Chemistry of Mesoporous Molecular Sieves

PROEFSCHRIFT

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The cover illustrates the biggest problem during washing of an as-synthesized mesoporous molecular sieve: foam.

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Six and a half miles until you stop.
42 years until you finish.

You run to think, to hear the birds, to be alone in a crowded world. To win the contest with that part of you that wants to stop. You run because it takes you to a place a car cannot go. To see the night shift worker trudge his way home as you breeze by. You run to help your mind distinguish between the important and the unimportant, what must be done and what can be put aside. To gain a sense of freedom. You run because you realise trying, and not winning, is everything. But most of all you do it because you are a runner and always will be. So you just continue on your way. Nearly home. Nowhere near finished.

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<tr>
<td>MCM-41</td>
<td>Mobil's Collection of Materials nr. 41</td>
</tr>
<tr>
<td>HMS</td>
<td>Hexagonal Mesoporous Silica</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Zeolite Socony Mobil nr. 5</td>
</tr>
<tr>
<td>USY</td>
<td>ultra-stable Y</td>
</tr>
<tr>
<td>FAU</td>
<td>faujasite</td>
</tr>
<tr>
<td>TEOS</td>
<td>tetrachloroethanol orthosilicate</td>
</tr>
<tr>
<td>CTACI</td>
<td>cetyltrimethylammonium chloride</td>
</tr>
<tr>
<td>TMAOH</td>
<td>tetramethylammonium hydroxide</td>
</tr>
<tr>
<td>TEAOH</td>
<td>tetraethylammonium hydroxide</td>
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<tr>
<td>TPAOH</td>
<td>tetrapropylammonium hydroxide</td>
</tr>
<tr>
<td>TMB</td>
<td>1,3,5-trimethylbenzene</td>
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<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
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<tr>
<td>MeOH</td>
<td>methanol</td>
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<tr>
<td>EtOH</td>
<td>ethanol</td>
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<tr>
<td>HPA</td>
<td>heteropolyacid</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>MAS</td>
<td>Magic-Angle Spinning</td>
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<tr>
<td>CP</td>
<td>Cross Polarization</td>
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<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>FT</td>
<td>Fourier Transform</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>AAS</td>
<td>Atomic Adsorption Spectroscopy</td>
</tr>
<tr>
<td>AES</td>
<td>Atomic Emission Spectroscopy</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer Emmett Teller</td>
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</table>
Industrial chemical processes are the cradle of catalysis research. The petrochemical and the fine-chemical industry take therefore a leading role in new catalyst technology.¹ Design and development of new catalysts is hereby of tremendous importance.² In the field of heterogeneous catalysis and adsorption processes a growing interest exists in porous materials with a precise and tailored structure e.g., zeolites and (pillared) clays.³ Potential applications of such molecular sieves are tailored to their pore dimensions. For a long time pore size restrictions have been limiting the number of applications involving large organic molecules. Therefore, novel ultra-large pore molecular sieves are required.⁴ The search for these materials was started several years ago and is successfully expanding.

1-1. Synthesis and mechanism of M41S and related materials

The discovery of the M41S materials by Mobil researchers,⁵,⁶ the first family of silicate- and aluminosilicate molecular sieves with ordered mesopores, has led to a booming research.⁷ The most extensively studied subgroup of the M41S family is the MCM-41 member which consists of a hexagonal array of uniform mesoporous channels with a size in the 15-100 Å range.⁶ Two other main subgroups are the cubic phase MCM-48 of the space group Ia3d and the nonstable lamellar phase. The latter phase can be stabilized via a post synthesis with tetraethyl orthosilicate (TEOS) resulting in the formation of MCM-50.⁸ The structural nature of MCM-41 materials leads to hexagonal reflections in the electron and the X-ray powder diffraction pattern of the low-order members of the hk0 subset. The unit cell constant a of these materials is given by 2d₁₀₀/√3. A typical X-ray diffractogram consists normally of a few peaks in the low-angle 2θ region, e.g. a main d₁₀₀ reflection and several weak high-order reflections like d₁₁₀, d₂₀₀ and d₂₁₀. The number of reflections is related to the quality of the MCM-41 material (vida infra).

The M41S materials expand the range of pore sizes of molecular sieves substantially (Figure 1.1). In the field of crystalline molecular sieves the metallophosphates VPI-5, cloverite and JDF-20 are the only ultra-large-pore sieves having a pore size of around 15 Å.⁹ Recently, UTD-1, a new high-silica large-pore zeolite has been synthesized with a pore diameter of 7.5 x 10 Å.¹⁰

The preparation of the mesoporous M41S materials has extended the structure-directing or templating concepts. Beside a few exceptions generally in zeolite synthesis the development of micropores
involves crystallization of (alumino-)silicate around a single molecule. These structure directing agents or templates are small amines or alkylammonium ions.\textsuperscript{11,12} In the syntheses of the M41S materials also functional templating agents are used. These templates are quaternary ammonium surfactant molecules of the type \( \text{C}_n\text{H}_{2n+1}\text{N}((\text{CH}_2)_n\text{X} \) (\( n \) is an even number from 6 to 22; \( \text{X} = \text{OH/Cl, OH, Cl, Br or HSO}_4 \)). A difference with zeolite preparation is that here associates of template molecules are applied.

Surfactants are large organic amphiphile molecules with a hydrophilic head group and a hydrophobic tail.\textsuperscript{13} A schematic phase diagram of cetyltrimethylammonium bromide (CTMABr), the most often applied MCM-41 templating agent, in water is shown in Figure 1.2. Surfactants tend to self-organize depending on the temperature and the concentration. At very low concentration \( c \) the surfactants are present as free molecules dissolved in solution and adsorbed at interfaces. At slightly higher concentrations, called the critical micelle concentration (CMC1), the individual surfactant molecules form small spherical aggregates (micelles). At higher concentrations (CMC2), where the amount of solvent available between the micelles decreases, spherical micelles can coalesce to form elongated cylindrical micelles. The outer surface of the
micelle is comprised of the hydrophilic heads of the surfactant molecules, while the tails of these molecules are directed toward the center of the micelle. At slightly higher concentrations, liquid-crystalline (LC) phases form. Initially, rodlike micelles aggregate to form hexagonal close-packed LC arrays. As the concentration increases, cubic bicontinuous LC phases are formed, followed by LC lamellar phases. At very high concentrations, in some systems, inverse phases can exist. Here water is solubilized at the interior of the micelle, and the headgroups point inward.

A 'liquid crystal templating' (LCT) mechanism (Figure 1.3) in which supramolecular assemblies of cationic alkytrimethylammonium surfactants serve as template components for the formation of MCM-41 materials has been postulated by Mobil workers.\textsuperscript{5,6} They suggest that the template is supposed to self-organize into a liquid-crystal phase, for instance hexagonal H\textsubscript{6} (cf. Figure 1.2) before being encapsulated by inorganic species which then condense into rigid walls. A system with large concentrations of surfactants (liquid-crystalline phase) seems to behave like this mechanism.\textsuperscript{14} The other pathway proposed that the inorganic species participate in the ordering process of the surfactant-inorganic mesophase and influence its
Chapter 1

morphology. The LCT mechanism was first proposed and based on (i) the close similarity between the morphology of the surfactant-inorganic mesophase and liquid crystals, (ii) the dependence of the pore size on the surfactant chain length and (iii) on the amount of auxiliary organics like 1,3,5-trimethylbenzene (TMB) acting as expander molecules. The support for pathway 2 was, however, growing by the facts that (i) M41S materials are often prepared in the presence of surfactant concentrations far below the CMC and (ii) hexagonal, cubic and lamellar structures may be formed by varying only the silica concentration indicating that no preexisting liquid-crystal phase is required.15,16

![Diagram](image)

**Figure 1.3.** LCT mechanism for the formation of MCM-41.5,16

The LCT mechanism has been confirmed by several researchers.15,19 Vartuli et al.16 studied the effect of the surfactant/silica molar ratio on the formation of mesoporous molecular sieves. As the surfactant to silica molar ratio increased from 0.5 to 2, the successive products obtained could be classified into four groups: MCM-41, MCM-48, thermally unstable lamellar phase and the cubic octamer [(CTMA)SiO2.5]8. The influence of the surfactant chain length (n = C6 to C16) and the reaction temperature on the formation of porous materials was investigated by Beck and co-authors.15 At 100 °C MCM-41 type materials were formed. Increasing the chain length resulted in better defined MCM-41. Formation of zeolite MFI appears at 150 °C using short chain surfactants (n = C6 and C8). At higher temperature (200 °C), zeolitic and dense-phase products were obtained.

Chen et al.20,21 postulated a silicate rod assembly model. The authors found that first rodlike micelles are coated with 2 to 3 monolayers of silica before they spontaneously self-organize into a hexagonal phase...
with further silica condensation during the calcination step. This was based on X-ray powder diffraction, thermogravimetric analysis, $^{29}$Si NMR, and in particular on in situ $^4$N NMR spectroscopy of precursor solutions having a surfactant concentration below CMC2.

Another variation on the LCT mechanism, also based on $^{14}$N NMR, was postulated by Steel et al.\textsuperscript{22} The authors assumed that first dissolved silicate species promote organization of the hexagonal mesophase. Then the silicate forms ordered layers with intercalated hexagonal mesophases. If the silicate to surfactant ratio is low, the silicate layer is thin, and is able to pucker into surfactant-silicate mesophases. Thick silicate layers were not able to pucker and the resulting product maintains lamellar.

A third model which is very similar to the previous one was reported earlier by Monnier et al. by using time-developed X-ray diffraction.\textsuperscript{21} This model directly addresses syntheses from solutions that have surfactant concentrations below CMC2, and preparations where shorter chain surfactants (e.g., $n = 12; X = \text{OH or Cl}$) that do not form rods are involved. The mechanism involves (i) cooperative nucleation of inorganic and organic species, (ii) liquid-crystal formation with inorganic anions and molecules, and (iii) polymerization and condensation of the inorganic entities. Using charged surfactants the initial step is preferential ion-exchange of the surfactant counterions with polycharged oligomeric silicate species. These silicate species serve as multidentate moieties and can bind several surfactant molecules and screen the repulsive forces between the head groups within an aggregate.

A more refined interplay of this charge screening is reported by Firouzi et al.\textsuperscript{24} This model comprises dynamic and often subtle interactions among the organic surfactants and inorganic species according to equilibrium thermodynamics which determines the ultimate structure and symmetry (Figure 1.4). A static template, like preorganized structures or even rodlike micelles, prior to adding the inorganic precursor for nucleation and growth of the inorganic phase, is not required. The authors showed unambiguously with $^{29}$Si NMR by employing $\text{Si}_n\text{O}_{2n+2}$ cubic octamers, that the as-synthesized silica structures contain uncondensed cubic octamers, which shows that condensation of the silicate framework is not essential to the formation of MCM-41. Fyfe and Fu showed that the cubic octamer could be used to directly synthesize lamellar and hexagonal phases.\textsuperscript{25} The authors reduced the framework charge by titrating the oxo-anions with acidic vapor which leads to step-by-step structural transformations: layered precipitate ($L_{0}$), to cubic ($V_1$, $\text{Ia3d}$), to lamellar ($L_0$), and to hexagonal ($H$) structures. These transformations are irreversible and demonstrate the liquid-crystalline nature of the phases. A transmission electron microscopy (TEM) examination of MCM-41 supported the transformation model described by Alfredsson et al. and showed a transition from lamellar to the hexagonal phase.\textsuperscript{26} However, several other researchers who used X-ray diffraction, TEM or small-angle X-ray scattering (SAXS) did not find that the formation of MCM-41 is preceded by any lamellar structure.\textsuperscript{27-30} Although the pH of the gel had to be adjusted, Matijasic and co-
authors observed a phase transition by using \textit{in situ} X-ray diffraction.\cite{31}

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure1.png}
\caption{Cooperative templating mechanism.\cite{7e,24}}
\end{figure}

Solid-phase transitions were observed by Huo \textit{et al.}\cite{32} They found that mesostructure transitions from lamellar to MCM-41 via elliptical-shaped channels (and backwards), and from MCM-41 to MCM-48 are possible. It is believed that these changes do not occur through dissolution to the liquid phase and new solid formation. The structural rearrangement of the surfactant phase was assumed to be caused by penetration of ethanol, provided by hydrolysis of TEOS, into the hydrophobic palisade regions of the surfactant arrays. Liu \textit{et al.} noticed formation of ordered mesoporous materials via heterogeneous nucleation.\cite{29} They demonstrated with TEM that colloidal silica particles, even a very small amount, promote the formation of ordered phases.

The pore size of MCM-41 is a function of the alkyl-chain length of the surfactant used. Varying the number \( n \) from 6 to 22, the pore diameter increases from 15 Å to 45 Å.\cite{5,21,15,30,33,36} Larger pore sizes are created
by using auxiliary organics or expander molecules.\textsuperscript{5,6} In this way hexagonal mesophases with regular pore diameters up to 100 Å can be prepared by dissolving hydrophobic molecules in the interior of the surfactant tubules prior to the extensive condensation of the MCM-41 silicate framework. A wide variety of such auxiliary agents have been investigated, such as paraffins, aromatics and alcohols.\textsuperscript{32,37} Particularly 1,3,5-trimethylbenzene (TMB) has been studied for this purpose. A linear increase in pore diameter has been achieved by increasing the TMB to surfactant molar ratio up to 2.5. Pores with a \( d \)-spacing of 120 Å have been imaged by TEM, although the pore mouths were quite elliptically shaped.\textsuperscript{6,7b}

Another way of pore size enlarging is reported by Khushalani \textit{et al.}.\textsuperscript{38} These authors prepared MCM-41 at relatively low temperature, e.g. 70 °C. The material was then annealed for 10 days in its own mother

Figure 1.5. Synthesis pathways using different combinations of surfactant and soluble inorganic species.\textsuperscript{42}
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liquid at 150 °C. The presynthesized MCM-41 gets restructured via silica dissolution, transport and redeposition. The pore-wall thickness remains approximately constant and the structure retained when calcined at 540 °C. Via this method pores were expanded from 30 Å to 70 Å. Large pores can also be generated by calcination of a wet surfactant-silicate gel with hexagonal mesopores.³⁹ This treatment results in a material with a bimodal mesopore size distribution with two maxima, at 30 Å and 110 Å, respectively.

Mesostructured porous silicas with pores in the micrometer region were synthesized by accurate control of different reaction parameters.⁴⁰,⁴¹ Via this way "tubules-within-a-tubule" or mesoporous macroscale structures were prepared.

M41S materials are normally prepared in strongly alkaline media. Under these basic conditions (pH 11-12), composite formation is dominated by strong, direct interactions between positively charged surfactant molecules and aggregates (S⁺) and negative inorganic silica solution species (I⁻) and the subsequent intermolecular interactions among the resulting molecular ion pairs (S'I'). Huo et al. were able to synthesize a broad range of mesoporous materials just by combining the appropriate charge balanced species.⁴² Figure 1.5 shows synthesis pathways by using different combinations of surfactant and soluble inorganic species. An interesting point from this scheme is that MCM-41 can be prepared in a strongly acidic solution via a counterion-mediated S'XI' pathway, although having weaker assembly forces compared to S'I'. In contrast to the prepared mesoporous metal-oxides, these silicate materials exhibit good thermal stability and structural

\[
\text{C}_{n}\text{H}_{2n+1}\text{NH}_2 + \text{Si(OEt)}_{4-x}(\text{OH})_x \rightarrow \text{Spontaneous rod-like micelle formation}
\]

Figure 1.6. S'I' templating mechanism according to Pinnavaia et al.⁷⁶,⁴³-⁴⁵
stability upon removal of the surfactant.

A completely new route to the preparation of mesoporous silicious materials is reported by Pinnavaia et al. A new concept of charge balance resulted in the discovery of a neutral templating route. These authors used nonionic surfactants such as primary amines and polyethylene oxide surfactants to prepare cylindrical nanoporous materials referred to as HMS and MSU-n, respectively. Hydrogen bonding interactions between neutral primary amine micelles (S") and neutral inorganic precursors (I") play a key role in determining the morphology of the mesophase (S^P'). Figure 1.6 illustrates the S^P' pathway, in which system the Si(OCH_3)_3(OH) species, formed by hydrolysis of TEOS, participate in H-bonding interactions with the lone pairs of surfactant amine head groups. This new organic-inorganic complex may be considered as an amphiphile with a very bulky head group which increases the likelihood for the formation of rod-like micelles. These micelles self-organize into a hexagonal packing followed by condensation of silanol groups and silica walls formation. Similar to the pore-size tuning of MCM-41 the pore size of HMS can be tuned by changing the amine surfactant chain length. Whereas the long-range order quality of MCM-41 is improving when the synthesis is applied under hydrothermal conditions (100 °C), HMS analogues afford only amorphous products under these conditions. Magic angle spinning (MAS) ^29Si NMR indicates that as-synthesized neutral HMS is much more extensively cross-linked than the as-synthesized charged frameworks of MCM-41 analogues. This improvement of the structure of the hexagonal arrays accounts also for the S^'X^- I' assembly. The HMS molecular sieves are best prepared at ambient temperature. The neutral character of HMS also allows an efficient and environmentally benign recovery of the template by solvent (ethanol) extraction.

Comparable phase transformation in the solid state from lamellar to hexagonal has also been reported for HMS-type materials. It appeared that the chain length of the amine, which determines the magnitude of the hydrophobic interaction, is crucial in determining the structure of the mesophase. Thereby is the lamellar phase favoured by long-chain amines.

A mesoporous material which possesses almost identical characteristics is the kanemite derived material referred to as FSM-16. This molecular sieve is initially prepared by intercalation of surfactants into the bilayers of kanemite via an ion-exchange process followed by a hydrothermal treatment.

Similar to zeolites, acid sites can be generated in the framework of mesoporous silicas by isomorphous substitution of trivalent cations of group IIIa such as Al^3+, B^3+ or Ga^3+ for Si^4+. Moreover, it is claimed that other cations e.g. Ti^4+ and Zr^4+ can be incorporated. Beside the patent literature (cf. ref. 7) a lot of open literature is dealing with the preparation of aluminosilicate MCM-41 materials. Various hydrothermal conditions and sources of silica and alumina were used. Janicke et al. found that aluminum incorporation succeeded better with aluminum isopropoxide (Al(i-OPr)_3) than with Catapal B (pseudo
boehmite.\textsuperscript{49} Another study on the influence of the aluminum source was carried out by Luan et al. by using different characterization techniques like, powder X-ray diffraction, \textsuperscript{29}Si and \textsuperscript{27}Al MAS NMR and TEM.\textsuperscript{50} These authors found that when \(\text{Al}_2(\text{SO}_4)_3\) was used all the framework aluminum was incorporated in the four-coordination state. This occurred to a lesser extent when Catapal alumina or NaAlO\textsubscript{2} was used. Other workers used beside the same characterization techniques, temperature programmed desorption (TPD) of \(n\)-butylamine and catalytic alkylation, and found that \(\text{Al(i-OPr)}_3\) was a better source for incorporation of aluminum than \(\text{Al}_2(\text{SO}_4)_3\) and pseudo boehmite.\textsuperscript{51} Also the use of NaAlO\textsubscript{2} gave a satisfying incorporation of aluminum in the framework.\textsuperscript{17} Nevertheless, it can be stated that aluminum incorporation depends not only on the type of precursor, but also on the synthesis conditions.

Incorporation of as much tetrahedral aluminum as possible in the MCM-41 framework was carried out by using mainly NaAlO\textsubscript{2}.\textsuperscript{53,54} Although the \textsuperscript{27}Al MAS NMR spectra and in some cases the crystallinity of the calcined MCM-41 materials was very moderate, Schmidt et al. claimed only on the basis of conventional one-pulse \textsuperscript{27}Al MAS NMR that very low Si/Al ratios were possible with all the framework aluminum tetrahedrally coordinated. The use of just one technique can, however, be misleading and such studies should definitely include TEM examinations.\textsuperscript{55,56} An elegant synthetic route to aluminosilicate MCM-41 with Si/Al ratios as low as 1 is reported by Fu et al. using \(\text{Al}_x\text{Si}_{8-x}(\text{OH})_x\text{O}_{20x-4}^+\ (0 \leq x \leq 4)\) precursors which possess a cubic structure. These precursors are actually building blocks from which MCM-41 can be prepared.

