
<td>7,27</td>
</tr>
<tr>
<td>MCM-41 -SO₃H</td>
<td>54</td>
<td>18</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>MCM-41 -SH</td>
<td>27</td>
<td>27</td>
<td>9</td>
<td>This work</td>
</tr>
<tr>
<td>MCM-41 -SO₃H</td>
<td>53</td>
<td>17</td>
<td>10</td>
<td>This work</td>
</tr>
</tbody>
</table>

The esterification of 1-octanol and dodecanoic acid was performed in three different experimental set-ups, an atmospheric batch slurry reactor, a stirred autoclave and a reaction pervaporation unit. The atmospheric batch esterifications were performed at 140 °C in a 25-ml glass reaction vessel equipped with a Liebig condenser which was thermostatically kept at 80 °C to enable removal of the water formed during the reaction. The reactants were used in a 1:1 molar ratio (0.035mol of both) and 5 wt% of catalyst was used. Eicosane (1.00 g, 3.5 mmol) was used as an internal standard. Kinetic data were obtained by performing the esterification reactions in a stirred stainless steel autoclave. The reactions were performed at 100 °C, 120 °C or 140 °C, using 0.163 mol of both substrates. Again 5 wt% catalyst was used.

The experiments with membrane removal were executed at the Akzo Nobel central research laboratory (Arnhem, The Netherlands). The experimental set-up consisted of a 1.5 l stirred reactor and a pervaporation unit consisting of a tubular microporous ceramic membrane (length, 1 m, outer diameter, 14 mm) prepared by ECN (Netherlands Energy Research foundation). The separating layer of this membrane consists of a very thin (< 0.5 μm) film of microporous amorphous silica on the outside surface of a multi-layer mesoporous alumina tube. The mean pore size of this layer is 0.3-0.4 nm. The reactor and the separation unit were heated to 120 °C. During reaction, the reaction mixture was continuously circulated along the membrane by means of a circulation pump at 400 l/h (see Figure 1). At the permeate side of the membrane a vacuum (10-20 mbar) was applied. The reactions were performed by charging the preheated reactor with dodecanoic acid (800 g, 4 mol), 1-octanol (572 g, 4.4 mol) and eicosane (65 g, 0.23 mol) as an internal standard. The circulation
pump was started after which, in the catalysed reaction, 5 wt% (based on the weight of the total reaction mixture) of MCM-41–SO₂H was added. The reactions were monitored by taking samples at suitable intervals which were analysed by GC analysis (CP Sil 5 CB, 50 m x 0.53 mm column). For the reactions performed in the pervaporation unit, the amounts of water present in the reaction mixture and in the permeate were determined by means of a Karl Fischer (KF) titration. The performance of a membrane both prior to and after the reaction was tested by measurement of the flux through the membrane and the selectivity towards water from a 5 wt% solution of water in 1-butanol. These tests were performed by loading the experimental set-up with 1.5 kg of the 1-butanol / water mixture and subsequently circulate it along the membrane. After use in an esterification reaction the membrane was washed by circulating 1 l of ethanol through the set-up for 15 min. This was repeated 3 times after which the set-up was dried by flushing with N₂.

Figure 1  Schematic representation of the reactor combined with the separation unit containing the pervaporation membrane [11].

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X-ray diffractograms were recorded on a Philips PW 1840 diffractometer using Cu Kα radiation. CP-MAS ²⁵Si and ¹³C NMR spectra were recorded on a Varian VXR-400S spectrometer, equipped with a 5 mm Doty probe. Mass spectra were recorded on a VG 70 SE mass spectrometer operating at 70 eV. N₂ adsorption / desorption isotherms were measured on a Quantachrome Autosorb-6B at 77K.

5.3 Results and discussion

MCM-41 was synthesised using a literature procedure [5]. X-ray and TEM analyses indicated that the material was of good quality. N₂ adsorption measurements showed the surface area to be 1100 m²/g. MCM-41 was functionalised with sulfonic acid groups using a literature procedure [7] (see Scheme 1).

![Functionalisation of MCM-41 with sulfonic acid groups.]

XRD measurements showed that the pore structure of the MCM-41 material was maintained. No loss in ordering could be observed upon modification of the material with sulfonic acid groups. N₂ adsorption data show that the surface area of the modified material dropped to 650 m²/g. This value corresponds with surface areas of modified mesoporous
materials as reported in the literature [28,6]. NMR data \(^{13}\)C and \(^{29}\)Si CP MAS) are in agreement with data presented in the literature (see Table 1). The weight difference between the MCM-41 material before and after functionalisation suggested a loading of 1.0 mmol sulfonic acid groups per g MCM-41. In order to get an impression of the thermal stability of the functionalised MCM-41, the material was placed in the vacuum chamber of a mass spectrometer after which the temperature was slowly raised. No organic fragments could be detected in the mass spectra at temperatures lower than 220 °C. At higher temperatures organic fragments caused by the decomposition of the alkylsulfonic acid groups were detected in the mass spectrometer.

The MCM-41(SO\(_3\)H) material proved to be an active and stable catalyst in the esterification of dodecanoic acid and 1-octanol. When the reaction mixture was filtered after 50% conversion, no reaction (apart from the blank reaction) was detected in the filtrate, indicating that there was no leaching of acid groups from the MCM-41 support. Furthermore, the catalyst could be re-used at least 2 times without loss of activity (see Figure 2).

![Graph](image.png)

Figure 2 Activity of the MCM-41 (SO\(_3\)H) catalyst in the esterification of dodecanoic acid and 1-octanol in a batch slurry reactor at 140°C. ■ Blank reaction, ◆ Catalysed reaction with fresh catalyst, ○ First reuse, x Second reuse.

The adjustable pore size of MCM-41 might offer the possibility to induce selectivity in reactions like the esterification of di- or tri-ols. This is only useful if there is virtually no
contribution of a blank (uncatalysed) reaction. For that reason some kinetic measurements were performed to find the temperature dependence of both the catalysed and the uncatalysed reaction. In order to avoid analysis problems, these reactions were performed with mono functionalised model reactants. Kinetic data were obtained by performing the esterifications at different temperatures in a closed autoclave. Initial rates were determined using the measuring points obtained during the first three hours of the reaction. The reaction rates at different temperatures were calculated assuming the reaction to be first order in both reactants.

The rate of the blank reaction is negligible at 100 °C and still very low at 120 °C. At 140 °C the blank reaction is considerable. In a catalysed esterification reaction at the latter temperature, the blank reaction will make a significant contribution to the total ester formation. By plotting ln k versus 1/T the Arrhenius plot is obtained, from which the activation energies can be calculated (see Figure 3).

![Graph](image)

Figure 3 The Arrhenius plot of the solvent free esterification of dodecanoic acid and 1-octanol. ◆ Catalysed, □ Blank.

The values were 61.20 kJ and 25.36 kJ for the blank and the catalysed reaction, respectively. The higher activation energy for the blank reaction compared to the catalysed
reaction implies that the temperature dependence of the former is much higher than that of the latter. Consequently, the blank reaction can be suppressed by applying a lower reaction temperature while at the same time maintaining an acceptable rate for the catalysed esterification reaction.

The esterification reactions performed in an atmospheric glass vessel (described earlier in this chapter) were performed at 140 °C. At this temperature water, formed during the esterification, evaporates from the reaction mixture at a sufficient rate. In order to suppress the blank reaction however, it is necessary to perform the reaction at a lower temperature. Consequently, other means of water removal have to be used, of which pervaporation using a ceramic membrane is an interesting option.