The incorporation of tetrahedral B\textsuperscript{3+} is successful with Si/B ratios as low as 5. The boron containing MCM-41 samples have to be treated more carefully than their Al analogues.\textsuperscript{59-63} Dry calcination conditions seem to be very important to suppress deboronation. These aspects count to a lesser extent for Ga-modified mesoporous silicate molecular sieves.\textsuperscript{64,65} The formation of Ga-MCM-41 materials is largely influenced by the pH of the gel mixture.

Similar to MCM-41 aluminum can be incorporated in the framework of HMS.\textsuperscript{66} Al(i-OPr)_3 is used as the aluminum source due to the neutral templating route of HMS materials. A big advantage of the synthesis of aluminosilicate HMS compared to MCM-41 is that the prepared material is sodium-free which allows the omittance of a troublesome ammonium ion-exchange procedure.

1-2. Characterization and properties of mesoporous materials.

A high temperature calorimetry study on siliceous MCM-41 showed that the enthalpies of MCM-41 materials at 298 K are only about 1 kJ/mol higher than that of zeolite Y.\textsuperscript{66} An MCM-41 sample calcined at 540 °C in air for 10 h showed, depending on the synthesis conditions of MCM-41, a decrease of up to 25%
STELLINGEN

1. Alleen zéér goed getrainde wetenschappers kunnen dit proefschrift in één adem uitlezen.

2. De vorming van water als bijproduct in de base gekatalyseerde Knoevenagel-condensatie maakt deze reactie niet geschikt voor het testen van watergevoelige cesiumoxide-beladen zeolieten in de vloeistoffase.


3. De claim MCM-41 te kunnen maken met een grote hoeveelheid tetraëdrisch-omringd aluminium is een zeer betrekkelijke conclusie als blijkt dat na het calcineren vrijwel al het aluminium octaëdrisch wordt.


4. Hoe graag menig onderzoeker het ook zou willen geloven, maar een amorf silica-alumina dat geen röntgendiffractiepatroon heeft, is echt geen MCM-41.


5. Gezien de zeer lage katalytische oxidatieve activiteiten van ijzer-flalocyanine complexen in zeoliet Y, de zogenaamde “ship-in-a-bottle” systemen, kan men deze materialen zeker niet beschouwen als een nabootsing van het enzym cytochrom P-450.


6. Het vermelden van peroxideconversies van 99 % die berekend zijn op basis van de omgezette hoeveelheid peroxide gedeelt door de hoeveelheid peroxide die aan het einde van de reactie overblijft, is een cosmetische beschrijving van de resultaten.


7. De door Posner en Augustine gegeven uitleg van de gemeten conversie in de aldol-condensatie van cyclo-octanon en benzaldehyde over zeoliet A: “de reactie heeft plaats gevonden in de poriemond van de zeoliet”, is een te verfijnde omschrijving van: “het buitenoppervlak van de zeoliet is aktief in deze reactie.”

8. Dat er in de periode 1994-1996 25% meer gevallen van kindermishandeling in Rotterdam aan het licht zijn gekomen dan de schatting was van het onderzoeksteam van het Sophia kinderziekenhuis, zegt wellicht meer iets over de kwaliteit van het onderzoeksteam, dan over de toename van het aantal gevallen van kindermishandeling.

*De Volkskrant*, 30 nov. 1996, pag. 9.

9. Gezien de geldende output-financiering bij de TU Delft dient niet de auteur te worden verplicht te trakteren op gebak bij acceptatie van een publicatie, zoals bij sommige onderzoeksgroepen het geval is maar de betrokken faculteit zelf.

10. Het sociale imago dat sommige grote chemische bedrijven graag uitdragen naar de mensen dient ook te gelden voor de manier waarmee zij omgaan met hun sollicitanten.

11. Door het steeds intensievere gebruik van de 'digitale snelweg' zal in de toekomst ook hier het gebruik van de vluchtroute geen overbodige luxe zijn.

12. De laagste rente is niet altijd de beste (*De Hypotheker*).

13. Er zouden wellicht minder auto-ongelukken gebeuren als iedere autobestuurder alleen WA-verzekerd zou zijn.


*K.R. Kloestra*
of the cell constant. This is in sharp contrast to crystalline silicates which change very little upon heating, for example cubic and hexagonal faujasite heated to 500 °C in air undergo a 0.3% and 1.3% volume increase, respectively, under the same conditions. As-synthesized MCM-41 materials are stable to about 900 °C in air with a cell constant contraction of 23%. Calcined MCM-41 materials were stable to ~800 °C when heated in dry air, and to ~700 °C when heated in air with 8 Torr of water. Kim et al. showed that the hydrothermal stability of an aluminosilicate MCM-41 with a Si/Al ratio of 39 could be increased by ion-exchange in the order Y^3+ (~900 °C) = Ca^{2+} > Na^+ (~800 °C). The stability of as-synthesized MCM-41 can be improved by successive acetic acid treatment resulting in enhanced condensation of the silanol groups. An improvement of the degree of framework condensation is confirmed by a decrease in the Q^3/Q^4 ratio (Q^3 = Si(OSi)_4OH and Q^4 = Si(OSi)_3), indicated by 29Si MAS NMR data. These calcined materials are stable in humid air with 20 Torr of water. The same authors also investigated the thermal stability of aluminosilicate MCM-41. Na^+ ion-exchanged MCM-41 is thermally more stable than in its H^+ mode. This will lead for the latter case therefore to more extraframework aluminum upon heating due to less stabilization as a result of the smaller size of the H^+ cations.

A completely different approach to improve the thermal and hydrothermal stability of MCM-41 is through textural control. In this case the pore walls of MCM-41 were made thicker by decreasing the OH to SiO_2 ratio which is actually decreasing the solubility of the silicate species. The pore-wall thickness, t = a - d_{\text{iso}}, varied from 4 to 16 Å. It is noteworthy to mention that HMS materials can have a pore wall thickness even up to 30 Å. HMS materials possess more unusual properties. Compared to the conventional mesoporous silicates prepared via charge balance templating, these materials are reported to have smaller crystallite domains and an improved textural mesoporosity due to extensive cross-linking of the siliceous framework, which results in a thermally more stable molecular sieve. TEM has proven to be a key technique for a proper characterization of mesoporous materials. By applying the Fresnel method on TEM images, Chen et al. were able to calculate the wall thickness.

The mechanical stability of pure silica MCM-41 is lower than that of zeolites and other porous materials. Applying an external pressure of 86 MPa, the ordered structure of activated MCM-41 is drastically altered. In spite of a reduction of 50% of the pore volume and the BET surface area, the pore size remained unaltered. Complete reduction of the structure was achieved at 224 MPa.

29Si MAS NMR is extensively used for the characterization of the framework structure of mesoporous molecular sieves. The 29Si NMR spectra of MCM-41 closely resemble those of amorphous silica suggesting a broad range of Si-O-Si (T-O-T) bond angles in this material. However, a more detailed study of M41S and amorphous silica gel showed on the basis of 29Si relaxation time constants by using variable contact time 29Si cross polarization (CP) NMR that both structures are not identical.
Figure 1.7. Formation of mesoporous materials containing (A) hexagonally and (B) more randomly ordered cylinders with the corresponding powder X-ray diffraction patterns.\textsuperscript{21}

Incorporation of aluminum in the framework of MCM-41 has even a more drastic influence on the range of T-O-T bond angles due to the limited flexibility of the O-Al-O angle compared to the O-Si-O angle. This brings along a dramatic decrease in the intensity and quality of the powder X-ray diffraction patterns and the TEM images\textsuperscript{60-57} and indicates that the structure of the prepared mesoporous materials is quite disordered (Figure 1.7).\textsuperscript{6,17-21} The degree of structural order of MCM-41 is also reflected by the sharpness of the capillary condensation step at $p/p_o = 0.4$ in the nitrogen adsorption isotherm which is usually type IV. In contrast to disordered MCM-41, a high quality MCM-41 material has a very steep inflection point at this step and a distinct hysteresis loop.\textsuperscript{41,44} Although disordered MCM-41 shows ill-defined X-ray patterns, it possesses roughly the same mesoporous features as BET surface area and pore volume. This indicates that TEM is almost a prerequisite in characterization of mesoporous molecular sieves.

Beside adsorption of nitrogen\textsuperscript{6,33,75,76} other adsorbates have been used such as argon,\textsuperscript{6,75} oxygen,\textsuperscript{75} cyclopentane,\textsuperscript{77} benzene,\textsuperscript{76} methane\textsuperscript{36,78} and water.\textsuperscript{79-81} The latter adsorbate gives an unusual type V hysteresis loop due to weak overall interaction of water with the mesoporous framework. Actually water adsorbs initially on the surface-hydroxy sites followed by capillary condensation.\textsuperscript{81}

From pyridine adsorption IR spectra and TPD of ammonia it is concluded that the acidity of aluminosilicate H-MCM-41 resembles that of amorphous silica-alumina, and is much lower than the acidity
of USY and mordenite. Furthermore, Bronsted acid sites of H-MCM-41 are rather weak and most of the acidity is original Lewis acidity. After calcination of MCM-41 the Lewis acidity has, depending on the procedure used, often increased which is indicative of an increase of the amount of extraframework aluminum. The acidity of H-MCM-41 is a little bit higher than that of a calcined non-ion exchanged MCM-41 (HNa-MCM-41). According to the same authors weak Bronsted acid sites interact at high temperature with Lewis acid sites resulting in formation of more catalytically reactive sites. Aluminosilicate HMS materials display enhanced Bronsted acidity compared to MCM-41 which acidity is generated via the neutral templating route. Similar to MCM-41 the Bronsted to Lewis acid ratio of HMS is not influenced by a decrease in Si/Al ratio.

In contrast to the acid properties the basic properties of MCM-41 have hardly been investigated. Na+ ion-exchanged MCM-41 (Na-MCM-41) appeared to possess weakly basic sites. Replacement of the extraframework Na+ ions for the more electropositive Cs+ ions hardly increased the basicity.

1-3. Catalytic applications of mesoporous molecular sieves

The use of ultra-large-pore molecular sieves such as MCM-41 and HMS in separation and catalysis applications can overcome to some extent the size limitations encountered with conventional zeolites. A common problem in catalysis with zeolites especially, when working in the liquid phase, is that diffusion of the reactant(s) is the rate limiting step. The term "configurational diffusion" was introduced by Weisz to denote intracrystalline migration. When the size of a sorbate is close to the pore size of the zeolite, the sorbate never escapes the influence of the zeolitic channel walls and the process is driven by concentration gradients rather than pressure gradients. In the Knudsen regime, a flow moves through a porous medium with a size in the range of 10 to 1000 Å, the border case of regular molecular diffusion. In a Knudsen flow a molecule will typically collide with a pore wall before hitting another molecule. Netrabukkana et al. measured the effective diffusivity of glucose and glucitol, dissolved in water, in zeolites, MCM-41 and silica gels. These authors observed that the effective diffusivity of glucose increased from $1.77 \times 10^{-9}$ to $1.08 \times 10^{-6}$ cm$^2$/s as the mean pore size increased from 7.4 to 116 Å. It is worth to mention that the molecular diffusivities of glucose and glucitol in water have values of $7.02 \times 10^{-6}$ and $7.65 \times 10^{-6}$ cm$^2$/s, respectively, and that the effective diffusivity for the linear glucitol ($\phi = 9.7$ Å including associated water) is three times lower than that for the cyclic glucose ($\phi = 8.6$ Å) over the same pore size range of the molecular sieves. One of the main contributions in retarding the diffusion of the solute within the mesoporous channels is hydrogen bonding between the pore wall and the solvent (water) and the solute. The low diffusion coefficient of water in MCM-41 compared to bulk water is thus related to the strong interaction of water with the pore surface.
By $^1$H NMR spin-echo measurements at -5 °C a self-diffusion coefficient is found in the range of $0.17 \times 10^{-6}$ to $2.3 \times 10^{-6}$ cm$^2$/s.

Beside the advantage that diffusion of solutes in MCM-41 materials behaves like a Knudsen flow, MCM-41 and related materials can be applied as a catalyst in reactions in which large organic molecules are involved. In acid catalysis a few examples are reported in which the advantages of the mesoporous channels of MCM-41 are clearly manifested. Armengol et al. used aluminosilicate H-MCM-41 for Friedel-Crafts alkylation of 2,4-di-tert.-butylphenol with cinnamyl alcohol.91 Interestingly, this reaction does not take place over H-Y zeolite. Alkylation of naphthalene with $n$-propanol on MCM-41, ZSM-5 and Y showed a four times higher conversion for the MCM-41 system indicating that mesoporosity is involved.92 A reaction in which much larger molecules are used is the tetrahydropyranylation of cholesterol, adamantanol-1-ol and 2-naphthol.93 Friedel-Crafts acylation of 2-methoxynaphthalene on MCM-41 with acetic anhydride is an example in which the weak Bronsted acid sites govern the product selectivities.94 At relatively low temperature only the 1-acylated product is produced. The free acid can be applied in acylation over MCM-41 with the combination of 1-naphthol and 2,6-dimethylbenzoic acid.95

Several papers have reported about hydrocarbon transformations such as catalytic cracking of $n$-heptane,96,97 cumene,96,97 gas oil96,97 and polypropylene,97 and propene oligomerization.99,100 Other interesting catalytic applications of MCM-41 materials are reported by Mobil researchers in the patent literature.74,84 Examples are propene oligomerization yielding C9 and C12 olefins, dealkylation of 1,3,5-tri-tert.-butylbenzene and alkylation of naphthalene with long-chain α-olefins.

Hydrocracking of vacuum gasoil has also been demonstrated on MCM-41 type materials. The used MCM-41 was loaded with nickel and molybdenum.101 These NiMo/MCM-41 systems appeared to be effective in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). Moreover, NiMo/MCM-41 was found to be more efficient at hydrocracking of gasoil than either NiMo/USY and/or amorphous silica-alumina loaded with NiMo.

MCM-41 is actually an excellent support, due to its large surface area, for different kinds of catalytic species for instance heteropoly acids such as H$_3$PW$_{12}$O$_{40}$.102,103 These strongly acidic systems exhibit a high catalytic activity and shape selectivity in liquid-phase phenol alkylation with isobutene and the more bulky styrene.103 A comparable approach is used in the functionalization of MCM-41 with 3-aminopropylsilane or other organic base moieties.104,105 These MCM-41 immobilized catalysts showed to be effective catalysts in the liquid-phase transesterification of glycerol.104
1-4. NIOK

Streamlining of graduate research and education belong to the main tasks of NIOK ("het Nederlands Instituut voor Onderzoek in de Katalyse"). Cooperation between NIOK and industry must lead eventually to clean and more efficient processes for both bulk and fine chemicals and therefore development of new catalytic systems. The original objective of the research-description is heterogeneous catalysis in the liquid-phase with (modified) MCM-41 materials. The main part of this thesis has been carried out within this framework. The interest and curiosity of the author to enlarge the number of applications of MCM-41 has also led to research in some closely related fields.

1-5. Survey of this thesis

In general, this thesis deals with explorative work on MCM-41. This includes studies on synthesis, characterization and the use of MCM-41 as a catalyst in acid and base catalyzed reactions. Also the potential of MCM-41 to serve as a support for catalytic active compounds is investigated.

The base and acid properties of alkali ion-exchanged MCM-41 are described in chapter 2. These materials are subjected to different type of liquid-phase reactions e.g. Knoevenagel condensation, aldol condensation, etc. The ease in converting large organic molecules is also demonstrated. Strongly basic mesoporous molecular sieves are prepared by calcination of a cesium acetate-impregnated MCM-41 giving MCM-41 with intraporous cesium oxide particles. Chapter 3 shows that these systems are very active in various Michael-type additions. A disadvantage of the cesium oxide loaded materials is the poor thermal stability and moisture sensitivity. A stable basic heterogeneous catalyst is achieved by addition of lanthana which results eventually in the binary CsLa-oxide supported on MCM-41. An extensive study concerning the synthesis, characterization and liquid-phase catalysis of and by this system is presented in chapter 4.

Chapter 5 extends the number of applications of MCM-41 and also HMS supported CsLa-oxides. A subtle interplay between both Cs’ and La’ ions leads to a novel rearrangement of ω-phenylalkanals to phenyl alkyl ketones. Also materials containing the strongly basic cesium oxide loaded on MCM-41, on HMS, and on related supports are able to isomerize these aldehydes in the liquid phase. Based on the reactivity of various related aldehydes a mechanism is proposed in which the phenyl group plays a key role.

The use of MCM-41 as an acid catalyst in fine-chemical reactions of large molecules is illustrated in chapter 6. Thereby, the tetrahydropyranylation of alcohols and phenols, a reaction to protect the OH group of functionalized intermediates in the synthesis of complex molecules, will be discussed. Chapter 7 deals with a thorough study on the synthesis of MCM-41 with low Si/Al ratios. An important issue that will be
discussed is: is all the NMR visible tetrahedral aluminum incorporated in the MCM-41 framework or not.

The impregnation of heteropoly acids onto MCM-41 and SiO₂ is described in chapter 8. A detailed study about transformation of supported Keggin-type H₃PW₁₂O₄₀ to dimeric heteropoly compounds during preparation is described and this is related to the activities of the composite system in liquid-phase catalysis.

Chapter 9 deals with the controlled framework-recrystallization of MCM-41 and HMS into a composite existing of a mesoporous molecular sieve with interporous nanocrystalline ZSM-5 structures. These porous nanocrystalline aluminosilicates (PNAs) show enhanced acidity and catalytic activity in cracking of n-hexane and cumene.

Overgrowth phenomena of MCM-41 on faujasite are described in chapter 10. These novel composites can be prepared either by a tandem-in situ synthesis or via precipitation on pre-synthesized faujasite crystals. These materials possess pores in the meso- as well in the microporous range and show to be more selective catalysts for the cracking of vacuum gasoil.

The final chapter, chapter 11, presents thermoporometry as a new tool in analyzing mesoporous MCM-41. This is a calorimetric procedure based on freezing point lowering of water in pores with a diameter larger than 15 Å. The data obtained correlate very well with standard nitrogen physisorption measurements.

References

7 Reviews:


General introduction


Chapter 1

General introduction

Chapter 1


2-1. Introduction

There is a growing interest in base catalysis by zeolites and related materials such as clays of the hydrotalcite type and microporous aluminophosphates. Beside acid catalysts there is a need for recyclable, water-stable solid base catalysts. Analogously to acid catalysis enhanced selectivity in base catalyzed reactions on these materials due to the pore size aperture might be obtained. Today there are just a few commercial base-catalyzed reactions in which zeolites are involved: the side-chain alkylation of toluene with methanol over alkali ion-exchanged X and Y first reported by Sidorenko et al. in 1976 and the synthesis of the five-membered heterocyclic compound 4-methylthiazole, an intermediate in the synthesis of the fungicide thiabendazole, from SO₂ and N-methylacetone imine on Cs-loaded X (Scheme (a) and (b), respectively).

![Chemical reaction diagrams](image)

From a mechanistic point of view the base catalyzed side-chain alkylation of toluene is reasonable well understood. It is proposed that methanol is first dehydrogenated catalytically to produce formaldehyde which is eventually alkylating toluene activated on the basic sites. It is proposed that interactions of the extraframework alkali ions with toluene causes an activation of toluene. Under the reaction conditions used (−400 °C) it is possible that toluene (pKₐ = 35) becomes more acidic which is also observed for other organic compounds bearing a weakly acidic proton. Hydrogen-deuterium exchange studies showed that the weakly acidic protons of toluene and acetone (pKₐ = 20) could be exchanged over the basic clay hydrotalcite.

Chapter 2

Regarding base catalysis by zeolites it is generally known that the average oxygen charge or basicity increases with increasing aluminum content of the zeolite and with increasing ionic radius of the exchanged alkali cation. Other factors which govern the structural or intrinsic basicity of a zeolite are bond angles (e.g. of the Si-O-Al bond), the length of the bonds and the spatial distribution of the framework aluminum. One of the strongest basic zeolites is therefore Cs-X due to its low Si/Al ratio and the type of extraframework cation. Zeolites with a stronger basicity can be prepared by isomorphous substitution of Al\(^{3+}\) for Ga\(^{3+}\) resulting in stronger negatively charged framework oxygens.