Prior to the esterification reaction the membrane was tested by a standard pervaporation test. Both the permeance and the selectivity of the membrane to water, from a 1-butanol / water mixture (5 wt% water), proved to be high. Table 2 shows data about the performance of the membrane, including the temperature of the separation unit, the vacuum on the permeate site, the flux per 10 min over 40 min and the wt% of water in the permeate.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>T (°C)</th>
<th>P perm side (mbar)</th>
<th>Flux (g/10 min)</th>
<th>wt% H₂O in permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>76</td>
<td>9</td>
<td>12.80</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td>74</td>
<td>8</td>
<td>7.01</td>
<td>94</td>
</tr>
<tr>
<td>30</td>
<td>74</td>
<td>8</td>
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<td>86</td>
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<tr>
<td>40</td>
<td>75</td>
<td>8</td>
<td>6.54</td>
<td>90</td>
</tr>
</tbody>
</table>

In Figure 4 the conversion plot of a blank and a catalysed esterification reaction in the pervaporation unit is presented. After 8 h a conversion higher than the equilibrium value, of 70%, was obtained.
**Figure 4** Conversion plot of the esterification of dodecanoic acid and 1-octanol performed in the pervaporation unit. ◆ MCM-41-SO₃H catalysed reaction, ■ Blank reaction.

The amount of water present in the reaction mixture varied from 1.3 % after 1 h of reaction to 0.4 % after 8 h of reaction. The flux remained almost constant at 10 g h⁻¹ over the entire experiment. The selectivity towards water was over 95 % during the first two h, but dropped during the course of the reaction (see Table 3). GC analysis of the permeate showed that besides water the other major component of the permeate was the ester. After 8 h reaction 44 g of water was obtained by permeation and according to KF titration another 14 g was still present in the reaction mixture. So in total 58 g of water had been formed indicating a conversion of 81 %. This value corresponds well with the conversion of 82 % as was determined by GC analysis of the reaction mixture.
Chapter 5

Table 3  Composition of the permeate during the esterification reaction.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>T (°C)</th>
<th>P perm side (mbar)</th>
<th>Flux (g/h)</th>
<th>wt% H₂O in permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>122</td>
<td>5</td>
<td>10.43</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>121</td>
<td>6</td>
<td>7.80</td>
<td>96</td>
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<tr>
<td>3</td>
<td>121</td>
<td>6</td>
<td>10.83</td>
<td>60</td>
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<td>4</td>
<td>122</td>
<td>7</td>
<td>10.15</td>
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<td>123</td>
<td>5</td>
<td>8.22</td>
<td>35</td>
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<td>7</td>
<td>123</td>
<td>7</td>
<td>5.51</td>
<td>52</td>
</tr>
<tr>
<td>8</td>
<td>123</td>
<td>7</td>
<td>9.60</td>
<td>35</td>
</tr>
</tbody>
</table>

The membrane proved to be remarkably stable. Although during the reaction increasing amounts of ester were found in the permeate, suggesting the membrane to become damaged, a BuOH/H₂O test after cleaning the set-up, showed the membrane was still intact (see Table 4). Apparently, more selective membranes, e.g. consisting of supported A zeolite, are required.

Table 4  Membrane performance in 1-BuOH/H₂O separation after use in an esterification reaction.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>T (°C)</th>
<th>P perm side (mbar)</th>
<th>Flux (g)</th>
<th>wt% H₂O in permeate</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>64</td>
<td>7</td>
<td>9.15</td>
<td>77</td>
</tr>
<tr>
<td>16</td>
<td>68</td>
<td>6</td>
<td>5.46</td>
<td>91</td>
</tr>
<tr>
<td>23</td>
<td>71</td>
<td>7</td>
<td>5.31</td>
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<tr>
<td>38</td>
<td>75</td>
<td>6</td>
<td>5.18</td>
<td>92</td>
</tr>
</tbody>
</table>
5.4 Conclusions

The present study shows that it is possible to shift the equilibrium of the esterification of dodecanoic acid and 1-octanol by selective removal of water from the reaction mixture using a microporous ceramic membrane. A heterogeneous catalyst could be applied without causing damage to the membrane. After use in a reaction the performance both in flux and water selectivity in a 1-BuOH/H₂O separation are comparable with the values obtained for the fresh membrane.

Further improvement requires highly water-selective membranes, e.g. based on zeolite A.
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MCM-41 supported TEMPO as an environmentally friendly catalyst in alcohol oxidation

ABSTRACT

A heterogeneous system for catalytic oxidations was developed by immobilising TEMPO onto the mesoporous material MCM-41. Prior to immobilisation, TEMPO was derivatised to 3-(trimethoxysilyl)propyloxy-TEMPO, by coupling 4-hydroxy-TEMPO and allyl bromide followed by hydrosilylation of the double bond. The catalytic activity of the immobilised catalyst was tested in the oxidation of α-methyl glucoside and α-octyl glucoside using hypochlorite as the oxidant. The catalyst was both active and stable under the reaction conditions. Complete oxidation of the primary alcohol group of α-methyl glucoside could be achieved in 10 minutes. Moreover, no significant decrease in activity upon immobilisation was found. The catalyst could be re-used five times without loss of activity. The oxidation of benzyl alcohol using the immobilised catalyst using oxygen as the oxidant and copper as co-catalyst was successful as well but proceeded relatively slow, probably because of difficulties in the re-oxidation of TEMPO.

Part of this work has been presented at the 1st FEZA conference held at 1-4 september 1999 in Eger, Hungary and has been published in Stud. Surf. Sci. Catal., 125 (1999) 465.
6.1 Introduction

In view of the growing awareness of the environmental impact of chemical processes and the resulting legislation, reduction of waste streams is needed. This gives impetus to the development of “green” chemistry by applying new catalytic processes, with practically no waste, and by exploiting natural non-exhaustible resources, such as carbohydrates. As early as in 1942 it was found that $\text{N}_2\text{O}_4$ preferentially oxidises primary alcohol groups in carbohydrates to obtain uronic acids [1,2]. Since this method has extensively been used for the oxidation of polysaccharides. Semmelhack et al. [3] found that the organic radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) could be used in the selective oxidation of primary alcohols to carbonyl compounds in the presence of secondary ones. Only recently this reagent has been introduced in sugar chemistry by Davis and Flitsch [4], who described the oxidation of partially protected monosaccharides. Our group, in cooperation with TNO-Food (Zeist), succeeded in highly selective conversion of primary alcohol towards carboxylate in polysaccharides, by catalytic TEMPO oxidation in aqueous medium using hypochlorite as the primary oxidant [5].

TEMPO is a stable radical which can be oxidised by several reagents [6] to yield a nitrosonium cation. The latter ion is a strong oxidant and shows a high selectivity towards oxidation of primary alcohols. During the oxidation of an alcohol the nitrosonium ion is reduced to the hydroxylamine which is subsequently re-oxidised to the nitrosonium ion by a suitable oxidant thereby closing the catalytic cycle. Hypochlorite is usually applied for oxidations in aqueous media and CuCl/O$_2$ for oxidations in organic media [7]. (see Figure 1).
The majority of publications on oxidations using nitroxy radicals deals with the oxidation of alcohols, though also oxidations of other functional groups, like amines and phosphines, have been reported [8].

Immobilisation of nitroxy radicals has been reported by several investigators, all using TEMPO-functionalised organic polymers [9,10,11,12,13]. In this chapter a route is presented to heterogenise TEMPO onto the mesoporous material MCM-41 [14,15,16]. Heterogenisation of TEMPO obviously has some process-technological advantages like an easy isolation and the possibility of re-use. MCM-41 was selected because of its very large surface area (>1000 m²/g) and the adjustable pore size (2-8 nm). The latter offers the possibility to induce shape selectivity. The amorphous character of the pore walls of the
MCM-41 material gives rise to a substantial number of silanol groups present at the pore wall, offering the possibility for grafting catalytically active groups [17]. Since the pore sizes of MCM-41 are rather large, bulky molecules, like for instance cyclodextrins, could probably be oxidised by the composite catalyst (further referred to as MCM-41/TEMPO). Oxidised cyclodextrins are assumed to have potential as host compounds for inclusion of various pharmaceuticals and as complexing agents for metal ions. Parent cyclodextrins are sparingly to moderately soluble in water particularly when an apolar compound is complexed in the cavity of the molecule. The solubility is substantially enhanced by oxidation of the primary alcohol groups to carboxylate groups. Another possible application of the hybrid catalyst might be in the production of carbohydrate based surfactants. Though most surfactants are still produced from petrochemical raw materials, it is expected that products based on renewable materials become increasingly important. Oxidation of alkyl glucosides would change the non-ionic character of those materials to anionic, thereby altering their application profile. In order to test the applicability of the MCM-41/TEMPO catalyst in non-aqueous media, the catalyst was also tested in the oxidation of benzyl alcohol in DMF.