The catalytic studies on the aluminosilicate MCM-41 molecular sieve have so far been focussed on acid catalysis (cf. chapter 1) and on redox catalysis. In general, acidity and basicity of zeolites is a conjugated system, though the Lewis base strength is less crystallinity-dependent than the Lewis acidity. It is observed that the extraframework Lewis acids (Na\(^{+}\) cations) are much more influenced by long-range stabilization effects, the crystallinity of the aluminosilicate, than the framework oxygens bearing the negative charge (Lewis bases). Considering the amorphous framework of MCM-41 it might be expected that MCM-41 materials possess basic properties. The influence of the type of extraframework alkali-cation is however probably less than in the case of zeolites. Here we report on the basic properties of alkali cation-exchanged MCM-41 material including a catalytic liquid-phase study. The performance of alkali ion-exchanged MCM-41 will be correlated to CO\(_2\) temperature programmed desorption data and to \(^{23}\)Na and \(^{133}\)Cs MAS NMR data of these materials.

2-2. Experimental

Materials

MCM-41 material was synthesized according to the following procedure: 24.2 g of a TMA/SiO\(_2\) solution (molar ratio TMA/SiO\(_2\) = 0.5; 10 wt% SiO\(_2\) = 2.4 g (Cab-oslil M5); 7.3 g of a 25 wt% solution of tetramethylammonium hydroxide (\(\text{TMAOH, purchased from Aldrich}\) was mixed with 9.5 g of sodium silicate (Aldrich; 27 wt% SiO\(_2\)). Subsequently 128 g of water and 6.7 g of silica (Cab-oslil M5) were added to the mixture. Under vigorous stirring 22.3 g of cetyltrimethylammonium bromide (ACROS) in 150 g of water was poured into the mixture. Finally, the gel was enriched with 1.14 g of sodium aluminate (Riedel-de Haën; 54 % Al\(_2\)O\(_3\) and 41 % Na\(_2\)O). The gel was stirred for 2 h at room temperature and subsequently kept statically in an oven at 100 °C overnight. The resulting solid was filtered and thoroughly washed with water, dried at 90 °C under vacuum, and calcined at 540 °C in dry air for 10 h. The calcined material, denoted as HNa-MCM-41, containing Si/Al and Na/Al ratios of 13.0 and 0.5 (ICP/AES-AAS elemental analysis), respectively, was ion-exchanged with 0.1 M aqueous NaCl (Baker) at room temperature for 2 days, recovered
by filtration, washed with distilled water and dried under vacuum at 80 °C. In this way the Na/Al ratio of the resulting Na-MCM-41 was raised to 1.0. H-MCM-41 was prepared by ion-exchange with 1 M aqueous NH₄NO₃ (Baker) at 80 °C for 20 h followed by calcination at 450 °C for 6 h. Cs-MCM-41 materials were obtained by stirring HNa-MCM-41 at room temperature for 20 h with an 0.1 M solution of CsCl (Baker) in water. The Cs/Al and Na/Al ratios of the Cs-MCM-41 sample were 0.8 and 0.2, respectively. The quality of the materials was determined by powder X-ray diffraction on a Philips PW 1840 diffractometer using monochromated CuKα radiation. The X-ray diffraction pattern of the MCM-41 material showed clearly the $d_{100}$- and $d_{110}$-spacing at 42 and 21 Å, respectively, which values are in agreement with literature data.⁹

**Techniques**

**CO₂ TPD**

Temperature programmed desorption (TPD) of carbon dioxide was performed on a Micromeritics 2900 TPD/TPR instrument. The materials were first activated at 600 °C for 5 h in dry air and subsequently cooled down to 110 °C under a helium flow. Then the activated materials were saturated with dry gaseous carbon dioxide at this temperature. Physisorbed carbon dioxide was removed by purging under a helium flow at 110 °C till a stable baseline was monitored (about 0.5 h). The TPD was performed under a helium flow (10 mL/min) by heating from 110 °C to 600 °C with a heating rate of 10 °C/min.

**²³Na NMR**

Solid-state 105.5 MHz $²³$Na MAS NMR spectra were recorded at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific Instruments 5 mm Solids MAS Probe. A recycle delay of 2.0 s, an acquisition time of 0.3 s and short 2.0 μs pulses, a spectral width of 100 kHz and a spin rate of 7 kHz were applied. The resonances were referenced to a 1 M solution of NaCl in water ($δ = 0$ ppm).

**¹³¹Cs NMR**

Solid-state 52.5 MHz $¹³¹$Cs MAS NMR spectra were performed in a similar way. A recycle delay of 0.5 s, an acquisition time of 0.3 s and short 2.5 μs ($-\pi/5$) pulses were used. The lines were referenced to a 1 M solution of CsCl in water.

**Reaction procedure**

HNa-MCM-41, Na-MCM-41 and Cs-MCM-41 were tested as base catalysts in the liquid-phase Knoevenagel condensation of benzaldehyde (Merek) with ethyl cyanoacetate (Aldrich) and with diethyl
malonate (Aldrich). The aldol condensation of benzaldehyde with various ketones (acetophenone, α-tetralone, isophorone and 2'-hydroxyacetophenone; all purchased from ACROS) was tested on Na-MCM-41 and H-MCM-41. The reactions were carried out with and without a solvent. The detailed reaction conditions for both test reactions are mentioned in the next paragraph. In all cases the progress of the reactions was monitored by GLC (CP-sil 5 column) and quantification was done via the internal standard method. The products were identified by GC-MS and reference samples. The MCM-41 samples were calcined at 450 °C for 10 h prior to use. All the reactants were used without further purification.

2-3. Results and discussion

**Base and acid catalysis in the Knoevenagel condensation**

The liquid-phase Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate was used to test the possibility of base catalysis by the Na⁺ and Cs⁺ ion-exchanged MCM-41 materials (Figure 2.1). Considering the pKₐs of dicyanomethane (pKₐ = 11.2) and diethyl malonate (pKₐ = 13.3)¹² the pKₐ ≤ 9 of ethyl cyanoacetate mentioned by Corma et al.¹¹ is subject to serious doubt. It would be more reasonable to assume a value of around 12, i.e. in between the pKₐs of dicyanomethane and diethyl malonate.

![Figure 2.1. Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate (R = CN) or diethyl malonate (R = CO₂Et).](image_url)

As shown in Table 2.1, carrying out the Knoevenagel reaction solvent-free, a conversion of 81% with a selectivity of 75% to the dehydrated product was obtained within 7 h. When testing the reaction over Na-MCM-41 in water at 100 °C a conversion of about 80% was obtained within 1.5 h with a selectivity of nearly 100% to the product. High activities were also observed in bi-phasic systems like THF-H₂O at 70 °C. That MCM-41 materials are active in aqueous media indicates that the basic sites are not deactivated by coordination of water molecules which is a result of the mild basicity of the MCM-41 materials and the weak coordination of the extraframework cations (*vida infra*). Unexpected solvent effects in Knoevenagel condensations have been found by several workers using xonolite, a basic clay,¹³ or silicon oxynitride
Base and acid catalysts by the sodium and cesium ion-exchanged MCM-41

(Si$_2$N$_2$O)$_4$. Homogeneous catalysis by leached basic entities can be excluded. In contrast to the recovered MCM-41 catalyst, the filtered reaction mixture demonstrated no activity after adding fresh reactants indicating that alkali ion-exchanged MCM-41 is a true heterogeneous basic catalyst. Likewise, H-MCM-41 is inactive indicating that extraframework alkali-cations are necessary in creating basic sites.

Various alkali-containing MCM-41 materials can be compared by expressing their specific activity $A$ as mol h$^{-1}$ mol$^{-1}$ alkali metal ($A_{\text{ak}}$) or as mmol h$^{-1}$ g$^{-1}$ MCM-41 ($A_{\text{wt}}$). Table 2.1 illustrates that Cs-MCM-41 is about two times more active than Na-MCM-41. However, a five times higher $A_{\text{ak}}$ was found when using the unexchanged HNa-MCM-41, though the $A_{\text{wt}}$ is comparable. Assuming the number of basic sites to be equal to the number of Na$^+$ cations, then the higher $A_{\text{ak}}$ of HNa-MCM-41 would indicate that not all the basic sites are involved in this reaction, which idea is strengthened by an almost identical $A_{\text{wt}}$ of HNa-MCM-41 and of Na-MCM-41. The small difference in activities between Na-MCM-41 and Cs-MCM-41 suggests that the type extraframework cation has little influence on the intrinsic basicity of MCM-41. This is in contrast with Faujasites where a significant increase in activity in the same Knoevenagel condensation was reported going from Li$^+$ ion-exchanged to Cs$^+$ ion-exchanged X and Y.$^1$ This is in agreement with the basicity and the ionization potentials of these cations which increase in the alkali series going from Li$^+$ to the large Cs$^+$ as observed by infrared studies of pyridine and pyrrole adsorption.$^{11}$ Alkaline ion-exchanged sepiolite basic clays show the same trend in the Knoevenagel condensation as observed for zeolites X and Y.$^{15}$

Table 2.1. Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate (Figure 2.1, R = CN) with various alkali-containing MCM-41 catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>amount (% m/m)</th>
<th>$t$ (h)</th>
<th>conversion (% m/m)</th>
<th>selectivity (%)</th>
<th>$A_{\text{ak}}$ (mol h mol$_{\text{alki}}^{-1}$)</th>
<th>$A_{\text{wt}}$ (mmol h g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MCM-41$^a$</td>
<td>5</td>
<td>1.5</td>
<td>90</td>
<td>100</td>
<td>7.3</td>
<td>24.3</td>
</tr>
<tr>
<td>Na-MCM-41$^b$</td>
<td>5</td>
<td>7</td>
<td>81</td>
<td>75</td>
<td>2.3</td>
<td>11.8</td>
</tr>
<tr>
<td>Na-MCM-41$^c$</td>
<td>5</td>
<td>3</td>
<td>72</td>
<td>99</td>
<td>4.7</td>
<td>15.5</td>
</tr>
<tr>
<td>HNa-MCM-41$^c$</td>
<td>5</td>
<td>3</td>
<td>61</td>
<td>95</td>
<td>24.9</td>
<td>14.1</td>
</tr>
<tr>
<td>Cs-MCM-41$^b$</td>
<td>1.6</td>
<td>7</td>
<td>67</td>
<td>60</td>
<td>5.3</td>
<td>12.9</td>
</tr>
<tr>
<td>Cs-MCM-41$^c$</td>
<td>5</td>
<td>3</td>
<td>72</td>
<td>98</td>
<td>7.5</td>
<td>18.4</td>
</tr>
</tbody>
</table>

$^a$H$_2$O at 100 °C; $^b$solvent-free at 150 °C, 20 mmol of ethyl cyanoacetate and 26 mmol of benzaldehyde; $^c$THF-H$_2$O at 70 °C, 15 mL of each solvent and 10 mmol of each reactant; $^d$specific activity at $t$ (mol h mol$_{\text{alki}}^{-1}$), $^e$specific activity at $t$ (mmol h g$^{-1}$ MCM-41).

In general, the first step in the condensation of benzaldehyde with the methyleneic compounds ethyl
cyanoacetate and diethyl malonate is formation of the methylenic carbanion via proton abstraction by the negatively charged basic oxygen sites of MCM-41 (Figure 2.2). Then the generated carbanion attacks the carbonyl group of benzaldehyde resulting in the formation of a carbon-carbon bond. The products formed are finally dehydrated to the α,β-unsaturated ester (Figure 2.2) even at quite low temperatures. It is very likely that the Lewis acid extraframework Na⁺ ions are responsible for the dehydration. Of course this mechanism is still speculative, but it can at least distinct between the formation of the α,β-unsaturated ester and the β-hydroxyester. Interestingly, the β-hydroxyester compound has never been observed in this study.

![Chemical Structures](Image)

**Figure 2.2.** Schematic presentation of the mechanism of the condensation of benzaldehyde with active methylenic compounds (R = CN: ethyl cyanoacetate and R = CO₃Et: diethyl malonate) on basic MCM-41 (represented as O-Si-O⁻-Al-O).

The less acidic diethyl malonate (pKₐ = 13.3; Figure 2.1, R = CO₃Et) was tested in the presence of Na-MCM-41 in a solvent-free system at 150 °C (20 mmol of ethyl malonate and 26 mmol of benzaldehyde), but only a 6% conversion after 3 h could be obtained due to the weak basicity of Na-MCM-41. Here no
activity of MCM-41 in aqueous media was noticed. In conclusion, Na-MCM-41 and Cs-MCM-41 possess basic sites with a strength to substract a proton with a $pK_a < 12$ and a few of them are able to substract a proton with a $pK_a < 13.3$.

Beside weakly basic sites Na-MCM-41 possesses also acid sites. This is reflected by the unexpected behaviour of Na-MCM-41 in a refluxing ethanolic solution of benzaldehyde and ethyl cyanoacetate. The latter remained unreacted in solution, while benzaldehyde was acetalized with two equivalents of ethanol (Figure 2.3). Within 30 min at reflux the reaction reached equilibrium conversion (60%; 5 wt% catalyst) with a selectivity of 100% to the diethyl acetal. The acetalization was also catalyzed by H-MCM-41 with essentially the same selectivity and $A_w$. Generally, acetalizations require acid sites of a low strength.\textsuperscript{16} We assume that in both cases the acetalization is acid catalyzed. In contrast to H-MCM-41, Na-MCM-41 contains no strong Bronsted acid sites, but both materials do contain weakly acidic silanol groups. The residual acidity of Na-MCM-41 stems therefore most probably from these framework silanol groups adjacent to the aluminum sites. Apparently these are strong enough to catalyze the acetalization of benzaldehyde with ethanol.\textsuperscript{17,18} That ordinary silanol groups are unable to catalyze the acetalization is demonstrated by the inactiveness of all-silica MCM-41 in this reaction. The presence of aluminum is therefore a prerequisite to create an active acidic MCM-41 catalyst. The reason why Na-MCM-41 prefers to catalyze the acetalization over the Knoevenagel condensation is probably that the $pK_a$ of the residual acid sites is lower than the $pK_a^*$ (= 14 - $pK_a$) of the basic sites. The temperature of the reaction mixture is probably also too low for the Na-MCM-41 material to catalyze the Knoevenagel reaction over its basic sites. Aluminosilicates MCM-41 with decreasing Si/Al ratios have been used for the acetalization of various aldehydes with trimethyl orthoformate.\textsuperscript{17} The combination of a high concentration of weak acid sites and the presence of mesopores makes the MCM-41 material a perfect candidate for the acetalization involving bulky reactants or products.\textsuperscript{17}

The alkylation of fructose with fatty alcohols is an example of this potential.\textsuperscript{18}

![Figure 2.3. Acetalization of benzaldehyde with ethanol.](image)

**Aldol condensations**

Generally, aldol condensations can be catalyzed by an acid or a base.\textsuperscript{20,21} This pertains also to the
Figure 2.4. Aldol condensation of benzaldehyde with acetophenone (R = H) or 2'-hydroxyacetophenone (R = OH).

crossed-aldo condensation of benzaldehyde and acetophenone, although quite rigorous conditions are reported to be required. Both Na-MCM-41 and H-MCM-41 were tested in the aldol condensation of benzaldehyde with acetophenone to chalcone (Figure 2.4a; R = H). Table 2.2 shows that H-MCM-41 as well

| catalyst     | t  | conversion<sup><sup>a</sup></sup><sup><sup>b</sup></sup> | selectivity<sup><sup>c</sup></sup> |<sup><sup>d</sup></sup> |<sup><sup>e</sup></sup> |<sup><sup>f</sup></sup> |<sup><sup>g</sup></sup> |
|--------------|----|------------------|-----------------|------------------|-------------------|------------------|
| H-MCM-41     | 1  | 21               | 96              | 28.8             |
|              | 3  | 50               | 92              | 21.9             |
|              | 6  | 72               | 90              | 14.6             |
| Na-MCM-41    | 1  | 18(15)           | 97(99)          | 24.3(23.1)       |
|              | 3  | 34(56)           | 92(98)          | 14.9(17.9)       |
|              | 6  | 53(73)           | 89(98)          | 9.9(14.2)        |

<sup>a</sup> Acetophenone; <sup>b</sup> Figure 2.4 R = H, between brackets the results of the reaction under nitrogen; <sup>c</sup> blank reaction shows only a trace of the product after 7 h at 150 °C; <sup>d</sup> selectivity to chalcone; <sup>e</sup> specific activity at t (mmol/h g<sub>MCM-41</sub>).
Na-MCM-41 were able to catalyze these reactions solvent-free at 150 °C. The identical $A_{\text{on}}$ of both catalysts suggests at first sight that the aldol condensation is in all cases acid catalyzed. Remembering the poor performance of Na-MCM-41 in the Knoevenagel condensation of benzaldehyde with diethyl malonate it is assumed at first sight that the acidity of the $\alpha$-protons of acetophenone is too low ($pK_a = 19$)\textsuperscript{13} for Na-MCM-41 to abstract this one. It is noteworthy that the reported $pK_a$ of 15.8 for acetophenone is too low.\textsuperscript{24} It is suggested, however, that the acidity of the $\alpha$-proton is increased via coordination of the carbonyl group with the Lewis acidic extra-framework Na\textsuperscript{+} ions and/or Al\textsuperscript{1,16,23,26} The significant improvement of the conversion of both reactants could be achieved by performing the reaction under nitrogen (Table 2.2, values in parentheses). This indicates that the catalyst deactivates due to blocking of the basic sites by benzoic acid, an oxidation product of benzaldehyde.\textsuperscript{15} This is further strengthened by the higher conversion of benzaldehyde compared to acetophenone when the reaction was carried out under air. The higher conversion of benzaldehyde in the former case is due to oxidation as a parallel reaction. The selectivities of around 90%

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{conversion_graph.png}
\caption{The conversion of benzaldehyde (circles) and acetophenone (triangles; Figure 2.4, $R = H$) over Na-MCM-41 under air (open markers) and under nitrogen (closed markers; solvent free, cf. Table 2.2).}
\end{figure}

at 6 h (Figure 2.5) and the hardly unchanged conversions after one day under air suggests that the catalyst deactivates.\textsuperscript{24} This indicates that the reaction is at least partly base-catalyzed by Na-MCM-41. The general mechanism of the acid-catalyzed aldol condensation of benzaldehyde with acetophenone is proposed to be an acid catalyzed nucleophilic addition of acetophenone (in its enol form) to the activated carbonyl group of benzaldehyde (Figure 2.6).\textsuperscript{15,17} The first step is therefore protonation of the carbonyl oxygen of benzaldehyde.
Figure 2.6. Mechanism of the acid (AH) catalyzed aldol condensation of benzaldehyde and acetophenone.

Interaction of acetophenone with the Lewis acidic aluminum sites via the carbonyl oxygen creates the enolate form of acetophenone. Coordination of acetophenone to the extraframework Na⁺ ions, which behave as weak Lewis acid sites, might also result in the enolate. The enol form of acetophenone behaves as a nucleophile and attacks the electron deficient carbonyl carbon of the activated benzaldehyde. The β-hydroxyketone is finally acid catalyzed dehydrated to the α,β-unsaturated ketone (chalcone). This reaction can also proceed over Lewis acidic extraframework Na⁺ ions. Considering the basicity of benzaldehyde and acetophenone it should be expected that acetophenone is being protonated (pKₐ of protonated compound is -7.1 and -6.15, respectively). However steric considerations on the transition state of the protonation step decide that benzaldehyde is preferentially protonated, because acetophenone is more crowded around the carbonyl group. It can be concluded that Na-MCM-41 might also be able to catalyze the aldol condensation by its Lewis acid sites and therefore Na-MCM-41 acts as a bifunctional Lewis acid/basic catalyst.

The basic catalyzed aldol condensation (Figure 2.7) starts with deprotonation of the α-proton of acetophenone followed by a nucleophilic addition at the carbonyl group of benzaldehyde. Considering the high pKₐ value of acetophenone activation of it by interaction with framework aluminum or Na⁺ ions to increase the acidity is most probably playing a role. Ab initio calculations on AlCl₃ coordinated acetophone and its enolate showed an increase in heat of formation of around 70 kcal/mol going from the former to the latter. Self-aldol condensation of acetophenone is not observed. A plausible reason for this is that the carbonyl carbon of acetophenone is less electrophilic than the one of benzaldehyde.

Na-MCM-41 and H-MCM-41 were also capable to catalyze the successive aldol condensation and intramolecular Michael addition to flavanone (Figure 2.4a and 2.4b; R = OH). In general, this reaction is cata-
Figure 2.7. Mechanism of the base (B) catalyzed aldol condensation of benzaldehyde and acetophenone.

Table 2.3. Aldol condensation of benzaldehyde with different ketones on Na-MCM-41 or H-MCM-41 catalyst (5 wt%) at 150 °C without solvent.