6.2 Experimental

6.2.1 Catalyst preparation

All chemicals were obtained from Acros, unless stated otherwise and used without further purification.

Synthesis of MCM-41. The MCM-41 material was synthesised following the procedure of Beck et al. [16]. Silica sources used were Cab-osil M-5 (fumed silica, Fluka) and a solution of sodium silicate (Aldrich). The templates cetyltrimethylammonium bromide and tetramethylammonium hydroxide (TMA) were obtained from Aldrich. MCM-41 was synthesised by heating the synthesis gel (molar composition: 1 SiO₂, 63.3 H₂O,
0.04 \((\text{TMA})_2\text{O}, 0.016 \((\text{C}_{16}\text{NMe}_3)_2\text{O})\) in a polypropylene bottle at 100°C for two days. The resulting material was thoroughly washed with water, dried and subsequently calcined in a stream of air at 540°C for 12 h.

*Synthesis of 4-allyloxy-TEMPO.* 4-Hydroxy-TEMPO (2.61 g, 15.15 mmol) was dissolved in 30 ml of THF and allowed to react with 1.1 equivalent of sodium hydride (Aldrich, 70% in mineral oil) suspension in 10 ml of THF. Prior to use the sodium hydride was washed 2 times with hexane in order to remove the mineral oil. After 2 h allyl bromide (1.83 g, 15.15 mmol) was added after which the mixture was stirred at ambient temperature. After 15 h the excess of sodium hydride was destroyed by adding MeOH (5 ml). The solvent was removed by evaporation giving an oil which was dissolved in dichloromethane and then poured into an ice and water slurry (25 ml) saturated with sodium hydrogencarbonate. The aqueous layer was extracted with dichloromethane (2×10 ml), the combined organic layers were washed with water (3×10 ml), dried over sodium sulfate and filtered. The solvent was removed by evaporation. Yield 92%.

*Synthesis of 3-(trimethoxysilyl)propyloxy-TEMPO.* 4-Allyloxy-TEMPO (2.12 g, 10 mmol) was added to a mixture of 5 mg of chloroplatinic acid and 80 mg of 2-propanol. Under cooling with an ice bath trimethoxysilane (2.44 g, 20 mmol) was added in 15 min. Then the reaction mixture was heated at 60°C for 5 h to complete the reaction. The crude reaction mixture was used as such in the immobilisation procedure.

*Immobilisation of 3-(trimethoxysilyl)propyloxy-TEMPO on MCM-41.* Calcined MCM-41 (2.5 g) was evacuated for 1 h at 90°C under vacuum and was suspended in 75 ml of dry toluene, after which 3-(trimethoxysilyl)propyloxy-TEMPO (0.87 g, 2.5 mmol) was added. After refluxing the suspension for 4 h the material was collected by filtration, washed with toluene and dried in air. The loading was determined by TGA.

*Synthesis of 4-Hydroxy-1,2,2,6,6-pentamethylpiperidine.* 4-Hydroxy-2,2,6,6-tetramethylpiperidine (2.08 g, 13.7 mmol) was dissolved in methanol (2 ml) after which methyl iodide (4.25 g, 30 mmol) was added. The reaction mixture was stirred for 25 h at ambient temperature. The white crystals that formed were collected by filtration and washed with 1:1 acetone diethyl ether. The solid was dissolved in aqueous NaOH (17.5 ml, 5%) solution which was extracted with diethyl ether (3×10 ml). The product was isolated
by evaporation of the diethyl ether. The yield was 66% and GC analysis showed the product to be 100% pure.

*Synthesis of 4-Allyloxy-1,2,2,6,6-pentamethylpiperidine.* The synthesis was carried out analogous to the synthesis of 4-allyloxy-TEMPO. $^{13}$C NMR (300.153 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ - 135.51; 116.48; 70.77; 68.79; 55.17; 46.81; 33.31; 28.16; 20.82

$^1$H NMR (300.153 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ - 5.94 (ddt, 1H, $J = 10.4$, 17.2, 5.5), 5.28 (ddt, 1H, $J = 17.2$, 1.8, 1.5), 5.16 (ddt, 1H, $J = 10.4$, 1.8, 1.4), 4.02 (dd, 2H, $J = 5.5$, 1.5, 1.4), 5.3 (s, 1H), 3.61 (tt, 1H, $J = 3.96$, 11.45), 2.24 (s, 3H), 1.87 (dd, 2H, $J \sim 3.96$, 11.5) 1.39 (dd, 2H, $J \sim 11.5$, 11.5), 1.62 (s, 6H), 1.02 (s, 6H).

*Synthesis of 4(trimethoxysilyl)propyloxy-1,2,2,6,6-pentamethylpiperidine.* The synthesis was carried out analogous to the synthesis of 3-(trimethoxysilyl)propyloxy-TEMPO. $^{13}$C NMR (300.153 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ - 71.07; 69.91; 55.13; 50.53; 46.89; 33.27; 28.16; 23.33; 20.85; 5.37

$^1$H NMR (300.153 MHz, CDCl$_3$) $\delta$ (ppm): $\delta$ - 3.57 (s, 9H), 3.42 (t, 2H, $J = 6.7$), 2.24 (s, 3H), 1.87 (dd, 2H, $J = 12.4$, 4.0, 1.67), 0.65 (t, 2H, $J \sim 6.7$), 1.16 (s, 6H), 1.25 (s, 6H) 1.36 (t, 2H, $J \sim 11.6$).

### 6.2.2 Characterisation

X-Band ESR spectra were obtained using a Bruker ER 100 apparatus operating at a frequency near 9.8 GHz equipped with a double cavity in TE001 mode. The determination of the g value was done by comparison with DPPH as a standard ($g=2.0036$). The number of spins was determined by comparison with a secondary standard ($\text{Na}_8(\text{Al}_8\text{Si}_6\text{O}_{24})\text{S}_2$). The ESR spectra were taken and interpreted by Dr. D. Brunel et al. at the “Ecole Nationale Supérieure de Chimie de Montpellier”

BET surface areas were measured by N$_2$ adsorption after degassing the sample for 12 h at 72°C using a Micromeritics ASAP 2000. TGA data were obtained using a Setaram SF 85 balance. NMR spectra of the oxidised products were recorded on a Varian VXR-400S.
6.2.3 Catalytic procedures

Carbohydrate oxidations. A typical carbohydrate oxidation procedure is: 5.82 mmol of the carbohydrate was dissolved in 30 ml of water, after which 22.5 ml of a 1.5M NaOCl solution in water (pH adjusted to 8), and 0.50 g of MCM-41/TEMPO (containing 0.3 mmol TEMPO) were added. Reactions were carried out at 0°C. The pH was maintained at 8 with by adding 1M aqueous NaOH using a pH-stat. Reaction products were isolated by addition of an appropriate amount of 2-propanol causing the products to precipitate as the sodium salts. The resulting solid was washed with 2-propanol, dried and subsequently analysed by NMR.

The oxidations of the cyclodextrins were performed using the same method. The amount of cyclodextrin used in a reaction corresponded to 5.82 mmol of primary alcohol groups. The oxidised cyclodextrin was isolated by ultrafiltration after which the water was evaporated and the product analysed by NMR.