<table>
<thead>
<tr>
<th>ketone</th>
<th>Catalyst</th>
<th>t/h</th>
<th>conversion* (% m/m)</th>
<th>selectivity* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2'-hydroxyacetophenone</td>
<td>Na-MCM-41</td>
<td>2</td>
<td>10(8)</td>
<td>72(77):28(23)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>25(27)</td>
<td>52(62):48(38)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>35(56)</td>
<td>33(37):67(63)</td>
</tr>
<tr>
<td>2'-hydroxyacetophenone</td>
<td>H-MCM-41</td>
<td>2</td>
<td>9</td>
<td>63 : 37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>26</td>
<td>55 : 45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>36</td>
<td>31 : 69</td>
</tr>
<tr>
<td>α-tetralone</td>
<td>Na-MCM-41</td>
<td>6</td>
<td>60</td>
<td>98</td>
</tr>
<tr>
<td>isophorone</td>
<td>Na-MCM-41</td>
<td>6</td>
<td>20</td>
<td>55</td>
</tr>
</tbody>
</table>

a) values in parentheses are the results of the reaction under nitrogen; b) selectivities 2'-hydroxychalcone : flavanone (Figure 2.4a,b; R = OI).

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Chapter 2

sites. On the other hand the strongly basic hydrotalcite had a large preference in producing the α,β-unsaturated ketone. Although, details have not been given it has been reported that Cs⁺ ion-exchanged amorphous silica-alumina systems are able to base-catalyze the aldol condensation of benzaldehyde with cyclooctanone.²⁸

Na-MCM-41 is also able to condense bulky substrates like α-tetralone with benzaldehyde quite easily and with a high selectivity to benzylidonetetralone (Figure 2.7a; Table 2.3). Allylic ketones like isophorone were converted less easily to benzylidene isophorone (Figure 2.7b) and this conversion was accompanied by a substantial amount of by-products. The catalyzed aldol condensation of both reactants by weakly alkaline solutions shows also a higher conversion of α-tetralone compared to isophorone. The pKₐ values of the enol and the keto form of cyclohexanone are 11.3 and 16.7, respectively.²⁹ It is expected that the corresponding pKₐs of α-tetralone do not differ very much. At least it can be suggested that the keto form is not acidic enough and activation via interaction with Lewis acid sites giving the enol form must occur to achieve proton abstraction by Na-MCM-41. The acidity of isophorone probably resembles that of toluene. In this case the question arises whether the reaction is base or acid catalyzed by Na-MCM-41.

![Diagram of Reaction](image)

**Figure 2.7.** Reactions of α-tetralone (a) and of isophorone (b) with benzaldehyde.

CO₂ TPD study

CO₂ temperature programmed desorption (TPD) is an often used technique for measuring the basicity of materials.¹² Interaction of CO₂ with basic O²⁻ can give a variety of carbonate species like mono- and bicarbonates, polydentates, or hydrogen carbonates.¹² Figure 2.8 shows the desorbed CO₂ of Na-MCM-41 and Cs-MCM-41 as a function of the temperature. The observation that Na-MCM-41 gives a large peak at 200 °C and that the TPD plot at high temperature does not return to the baseline suggests that Na-MCM-
any CO\textsubscript{2} desorption which would suggest that Na-MCM-41 is much more basic than Cs-MCM-41. This is however very unlikely considering the catalytic experiments. Similar observations have been made for Na-X compared to CsNa-X and for Na-Y compared to CsNa-Y, whereby the Na\textsuperscript{+} ion-exchanged zeolite showed a much higher amount and temperature of CO\textsubscript{2} desorption than the X or Y zeolites with a certain Cs\textsuperscript{+} exchange level.\textsuperscript{1,30} This agrees with the decreasing heat of adsorption of CO\textsubscript{2} on cationic zeolites going from Li\textsuperscript{+} to K\textsuperscript{+}, however, it is not in harmony with the order of basicity derived by theoretical and experimental results. Apparently in contrast with oxides, CO\textsubscript{2} is not the most appropriate probe to measure the basicity of zeolites and related materials.\textsuperscript{1,29} The amount of desorbed CO\textsubscript{2} from Na-MCM-41, which is much larger than that from Cs-MCM-41, precisely corresponds to one molecule of CO\textsubscript{2} per 2 Na\textsuperscript{+} ions. This indicates that a special type of extraframework sodium carbonate species is formed. On the other hand, the thermal decomposition diagram of Na\textsubscript{2}CO\textsubscript{3} supported on SiO\textsubscript{2} shows several maxima at higher temperatures. This was however not a mono-layer. Surprisingly, HNa-MCM-41 gave the same CO\textsubscript{2}/Na ratio, but a lower amount of desorbed CO\textsubscript{2}. Regarding the decrease of the heat of adsorption of CO\textsubscript{2} on alkali-containing zeolites going from small to larger alkali cations, it is still difficult to understand why Na-MCM-41 and Cs-MCM-41 show an almost similar activity in the Knoevenagel condensation. The reasons that Na-MCM-41 displays a larger CO\textsubscript{2} desorption than Cs-MCM-41 are probably the poor local crystallinity around the extra-framework Na\textsuperscript{+} cations and a weaker bonding of Na\textsuperscript{+} ions to the negatively charged framework oxygens (see the $^{29}$Na NMR
data) compared to the Cs⁺ cations. As the Lewis basic sites are considered to be the oxygens adjacent to the oxygens connected directly to the extra-framework alkali cations, these basic sites are more negatively charged when Cs⁺ cations are bonded at the framework. Therefore, the Cs⁺ cations are expected to induce stronger basic sites, but probably the CO₂ probe is too large to approach these basic sites due to the size of the extraframework Cs⁺ cations and the shape of the negatively charged sites.

²³Na and ¹³³Cs NMR

To get more insight in the complex behaviour of the extraframework cations in MCM-41 these materials were subjected to ²³Na and ¹³³Cs NMR measurements (Figure 2.8 and 2.9, respectively). Table 2.4 shows the ²³Na MAS NMR data of Na-MCM-41 and the ¹³³Cs MAS NMR data of Cs-MCM-41. The sharp linewidth of the ²³Na resonance at -3 ppm of hydrated Na-MCM-41 represents an average chemical shift due

![Diagram of Na-MAS NMR spectra]

Figure 2.8. ²³Na MAS NMR spectra of (a) hydrated Na-MCM-41 and (b) dehydrated Na-MCM-41.
Figure 2.9. $^{133}$Cs MAS NMR spectra of (a) hydrated Cs-MCM-41 and (b) dehydrated Cs-MCM-41 (asterisks indicate spinning sidebands).

to the rapid motion of the Na$^+$ cations. Considering the large quadrupole moment ($eq = 1.2 \times 10^{-29}$ m$^2$), the low spin number of the $^{23}$Na ($I = 3/2$) and the absence of spinning sidebands, the broad resonance after dehydration does not result from averaging. $^{24}$Hydrated Cs-MCM-41 shows also a resonance in the lower up-field region of the $^{133}$Cs spectrum ($eq = -0.03 \times 10^{-29}$ m$^2$; $I = 7/2$), namely at -14 ppm, and a very small linewidth (0.2 kHz). Again spinning sidebands are not present, which suggests that the extraframework Cs$^+$ cations are in a quasi isotropic environment due to the high mobility of these hydrated cations.$^{32-40}$ On dehy-

Table 2.4. $^{23}$Na and $^{133}$Cs MAS NMR data of hydrated and dehydrated Na-MCM-41 and Cs-MCM-41 materials, respectively.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$\delta_{\text{hydrated}}$ (ppm)</th>
<th>$\Delta v_{1/2}$ (kHz)$^b$</th>
<th>$\delta_{\text{dehydrated}}$ (ppm)</th>
<th>$\Delta v_{1/2}$ (kHz)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MCM-41</td>
<td>-3$^c$</td>
<td>0.3</td>
<td>-13$^c$</td>
<td>1.8</td>
</tr>
<tr>
<td>Cs-MCM-41</td>
<td>-14$^c$</td>
<td>0.2</td>
<td>-88$^c$</td>
<td>2.4</td>
</tr>
</tbody>
</table>

a) Dehydrated at 450 °C; b) peakwidth at half height; c) no spinning sidebands are observed; d) spinning sidebands.
dration, the \(^{133}\)Cs resonance shifts to -88 ppm accompanied by considerable line broadening (2.4 kHz) and the appearance of spinning sidebands. This implies that the Cs\(^+\) cations have lost their high mobility and now sense different chemical surroundings with their associated shielding anisotropies. The observed chemical shift of both nuclei on hydration can be ascribed mainly to the electron back-donation of the water ligands to the cations and to a lesser extent to the configuration of the water ligands to the nuclei.\(^{32}\) Keeping in mind the higher sensitivity of \(^{133}\)Cs nuclei compared to \(^{23}\)Na nuclei it is suggested, on the basis of these NMR results and the CO\(_2\) TPD data, that the extraframework Na\(^+\) cations are more mobile than extraframework Cs\(^+\) cations. Cation exchange dynamics, motion and exchange of cations, have been reported for different Na\(^+\) and/or Cs\(^+\) ion-exchanged zeolites: A, \(^{33,34}\)mordenite, \(^{30}\)ZSM-5 \(^{37}\)and Y \(^{38,39}\)and vermiculite clay.\(^{32}\) The interparticle cation mobility at high temperature is illustrated by a \(^{133}\)Cs MAS NMR study on a fluid cracking catalyst containing beside kaolin, pollucite (cesium analcime) and USY, which showed that Cs\(^+\) cations had migrated from pollucite to USY after the cracking test.\(^{40}\)

2-4. Conclusions

Sodium and cesium cation-exchanged MCM-41 are shown to be mild, selective, water-stable and recyclable catalysts for the base-catalyzed Knoevenagel condensation and the acid-catalyzed acetalization. The aldol condensation is probably base and acid catalyzed by Na-MCM-41. Both, Na-MCM-41 and the slightly more basic Cs-MCM-41 possess weakly basic sites and acidic silanol groups adjacent to the aluminum sites. The capability of alkali cation-exchanged MCM-41 to perform catalysis in aqueous media is most probably due to the weak coordination of solvated extraframework cations.

References

Solid mesoporous base catalyst comprising of MCM-41 supported intraporous cesium oxide*

3-1. Introduction

Though base catalysis with alkali ion-exchanged zeolites is known for years, extensive studies on this subject have been started, in contrast with acid catalysis, quite recently.¹,² A reason for this might be the growing importance of selectivity aspects in base catalyzed reactions. The aldol condensation of acetone can be performed over A, X, Y or L-zeolites.³ Where zeolite X and Y preferentially produce isophorone, the unidimensional pore-sized L-zeolite produces just half the amount of isophorone at the benefit of mesityl oxide. The small pore zeolite A has even a larger preference for the formation of the latter.² It is however improbable that these compounds can desorb from the zeolite A pores. Beside the type of zeolite, the intrinsic basicity of the zeolites can be tuned by selecting the appropriate type of extraframework cation.¹ The basicity of zeolites is limited by their chemical composition, but it can be improved substantially by the introduction of basic oxides.¹⁻¹¹ Incorporation of different type of oxides in zeolite X, Y and ZSM-5 has been reported, e.g. MgO,¹,² Na₂O,⁴⁻¹¹ K₂O,⁴⁻¹¹ Rb₂O,⁴⁻¹¹ and Cs₂O¹⁻¹⁰ Intrazeolitic cesium oxide is the most extensively studied system due to the high basicity and the insensitivity to carbon dioxide poisoning, which is the largest problem of the use of oxides as a catalyst.¹⁻¹⁰ Also other basic species have been impregnated on zeolites such as sodium clusters¹⁻¹² and lanthanide amides.²,¹³,¹⁴,¹⁵ The most intensively studied zeolites are X and Y due to their large amount of framework aluminum and the presence of internal cages (12 Å) making them a stable and suitable support for cesium oxide particles.³⁻¹⁰ The general method to prepare these materials is by impregnating the zeolites with cesium acetate followed by heating at high temperature which leads to decomposition of cesium acetate into cesium oxide and carbon dioxide.

Catalysis by basic zeolites with or without intraporous cesium oxide particles is limited to relatively small molecules due to the pore size restrictions of the zeolitic support.¹⁻² In the previous chapter the basic and acid properties of the alkali-exchanged mesoporous material MCM-41 in several organic reactions were reported. These MCM-41 type mesoporous molecular sieves showed excellent performances due to their mild basicity.¹⁵ Considering the strong basicity of Cs-loaded zeolites, the basicity of MCM-41 might also be in-

creased by incorporation of cesium oxide particles. Here a detailed study on the cesium oxide-MCM-41 systems is described. The cesium oxide-MCM-41 materials were subjected to various characterization techniques and correlated to their activities in two Michael-type addition reactions: the addition of diethyl malonate to chalcone and the two step-addition of diethyl malonate to neopentyl glycol diacrylate. Selectivity aspects due to the pore aperture of the MCM-41 support could be investigated in the latter two-step reaction.

3-2. Experimental

Catalyst preparation

The starting MCM-41 was synthesized by mixing 16.8 g TMA-SiO₂ solution [TMAOH/SiO₂ = 0.5; 10 wt% SiO₂ (Cab-oil M5 from Fluka) and tetramethylammonium hydroxide (TMAOH; Aldrich)] with 6.60 g of sodium silicate (Aldrich; 27 wt% SiO₂). Subsequently 31 g of water and 4.56 g of silica were added to the mixture. Under vigorous stirring 15.5 g of cetyltrimethylammonium bromide (ACROS) in 104 g of water was poured in the mixture. Finally the gel was enriched with an appropriate amount of sodium aluminate (Riedel-de Hae; 54 % Al₂O₃ and 41 % Na₂O) to obtain the desired Si/Al ratio. The gel was stirred for 2 hours at room temperature and subsequently kept in an oven at 100 °C statically overnight. The resulting solid was filtered and thoroughly washed, dried at 90 °C under vacuum, and calcined at 540 °C under air for 10 h.

The cesium-impregnated MCM-41 materials, denoted Cs/MCM-41, were prepared by impregnating MCM-41 materials in a concentrated solution of cesium acetate (ACROS). Different loadings were achieved by applying different molarities. The mixtures were shaken overnight at room temperature and centrifuged after the upper layer was removed by decantation. The solids were finally dried at 100 °C under vacuum.

The sodium and cesium ion-exchanged MCM-41 samples (denoted Na-MCM-41 and Cs-MCM-41, respectively) were prepared according to reference 16 by using aqueous NaCl or CsCl (Baker), respectively.

LA-SHPV, a commercial silica-alumina cracking catalyst, a generous gift from Akzo Nobel Chemicals, was used as a cesium oxide support for comparison in catalysis. The chemical composition is: 12.0 wt% Al₂O₃, the surface area = 539 m²/g and pore volume H₂O = 1.34 ml/g. The LA-SHPV material was impregnated in a 2 M aqueous solution of CsOAc at room temperature. Then the mixture was filtrated and dried at 80 °C.

Reference cesium oxide was purchased from Aldrich.
Solid mesoporous base catalyst comprising of MCM-41 supported intraporous cesium oxide

Characterization

X-ray powder diffraction

Some of the samples were characterized by powder X-ray diffraction on a Philips PW 1840 diffractometer using monochromated CuKα radiation. Patterns were recorded from 1° to 40° (2Θ) with a resolution of 0.02° and a count time of 1 s at each point.

133Cs NMR spectroscopy

Solid-state 133Cs MAS NMR spectra were recorded at room temperature on a Varian VXR-400s spectrometer, equipped with a Doty Scientific 5 mm solids MAS probe. A resonance frequency of 52.5 MHZ, a recycle delay of 1.0 s, an acquisition time of 0.1 s and short 2 μs pulses, a spectral width of 100 KHz and a spin rate of 4-7 KHz were applied. The lines were referenced to a 1M solution of CsCl in water (0 ppm).

CO₂ temperature programmed desorption

Temperature programmed desorption (TPD) of carbon dioxide was performed on a Micromeritics 2900 TPD/TPR instrument. First the materials were calcined at 600 °C for 5 h under a helium flow. During cooling down to 110 °C the activated materials were saturated with dry carbon dioxide. Physisorbed carbon dioxide was removed by purging under a helium flow at 110 °C until a stable baseline was monitored (about half an hour). The TPD was performed under a helium flow (10 mL/min) by heating from 110 to 600 °C with a heating rate of 10 °C/min.

Nitrogen physisorption

Multipoint BET surface areas, pore volumes and pore size distributions of the materials were calculated from N₂ adsorption/desorption isotherms at -196 °C using a Quantochrome Autosorb 6 apparatus. The samples were outgassed for 16 h under vacuum at 350 °C prior to use.

Catalytic testing

The substrates used were dried on zeolite NaA. A Cs/MCM-41 sample was calcined in situ at 500 °C under vacuum for 6 h. At t=0 the activated sample (6 wt% with respect to the total amount of reactants) was added to a stirred mixture of 10 mmol of diethyl malonate (1.61 g; Aldrich), 5 mmol neopentyl glycol diacrylate (1.06 g; Aldrich) in 15 ml of toluene (ACROS) at room temperature under a nitrogen atmosphere. The course of the reaction, which was conducted at room temperature or under reflux, was monitored by GC (CP sil 5CB column). The products were analyzed by GC-MS (VG70-250S/SE instrument).
3-3. Results and discussion

Characterization

X-ray powder diffraction was carried out on the original MCM-41 support and Cs/MCM-41, the calcined cesium acetate impregnated MCM-41 materials, with various Cs loadings to study the resistance of the MCM-41 support to the impregnation procedure. The parent MCM-41 showed clearly the $d_{100}$ spacing at 40 Å and the high order reflections (Figure 3.1). The $d_{100}$ spacings of the impregnated Cs/MCM-41 materials are located at the same position, but have a lower intensity. This phenomenon is probably due to X-ray scattering by the high electron density of the large intraporous Cs$^+$ cations\textsuperscript{6,10} and is not an indication of any lack of mesoporosity (\textit{vide infra}). The decrease of the high order diffraction peaks going to higher Cs loadings of Cs/MCM-41 is consistent with observations on MCM-41 materials impregnated with heteropoly acid\textsuperscript{8} and indicates that the cesium oxide particles are mainly located inside the mesoporous. The intact MCM-41 support and the homogeneous dispersion of the intraporous cesium oxide particles were confirmed by transmission electron microscopy (not shown).

![X-ray diffractograms](image)

Figure 3.1. X-ray diffractograms of a) a parent MCM-41 with Si/Al = 21; b) 5.7 wt% Cs/MCM-41; c) 9.4 wt% Cs/MCM-41 and d) 15.5 wt% Cs/MCM-41 (all the materials are calcined at 500 °C).

Solid state $^{133}$Cs MAS NMR was performed to investigate the nature of Cs in the Cs/MCM-41
Solid mesoporous base catalyst comprising of MCM-41 supported intraporeous cesium oxide

materials. Figure 3.2 shows the $^{133}$Cs MAS NMR spectra of Cs ion-exchanged and Cs added MCM-41 samples. Hydrated Cs ion-exchanged MCM-41 (Figure 3.2a) shows a resonance at -14.4 ppm with a very small line width indicating very mobile Cs species (cf. chapter 2). Upon dehydration the resonance shifts to -88 ppm (Figure 3.2b) and line broadening appears as a consequence of a different geometry. $^{133}$Cs MAS NMR has also been used to study the motion and position of extraframework Cs$^+$ cations in Cs-A,\textsuperscript{19,21} Cs-mordenite,\textsuperscript{22} Cs-ZSM-5,\textsuperscript{23} Cs-Y\textsuperscript{24} and Cs-vermiculites.\textsuperscript{25} Thereby is found that in the hydrated state of Cs$^+$ ion-exchanged molecular sieve the Cs$^+$ ions show a high mobility and can move to particular exchange sites.