Benzyl alcohol oxidation. Benzyl alcohol (1.08 g, 10 mmol) was dissolved in 25 ml of DMF after which CuCl (24.8 mg 0.25 mmol) and 0.25 g of MCM-41/TEMPO (0.15 mmol) were added. The system was stirred under an oxygen atmosphere for 48 h at room temperature, after which the catalyst was removed by filtration. The reaction mixture was analysed by GC. The speed of agitation (500-1000 rpm) had no influence on the reaction rate, indicating that oxygen diffusion is not rate limiting.

6.3 Results and discussion

6.3.1 Synthesis of immobilised TEMPO.

MCM-41/TEMPO was obtained from 4-hydroxy-TEMPO as the starting compound. An ether synthesis yielded 4-allyloxy-TEMPO, which was subsequently hydrosilylated
using trimethoxysilane and chloroplatinic acid as the catalyst [18,19]. Reaction with evacuated MCM-41 in dry toluene for 4 h at reflux temperature yielded the MCM-41/TEMPO catalyst [20,21] (See Figure 2).

Figure 2  Synthesis of MCM-41/TEMPO.

Independently Brunel et al. developed another procedure to immobilise TEMPO onto silica where the tethering to the silica surface involved a propylamide-sequence [22].

6.3.2 Characterisation

Due to the radical nature of the starting material and the intermediate products shown in Figure 2, NMR analysis was not possible. To enable characterisation by NMR, the same synthesis route was performed, starting from 1,2,2,6,6-pentamethylpiperidine. The first step gave 4-allyloxy-1,2,2,6,6-pentamethylpiperidine and the second step led to the formation of
4(trimethoxysilyl)propyloxy-1,2,2,6,6-pentamethylpiperidine. Both products were identified by their $^1$H and $^{13}$C NMR spectra.

Nitrogen isotherms of both parent and TEMPO loaded MCM-41 exhibit type IV behaviour as expected for regular mesoporous systems. Because of the grafting of the MCM-41 walls by organic moieties, the surface area of the TEMPO loaded MCM-41 (600 m$^2$/g) is lower than that of the parent material (1100 m$^2$/g). ESR studies showed a g value of 2.0060 which is virtually the same as reported by Brunel et al. for TEMPO on silica systems [22]. The spin content was found to be $0.3 \times 10^{20}$ spins per g. Keeping in mind the Avogadro number, the spin equivalent was calculated to be 0.05. This value seems very low and contrasts with TGA data, which suggest a loading of 0.6 mmol/g. Probably this discrepancy results from a reduction of the nitroxide function either by trimethoxysilane during the hydrosilylation step or by methanol which is formed during the grafting procedure.

6.3.3 Oxidation of $\alpha$-methyl glucoside with the MCM-41/TEMPO hypochlorite system.

Following conditions described in the literature [4,23], initially pH 9 was applied in the oxidation of $\alpha$-methyl glucoside. At this pH the hypochlorite/hypochlorous acid equilibrium lies almost completely on the side of hypochlorite, the active species in the re-oxidation of TEMPO towards the nitrosonium ion. Although no relation between OCl$^-$ concentration and rate of oxidation exists [24], it is important to keep the hypochlorous acid concentration as low as possible. Hypochlorous acid is the active species in oxidative glycol cleavage, a side reaction which predominates at lower pH [25]. MCM-41/TEMPO proved to be active in the oxidation of $\alpha$-methyl glucoside, selectively yielding 1-O-methyl glucuronate (see Figure 3).
Figure 3 Oxidation of α-methyl glucoside.

The immobilised TEMPO catalyst proved to be only slightly less active than the homogeneous TEMPO catalyst (see Fig. 4). In both cases full conversion was achieved in 10 min. Although there was no significant decrease in activity upon re-use, filtration experiments showed leaching of small amounts of TEMPO from the catalyst. This occurred both with fresh and with re-used catalyst. Most likely the supporting MCM-41 material slowly dissolves at pH 9, thereby releasing some of the immobilised TEMPO.

In order to avoid dissolution of the MCM-41 framework a lower pH value (pH 8) was applied, keeping the other reaction conditions the same. Because of the higher amounts of hypochlorous acid present at lower pH the side reaction, oxidative glycol cleavage, starts to play a role [25]. It appeared that, upon decreasing the reaction temperature from ambient temperature to 0°C, this reaction was suppressed sufficiently. At pH 8 α-methyl glucoside was selectively oxidised to 1-O-methyl glucuronate, although the reaction rate was slightly lower than that of the reactions performed at pH 9. As can be seen in Figure 4 an induction period occurred when the oxidation reaction is performed at pH 8. This could also be observed when the reaction was performed at pH 9 although it was much less pronounced. This induction period is in agreement with the suggestion that the majority of TEMPO was reduced during the synthesis of the hybrid catalyst. Presumably the first step in the oxidation of α-methyl glucoside is the reoxidation of TEMPO and the formation of the nitrosonium ion, resulting in a small induction period.
Figure 4  Comparison of the activity of MCM-41/TEMPO at pH 8 (▲), pH 9 (●) and the homogeneous system at pH 9 (■) in the oxidation of α-methyl glucoside at 0 °C.

In Figure 5 a leaching test of the MCM-41/TEMPO system at pH 8 and 0°C is presented. Both curves are conversion plots of the oxidation of α-methyl glucoside, using fresh MCM-41/TEMPO and applying excess of α-methyl glucoside.

Figure 5  Leaching test of the MCM-41/TEMPO system at pH 8 and 0°C, using standard conditions for α-methyl glucoside oxidation but with 5 ml NaOCl (● Reaction mixture filtered after 20 min, ■ Unfiltered reaction mixture).
After 20 min one of the reaction mixtures was filtered. To both reaction mixtures fresh NaOCl (7.8 ml, 1.5 M) was added, resulting in a re-start of the unfiltered reaction mixture (solid line). The reaction mixture from which the catalyst was removed by filtration showed no activity (dotted line), proving that no leaching had occurred. The high selectivity towards oxidation of the primary alcohol group can be explained by the approach of the alcohol function to the active center of TEMPO in the nitrosonium form, which is stERICally much more favourable for the primary alcohol groups than for the secondary ones (see Figure 6).

![Figure 6](image)

**Figure 6** Approach of the catalytic center of TEMPO (nitrosonium ion, below) by an \(\alpha\)-methyl glucoside molecule (above).

### 6.3.4 Oxidation of other carbohydrates.

Other carbohydrates could be oxidised using the MCM-41/TEMPO catalyst as well. \(\alpha\)-Octyl glucoside could easily be oxidised with the same >99% selectivity towards the
oxidation of the primary alcohol as α-methyl glucoside. The reaction rate was less than for the oxidation of α-methyl glucoside but still acceptable (see Figure 7).

The oxidation of sucrose proved to be possible as well, although the reaction rate was lower than in the oxidation of α-methyl glucoside. After 8 h there was still some incompletely oxidised sucrose present in the reaction mixture. Oxidation of a disaccharide containing an unprotected anomic center (lactose) resulted in a mixture of products. $^{13}$C NMR showed a large amount of different carboxyl groups, suggesting that not only the primary alcohol groups were oxidised. Moreover, the amount of base consumed during the reaction exceeded the total amount of primary alcohol groups present, supporting the suggestion that other groups, most likely the C1 aldehyde group, were oxidised as well.

![Conversion plot of the oxidation of α-octyl glucoside](image)

**Figure 7** Conversion plot of the oxidation of α-octyl glucoside (For the conditions, see experimental part).

### 6.3.5 Oxidation of β-cyclodextrin.

β-Cyclodextrin (see Figure 8) could be oxidised by the MCM-41/TEMPO, hypochlorite system, but the reaction was slow.
Figure 8  \( \beta \)-cyclodextrin.

The diameter of this cyclic oligosaccharide (7 glucose units, \( \alpha \) 1-4 connected) is 15.4 Å and it thus should have easy access to the MCM-41 TEMPO system. After 8 h the reaction stopped although a quantitative conversion to the heptacarboxylate was not reached. Quantitative \( ^{13}\text{C} \) NMR (see Figure 9) showed 80% carboxylic acid (180 ppm) and 20% primary alcohol groups (60 ppm). This corresponds with an average oxidation of 5.6 out of 7 primary alcohol groups which is the same degree of oxidation as was obtained in the homogeneously catalysed reaction [26].

Figure 9  \(^{13}\text{C} \) NMR spectrum of oxidised \( \beta \)-cyclodextrin as sodium carboxylate.
The incomplete oxidation in the latter case was suggested to be caused by the formation of a β-cyclodextrin/TEMPO inclusion complex as shown in Figure 10.

![Schematic drawing of a β-cyclodextrin/TEMPO inclusion complex.](image)

Figure 10  Schematic drawing of a β-cyclodextrin/TEMPO inclusion complex.

ESR studies showed that TEMPO forms an inclusion complex with β-cyclodextrin with the NO function pointing upwards and with the NO vector along the symmetry axis of the host molecule [27]. This orientation was confirmed by NMR relaxation measurements [28]. However in the heterogenised system, TEMPO is linked to the support via the C6 carbon and thus such a complex cannot be formed. A more likely cause for the inability to achieve complete oxidation is that the increasing amount of negative charge on the cyclodextrin ring in combination with the ridgid structure of the cyclodextrin ring makes it increasingly difficult for the cyclodextrin to approach the catalytic center of TEMPO thereby rendering a complete oxidation of all primary alcohol groups difficult. Thus, also for electrostatic reasons, with increasing degree of oxidation of the cyclodextrin ring it can be expected that activation energy for the next oxidation increases.
6.3.6 Oxidation of benzyl alcohol using the MCM-41/TEMPO CuCl/O\textsubscript{2} system\textsuperscript{*}

Oxygen was used as the oxidant for the oxidation of benzyl alcohol and copper(I) chloride as the co-catalyst for the re-oxidation of TEMPO. TEMPO immobilised on MCM-41 proved to be active in the oxidation of benzyl alcohol. Table 1 shows the conversion and selectivity towards benzaldehyde after 48 h. Included are also the blank reaction and a reaction with only CuCl. In GC analysis no traces of TEMPO derivatives were detected indicating that no leaching had occurred. As shown in Table 1, when comparing with CuCl, the MCM-41/TEMPO CuCl combination increases the reaction rate as well as the selectivity towards the aldehyde. There is no over-oxidation to benzoic acid which can be ascribed to the absence of water. TEMPO cannot catalyse the direct oxidation of the aldehyde since it is not capable to catalyse oxygen-transfer reactions. In water however, the aldehyde will be present as a hydrate which can be converted to the carboxylate by a simple hydrogen transfer reaction. When only CuCl was used as the catalyst the activity was low and considerable over-oxidation to benzoic acid occurred.

Table 1 Benzyl alcohol oxidation using oxygen as the primary oxidant\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion after 48h (%)</th>
<th>Selectivity to benzaldehyde (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>CuCl</td>
<td>1.2</td>
<td>50</td>
</tr>
<tr>
<td>TEMPO, CuCl\textsuperscript{b}</td>
<td>94\textsuperscript{c}</td>
<td>&gt;99</td>
</tr>
<tr>
<td>MCM-41/TEMPO, CuCl</td>
<td>35</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

\textsuperscript{a} conditions, see experimental part

\textsuperscript{b} 10 mmol benzyl alcohol, 0.5 mmol TEMPO and 5 mol% CuCl in 25 ml DMF (ref. 25).

\textsuperscript{c} conversion after 4 h

\textsuperscript{*} These experiments have been performed in cooperation with Drs. A. Dijksman (group of Prof. R.A. Sheldon, Delft University of Technology).
The activity of the MCM-41/TEMPO CuCl combination appears to be much lower than that of a comparable homogeneous system described in the literature [29]. This may be ascribed to difficulties in the re-oxidation of TEMPO since the active species in the oxidation reaction is the same as in the case of the oxidations performed in aqueous media, where practically no decrease in activity upon immobilisation was observed. Possibly, diffusion of the copper (II) into the MCM-41 pores is relatively slow and cannot keep up with the rate of the oxidation reaction, thereby becoming the rate limiting step.

6.4 Conclusions

MCM-41 supported TEMPO proved to be catalytically active in the oxidation of primary alcohols towards carboxylates (in water) and to aldehydes (in DMF). The catalyst could successfully be applied with high selectivity for the oxidation of two 1-O-alkyl glucosides. The selectivity towards oxidation of the primary alcohol group dropped however, when carbohydrates containing a free anomeric center were oxidised. In the oxidations in aqueous media using hypochlorite as the oxidant, the catalyst proved to be stable up to pH 8. When these oxidations were carried out at 0°C no oxidative glycol cleavage was observed. For the reactions performed in water immobilisation of the TEMPO catalyst on MCM-41 did not lead to loss in activity upon re-use.

The MCM-41/TEMPO catalyst could also be applied in the oxidation of other substrates performed in non-aqueous media (e.g. the oxidation of benzyl alcohol in DMF). The activity however, was only modest, probably because of difficulties in the re-oxidation step.
References

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7 Reductive etherification of substituted cyclohexanones with secondary alcohols catalysed by zeolite H-MCM-22

ABSTRACT

Zeolite MCM-22 is an active and regenerable catalyst exhibiting a remarkably shape selective reductive etherification of cyclohexanones with bulky substituents at the 4-position, employing secondary alcohols as reductants. The mechanism is proposed to proceed via the formation of a hemiacetal followed by an MPV-like reduction.

This work has been published in condensed form in Chem. Commun. (1997) 1989.
7.1 Introduction

Zeolite MCM-22 has recently been introduced as a unique biporous zeolite [1]. It has been shown [2,3] that it contains a layered structure of two independent pore systems: one with sinusoidal 10-membered ring channels extended in two dimensions, and one consisting of large 12-membered ring supercages (7.1x7.1x18.1 Å), connected by 10-membered ring channels. The material has a high thermal stability, a BET surface area of > 400 m² g⁻¹ and a sorption capacity of 0.16 ml g⁻¹ [4,5], which make it potentially suitable for catalysis. MCM-22 in its acidic form has already been claimed to be active in, for example, the conversion of lower olefins to heavier hydrocarbons, and of aliphatic hydrocarbons to aromatics, the disproportionation of toluene and the alkylation of benzene [6,7]. Another interesting application of MCM-22 is as a precursor for the synthesis of MCM-36. MCM-22 crystallises as a layered material, which condenses upon template removal (calcination). By swelling and pillaring these layers prior to calcination one creates a hybrid micro- and mesoporous material [8]. An interesting material ITQ-2, is formed by delamination of the MCM-22 precursor material [9]. This material is expected to combine the acid characteristics of a zeolite with a better accessibility. MCM-22 can also be synthesised as an all silica zeolite although a different template is needed then [10].