The calcined Cs/MCM-41 samples show a $^{133}$Cs resonance shift from 21 ppm via 48 ppm (Figure 3.2c and d) to 89 ppm (not shown) by increasing the Cs content from 12.4 wt% to 32.5 wt% Cs indicating occluded Cs$_2$O particles.\textsuperscript{8} A physical mixture of 40 wt% Cs$_2$O/SiO$_2$ shows a resonance at 109 ppm. The resonances at -18.5 ppm and -4.2 ppm are tentatively assigned to partially hydrated cesium species formed by reaction of cesium oxide with moisture during transfer of the materials in the probe. Fully hydrated Cs/MCM-41 materials by contacting them in air show resonances around 13 to 18 ppm. When a hydrated

![Figure 3.2. $^{133}$Cs MAS NMR spectra of a) hydrated Cs-MCM-41; b) dehydrated Cs-MCM-41 (asterisks are spinning sidebands); c) calcined Cs/MCM-41 (12.4 wt% Cs); d) calcined Cs/MCM-41 (21.9 wt% Cs).](image-url)
Cs/MCM-41 (21.9 wt% Cs) is calcined again, then the \(^{133}\)Cs resonance does not appear at its original position before hydration, but shifts about 13 ppm units downfield to 61 ppm. This indicates a reorganization of the Cs atoms forming probably (larger) cesium oxide clusters. \(^{133}\)Cs MAS NMR data of Cs loaded zeolite X showed the same correlation as found for Cs/MCM-41 materials.\(^8\) By increasing the Cs loading the \(^{133}\)Cs resonance of the cesium oxide shifts downfield. This indicates that the intraporous cesium oxide particles are becoming of the bulk oxidic type as a result of a growing particle size. Zeolite X loaded with cesium oxide, showed less broad resonances which might be the result of a high local symmetry around the intraporous cesium oxide particles compared to cesium oxide particles inside MCM-41, where the framework has more an amorphous character.

The basic strength and the accessibility of the cesium oxide particles were measured by CO\(_2\) temperature programmed desorption (TPD).\(^{12,4,8,11}\) TPD plots of some Cs-containing MCM-41 samples are illustrated in Figure 3.3. Cs-MCM-41 shows hardly any CO\(_2\) desorption. Upon increasing the Cs loading the amount of desorbed CO\(_2\) increases and the maximum peak temperature (\(T_{\text{max}}\)) shifts to higher temperatures. This indicates that stronger basic sites are generated by thermal decomposition of impregnated cesium acetate. Cs/MCM-41 with higher Si/Al ratios showed in general a lower \(T_{\text{max}}\), indicating that the amount of framework aluminum influences the basicity of the intraporous cesium oxide particles. A remarkable result was found for Na\(^+\) ion-exchanged MCM-41 (cf. chapter 2).\(^{16}\) Na-MCM-41 gives a strong and relatively sharp

![Figure 3.3 CO\(_2\) TPD plots of alkali-containing MCM-41 with Si/Al = 12.5. a) Na-MCM-41; b) Cs-MCM-41; c) Cs/MCM-41 (19.2 wt% Cs); d) Cs/MCM-41 (27.5 wt% Cs).](image-url)
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peak in the CO₂ TPD plot. The desorbed amount of CO₂ corresponds to 1 CO₂ per 2 Na atoms, suggesting formation of framework-bonded sodium carbonate-like species and indicates very loosely bounded Na⁺ cations. The shift of Tₘₚₓ to higher temperature and the increase in the amount of desorbed CO₂ agree with reported CO₂ TPD data of Cs loaded X.⁸

The correlation between the number of Cs atoms per desorbed CO₂ and the Cs loading is depicted in Figure 3.4. If MCM-41 contains a monolayer of Cs₂O, then a desorption of 1 CO₂ per 2 Cs atoms would be expected if O²⁻ is considered as the basic site.¹² A desorption ranging from 1 to 2.2 CO₂ per 2 Cs atoms

![Graph showing desorption of CO₂ and BET area as a function of Cs loading](image)

**Figure 3.4.** Amount of CO₂ (open markers) and BET area (closed markers) as a function of the cesium loading of MCM-41. ▼ and V denote Cs/MCM-41 with Si/Al = 13, ▲ and Δ denote Cs/MCM-41 with Si/Al = 21 and, ● and ○ denote Cs/MCM-41 with Si/Al = 25 (the most left open-circle represents Cs⁺ ion-exchanged MCM-41).

is found for the lower Cs loadings of around 10 wt% (corrected for the Cs⁺ ion-exchange capacity of MCM-41, the most left open circle in Figure 3.4) indicating a reasonably homogeneous dispersion of cesium oxide inside MCM-41. Less CO₂ is desorbed at high Cs loadings which is probably a consequence of formation of cesium oxide clusters. These results are fairly well in agreement with CO₂ TPD data of Cs loaded Y which showed a decrease in desorbed amount of CO₂ by increasing the Cs content which is, however, not the case for Cs loaded X.⁹ X¹⁰ The authors proposed that at high Cs loading the intraporous cesium oxide particles inside Y are situated as a cluster of the form (Cs₂O)₂ and not as Cs₂O.⁹
### Table 3.1. Nitrogen physisorption data of various Cs containing MCM-41 samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>Cs content (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>BET surface (m²/g)</th>
<th>(V_{cum})&lt;sup&gt;b&lt;/sup&gt; (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41&lt;sup&gt;c&lt;/sup&gt;</td>
<td>-</td>
<td>1069</td>
<td>0.819</td>
</tr>
<tr>
<td>Cs-MCM-41</td>
<td>3.7</td>
<td>957</td>
<td>0.471</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>12.4</td>
<td>510</td>
<td>0.248</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>21.9</td>
<td>176</td>
<td>0.094</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>24.2</td>
<td>42</td>
<td>0.002</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>32.5</td>
<td>70</td>
<td>0.034</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>45.4</td>
<td>24</td>
<td>0.004</td>
</tr>
<tr>
<td>MCM-41&lt;sup&gt;d&lt;/sup&gt;</td>
<td>-</td>
<td>1072</td>
<td>0.855</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>5.7</td>
<td>803</td>
<td>0.405</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>9.4</td>
<td>656</td>
<td>0.322</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>15.3</td>
<td>448</td>
<td>0.190</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>23.6</td>
<td>214</td>
<td>0.084</td>
</tr>
<tr>
<td>MCM-41&lt;sup&gt;*&lt;/sup&gt;</td>
<td>-</td>
<td>1087</td>
<td>0.892</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>15.6</td>
<td>534</td>
<td>0.304</td>
</tr>
<tr>
<td>MCM-41&lt;sup&gt;*&lt;/sup&gt;</td>
<td>-</td>
<td>1002</td>
<td>0.785</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>19.2</td>
<td>423</td>
<td>0.188</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>27.5</td>
<td>206</td>
<td>0.089</td>
</tr>
</tbody>
</table>

<sup>a</sup> Measured by flame AES; <sup>b</sup> cumulative pore volume; <sup>c</sup> Si/Al = 25; <sup>d</sup> Si/Al = 21; <sup>e</sup> Si/Al = 13.

Table 3.1 illustrates the nitrogen physisorption data of some calcined Cs/MCM-41 materials. The BET surface areas and pore volumes decrease with increasing Cs content. At a certain amount of Cs the BET surface area (and also the pore volume) decreases dramatically. The border case at which this happens depends on the Si/Al ratio of the MCM-41 support. In contrast to Cs/MCM-41 with 24.2 wt% Cs and a Si/Al ratio of 25, Cs/MCM-41 with 27.5 wt% Cs and a Si/Al ratio of 13 shows no collapse of the mesoporous framework. Duplicate measurements, carried out on some Cs/MCM-41 samples by pre-evacuating for a second time for 16 h under vacuum at 350 °C, indicated that all the BET areas decrease significantly (about 70%). This indicates that the occluded cesium oxide particles react with the MCM-41 framework probably
forming cesium silicate species. A drastic decrease in the surface area and micropore volume of Cs loaded Y and ZSM-5 after calcination has also been reported by several workers.\textsuperscript{7,9,10} \textsuperscript{29}Si and \textsuperscript{27}Al MAS NMR experiments on these materials show that both framework silicon and aluminum are involved in the low stability of these zeolites. Thus the collapse of the framework is rather a result of breaking of the Si-O-Si bonds than of the Si-O-Al bonds.\textsuperscript{7} Therefore formation of local cesium silicates or aluminates could not be excluded. Comparing the stability of Y and ZSM-5 with that of X suggests that the lower the Si/Al ratio, the more stable the zeolite framework is with respect to occluded cesium oxide. In the case of Cs/MCM-41, which is generally less stable than a zeolite, the same reason might be expected for the collapse of the framework.

The correlation between the BET surface areas and the cesium atom loading is illustrated in Figure 3.4. The BET surface area decreases linearly with the Cs content and therefore the decrease in surface area and pore volume at moderate Cs loadings is rather the result of the expression of area per weight than a collapse of the framework. A horizontal line is observed for loadings higher than 22 wt\% Cs for MCM-41 with Si/Al = 25. The border case for the more aluminum rich MCM-41 with Si/Al = 13 is probably around 35 wt\% Cs. A comparable correlation is found for Cs-loaded Y.\textsuperscript{9,10} Completely filled pores were observed at a Cs content of 16 Cs atoms per unit cell which corresponds roughly to 55 wt\% Cs.

Catalysis

The activity of some of the Cs/MCM-41 materials was first tested in the base catalyzed Michael addition of the bulky chalcone with the weakly acidic (pK$_a$ = 13.3) diethyl malonate (26 mmol and 20 mmol, respectively; 2\% m/m catalyst; Figure 3.5).\textsuperscript{16} Here Cs/MCM-41 (20 wt\% Cs) gave an excellent performance at 150 °C in the absence of solvent: a conversion of 87% with a selectivity of 91% within 30 min could be achieved. The much more acidic ethyl cyanoacetate (pK$_a$ < 9) could be converted completely within 5 min at the same conditions. This reaction indicates that Cs loaded MCM-41 is able to convert large substrates in reasonable reaction times. In general, catalysis of Michael additions are very well served by the moisture sensitive cesium oxide containing materials, because water is not involved in these reactions. Though only

\[
\text{Ph-CH} = \text{CH-Ph} + \text{H}_2\text{C-CO}_2\text{Et} \rightarrow \text{Ph-CH} = \text{CH-CO}_2\text{Et}
\]

\[
\text{Et}_2\text{C-CH-CO}_2\text{Et}
\]

\textbf{Figure 3.5.} Michael addition of chalcone with diethyl malonate.

\textbf{47}
initial reaction rates have been measured, the reported Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate over Cs-loaded X and Y is not the most suitable probe reaction due to water formation.\textsuperscript{5,9}

In the liquid-phase alkylation of 4-\textit{tert}-butyl phenol by styrene on MCM-41 supported heteropoly acid,\textsuperscript{18} a high preference for the formation of the less bulky mono-alkylated product was found. Regioselectivity in base-catalyzed reactions of bulky molecules on Cs/MCM-41 due to the partly occupied mesoporous framework of the MCM-41 support might also be expected. The liquid-phase Michael addition on neopentyl glycol diacrylate, possessing two isolated activated double bonds, with diethyl malonate was used as the probe reaction (Figure 3.6). The reaction of neopentyl glycol diacrylate with diethyl malonate can lead to the mono-adduct 1 and in a consecutive reaction to bis-adduct 2. In case of shape-selectivity product

\[
\begin{align*}
\text{CH}_2=\text{CH} & \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2 & \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_2 \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_2 \\
\text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} \\
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{C} \quad \text{CO}_2\text{Et} \\
\text{CO}_2\text{Et} & \quad \text{CO}_2\text{Et} \\
\end{align*}
\]

Figure 3.6. Two-step Michael addition of neopentyl glycol diacrylate with diethyl malonate.

1 should be produced in a larger amount. Table 3.2 illustrates the performance of the used catalysts. All the Cs/MCM-41 materials are quite active in this reaction. The activity of Cs/MCM-41 increases with increasing Cs content and decreasing Si/Al ratio which is reflected by the required reaction temperature. These observations agree with CO\textsubscript{2} TPD data (\(T_{\text{max}}\)). The influence of the MCM-41 support compared to bulk cesium oxide is illustrated by the selectivity 1:2. Cs/MCM-41 with Cs contents below 25 wt\% showed a high preference to the mono-adduct 1. Using the higher loaded 28 wt\% Cs/MCM-41 at 110 °C the selectivity decreases drastically due to the high basicity of the catalyst combined with less pore volume. The selectivity to 1 could be improved substantially by decreasing the reaction temperature (\(T_{\text{reaction}}\)) to 20 °C. The reason

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Table 3.2. Liquid-phase Michael addition of neopentyl glycol diacylate with diethyl malonate in toluene over various Cs/MCM-41 materials, Cs loaded LA-SHPV and bulk cesium oxide.a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cs cont. (wt%)</th>
<th>$T_{\text{reaction}}$ (°C)</th>
<th>$A_{\text{Cs-atom}}$ (mol/mol$_{\text{Cs}}$ h)$^c$</th>
<th>$A_{\text{wt}}$ (mmol/g.h)$^d$</th>
<th>$t$ (min)$^e$</th>
<th>conv. (%) $m/m$</th>
<th>selec. (%) $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs/MCM-41$^b$</td>
<td>19</td>
<td>110</td>
<td>10</td>
<td>7</td>
<td>60</td>
<td>36</td>
<td>85.15</td>
</tr>
<tr>
<td>Cs/MCM-41$^i$</td>
<td>24</td>
<td>110</td>
<td>45</td>
<td>25</td>
<td>15</td>
<td>41</td>
<td>63.37</td>
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<tr>
<td>Cs/MCM-41$^b$</td>
<td>28</td>
<td>110</td>
<td>299</td>
<td>128</td>
<td>30</td>
<td>96</td>
<td>15.85</td>
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<td></td>
<td>20</td>
<td></td>
<td>25</td>
<td>12</td>
<td>30</td>
<td>38</td>
<td>98.02</td>
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</tr>
<tr>
<td>Cs/LA-SHPV$^j$</td>
<td>36</td>
<td>20</td>
<td>84</td>
<td>630</td>
<td>10</td>
<td>46</td>
<td>25.75</td>
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<tr>
<td>Cs$_2$O$^k$</td>
<td>94</td>
<td>20</td>
<td>1266</td>
<td>1342</td>
<td>5</td>
<td>62</td>
<td>0.60$^l$</td>
</tr>
</tbody>
</table>

a) Reaction formulation and conditions see experimental part; b) reaction temperature; c) specific activity $A_{\text{Cs-atom}}$ at 30% m/m neopentyl glycol diacylate conversion; d) specific activity $A_{\text{wt}}$ at 30% m/m neopentyl glycol diacylate conversion; e) reaction time; f) conversion of neopentyl glycol diacylate at r, g) selectivity ratio of the mono-adduct 1 to the bis-adduct 2; the overall selectivity to both products is around 85% - 90%; h) Si/Al = 13; i) Si/Al = 22; j) Cs loaded LA-SHPV containing 12.0 wt% Al$_2$O$_3$; k) 8 wt% bulk cesium oxide based on total amount of substrates; l) accompanied by formation of 40 % of byproducts.

for this high selectivity is probably the poor accessibility of the active sites which is reflected by the low pore volume (0.089 cm$^3$/g) of the catalyst due to the high Cs loading of 28 wt%. Figure 3.4 illustrates that this is certainly not the result of a collapse of the framework structure of the MCM-41 support, but that this is the Cs loading. Probably, this material contains large Cs clusters which have actually a low effective number of strongly basic surface-sites per cluster which is reflected by the much higher $A_{\text{Cs-atom}}$ (specific activity defined as mol/mol$_{\text{Cs-atom}}$ h) compared to the $A_{\text{wt}}$ (specific activity defined as mmol/g.h). The low Cs loaded MCM-41 materials have a lower ratio $A_{\text{Cs-atom}}$ to $A_{\text{wt}}$ indicating that more of the intraporous cesium oxide is involved in catalysis. That the combination of basicity and mesoporosity is responsible for the achieved selectivity in this reaction is illustrated by the Cs loaded LA-SHPV, an amorphous silica-alumina cracking catalyst. This material showed a low selectivity to 1 and a comparable activity compared to 28 wt% Cs/MCM-41 tested at 110 °C. Bulk Cs$_2$O shows also a higher preference for the bis-adduct 2, but this was
accompanied with a substantial formation of byproducts due to the very strong basicity.

3-4. Conclusions

Cesium oxide loaded MCM-41 materials seem to be promising catalysts for base catalyzed reactions for the production of fine chemicals. The presence of cesium oxide particles is responsible for the strong basicity of these materials. The influence of the mesoporous framework of the MCM-41 support is illustrated by the regioselectivity in the two step Michael-type addition of diethyl malonate to neopentyl glycol diacrylate. Thereby not only the aperture of the MCM-41 support plays a role, but also the Cs loading on MCM-41. A disadvantage of the Cs-loaded MCM-41 materials is the poor high temperature-regenerability of the material leading to a drastic decrease of the surface area and pore volume.

References

Solid mesoporous base catalyst comprising of MCM-41 supported intraporous cesium oxide

Binary cesium-lanthanum oxide supported on MCM-41: a new stable heterogeneous basic catalyst*

4-1. Introduction

Heterogeneous base catalysis is a growing field of interest. Alkaline (earth) oxides, rare earth oxides, special zeolites and clays have been used as base catalysts. The zeolites are used generally in their alkaline ion-exchanged form or serve as a support for small alkaline oxide particles. The zeolitic systems are insensitive to carbon dioxide poisoning and are moderately moisture sensitive. However, a limitation of these microporous materials is the pore accessibility. The mesoporous molecular sieve MCM-41 has proven to be a promising candidate for the catalytic conversion of large molecules. Sodium and cesium ion-exchanged MCM-41 is weakly basic; its basicity was improved by intraporous cesium oxide particles. These strongly basic mesoporous systems are able to catalyze the Michael addition with enolates of a relatively weak acidity (pKa ≤ 13.3). The stability of these catalysts is rather poor which counts generally for cesium oxide supported on molecular sieves containing a small amount of framework aluminium.

Binary oxides containing alkaline metals might have interesting properties compared to the corresponding single oxide, for instance an increased stability and improved catalytic behaviour. Preparation of binary oxides and other related oxidic materials has been reviewed recently. Stable binary lithium-lanthanide oxides have been prepared via mixtures of their metal salts or via mixtures of the corresponding single oxides. Characterization of LiLnO₂ (Ln = La, Nd and Sm) after use in the oxidative coupling of methane (OCM) at 750 °C, revealed that the structure of these catalysts was retained. The yttrium analogue LiYO₂ appeared to undergo partial transformation into an amorphous phase at the reported reaction conditions. All the LiLnO₂ compounds showed interesting performances in OCM. The use of CsLaO₂ has not been reported. Like most of the binary alkali-lanthanum oxides CsLaO₂ possesses a structure of the NaFeO₂ type, an ordered rock salt structure consisting of mixed cation layers of closest-packed O²⁻.

Binary CsLa-oxide supported on MCM-41 might have interesting performances in base catalyzed reactions like the Michael addition. The objective of this work was to prepare a stable basic catalyst of the MCM-41 type by impregnation of stoichiometric amounts of cesium and lanthanum. The physicochemical

properties of the intraporous cesium lanthanum mixed-oxide particles were investigated by a variety of
colorization techniques and by testing these composites in base-catalyzed liquid phase reactions. Binary
alkali-lanthanum oxides containing sodium, potassium or rubidium were prepared in a similar way inside the
MCM-41 material to study some properties of these composite systems and compare them with the cesium
analogue.

4-2. Experimental

Catalyst preparation

The MCM-41 support was synthesized by mixing 16.8 g TMA-SiO$_2$ solution (TMA/SiO$_2$ = 0.5; 10
wt% SiO$_2$; tetramethylammonium hydroxide (TMAOH) purchased from Aldrich and the silica source was
Cab-o-sil M5 from Fluka) with 6.6 g of sodium silicate (Aldrich; 27 wt% SiO$_2$). Subsequently 31 g of water
and 4.6 g of silica were added to the mixture. Under vigorous stirring 15.5 g of cetyltrimethylammonium
bromide (ACROS) in 104 g of water was poured in the mixture. Finally the gel was enriched with the
appropriate amount of sodium aluminate (Riedel-de Haeen; 54 % Al$_2$O$_3$ and 41 % Na$_2$O) to obtain the desired
Si/Al ratio. The gel was stirred for 2 hours at room temperature and subsequently kept, without stirring, in
an oven at 100 °C overnight. The resulting solid was filtered and thoroughly washed with water, dried at 90
°C under vacuum, and calcined at 540 °C in air for 10 h.

MCM-41 samples containing only one of the metals cesium or lanthanum, denoted Cs/MCM-41and
La/MCM-41, respectively, were prepared by stirring 1.0 g of MCM-41 in a solution containing the
appropriate amount of cesium acetate (CsOAc; ACROS) or lanthanum nitrate hexahydrate (Merck) in 4 g
of methanol for 3 h at 60 °C. The solvent was removed quickly under vacuum in a rotary evaporator and the
materials were subsequently calcined at 500 °C for 5 h in air.