Here we report on the use of H-MCM-22 as a bifunctional catalyst in the reductive etherification of cyclohexanones having bulky substituents at the 4-position using secondary alcohols as reductants. The zeolite appears to be active for both the acid-catalysed conversion of the ketones to (hemi)-acetals and a consecutive Meerwein-Ponndorf-Verley (MPV)-type hydride transfer to yield ethers. Until now two catalysts were always required to achieve this, i.e. a Brönsted acid for the acetalisation and a transition metal for the reduction step [11,12]. Various solid catalysts including zeolites have been applied in acid-catalysed acetal formation [13] and in the MPV reaction [14,15]. However, the combination of both properties in a single zeolite, enabling the direct synthesis of ethers from ketones is novel.
7.2 Experimental

All chemicals were obtained from Aldrich unless stated otherwise and used without further purification. MCM-22 with a Si/Al ratio of 15 was synthesised using a literature procedure [16]. The synthesis gel was prepared by slowly adding a solution of H₂SO₄ (98 wt%) in 5 ml of water to a solution of 0.53 g NaOH and 0.86 g sodium aluminate (Riedel-de Haën) in 20 g of water. The resulting solution was added to a suspension of 8.8 g silica (Cab-osil M-5 (Fluka)) in 85 g water, after which 4.8 g hexamethylenimine was added. The synthesis mixture was aged overnight followed by a 12 day hydrothermal treatment at 150 °C under continuous agitation. The resulting solid was dried at 60 °C in vacuo and subsequently calcined in a flow of air at 540 °C for 12 h, yielding 4 g of MCM-22. The acidic form was obtained by four-fold ion-exchange with 1 M aqueous ammonium nitrate at 80 °C for 12 h followed by calcination as described above. A sample of the Na form was prepared by a four fold ion-exchange in a 1 M aqueous solution of NaCl. Reactions were conducted by refluxing 9 mmol of ketone, 1 g of catalyst, and 1.6 mmol of 1,3,5-tri-tert-butylbenzene as internal standard in 70 ml 2-propanol or 2-butanol. Water was continuously removed by refluxing the reaction mixture over a bed of zeolite Na-A. The reactions were monitored by GC (CP wax 52 CB column). Products were identified by GC-MS and by comparison with reference samples. X-ray diffractograms were recorded on a Philips PW 1840 diffractometer using Cu Kα radiation. Transmission Electron Microscopy (TEM) was performed using a Philips CM 30 ST or a CM 30 T electron microscope operated at 300 kV. Samples were prepared for TEM by placing droplets of a suspension of the sample in ethanol on a polymer microgrid supported on a Cu grid. MAS NMR spectra were recorded on a Varian VXR-400S spectrometer, equipped with a 5 mm Doty probe. Identification of the reaction products was done using mass spectroscopy. Mass spectra were recorded on a VG 70 SE, operating at 70 eV.
7.3 Results and discussion

XRD and the NMR \(^{29}\text{Si}\) and \(^{27}\text{Al}\) spectra of the MCM-22 material were in agreement with literature data [17]. The \(^{27}\text{Al}\) NMR spectra indicated the presence of some extra-framework aluminium (\(\delta = -1.0\)). TEM measurements showed the material to consist of small disk-like particles (130 x 130 x 15 nm) which is in agreement with reported SEM data [2] (see Figure 1).

![Image](image_url)

Figure 1 Transmission Electron Micrographs showing the disk-like morphology of MCM-22.

Zeolites (H-Beta, H-Y) and (ordered) silica-aluminas (MCM-41, HA-HPV) are known to catalyse the Meerwein-Ponndorf-Verley reduction. Over zeolite H-MCM-22 a totally different reaction took place. H-MCM-22 proved to be active and selective in the reductive etherification of 4-tert-butylcyclohexanone, with 2-propanol or 2-butanol, giving the corresponding ethers with a cis/trans ratio of 60/40 (see Figure 2 and Table 1). Only small amounts (\(\sim 5\%\)) of 4-tert-butylcyclohexanol, formed by direct MPV reduction, were
observed. Continuous removal of water from the reflux by a bed of zeolite Na-A significantly increased both the conversion and the selectivity to the ether (Table 1). The catalyst could be re-used, following regeneration at 450 °C for 12 h in air, without any loss in activity or crystallinity.

![Reductive etherification of 4-tert-butylocyclohexanone.](image)

Figure 2  Reductive etherification of 4-tert-butylocyclohexanone.

The size and the shape of the ketone substrate appears to be decisive for the course of the reaction. For example, 4-phenylcyclohexanone and 4-methylcyclohexanone could be etherified, although with poor conversions and selectivity. On the other hand, 4-(trimethylsilyl)cyclohexanone, with a similar size and shape as 4-tert-butylocyclohexanone, reacted smoothly.

Secondary alcohols are found to be required as hydride donors. With methanol only acetal formation occurred. Acid sites appear to be essential since with Na-MCM-22 as a catalyst in the etherification of 4-tert-butylocyclohexanone only 5 % yield was obtained after 24 h. The reductive etherification is irreversible. Starting from the 4-tert-butylocyclohexyl isopropyl ether (cis/trans mixture), water and acetone in 2-propanol in the presence of zeolite H-MCM-22 no reaction occurred.
Table 1  Reductive etherification of various 4-substituted cyclohexanones with secondary alcohols and H-MCM-22 as the catalyst.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conversion (%)</th>
<th>Selectivity to ether (%)</th>
<th>Selectivity to alcohol (%)</th>
<th>TON\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-tert-butylcyclohexanone</td>
<td>100</td>
<td>78</td>
<td>6</td>
<td>7.3</td>
</tr>
<tr>
<td>4-tert-butylcyclohexanone\textsuperscript{c}</td>
<td>22</td>
<td>19</td>
<td>35</td>
<td>1.6</td>
</tr>
<tr>
<td>4-tert-butylcyclohexanone\textsuperscript{d}</td>
<td>98</td>
<td>87</td>
<td>9</td>
<td>8.2</td>
</tr>
<tr>
<td>4-tert-butylcyclohexanone\textsuperscript{e}</td>
<td>6</td>
<td>65</td>
<td>29</td>
<td>0.3</td>
</tr>
<tr>
<td>4-tert-butylcyclohexanone\textsuperscript{f}</td>
<td>96</td>
<td>93</td>
<td>6</td>
<td>7.0</td>
</tr>
<tr>
<td>4-phenylcyclohexanone\textsuperscript{g}</td>
<td>15</td>
<td>20</td>
<td>0</td>
<td>1.1</td>
</tr>
<tr>
<td>4-phenylcyclohexanone\textsuperscript{d,g}</td>
<td>15</td>
<td>20</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>4-methylcyclohexanone\textsuperscript{g}</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>1.5</td>
</tr>
<tr>
<td>4-methylcyclohexanone\textsuperscript{d,g}</td>
<td>12</td>
<td>60</td>
<td>0</td>
<td>1.3</td>
</tr>
<tr>
<td>4-(trimethylsilyl)cyclohexanone</td>
<td>&gt;95</td>
<td>60</td>
<td>&lt;5</td>
<td>4.8</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: 9 mmol ketone (4-tert-butyl-, 4-phenyl-, 4-methyl-, or 4-(trimethylsilyl)cyclohexanone), 1 g catalyst, and 1.6 mmol 1,3,5-tri-tert-butylbenzene as an internal standard, in 70 ml 2-propanol under reflux and stirring. Water abstraction from the vapour phase by a soxhlet apparatus filled with zeolite NaA. \textsuperscript{b} Based on the total number of aluminium sites present in 1 g catalyst. \textsuperscript{c} Without removal of water. \textsuperscript{d} Regenerated catalyst. \textsuperscript{e} Reaction with Na-MCM-22 as catalyst. \textsuperscript{f} Reaction with 2-butanol at 99 °C. \textsuperscript{g} Conversions are corrected for the amount of substrate in the vapour phase and the amount adsorbed by the catalyst.

As mentioned above several zeolites, especially zeolite H-Beta, perform well in MPV reductions [18]. The mechanism is thought to involve a lattice-connected, but dynamic aluminium, to which iPrOH as alkoxide and ketone are coordinated (See Figure 3). However, a mechanism involving MPV reduction of the cyclohexanone, followed by acid-
catalysed etherification by the solvent can be excluded, since no etherification occurred when 4-tert-butylcyclohexanol (cis/trans mixture) was subjected to similar reaction conditions. It is postulated that the reaction proceeds via Brönsted acid-catalysed formation of a hemiacetal followed by a Lewis acid-catalysed, MPV-like hydride transfer to yield the ether (see Figure 4).

![Transition state for the formation of cis-4-tert-butylcyclohexanol by MPV reduction catalysed by zeolite H-Beta.](image)

**Figure 3** Transition state for the formation of cis-4-tert-butylcyclohexanol by MPV reduction catalysed by zeolite H-Beta.

![Proposed reaction scheme for the reductive etherification reaction.](image)

**Figure 4** Proposed reaction scheme for the reductive etherification reaction.

R₁ = t-Bu, Ph, Me, SiMe₃
R₂ = iPr, s-Bu
H⁺ = zeolite OH
H' = activated H of secondary alkoxide coordinated to Al.
The involvement of (hemi) acetals is supported by the almost instantaneous formation of both the dimethyl and the mixed methyl/isopropyl acetals upon reaction of 4-tert-butylcyclohexanone with a mixture of methanol and 2-propanol (molar ratio 1:1). These acetals were slowly converted into the methyl ethers with only very small amounts of the isopropyl ether. With 4-phenyl- and 4-methylcyclohexanone, dissolved in a 1:1 mixture of methanol and 2-propanol in the presence of zeolite H-MCM-22, acetal formation also occurred; however, only trace amounts of ether were formed together with some cyclohexene derivatives (see Figure 5). The di-isopropyl acetal was not observed in any reaction although this acetal can easily be prepared homogeneously [13]. The di-isopropyl acetal of any of the ketones is assumed to be too bulky to leave the large cages of H-MCM-22.

Figure 5    Scheme of acetal formation.
It has been reported in the literature [19] that MCM-22 crystals contain 12 membered ring pockets on the external surface. The abundance and depth (7 Å) may be sufficient to accommodate large organic molecules and promote their catalytic conversion. It is unlikely that these pockets are involved in the reactions described in this chapter since in that case one would expect the formation of the di-isopropyl acetics.

The role of 2-propanol as hydride donor was demonstrated by a reaction in (2-²H)2-propanol (25 % labeling). GC-MS and ²H-NMR of the reaction product 4-tert-butylcyclohexyl isopropyl ether showed that the C1-position of the cyclohexane ring and the secondary carbon of the isopropoxy group were 25 % deuterated.

It remains unclear why H-MCM-22 shows this unusual behaviour, while various other solid acids yield only the MPV reduction products.[18] Possibly the number of Brönsted acid sites in H-MCM-22 greatly exceeds the number of sites capable of catalysing the MPV reduction, resulting in the fast formation of (hemi) acetals followed by a slow conversion to the ethers. An explanation for the remarkable shape selectivity of the reaction (the advantageous effect of a bulky 4-alkyl or 4-trimethylsilyl group) may be that it takes place in the zeolite supercages (see Figure 6).

Figure 6  4-tert-butylcyclohexanone docking in an MCM-22 supercage.
The aluminium site in MCM-22, required for the hydride transfer, is assumed to be located mostly at the entrance of the MCM-22 supercage. [20] When 4-tert-butyl- (or 4-trimethylsilyl-)cyclohexanone is adsorbed into the zeolite cage it may dock into an orientation which brings the carbonyl group in close proximity to that site. In this tentative mechanism the aluminium atom plays a threefold role: activation of the ketone, stabilisation of the carbocation intermediate formed after the elimination of water and mediation of the hydride transfer. By contrast, the 4-methyl- and 4-phenylcyclohexanones may not be induced to adopt this specific orientation.

7.4 Conclusions

H-MCM-22 is an active catalyst in the reductive etherification of substituted cyclohexanones. The mechanism is proposed to proceed via the formation of a hemiacetal followed by an MPV-like reduction.
References

Summary

Micro and meso porous materials as catalysts for fine and oleochemical conversions

The research described in this thesis was carried out within the framework of the IOP on Catalysis, as a part of the project devoted to the development of new solid acid catalysts for the conversion of oleochemicals, of which the esterification reaction was the most important. During the course of the research, the scope was extended to micro- and mesoporous materials as catalysts for fine and oleochemical conversions.

Chapter 1 gives an introduction to micro- and mesoporous materials and their use as catalysts (and catalysis in general). Furthermore, information is provided about esters and esterification and on oleochemicals.

Chapter 2 describes the use of zeolites, more specifically of zeolite Beta in liquid and gas phase esterifications. The main issue is the influence of the hydrophobicity of the zeolites on their activity in the esterification reactions. It was found that this parameter is a key factor for the zeolites activity in liquid phase esterification reactions. Hydrophilic zeolites proved to be inactive in the liquid phase esterification of apolar reactants. This is ascribed to strong adsorption of water, formed during the reaction, which prohibits adsorption of reactants. With polar reactants the influence of the hydrophobicity decreased, probably because those reactants are able to supersede the water. In gas phase reactions (performed by R. Koster from the group of Prof. A. Bliek, University of Amsterdam), with relatively low molecular mass reactants, no influence of the hydrophobicity of the zeolites was observed.

Chapter 3 discusses the use of MCM-41 supported heteropoly acids (HPA) as catalysts for esterification reactions. In both the liquid phase esterification of 1-propanol and hexanoic acid and the gas phase esterification of acetic acid and 1-butanol high activities were obtained. Characterisation of a spent catalyst showed however that the initially high dispersion of HPA units was lost during the reactions. This occurred both in the liquid- and
gas phase experiments, although it was less pronounced in the gas phase. It is expected that water, formed during the esterification, acts as a HPA mobiliser, leading to the formation of large HPA clusters on the outer surface of the MCM-41 support.

In chapter 4 a new material, with potential catalytic activity, is reported. Impregnation of MCM-41 with tetrapropylammonium hydroxide, followed by a hydrothermal treatment led to the formation of 3 nm particles in the MCM-41 porewall which could be observed with TEM. Although there is no solid proof, there are strong indications that those 3 nm particles possess a ZSM-5 structure. Several hurdles still have to be taken of which the most important are the limited stability of the MCM-41 framework during the hydrothermal treatment, and the limited stability of the 3 nm particles upon calcination. Nevertheless, this material could be very valuable.

Chapter 5 focuses on the use of a mesoporous solid acid catalyst, in combination with a ceramic membrane, in the esterification of dodecanoic acid and 1-octanol. The hybrid catalyst, MCM-41 containing sulfonic acid groups, was found to be active and stable in the above mentioned reaction. The use of a pervaporation membrane opened the possibility to remove water during the reaction at a lower reaction temperature. The membrane was initially selective towards water and showed a good flux, thus leading to a conversion higher than the equilibrium value.

The knowledge gained on MCM-41 during the course of this research was used to immobilise the oxidation catalyst TEMPO. Chapter 6 describes the derivatisation of TEMPO, the subsequent immobilisation on MCM-41, the characterisation of the hybrid catalyst and catalytic tests. No significant decrease in activity upon immobilisation was found and the catalyst could readily be re-used when the reactions were performed in water and hypochlorite was used as the oxidant. When the oxidation was performed in DMF using oxygen as the oxidant and copper as a co-catalyst the reaction proceeded relatively slowly, probably because of slow reoxidation of TEMPO with this co-catalyst.

Chapter 7 deals with zeolite MCM-22, which showed a remarkable shape selectivity in the reductive etherification of substituted cyclohexanones, using 2-propanol or 2-butanol as the reductant. When cyclohexanones containing bulky substituents on the 4 position were employed, the cyclohexanone was converted to the corresponding 2-propyl or 2-butyl ether.
This reaction is proposed to proceed *via* the formation of a hemiacetal, followed by an MPV-like reduction.