CsLa/MCM-41 materials, containing equimolar amounts of both cesium and lanthanum, were
prepared in three different ways, namely (i) one-step wet impregnation, (ii) one-step solid-state impregnation
and (iii) two-step wet impregnation. The first method is by stirring 1.0 g of MCM-41 in a methanolic solution
containing equimolar amounts of CsOAc and La(NO$_3$)$_3$·6H$_2$O for 3 h at 60 °C, followed by quickly drying
and subsequently calcination at 500 °C for 5 h in air. These samples will be denoted CsLa/MCM-41A.

The second way is by solid-state impregnation. The MCM-41 support was ground carefully with the
appropriate amounts of CsOAc and La(NO$_3$)$_3$·6H$_2$O, and the mixture was calcined at 500 °C (1 °C/min
heating rate) for 5 h in air. These samples will be denoted CsLa/MCM-41B.

The third route is first preparing monometallic lantha containing MCM-41 (La/MCM-41; see
above) and subsequently impregnating this with CsOAc and calcining the materials again at 500 °C. These
Binary cesium-lanthanum oxide supported on MCM-41: a new stable heterogeneous basic catalyst

materials are denoted CsLa/MCM-41C. All the CsLa/MCM-41 materials were loaded with about 5 wt% cesium and 5 wt% lanthanum.

The Na and Cs ion-exchanged MCM-41 samples (Na-MCM-41 and Cs-MCM-41, respectively) were prepared according to reference 14 by using aqueous NaCl (Baker) or CsCl (ACROS).

All-silica NaLa/MCM-41, KLa/MCM-41 and RbLa/MCM-41 were prepared similarly to the first method (i), namely by using stoichiometric amounts of the corresponding alkali acetate and lanthanum nitrate hexahydrate (based on 5 wt% La).

Bulk CsLaO₂ was prepared by mixing the appropriate amounts of CsOAc and La(NO₃)₂·6H₂O in an alcoholic solution at room temperature for a few hours followed by drying and calcining at 500 °C for 5 h. This binary oxide showed diffraction peaks corresponding with literature data. Binary MLaO₂ or M₂O-La₂O₃ (M = Na, K or Rb) were prepared in a similar way. Reference cesium oxide and lanthana were purchased from Aldrich.

Characterization

Structural characterization was performed by powder X-ray diffraction on a Philips PW 1840 diffractometer using monochromated CuKα radiation. Patterns were recorded from 1° to 40° (2Θ) with a resolution of 0.02° and a count time of 1 s at each point.

Differential scanning calorimetry and thermogravimetrical analysis (DSC-TGA) was carried out with an STA-1500 H thermobalance (PL Thermal Sciences). Experiments were performed at a heating rate of 10 °C/min in an air flow of about 50 mL/min.

Solid-state 52.5 MHz ¹³³Cs MAS NMR spectra were recorded at room temperature on a Varian VXR-400S Spectrometer, equipped with a Doty Scientific Instruments 5 mm Solids MAS Probe. A recycle delay of 0.5 s, an acquisition time of 0.3 s and short 2.5 μs (≈ π/5) pulses, a spectral width of 100 KHz and a spin rate of 4-7 KHz were applied. The lines were referenced to a 1M solution of CsCl in water (δ = 0 ppm).

Recording of solid-state 105.5 MHz ¹¹⁷Na MAS NMR spectra and 130.6 MHz ⁸⁷Rb MAS NMR spectra was performed in a similar way. For both nuclei a recycle delay of 2.0 s, an acquisition time of 0.3 s and short 2.0 μs pulses were used. The resonances were referenced to a 1M solution of NaCl or RbCl (δ = 0 ppm), respectively.

Temperature programmed desorption (TPD) of carbon dioxide was performed on a Micromeritics 2900 TPD/TPR instrument. The calcined materials were first activated at 600 °C for 5 h and subsequently cooled down to 110 °C under a helium flow. Then the activated materials were saturated with dry gaseous
carbon dioxide at this temperature. Physisorbed carbon dioxide was removed by purging under a helium flow at 110 °C till a stable baseline was monitored (about half an hour). The TPD was performed under a helium flow (10 mL/min) by heating from 110 °C to 600 °C with a heating rate of 10 °C/min.

Multipoint BET surface areas, pore volumes and pore size distributions of the materials were calculated from N₂ adsorption/desorption isotherms at -196 °C using a Quantochrome Autosorb 6 apparatus. The samples were outgassed for 16 h under vacuum at 350 °C prior to use.

Catalytic testing

The Michael additions were carried out as follows. A round-bottomed flask containing a mixture of 10 mmol of ethyl cyanoacetate, 10 mmol of ethyl acrylate (or another α,β-unsaturated ester), internal standard and 20 mL of ethanol was heated to reflux. At t = 0 the metal oxide containing MCM-41 (5% m/m with respect to the total amount of reactants) was added to the stirred mixture. The course of the reaction was monitored by GC (CP sil 5CB column). The products were identified by GC-MS, ¹H NMR and ¹³C NMR.

The Knoevenagel condensations were done in the same way, with 10 mmol of benzaldehyde instead of ethyl acrylate and 30 mL of solvent. The solvents used were ethanol or mixtures of H₂O:THF = 1 (THF = tetrahydrofuran) or H₂O:dioxane = 1.

4.3. Results and discussion

Preparation and structural characterization of CsLa/MCM-41

The MCM-41 supported binary cesium-lanthanum oxides were prepared via three different routes (see Experimental section). To study any influence of the framework aluminium content on the stability on the impregnated materials, MCM-41 materials with three different Si/Al ratios (15, 30 and ∞) were used. The first method, via a one-step wet impregnation in methanol, yielded an intraporous homogeneously dispersed binary CsLa-oxide after calcination. In a separate experiment it was found that an equimolar mixture of cesium acetate and lanthanum nitrate after calcination gave the colorless binary mixed oxide CsLaO₂. When the molar amounts of cesium acetate were less than the molar amounts of lanthanum nitrate the same CsLa mixed oxide was formed along with lanthana (confirmed by ¹³Cs MAS NMR). Larger amounts of cesium acetate give CsLaO₂ and Cs₂(CO₃)₂. The classical preparation method for CsLaO₂ is mixing stoichiometric amounts of Cs₂O with La₂O₃ and heating this mixture at 550 °C. Other binary alkali-lanthanide oxides can be prepared via thermal decomposition of the corresponding metal salts and resulted in the same binary oxide product as via the normal route.
Figure 4.1 X-ray powder diffractograms of various CsLa/MCM-41 samples and their parent support (lowest pattern). In each box is the second pattern associated with method A, the third pattern is associated with method B and the upper pattern is associated with method C. A-D all-silica MCM-41 materials; E-H are MCM-41 materials with Si/Al =30; I-L are MCM-41 materials with Si/Al =15.
Chapter 4

The second route in loading the MCM-41 with oxides is by a solid state-like impregnation at 500°C. In this way oxides disperse spontaneously on the internal surface of zeolites and MCM-41. Theoretically it should also be possible to impregnate MCM-41 with an equimolar mixture of cesium acetate and lanthanum nitrate by using this technique. To investigate whether it is possible to prepare intraporous dispersed cesium oxide particles on a lanthanum oxide layer, MCM-41 was also impregnated in two steps. Lanthana tends to spread in a monolayer on silica after thermal decomposition of the silica impregnated lanthanum nitrate salt. The first step is loading MCM-41 with the lanthanum nitrate and subsequently calcining the material. The achieved intraporous lanthana possesses a high degree of lattice disorder which leads to a very active oxide. The last step is impregnating the LaOx loaded material with cesium acetate and calcining it again. Methanol was used as solvent for all the wet impregnations. Loading MCM-41 with a larger salt content resulted in disruption of the MCM-41 framework structure probably due to too strong interactions of the impregnated compounds. It was observed that when these experiments were done in water the MCM-41 framework structure was destroyed by the low pH caused by ionization of hydrated lanthanum cations.

Powder X-ray diffraction was carried out on the original MCM-41 supports and the calcined impregnated MCM-41 materials to examine the crystallinity of the impregnated MCM-41 materials. Figures

![Graph](image)

**Figure 4.2.** Sorption isotherms of nitrogen at -196 °C on a) parent all-silica MCM-41; b) CsLa/MCM-41A; c) CsLa/MCM-41B (dotted line); d) CsLa/MCM-41C.

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4.1A,E,I. show the X-ray diffractograms of the original supports. There is an increase in 'crystallinity' of the three parent MCM-41 supports going up in Si/Al ratio.\textsuperscript{26,29} All-silica MCM-41 seems to be less stable with respect to the one-step wet impregnation compared to the aluminosilicate MCM-41, which is reflected in the decrease of intensity of the $d_{100}$-spacing by a factor 3 (Figure 4.1B). We note that a decrease in X-ray peak intensity is not necessarily an indication of a partial collapse or a lower regularity of the unidimensional pore arrangement.\textsuperscript{30,31} Also consideration should be given to the high electron density of Cs and La loaded molecular sieves when using X-ray diffraction.\textsuperscript{5} Variation in peak intensities in the X-ray diffractograms has also been observed for cesium oxide loaded zeolite X.\textsuperscript{7} The all-silica MCM-41 support displays a better resistance to the solid-state impregnation treatment (Figure 4.1C). This phenomenon is also observed for the other two MCM-41 supports (Figure 4.1G and K). The effect of the two-step wet impregnation on the crystallinity is somewhat comparable with the one-step impregnation. Again the two aluminosilicate MCM-41 samples show the largest preservation of the hexagonal ordering of the framework (Figure 4.1D,H,L). X-ray crystalline CsLaO$_x$ is not observed in any of the impregnated MCM-41 materials whatever the technique used. This shows that the critical dispersion capacity of CsLaO$_x$ on the surface of MCM-41 is not exceeded.\textsuperscript{24}

The adsorption/desorption isotherms of nitrogen on the original all-silica MCM-41 and the corresponding impregnated CsLaO$_x$/MCM-41 materials are illustrated in Figure 4.2. The inflection point of the parent MCM-41 becomes less sharp and shifts to lower relative pressure indicating the creation of smaller mesopores by the impregnation. The decrease in adsorbed nitrogen, expressed as volume per mass unit, should therefore be considered with care. The preservation of the mesoporous framework structure of sample CsLa/MCM-41B and CsLa/MCM-41C, mentioned earlier, is indicated by the shape of the isotherms. The overall influence of the impregnation steps and the calcination treatment on the pore size, pore volume and BET area is summarized in Table 4.1. The large BET surface area of all the CsLa/MCM-41 materials is retained after re-evacuation at high temperature indicating intrapore thermally stable oxide clusters. This contrasts with the reported instability of the Cs/MCM-41 after a second heat treatment.\textsuperscript{15} The decrease in the cumulative mesopore volume and pore size ($d_v$) is in harmony with the presence of the oxide particles inside the pores.\textsuperscript{32,33} The pore size is actually the mean Broekhoff-De Boer diameter assuming cylindrical pores\textsuperscript{34} which appeared in earlier studies to give a reliable pore dimension.\textsuperscript{35,36}

Figure 4.3 shows the DSC-TGA behaviour of CsLa/MCM-41A, an all-silica MCM-41 loaded with cesium acetate and lanthanum nitrate via the one step wet impregnation. A clear exotherm occurs at around 375 °C probably from the decomposition of cesium acetate.\textsuperscript{5} The gradual weight loss between 400 °C and 600 °C might stem from the endothermic decomposition of lanthanum nitrate.\textsuperscript{37} The formation of CsLaO$_x$ occurs probably after the final decomposition of lanthanum nitrate.
Table 4.1. Nitrogen physisorption data of various CsLa/MCM-41 materials

<table>
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<tr>
<th>Sample</th>
<th>Si/Al ratio</th>
<th>Impreg. method</th>
<th>( V_p ) (cm(^3)/g)</th>
<th>( d_p ) (Å)</th>
<th>BET area (m(^2)/g)</th>
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<td>35</td>
<td>699</td>
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<td>847</td>
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<td>3(^f)</td>
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<td>33</td>
<td>662</td>
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a) 1 = one step wet impregnation, 2 = solid-state impregnation and 3 = two steps wet; impregnation; b) cumulative pore volume (between p/p\(_0\) = 0.02 and 0.7); c) the mean Broekhoff-De Boer (assuming cylindrical pores) diameter; \(^{14}\) d) duplicate physisorption measurements after a second re-evacuation cycle at high temperature; e) first step of method 3; f) second step of method 3.

\(^{133}\)Cs NMR

Solid state \(^{133}\)Cs MAS NMR was performed to investigate the nature of Cs in the CsMCM-41 materials. Figure 4.4 shows the \(^{133}\)Cs NMR spectra of Cs\(^+\) ion-exchanged and CsLa/MCM-41 materials. Hydrated Cs\(^+\) ion-exchanged MCM-41 (Figure 4.4a) shows a resonance at -14 ppm with a very small linewidth of 0.2 kHz. The absence of spinning sidebands indicates that the Cs\(^+\) cations are in a quasi isotropic environment due to the high mobility of the hydrated extra-framework Cs\(^+\) cations.\(^{38-42}\) On dehydration, the resonance shifts to -88 ppm (Figure 4.4b) accompanied by considerable line broadening (2.4 kHz) and the appearance of spinning sidebands. This indicates that the Cs\(^+\) cations have lost their high mobility and now sense different chemical surroundings with their associated shielding anisotropies. The MCM-41 supported CsLaO\(_x\) (Fig. 4.4d,e) shows a resonance between -40 and -20 ppm, depending on the Si/Al ratio of the MCM-
Figure 4.3. DSC-TGA diagram of all-silica MCM-41 impregnated with cesium acetate and lanthanum nitrate (CsLa/MCM-41A; method A).

41 support (Table 4.2). The nature of $^{133}$Cs is probably here less ionic compared to Cs$^+$ ion-exchanged MCM-41. Bulk CsLaO$_2$ (Figure 4.4c) exhibits a chemical shift at -21 ppm with a linewidth at half height of 0.4 kHz. The increase of the linewidth in the supported systems suggests that the $^{133}$Cs ions in CsLa-mixed oxides are in a less symmetrical environment. Cs species in all-silica MCM-41 are less shielded than in the aluminosilicate MCM-41 samples and show a similar resonance as in bulk CsLaO$_2$. The latter observation suggests that the Cs species have hardly any or no interaction with the silica type support. This supports the idea that lanthanum is bonded to the MCM-41 support. The behaviour of the $^{133}$Cs resonance, shifting to highfield by increasing the framework aluminium content, suggests that the Cs species are becoming more electropositive which results in a longer Cs-O bond. Considering the difference in chemical shift, there is an interaction of the AlO' with the Cs' cations. Broadening of the peak on increasing the aluminium content of the MCM-41 support is probably due to heteronuclear dipolar coupling with the aluminium. Studies on silica and alumina supported europium oxides show that the bonding of Eu$^{3+}$ to SiO$_2$ is more covalent (less ionic) than that to Al$_2$O$_3$. In contrast to Cs ion-exchanged MCM-41 and CsO$_2$/MCM-41 $^{133}$Cs resonances of CsLa/MCM-41
Figure 4.4. $^{133}$Cs MAS NMR spectra. a) hydrated Cs ion-exchanged MCM-41; b) dehydrated Cs ion-exchanged MCM-41; c) bulk CsLaO$_2$; d) CsLa/MCM-41A with Si/Al = $\infty$; e) dehydrated CsLa/MCM-41A with Si/Al = $\infty$; f) CsLa/MCM-41B with Si/Al = $\infty$; g) CsLa/MCM-41C with Si/Al = $\infty$ and h) CsLa/MCM-41A with Si/Al = 15.
are hardly influenced by hydration (Table 4.2) suggesting that the bonding of Cs⁺ cations with lattice oxygen anions in CsLa-mixed oxide is stronger than that of Cs⁺ with the framework oxygens in Cs⁺ ion-exchanged MCM-41 (Figure 4.4a,b). This is also reflected by the unaffected peak width after dehydration. Bulk CsLaO₂ is sensitive to moisture and becomes sticky upon hydration in agreement with the reported hygroscopic properties of CsLaO₂. The insensitivity to hydration of the supported CsLa-mixed oxides might be due to the interaction of the binary oxide particles with the MCM-41 framework causing a stabilization of the CsLaOₓ lattice. A somewhat comparable observation is found for SiO₂ supported NiO which is much more difficult to reduce than bulk NiO. It is surprising that all the CsLa/MCM-41C samples show a resonance similar to that of the CsLa/MCM-41A samples. This indicates that both wet- impregnation techniques lead to the same binary oxide. The prepared LaOₓ layer inside MCM-41 is probably reactive enough to be converted into a CsLa-mixed oxide. A comparable impregnation technique is reported for the preparation of highly dispersed BaO particles on La₂O₃, namely impregnation of lanthana with barium nitrate followed by drying and calcination. However, the authors did not observe a binary metal-oxide phase like BaLa₂O₄.

Table 4.2. Cs MAS NMR data of various Cs and La-containing MCM-41 samples.

<table>
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<tr>
<th>sample</th>
<th>Si/Al ratio</th>
<th>δ_{hydr} (ppm)</th>
<th>Δν_{1/2} (kHz)a</th>
<th>δ_{dehydr} (ppm)</th>
<th>Δν_{1/2} (kHz)a</th>
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<td>-21</td>
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<td>CsLa/MCM-41A</td>
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<td>-39</td>
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<tr>
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<td>1.7, 1.4</td>
<td>-23, -53</td>
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<td>48</td>
<td>11</td>
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</table>

a) Peakwidth at half height; b) Cs⁺ ion-exchanged MCM-41; c) 5.0 wt% Cs; d) 12.4 wt% Cs; e) 21.9 wt% Cs.
MCM-41 loaded samples prepared by solid-state impregnation exhibit two resonances, at -20 and -44 ppm, indicating two different Cs-containing oxides. Comparing $^{133}\text{Cs}$ MAS NMR data of CsLa/MCM-41 (i = A, B and C) with those of Cs/MCM-41 a large difference in chemical shift is observed. The former shows a resonance at around -30 ppm and the latter at around +20 ppm. Thus in a cesium oxide lattice $^{133}\text{Cs}$ is more deshielded than in CsLaO$_x$ on MCM-41 or in other words shorter Cs-O bonds seem to be present.

$\text{CO}_2$ TPD

The basic strength and the accessibility of the basic sites of the CsLaO$_x$ particles were measured by $\text{CO}_2$ temperature programmed desorption (TPD). The desorbed $\text{CO}_2$ as a function of the temperature of several materials prepared is shown in Figure 4.5. Considering ion-exchanged MCM-41 an interesting phenomenon is observed (Figure 4.5-1,2). In contrast to Cs-MCM-41, Na-MCM-41 gives an intense peak at 200 °C and a desorbed amount of $\text{CO}_2$ (Table 4.3) corresponding to one molecule of $\text{CO}_2$ per 2 Na$^+$ ions. This suggests that supported sodium carbonate-like species are formed. On the other hand, the thermal de-

![Figure 4.5. TPD plots of $\text{CO}_2$ on various CsLa/MCM-41 (solid lines) and other basic materials (dotted lines): 1) Cs ion-exchanged MCM-41; 2) Na ion-exchanged MCM-41; 3) CsLa/MCM-41A with Si/Al = 30; 4) CsLa/MCM-41B with Si/Al = 30; 5) CsLa/MCM-41C with Si/Al = 30; 6) La/MCM-41; 7) Cs/MCM-41; 8) bulk CsLaO$_2$.](image)
composition diagram of Na\textsubscript{2}CO\textsubscript{3} supported on SiO\textsubscript{2} show several maxima at higher temperatures. It is known that alkali ion-exchanged zeolites X and Y are basic, particularly CsX, which contains a high amount of framework aluminium. Despite their basicity these zeolites show hardly any CO\textsubscript{2} desorption.\textsuperscript{1,4} The reason why Na-MCM-41 displays a large CO\textsubscript{2} desorption, in contrast to its moderate basicity, is probably the poor local crystallinity around the extra-framework Na\textsuperscript{+} cations and a weaker bounding of Na\textsuperscript{+} cations to the negatively charged framework oxygens (see \textsuperscript{23}Na NMR data) compared to Cs\textsuperscript{+} cations.\textsuperscript{45} As the Lewis base sites are considered to be oxygens adjacent to the oxygens connected directly to the extra-framework alkali cations, these basic sites are more negatively charged when Cs\textsuperscript{+} cations are bonded at the framework. So Cs\textsuperscript{+} is expected to induce stronger basic sites, but probably the CO\textsubscript{2} probe is too large to approach these.\textsuperscript{45} Earlier we reported that strong basic sites in MCM-41 are created by impregnation with cesium acetate followed by

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<th>sample</th>
<th>Si/Al</th>
<th>ratio metal per desorbed CO\textsubscript{2}</th>
<th>desorbed CO\textsubscript{2}</th>
<th>T\textsubscript{\text{max}}</th>
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</tbody>
</table>

a) Ion-exchanged MCM-41; b) 3.1 wt% La; c) 5.8 wt% La; d) 15.0 wt% La; e) 9.4 wt% Cs; f) 19.2 wt% Cs.
thermal decomposition.\textsuperscript{16} The CsLa/MCM-41A materials show a broad peak around 195°C suggesting a lower additional basicity compared to Cs/MCM-41 (Table 4.3). The basicity of CsLa/MCM-41 is more comparable with that of La/MCM-41 than with that of Cs/MCM-41, which is in harmony with the fact that the basic nature of CsLaO\textsubscript{x} has more lanthanide character than cesium oxide character (Figure 4.5-6,7). Energies of solution of alkali-metal dopants with oxygen vacancy compensation correspond well with those of binary metal oxides.\textsuperscript{46} These calculations underline the observed basic nature of the CsLaO\textsubscript{x} supported MCM-41 which exhibits the character of La\textsubscript{2}O\textsubscript{3} modified by the addition of Cs\textsubscript{2}O.

The accessibility of the CsLa-mixed oxides is correlated with the amount of desorbed CO\textsubscript{2} per metal atom. Thereby a reasonable correlation is achieved (Table 4.3), indicating that small oxide clusters are formed inside MCM-41. The stability of the CsLa-mixed oxides was studied by duplicate TPD experiments. In contrast to Cs/MCM-41,\textsuperscript{16} all CsLa/MCM-41 samples show much greater stability reflected by the desorption of a similar amount of CO\textsubscript{2} desorbed per incorporated metal after duplicate measurements. Bulk CsLaO\textsubscript{x} showed one peak at 400°C (Figure 4.5). The amount desorbed CO\textsubscript{2} corresponds to 99 metal atoms. These data are consistent with the common fact that supported metal oxides possess a lower basicity and a larger accessibility of the basic sites than bulk oxides due to the dispersity of small oxide clusters.\textsuperscript{17,41}

The CsLa/MCM-41B samples, prepared by solid state impregnation at high temperature, show two maxima in the TPD diagram. One peak at 195°C and one at 400°C. The former peak is probably dispersed CsLa-mixed oxide and the latter peak might be crystallites of XRD-invisible CsLaO\textsubscript{x} (\textit{vide infra}) showing a peak comparable with bulk CsLaO\textsubscript{x}. The tendency of metal salts to form large metal oxide particles is not uncommon during solid-state thermolysis.\textsuperscript{25}

\textit{Other MLa/MCM-41 systems (M = Na, K and Rb) and Na-MCM-41}

The basicity of CsLa/MCM-41A was compared with that of alkali-lanthanum-oxide containing all-silica MCM-41 (MLa/MCM-41; M = Na, K and Rb). Figure 4.6a-d show the CO\textsubscript{2} TPD plots of MLa/MCM-41 which are normalized to the atomic weight and the duplicate measurements (Figure 4.6a-d). Desorption occurs at higher temperatures for M = Rb and Cs, indicative of a higher basicity. A strong decrease in the amount of desorbed CO\textsubscript{2} for the duplicate measurements suggests clustering of the oxidative particles. CsLa/MCM-41A shows also a decrease in peak intensity, but an increase in the amount of desorbed CO\textsubscript{2} at the higher temperature region can be observed. The profile of the CO\textsubscript{2} TPD plot from NaLa/MCM-41, which possesses two distinct maxima, indicates the presence of several types of oxidative species.\textsuperscript{23}Na MAS NMR on bulk NaLaO\textsubscript{x} and NaLa/MCM-41 revealed indeed different \textsuperscript{23}Na resonances (Table 4.4). Beside the resonance of hydrated Na\textsuperscript{+} a large resonance at -6.7 ppm was observed. Rehydration of the samples occurred
Figure 4.6. TPD plots of CO₂ on various all-silica MLa/MCM-41 (M = Na, K, Rb or Cs) and their duplicate measurements (index '). a) NaLa/MCM-41; b) KLa/MCM-41 (dotted line); c) RbLa/MCM-41 (dashed line) and d) CsLa/MCM-41A.

during transfer in the spinner. Comparing hydrated NaLa/MCM-41 with hydrated Na-MCM-41 shows that the nature of the Na⁺ ions are comparable in both materials. This suggests that hydrated NaLa/MCM-41 does not contain a NaLa-mixed oxide. The small line at -2.5 ppm of hydrated Na-MCM-41 (0.3 kHz) represents an average chemical shift due to the rapid motion of the Na⁺ ions.⁴⁷ Dehydrated Na-MCM-41 shows a resonance at -13.4 ppm with a linewidth of 1.8 kHz. Considering the large quadrupole moment and low spin number of ²³Na, it can be suggested that the latter line does not result from averaging. This indicates that in the dehydrated state the Na⁺ cation mobility has decreased drastically. RbLaO₂ shows in the ⁸⁷Rb MAS NMR spectrum two resonances: a main resonance at -39.1 ppm and a shoulder at -35.5 ppm, probably due to hydration. In contrast, the CO₂ TPD profile of KLa/MCM-41 contains just one maximum, so this binary oxide might consist of one K-species. XPS studies on binary NaLa-oxide and ternary NaLaNb-oxide catalysts revealed that sodium seems situated as amorphous Na₂O on the surface or in the bulk of the catalysts.⁴⁸ In general it is expected that the role of Na is to poison the La₂O₃ surface.⁴⁶ The presented results for the binary KLa-oxide and RbLa-oxide are in agreement with reported calculations suggesting formation of an MLaO₂ (M = K or Rb) compound at a 1:1 atomic-ratio.⁴⁶
Table 4.4. $^{23}$Na and $^{87}$Rb MAS NMR data of hydrated Na-MCM-41 and (MCM-41 supported) MLaO$_x$ (M = Na or Rb).

<table>
<thead>
<tr>
<th>sample</th>
<th>$^{23}$Na $\delta$ (ppm)*</th>
<th>$^{87}$Rb $\delta$ (ppm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-MCM-41$^{b}$</td>
<td>-2.5 (-13.4)$^{e}$</td>
<td>$^{87}$Rb</td>
</tr>
<tr>
<td>NaLaO$_x$</td>
<td>4.3, -0.2, -22.6$^{d}$</td>
<td></td>
</tr>
<tr>
<td>NaLa/MCM-41</td>
<td>-6.7, -15$^{e}$</td>
<td>-35.5,$^{6e}$ -39.1</td>
</tr>
<tr>
<td>RbLaO$_x$</td>
<td></td>
<td>not detected$^{f}$</td>
</tr>
<tr>
<td>RbLa/MCM-41</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) No spinning sidebands are observed; b) Na$^+$ ion-exchanged MCM-41; c) dehydrated Na-MCM-41 at 450°C; d) hydrated alkali oxide; e) shoulder; f) spectral width of 100 KHz.

In summary it can be concluded that MCM-41 is loaded with a thermally stable CsLaO$_x$ layer structure which is independent of the wet-impregnation technique used. These mixed oxides are probably anchored on the pore walls of the support via La-O bonds.$^{36,49}$ On the basis of the $^{133}$Cs NMR data it might be suggested that the Cs$^+$ cations are situated in the toplayer of the binary oxide and not as a single surface Cs$_2$O species. Hereby new basic sites are generated compared to lanthana-containing MCM-41. This hypothesis is underlined by the observation that La/MCM-41 is inactive in the base catalyzed liquid phase reactions tested in contrast with CsLa/MCM-41 (vide infra). Supported lanthana has the tendency to spread in a monolayer onto silica, the intraporous CsLaO$_x$ is assumed to be dispersed in a submonolayer.$^{24,27}$

**Liquid phase catalysis**

The catalytic properties of the CsLa/MCM-41 materials were tested in liquid phase Michael additions and Knoevenagel condensations. CsLa/MCM-41 was found to catalyze the Michael addition of vinyl cyanacetate to ethyl acrylate (Figure 4.7). Besides formation of the mono-adduct 1, compound 2, a bis-adduct achieved by a double Michael-type addition,$^{50}$ is produced consecutively. The selectivity (at 30% m/m ethyl acrylate conversion) to 1 is slightly lower using mesoporous CsLa/MCM-41 than when applying silica-supported CsLa-mixed oxide. Various catalysts can be compared by expressing their specific activity $A_{st}$ as mmol/h.g. Table 4.5 illustrates that CsLa/MCM-41B gives a higher specific activity than the weaker basic CsLa/MCM-41A and CsLa/MCM-41C. It is noteworthy that CsLa/SiO$_2$ requires a higher metal loading to achieve an activity comparable with CsLa/MCM-41. The highest specific activity was observed for Cs/MCM-41, but this is accompanied by a poor selectivity to both 1 and 2 due to much by-product formation.
Binary cesium-lanthanum oxide supported on MCM-41: a new stable heterogeneous basic catalyst

Figure 4.7. Two-step Michael addition of ethyl cyanoacetate to ethyl acrylate.

In contrast to the Knoevenagel condensation of ethyl cyanoacetate with benzaldehyde,\textsuperscript{15} Na\textsuperscript+ ion-exchanged MCM-41 (Na-MCM-41) was inactive in the present Michael addition. Although the basicity of CsLa/MCM-41 is quite mild, it shows a very good performance in this reaction. This indicates that addition of CsLaO\textsubscript{x} enhances the activity of MCM-41 substantially in the Michael addition with the low reactive ethyl acrylate.
Table 4.5. Michael addition of ethyl acrylate (10 mmol) and ethyl cyanoacetate (10 mmol) with either MCM-41 or SiO₂-supported cesium oxide or cesium/lanthanum oxide in refluxing ethanol at 30% m/m ethyl acrylate conversion.

<table>
<thead>
<tr>
<th>catalyst*</th>
<th>Si/Al ratio</th>
<th>( A_{\text{wt}} ) (mmol/h.g)(^b)</th>
<th>selectivity 1 : 2 (%)(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsLa/MCM-41A(^d)</td>
<td>∞</td>
<td>39.3</td>
<td>60 : 40</td>
</tr>
<tr>
<td>CsLa/MCM-41B(^d)</td>
<td>∞</td>
<td>62.2</td>
<td>47 : 53</td>
</tr>
<tr>
<td>CsLa/MCM-41C(^d)</td>
<td>∞</td>
<td>39.3</td>
<td>43 : 57</td>
</tr>
<tr>
<td>CsLa/MCM-41C(^d)</td>
<td>∞</td>
<td>40.6</td>
<td>44 : 56</td>
</tr>
<tr>
<td>Cs/MCM-41(^f)</td>
<td>12</td>
<td>954</td>
<td>8 : 33*</td>
</tr>
<tr>
<td>CsLa/SiO₂(^h)</td>
<td>∞</td>
<td>32.0</td>
<td>64 : 36</td>
</tr>
<tr>
<td>Cs/SiO₂(^i)</td>
<td>∞</td>
<td>289</td>
<td>36 : 42*</td>
</tr>
</tbody>
</table>

\(a\) 5% m/m catalyst based on total amount of substrates; \(b\) specific activity at 30% m/m ethyl acrylate conversion; \(c\) Product selectivity at 30% m/m ethyl acrylate conversion; \(d\) 5% m/m Cs and 5% m/m La on MCM-41; \(e\) re-used CsLa/MCM-41C catalyst after a second re-activation cycle at 500 °C for 5h; \(f\) 5% m/m Cs on MCM-41; \(g\) formation of by-products; \(h\) Cab O-sil M5 loaded with 20 wt% of Cs metal and 20 wt% of La metal; \(i\) Cab O-sil M5 loaded with 5% m/m Cs.

The anion of ethyl cyanoacetate does not react simply with α,β-unsaturated ketones; this reaction can only proceed when either the anionic intermediate is stabilized by another electronegative element or when the α,β-unsaturated ketone is sufficiently activated via coordination to a Lewis acid center. The performance of CsLa/MCM-41 is ascribed to the presence of lanthanum which activates the ethyl acrylate by coordination to the ester oxygens.\(^{31,32}\) The product selectivities are probably also controlled by the mesoporous MCM-41 support. The reaction of the less activated ethyl trans-crotonate (Figure 4.8) was not achieved. However, ethyl trans-cinnamate could be reacted with ethyl cyanoacetate in a reasonable conversion of 20% m/m after 2h at high temperature (160 °C; cyclohexanone as solvent). Electronic effects or shielding of the double bound

![Structure of ethyl trans-crotonate (left) and ethyl trans-cinnamate (right).](image)

Figure 4.9. Structure of ethyl trans-crotonate (left) and ethyl trans-cinnamate (right).
by the β-alkyl/aryl group of the α,β-unsaturated ketones might be responsible for the lower activity and the observed selectivities. Pore size effects also may not be excluded as indicated by the selectivity of the reaction with ethyl trans-cinnamate giving exclusively the corresponding mono-adduct. Pore size effects were reported earlier for Cs/MCM-41 in the double Michael addition of diethyl malonate with neopentyl glycol diacrylate.16

The basicity of CsLa/MCM-41 is too weak to catalyze the Michael addition of diethyl malonate (pK_a = 13.3) with ethyl acrylate under the studied conditions. This strengthens the observation that the supported CsLa-oxides are not subject to leaching towards homogeneous cesium hydroxide. We noted that a stoichiometric amount of homogeneous CsOH with respect to the Cs loading of CsLa/MCM-41 (40 μmol of CsOH) catalyses the reaction under the same conditions within one hour, this was, however, accompanied with a substantial amount of by-products.

The re-usability of the CsLa/MCM-41 catalysts was studied by filtering a reaction mixture, washing with acetone and re-activating the catalyst at 500 °C for 5 h. Thereby no weight loss was observed after the heating cycle. The performance of re-used CsLa/MCM-41C catalyst is given in entry 4 in Table 4.5. A similar A_\text{act} was observed which reflects again the thermal stability of these materials during regeneration and also supports the assumed binding of the binary oxides to the MCM-41 framework.

![Figure 4.9](image)

**Figure 4.9.** Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate (R = CN) or ethyl acetoacetate (R = COMe).

The Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate (pK_a ≤ 9) served to study the capability of CsLa/MCM-41 to be used in aqueous media (Figure 4.9). All the CsLa/MCM-41A catalysts gave large conversions (Table 4.6) together with >99 % selectivity to the α,β-unsaturated esters under mild conditions. Apperently the second step (dehydration of the alcohol intermediate) in the Knoevenagel condensation is fast. Interestingly, CsLa/MCM-41A showed a better performance in ethanol than in H_2O/THF (1:1 v/v). Unexpected solvent effects were also found in the Knoevenagel condensation catalyzed by silicon oxynitride53 and the basic clay xonolite.54 The former showed a higher conversion in ethanol than in THF. Xonolite was active in the following order H_2O > ethanol > THF. We already reported that the ba-
Table 4.6. Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate or ethyl acetoacetate (R = CN or COMe, respectively) with CsLa/MCM-41, Na-MCM-41 and Cs-MCM-41 in three refluxing protic solvents.

<table>
<thead>
<tr>
<th>catalyst(a)</th>
<th>Si/Al ratio</th>
<th>R(b)</th>
<th>solvent(c)</th>
<th>conversion ((% m/m)^d)</th>
<th>(A_{\text{act}}) ((\text{mmol/\text{h.g}})^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsLa/MCM-41A</td>
<td>∞</td>
<td>CN</td>
<td>EtOH</td>
<td>86</td>
<td>89.2</td>
</tr>
<tr>
<td>CsLa/MCM-41A</td>
<td>30</td>
<td>CN</td>
<td>EtOH</td>
<td>95</td>
<td>97.8</td>
</tr>
<tr>
<td>CsLa/MCM-41A</td>
<td>∞</td>
<td>CN</td>
<td>H(_2)O/THF</td>
<td>58</td>
<td>51.7</td>
</tr>
<tr>
<td>CsLa/MCM-41A</td>
<td>∞</td>
<td>CN</td>
<td>H(_2)O/THF</td>
<td>46</td>
<td>54.3</td>
</tr>
<tr>
<td>CsLa/MCM-41A</td>
<td>30</td>
<td>CN</td>
<td>H(_2)O/THF</td>
<td>53</td>
<td>55.5</td>
</tr>
<tr>
<td>Na-MCM-41(b)</td>
<td>13</td>
<td>CN</td>
<td>H(_2)O/THF</td>
<td>40</td>
<td>30.1</td>
</tr>
<tr>
<td>Cs-MCM-41(b)</td>
<td>13</td>
<td>CN</td>
<td>H(_2)O/THF</td>
<td>55</td>
<td>43.3</td>
</tr>
<tr>
<td>CsLa/MCM-41A</td>
<td>30</td>
<td>COMe</td>
<td>H(_2)O/dioxane</td>
<td>21</td>
<td>20.7</td>
</tr>
</tbody>
</table>

\(a\) 5% \(m/m\) catalyst based on total amount of substrates (10 mmol of each); b) Reactant R = CN is ethyl cyanoacetate and R = COMe is ethyl acetoacetate; c) the ratio of the solvent mixtures are 1:1 \(v/v\); d) enolate conversion after 1 hour; e) specific activity after 1 hour; f) 4% \(m/m\) re-used CsLa/MCM-41A catalyst after filtration and drying; g) ion-exchanged MCM-41.

Sicity of alkali ion-exchanged MCM-41 was high enough to catalyze also this reaction.\(^{15}\) Table 4.6 illustrates that the specific activities \(A_{\text{act}}\) of Na-MCM-41 and Cs-MCM-41 in H\(_2\)O/THF are somewhat lower than that of CsLa/MCM-41. A larger difference, about a factor 5, would be achieved if the specific activity was expressed as mol/h.mol\(_{\text{ka,mol}}\). Weaker acidic enolates like ethyl acetoacetate (pK\(_{a}\) = 10.5; 8.0 % enol)\(^{35}\) could also be deprotonated under less severe conditions (solvent: H\(_2\)O/dioxane 1:1, 100 °C).

The re-use of the CsLa/MCM-41A catalyst is again demonstrated by a similar \(A_{\text{act}}\) after filtration (entry 4 in Table 4.6) while the filtrate showed no activity. In all cases no indication of catalysis by leached homogeneous basic metallic species was found.

The CsLa/MCM-41 materials were tested in ordinary glass reactors without taking any special precautions (CO\(_2\)-free atmosphere and dry glassware).\(^1\) This confirms again that these MCM-41 supported CsLa-mixed oxides are easy to handle in sharp contrast with La/MCM-41. The lanthana supported MCM-41 materials appeared to be inactive in all the mentioned liquid phase reactions. This pertains to a much lesser extent to the earlier reported Cs/MCM-41 materials which are very active in liquid phase catalysis, but are very moisture sensitive.\(^{16}\)
4.4. Conclusions

Heterogeneous mesoporous stable basic catalysts are prepared by impregnation of MCM-41 with equimolar amounts of cesium acetate and lanthanum nitrate followed by drying and calcination. Loading of CsLaO₅ on MCM-41 via solid state-like impregnation at high temperature can also be achieved. CsLa/MCM-41 materials possess small intraporous thermally stable CsLaO₅ clusters with a submonolayer-shape having a mild basicity. The use as a basic catalyst in aqueous media is displayed in the Knoevenagel condensation. The combination of the CsLaO₅ layer and the mesoporous framework alters the product selectivity in the two-step Michael addition of ethyl acrylate and ethyl cyanoacetate. The catalysts can be re-used after a solvent flush and a high temperature cycle without loss of activity.