**Concluding remarks**

In this thesis new catalytic materials and methods are described for conversion of fine and oleochemicals. These new heterogeneous catalysts offer advantages over the presently used homogeneous catalysts. They are however, not per definition environmentally more benign than their homogeneous counterparts. Especially the synthesis of MCM-41 based catalysts involves significant emissions during the calcination step. Furthermore, due to the cost of the template used and the fact that this can not be re-used, MCM-41 based catalysts are for many applications unacceptably expensive. Cheap alternatives for MCM-41 have however already been reported and it is expected that most of the modifications of MCM-41 which are described in this thesis are possible on those new materials as well. This might lead to new materials which are interesting not only from a scientific point of view. Finally, one can conclude that, although this research did not lead to directly applicable new catalysts, scientific progress has been made, which in the future can contribute to greener, more sustainable chemical processes.
Samenvatting

Micro- en mesoporeuze materialen als katalysatoren voor de synthese van fijn- en oleochemicaliën

Het onderzoek dat in dit proefschrift beschreven staat werd uitgevoerd in het kader van het Innovatiegerichte Onderzoeksprogramma Katalyse, als onderdeel van het project gericht op de ontwikkeling van nieuwe vaste zure katalysatoren welke gebruikt kunnen worden voor de synthese van oleochemicaliën, waarbij de synthese van esters voorop stond. Gedurende het onderzoek werden ook de katalytische synthese van enkele fijnchemicaliën in het onderzoek betrokken hetgeen leidde tot de huidige titel: micro- en mesoporeuze materialen voor de synthese van fijn- en oleochemicaliën.

In hoofdstuk 1 wordt een introductie gegeven over micro-en mesoporeuze materialen en het gebruik daarvan als katalysator. Verder zijn enkele pagina’s gewijd aan esters, de veresteringsreactie en aan oleochemicaliën.

Hoofdstuk 2 beschrijft het gebruik van zeolieten en in het bijzonder zeoliet Beta als katalysator in vloeistof- en gasfase veresteringsreacties. Het is gebleken dat in vloeistoffase reacties de hydrofobiciteit van een zeoliet van doorslaggevend belang kan zijn. Hydrofiele zeolieten bleken inactief te zijn in de verstering van apolaire reactanten. Dit kan worden toegeschreven aan een sterke adsorptie aan de zeoliet van het water dat gevormd wordt tijdens de reactie. Hierdoor wordt adsorptie van reactanten verder verhinderd. Wanneer polaire reactanten worden gebruikt is de invloed van de hydrofobiciteit van de katalysator minder, daar deze reactanten in staat zijn het gevormde water te verdringen. In gasfase verstering (uitgevoerd door R. Koster in de groep van prof. A. Bliek, Universiteit van Amsterdam) van reactanten met een laag molecuulgewicht werd geen invloed van de hydrofobiciteit van de katalysator waargenomen.

Hoofdstuk 3 laat zien dat bij het gebruik van MCM-41 gedragen heteropolyzuren als katalysator enige voorzichtigheid geboden is. In zowel vloeistof- als gasfase veresteringen
van respectievelijk 1-propanol en hexaanzuur en 1-butanol en azijnzuur bleek de genoemde katalysator zeer actief. Bij karakterisering van een gebruikte katalysator bleek echter dat de initiële hoge dispersie van het heteropolyzuur verloren was gegaan en dat op het MCM-41 buitenoppervlak grote clusters heteropolyzuur gevormd waren. Dit effect was bij zowel vloeistof- als bij gasfase reacties waarneembaar, hoewel het bij gasfase reacties minder sterk was. Het is zeer waarschijnlijk dat het water dat gevormd wordt tijdens de reactie een belangrijk aandeel heeft in de vorming van deze clusters.

Hoofdstuk 4 behandelde een nieuw materiaal dat in potentie als katalysator gebruikt kan worden. Het impregneren van MCM-41 met tetrapropylammoniumhydroxide gevolgd door een hydrothermale behandeling leidde tot de vorming van 3 nm deeltjes in de MCM-41 poriewand. Hoewel hard bewijs ontbreekt zijn er sterke aanwijzingen dat deze 3 nm deeltjes een ZSM-5 structuur hebben. Verschillende problemen zullen nog overwonnen moeten worden, waarvan de beperkte stabiliteit van MCM-41 gedurende de hydrothermale behandeling en de beperkte stabiliteit van de 3 nm deeltjes gedurende de calcinering de belangrijkste zijn. Desondanks, kan dit materiaal uitgroeien tot een waardevolle katalysator.

Hoofdstuk 5 richt zich op het gebruik van een mesoporeus vast zuur als katalysator, in combinatie met een keramisch pervaporatiemembraan, in de verstering van dodecaanzuur en 1-octanol. De katalysator, MCM-41 gefunctionaliseerd met sulfonzure groepen, bleek actief in de genoemde reactie en stabil en onder de toegepaste condities. Het gebruik van een pervaporatiemembraan bood de mogelijkheid de reactie bij een lagere temperatuur uit te voeren zonder dat problemen met het afvoeren van het water uit het reactiemengsel ontstonden. Het membraan combineerde een goede flux met een aanvankelijk hoge selectiviteit naar water, waardoor hoge conversies bereikt konden worden.

De kennis aangaande MCM-41, welke werd vergaard gedurende het verloop van dit onderzoek, werd gebruikt voor de immobilisatie van de oxidatiekatalysator TEMPO. Hoofdstuk 6 rapporteert over de derivatisering van TEMPO gevolgd door de immobilisatie op MCM-41. Zowel de karakterisering van de nieuwe katalysator als enkele katalytische tests worden beschreven. Alkylglucosides konden met hoge selectiviteit op de 6-plaats geoxideerd worden naar de overeenkomstige carbonzuren, welke in potentie als surfactant gebruikt kunnen worden. Bij gebruik van hypochloriet als oxidant leidde het immobiliseren van TEMPO nauwelijks tot een achteruitgang in de activiteit en kon de katalysator zonder
problemen worden hergebruikt. Wanneer de reactie werd uitgevoerd in DMF met zuurstof als oxidant en koper als co-katalysator verliep de reactie relatief langzaam, vermoedelijk door een langzamere re-oxidatie van TEMPO.

Hoofdstuk 7 behandelt zeoliet MCM-22 welke een opvallende vormselectiviteit vertoonde in de reductieve verethering van 4-gesubsribueerde cyclohexanon en, gebruik makend van 2-propanol of 2-butanol als reductant. Wanneer cyclohexanon met grote substituente (t-butyl, trimethylsilyl) op de 4-positie werden gebruikt, werd het cyclohexanon omgezet naar de corresponderende 2-propyl of 2-butylether. Gepostuleerd wordt dat dat deze reactie verloopt via de vorming van een hemiacetal gevolgd door een MPV-achtige reductie.

Slotconclusies

In dit proefschrift worden nieuwe materialen en methoden beschreven die gebruikt kunnen worden voor de synthese van fijn- en oleochemicaliën. Deze nieuwe heterogene katalysatoren hebben enkele voordelen ten opzichte van de momenteel veel gebruikte homogene katalysatoren. Deze heterogene katalysatoren zijn echter niet per definitie milieuvriendelijker dan hun homogene tegenhangers. Bij de synthese van op MCM-41 gebaseerde katalysatoren treden bij de calcineringsstap ongewenste emissies op die om uitgebreide afgaszuivering vragen. Bovendien is dit type katalysatoren relatief duur vanwege het dure tempaatmolecuul dat gebruikt wordt en het feit dat deze tempatlen niet hergebruikt kunnen worden. Goedkopere alternatieven voor MCM-41 zijn echter al bekend en het is waarschijnlijk dat het merendeel van de in dit proefschrift beschreven modificaties aan MCM-41 ook bij deze nieuwe materialen toegepast kunnen worden. Dit kan leiden tot materialen welke niet alleen wetenschappelijk gezien interessant zijn. Afsluitend kan geconcludeerd worden dat hoewel dit onderzoek niet heeft geleid tot nieuwe direct toepasbare katalysatoren, er wetenschappelijke vooruitgang geboekt is die in de toekomst kan bijdragen aan groenere en duurzamere chemische processen.
Dankwoord

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List of Publications


CURRICULUM VITAE


Vanaf 1 juni is de auteur werkzaam bij Avantium Technologies in Amsterdam.