References

Chapter 4

30. See chapter 3.
Novel isomerization of ω-phenylalkanals to phenyl alkyl ketones over cesium (lanthanum) oxide supported on mesoporous aluminosilicate molecular sieves and related materials*

5-1. Introduction

Aldehyde isomerization over solid catalysts is an interesting and attractive route to ketones.¹ Some examples of branched-aldehyde isomerizations over different types of catalyst have been reported. The pentasil zeolites B-MFI and Fe-MFI are active at high temperature (400 °C) in this reaction and show high selectivities to the corresponding ketones.¹ ² A less selective catalyst is the K₂CO₃ promoted CrZnMn-oxide system.³ In this case the reactions were also carried out in the gas-phase at high temperatures and under addition of water vapour.¹ ³ In contrast to the radical mechanism proposed for the latter case,³ the mechanism of the aldehyde-ketone isomerization over pentasil zeolites is proposed to go exclusively via an α-methyl, α-phenyl or a α-benzyl shift,¹ because a hierarchical order in R-shift was observed for aromatic aldehydes over pentasil zeolites. Rearrangement of 2-phenylpropanal gave a methyl shift instead of a phenyl shift which results in the selective formation of phenylacetone.¹ ²

![Chemical Structure](image)

Recently we reported on the strongly basic properties of cesium oxide supported on MCM-41,⁴ ⁵ a mesoporous molecular sieve of the M41S family.⁶ A disadvantage of this system was the poor regenerability which was reflected by a loss in surface area and by clustering of the oxide particles.⁵ We succeeded to improve the thermal stability substantially and to lower its moisture sensitivity by addition of equimolar amounts of lanthanum which gave the MCM-41 supported binary cesium-lanthanum oxide.⁷ In spite of their mild basicity these CsLa/MCM-41 materials showed an interesting performance in the liquid-phase Michael addition of ethyl cyanoacetate to ethyl acrylate under mild conditions.⁷

Novel isomerization of α-phenylalkanals to phenyl alkyl ketones over cesium (lanthanum) oxide on...

Here we report on the unexpected behaviour of the binary CsLa-oxide supported on mesoporous aluminosilicate MCM-41\textsuperscript{8} and HMS\textsuperscript{8} materials, and on an amorphous silica-alumina (ASA) support in the presence of aromatic aldehydes in the liquid phase. All these basic catalysts rearranged selectively the α-phenylalkanals to phenyl alkyl ketones in the liquid phase. Factors like basicity and the presence of mesopores have an influence on the activity and selectivity to the phenyl alkyl ketone and the α,β-unsaturated ketone, a side-product resulting from the aldol condensation. A tentative mechanism is advanced which explains the novel rearrangement.

5-2. Experimental

Materials

The mesoporous aluminosilicate MCM-41 and HMS materials having both a Si/Al ratio of 15 were prepared according to the literature procedures of 7 and 8, respectively. The amorphous silica-alumina (ASA) supports were kindly donated by Akzo Nobel Chemicals Amsterdam, The Netherlands. These are a low alumina containing ASA (LA-SHPV; denoted as ASA1) with 12.0\% of Al\textsubscript{2}O\textsubscript{3} and a high alumina containing ASA (HA-SHPV; denoted as ASA2) with 25.0\% of Al\textsubscript{2}O\textsubscript{3}. The ASAs were prepared, according to the manufacturer, by precipitating alumina on silica particles. The γ-Al\textsubscript{2}O\textsubscript{3} was purchased from Merck.

The supported CsLa-oxide materials were prepared as follows. A mixture containing 5 g of the support, 5 wt\% Cs (added as cesium acetate, ACROS), an equimolar amount of lanthanum nitrate hexahydrate (Merck) and 10 g of methanol was stirred at room temperature. After 3 h the methanol was evaporated quickly under vacuum and the material was subsequently calcined at 500 °C for 5 h. The cesium oxide containing materials were prepared in the same way except that lanthanum nitrate was omitted. Both MCM-41 and HMS were Na\textsuperscript{+} ion-exchanged in a 1M NaCl aqueous solution at 60 °C overnight, and the materials obtained will be denoted as Na-MCM-41 and Na-HMS, respectively. The acid sites of the two ASA supports and that of γ-Al\textsubscript{2}O\textsubscript{3} were neutralized with 0.1M NaOH aqueous solution, washed and dried prior to the metal salt-impregnation.

Techniques

Structural characterization was performed by powder X-ray diffraction on a Philips PW 1840 diffractometer using monochromated CuKα radiation. Patterns were recorded from 1° to 40° (2θ) with a resolution of 0.02° and a count time of 1 s at each point.

Temperature programmed desorption (TPD) of carbon dioxide was performed on a Micromeritics 2900 TPD/TPR instrument. The calcined materials were first activated at 600 °C for 5 h and subsequently
cooled down to 110 °C under a helium flow. Then the activated materials were saturated with dry gaseous carbon dioxide at this temperature. Physiosorbed carbon dioxide was removed by purging under a helium flow at 110 °C till a stable baseline was monitored (about half an hour). The TPD was performed under a helium flow (10 mL/min) by heating from 110 °C to 600 °C with a heating rate of 10 °C/min.

Multipoint BET surface areas, pore volumes and pore size distributions of a number of materials were calculated from N₂ adsorption/desorption isotherms at -196 °C using a Quantochrome Autosorb 6 apparatus. The samples were outgassed for 16 h under vacuum at 350 °C prior to use.

Catalysis

Phenylacetaldehyde, phenylacetone and 2-phenylpropanaldehyde were purchased from Aldrich and 3-phenylpropanaldehyde from Merck. All the commercial reactants were distilled prior to use. The non-commercially available reactants 4-phenylbutyraldehyde and 2-(4-methoxyphenyl)acetaldehyde were prepared according to 9 from the corresponding primary alcohol purchased from Fluka and Aldrich, respectively, by using oxaly chloride and dimethyl sulfate. The 2- and 3-methoxy-substituted phenylacetaldehydes and 2,6-dichlorophenylacetaldehyde were prepared according to 10 from the corresponding benzyl cyanide purchased from Aldrich and ACROS.

The pre-activated catalysts (1 wt% with respect to the total amount of ω-phenylalkanals) were allowed to react with 5 g of the ω-phenylalkanal in a dry glass reactor at 100 °C under air. No solvents were applied. The course of the reaction was monitored by GLC using a capillary CP silica column. Aliquots were taken at suitable time intervals and were analyzed by GC-MS. Products were isolated by vacuum distillation or column chromatography and characterized by ¹H and ¹³C NMR.

5-3. Results

Catalysis

Studying the conversion of phenylacetaldehyde over the supported cesium oxide and binary cesium-lanthanum oxide catalysts containing 5 wt% Cs and 10 wt% CsLa (Cs : La atomic ratio = 1 : 1), respectively, in the solvent-free procedure at 100 °C two main products, acetophenone (1) and 2,4-diphenyl-2-butenal (2), were observed (Figure 5.1). The presence of acetophenone implies an isomerization of phenylacetaldehyde, whereas 2 will be formed by the commonly encountered base catalyzed self-aldol condensation leading to 2,4-diphenyl-3-hydroxybutanal followed by dehydration (Figure 5.1). In all cases traces of ethylbenzene were observed.

Table 5.1 illustrates the performance of various basic catalysts in the liquid-phase conversion of
Novel isomerization of ω-phenylalkanals to phenyl alkyl ketones over cesium (lanthanum) oxide on...

![Chemical structures](image)

Figure 5.1. The reactions of phenylacetaldehyde over Cs en CsLa-oxide containing catalysts.

Phenylacetaldehyde. All the catalysts tested are very active systems as indicated by the specific activity $A_{sp}$.

Table 5.1. The performance of phenylacetaldehyde on various CsLa-oxide and Cs-oxide supported catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$A_{sp}$ (mmol.g$^{-1}$.h$^{-1}$)$^a$</th>
<th>product selectivity (%)$^b$</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs/MCM-41</td>
<td>954</td>
<td>36.4</td>
<td>32.8</td>
<td></td>
</tr>
<tr>
<td>Cs/Na-MCM-41</td>
<td>736</td>
<td>46.4</td>
<td>12.8</td>
<td></td>
</tr>
<tr>
<td>Cs/HMS</td>
<td>209</td>
<td>61.2</td>
<td>25.6</td>
<td></td>
</tr>
<tr>
<td>Cs/Na-HMS</td>
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<td>59.3</td>
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<td></td>
</tr>
<tr>
<td>Cs/ASA1</td>
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<td>15.1</td>
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<tr>
<td>Cs/ASA2</td>
<td>3384</td>
<td>60.3</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Cs/Al$_2$O$_3$</td>
<td>1589</td>
<td>-</td>
<td>42.0</td>
<td></td>
</tr>
<tr>
<td>CsLa/MCM-41</td>
<td>309</td>
<td>36.5</td>
<td>40.6</td>
<td></td>
</tr>
<tr>
<td>CsLa/Na-MCM-41</td>
<td>373</td>
<td>50.1</td>
<td>37.8</td>
<td></td>
</tr>
<tr>
<td>CsLa/HMS</td>
<td>719</td>
<td>65.9</td>
<td>37.8</td>
<td></td>
</tr>
<tr>
<td>CsLa/Na-HMS</td>
<td>425</td>
<td>39.0</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>CsLa/ASA1</td>
<td>250</td>
<td>11.1</td>
<td>78.4</td>
<td></td>
</tr>
<tr>
<td>CsLa/ASA2</td>
<td>702</td>
<td>31.3</td>
<td>23.6</td>
<td></td>
</tr>
<tr>
<td>CsLa/Al$_2$O$_3$</td>
<td>1041</td>
<td>33.1</td>
<td>29.4</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Specific activity at 30% phenylacetaldehyde conversion; $^b$ by-product is ethylbenzene.
expressing the number of mmol substrate converted per gram catalyst per hour. The Al₂O₃ and the high alumina-containing ASA2 systems show the highest activities, but the selectivities to the side-product ethylbenzene are in both cases substantial. It was checked that in the absence of a catalyst no conversion is occurring. Considering the mesoporous catalysts it can be noticed that the most active catalyst is Cs/MCM-41. The cesium analogue Cs/HMS shows a lower activity, but a largely improved selectivity to acetophenone. A worsening rather than an improvement of the activity was achieved when the extraframework H⁺ ions were ion-exchanged with Na⁺ ions. A similar phenomenon was observed for MCM-41 although the decrease in activity here is much less. Therefore it is suggested that the cesium oxide particles are most probably situated near the aluminum sites of the framework and that Na⁺ ions influence the basicity of the supported metal oxides (vida infra).

Generally the basicity of the supported CsLa-oxides is lower than that of the Cs oxide analogues (as shown by CO₂-TPD). Consequently the activities of the CsLa-oxide systems are lower than those of the Cs-oxide ones. In general the mesoporous Cs and CsLa-oxide catalysts show a higher selectivity to acetophenone

Table 5.2. 3-phenylpropionaldehyde over various CsLa-oxide and Cs-oxide supported mesoporous catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>( A_{\text{wt}} ) (mmol g⁻¹ h⁻¹)</th>
<th>product selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>25.8</td>
<td>60.1</td>
</tr>
<tr>
<td>Cs/Na-MCM-41</td>
<td>24.4</td>
<td>67.8</td>
</tr>
<tr>
<td>Cs/HMS</td>
<td>15.7</td>
<td>53.0</td>
</tr>
<tr>
<td>Cs/Na-HMS</td>
<td>12.8</td>
<td>24.2</td>
</tr>
<tr>
<td>Cs/ASA1</td>
<td>16.3</td>
<td>68.4</td>
</tr>
<tr>
<td>Cs/ASA2</td>
<td>28.3</td>
<td>66.4</td>
</tr>
<tr>
<td>Cs/Al₂O₃</td>
<td>34.3</td>
<td>72.0</td>
</tr>
<tr>
<td>CsLa/MCM-41</td>
<td>16.4</td>
<td>77.1</td>
</tr>
<tr>
<td>CsLa/Na-MCM-41</td>
<td>16.8</td>
<td>33.7</td>
</tr>
<tr>
<td>CsLa/HMS</td>
<td>23.5</td>
<td>60.3</td>
</tr>
<tr>
<td>CsLa/Na-HMS</td>
<td>19.4</td>
<td>53.0</td>
</tr>
<tr>
<td>CsLa/ASA1</td>
<td>11.1</td>
<td>57.3</td>
</tr>
<tr>
<td>CsLa/ASA2</td>
<td>23.8</td>
<td>78.5</td>
</tr>
<tr>
<td>CsLa/Al₂O₃</td>
<td>16.3</td>
<td>44.0</td>
</tr>
</tbody>
</table>

a) Specific activity at 2 h reaction time.
Novel isomerization of \(\omega\)-phenylalkanals to phenyl alkyl ketones over cesium (lanthanum) oxide on...

1 than to the more bulky \(\alpha,\beta\)-unsaturated aldehyde 2. The HMS systems show even a larger preference in producing 1. Cs/ASA2 is exceptional in showing a very low selectivity to 2 together with a high selectivity to 1. Ethylbenzene is produced as a minor product except over Cs/Al₂O₃ and Cs/ASA1.

Remembering the considerable high specific activity of ASA2 and Al₂O₃ systems in the conversion of phenylacetaldehyde here the catalysts show activities which differ actually not very much from those of the other catalysts. Within the supported Cs-oxide series, the Cs/HMS and Cs/Na-HMS materials show, beside the lowest \(A_{\text{a}}\), a high selectivity to the \(\alpha,\beta\)-unsaturated aldehyde 4.

The conversion of 3-phenylpropionaldehyde is depicted in Table 5.2. Generally, this reaction proceeds more slowly than that of phenylacetaldehyde which is reflected by the lower \(A_{\alpha}\) of the catalysts. In line with the previous reaction, mainly propiophene, 3, and the dehydrated aldol product 2-benzyl-4-phenyl-2-butenal, 4, are produced (Figure 5.2). Besides, very small amounts of propylbenzene are noticed.

![Figure 5.2. The reactions of 3-phenylpropionaldehyde over Cs en CsLa-oxide containing catalysts.](image)

Finally in this series Ph(CH₂)ₙCHO (1 \(\leq\) n \(\leq\) 3), the conversion of 4-phenylbutyraldehyde was

![Figure 5.3. The reactions of 4-phenylbutyraldehyde over Cs and CsLa-oxide containing catalysts.](image)
**Table 5.3.** 4-phenylbutyraldehyde over various CsLa-oxide and Cs-oxide supported mesoporous catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$A_w$ (mmol·g$^{-1}$·h$^{-1}$)$^a$</th>
<th>product selectivity (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs/MCM-41</td>
<td>8.4</td>
<td>83.7</td>
<td>16.3</td>
<td></td>
</tr>
<tr>
<td>Cs/HMS</td>
<td>3.6</td>
<td>74.3</td>
<td>25.7</td>
<td></td>
</tr>
<tr>
<td>CsLa/MCM-41</td>
<td>4.7</td>
<td>80.6</td>
<td>19.4</td>
<td></td>
</tr>
<tr>
<td>CsLa/Na-MCM-41</td>
<td>4.9</td>
<td>81.2</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td>CsLa/ASA1</td>
<td>7.3</td>
<td>83.7</td>
<td>16.3</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Specific activity at 2 h 4-phenylbutyraldehyde conversion.

monitored in order to examine in this type of reaction any systematics. Figure 5.3 illustrates that also this reaction gave the rearranged compound, butyrophenone, 5, and formation of the $\alpha,\beta$-unsaturated aldehyde 2-(ethylphenyl)-6-phenyl-2-hexenal, 6. All the tested catalysts show almost the same product selectivity (Table 5.3) and no traces of butylbenzene could be detected.

Several related reactants were tested in order to elucidate the mechanism of this unknown reaction. First, phenylacetone did not rearrange to propiophenone, but remained unconverted at temperatures up to 170 °C. When 2-phenylpropionaldehyde was subjected to the oxide catalysts only self-aldol condensation was observed leading to 2,4-diphenyl-3-hydroxy-2-methyl-pentanal. In case of an intramolecular aromatic substitution in the case of the phenylacetaldehyde to acetophenone rearrangement substituents at the phenyl group might have an effect on the product distribution and also on the rate of the reaction. It appeared that (3-methoxyphenyl)acetaldehyde was inactive whereas (4-methoxyphenyl) acetaldehyde gave exclusively 4-methoxyacetophenone 7 (Figure 5.4). Table 5.4 shows that the performances of all the Cs and CsLa-oxide containing catalysts are similar. Interestingly the conversion of (2-methoxyphenyl)acetaldehyde over the metal-oxide catalysts gives only the dehydrated-aldol product 2,4-di-(2-methoxyphenyl)-2-butenal and not the corresponding phenyl alkyl ketone. Formation of its substituted ethylbenzene compound was not observed.

![Reaction Scheme](image)

**Figure 5.4.** The reaction of (4-methoxyphenyl)acetaldehyde over Cs and CsLa-oxide containing catalysts.
Table 5.4. The conversion of (4-methoxyphenyl)acetaldehyde over various CsLa-oxide and Cs-oxide supported mesoporous catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$A_{\text{wt}}$ (mmol g$^{-1}$ h$^{-1}$)$^a$</th>
<th>product selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs/MCM-41</td>
<td>2.8</td>
<td>100</td>
</tr>
<tr>
<td>Cs/HMS</td>
<td>0.7</td>
<td>100</td>
</tr>
<tr>
<td>CsLa/MCM-41</td>
<td>1.3</td>
<td>100</td>
</tr>
<tr>
<td>CsLa/Na-MCM-41</td>
<td>1.4</td>
<td>100</td>
</tr>
<tr>
<td>CsLa/Na-HMS</td>
<td>1.9</td>
<td>100</td>
</tr>
<tr>
<td>CsLa/ASA1</td>
<td>2.5</td>
<td>100</td>
</tr>
</tbody>
</table>

a) Specific activity at 2 h reaction time.

When both ortho positions of phenylacetaldehyde contain a chloro substituent, again mainly aldol condensation takes place followed by dehydration giving 2,4-di-(2,6-dichlorophenyl)-2-butenal (8; Table 5.5).

Table 5.5. The conversion of (2,6-dichlorophenyl)-2-acetaldehyde over various CsLa-oxide and Cs-oxide supported mesoporous catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>$A_{\text{wt}}$ (mmol g$^{-1}$ h$^{-1}$)$^a$</th>
<th>selectivity to 8 (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs/MCM-41</td>
<td>3.2</td>
<td>72.4</td>
</tr>
<tr>
<td>Cs/HMS</td>
<td>1.2</td>
<td>74.1</td>
</tr>
<tr>
<td>CsLa/MCM-41</td>
<td>3.2</td>
<td>73.6</td>
</tr>
<tr>
<td>CsLa/Na-MCM-41</td>
<td>3.5</td>
<td>74.4</td>
</tr>
<tr>
<td>CsLa/HMS</td>
<td>4.5</td>
<td>74.1</td>
</tr>
<tr>
<td>CsLa/ASA1</td>
<td>5.6</td>
<td>83.0</td>
</tr>
</tbody>
</table>

a) Specific activity at 2 h reaction time; b) 2,4-di-(2,6-dichlorophenyl)-2-butenal.

Catalysts characterization

The X-ray diffraction patterns of the mesoporous aluminosilicates are in agreement with earlier reported data$^2$ and are therefore not depicted.

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### Table 5.6. CO₂ and NH₃ TPD data of various Cs and CsLa-containing catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Desorbed CO₂ (µmol/g)ᵃ</th>
<th>Ratioᵇ</th>
<th>Tₘₐₓ (°C)ᶜ</th>
<th>Desorbed NH₃ (µmol/g)ᵈ</th>
<th>Ratioᵉ</th>
<th>Tₘₐₓ (°C)ᶠ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs/MCM-41</td>
<td>110</td>
<td>3.2</td>
<td>193</td>
<td>80</td>
<td>4.4</td>
<td>225</td>
</tr>
<tr>
<td>Cs/Na-MCM-41</td>
<td>70</td>
<td>4.3</td>
<td>188</td>
<td>100</td>
<td>3.0</td>
<td>189</td>
</tr>
<tr>
<td>Cs/HMS</td>
<td>90</td>
<td>3.8</td>
<td>210</td>
<td>150</td>
<td>2.2</td>
<td>184</td>
</tr>
<tr>
<td>Cs/Na-HMS</td>
<td>175</td>
<td>4.8</td>
<td>175</td>
<td>80</td>
<td>5.5</td>
<td>172</td>
</tr>
<tr>
<td>Cs/ASA1</td>
<td>90</td>
<td>3.6</td>
<td>203</td>
<td>120</td>
<td>3.1</td>
<td>154</td>
</tr>
<tr>
<td>Cs/ASA2</td>
<td>12</td>
<td>3.1</td>
<td>202</td>
<td>570</td>
<td>0.6</td>
<td>132</td>
</tr>
<tr>
<td>Cs/Al₂O₃</td>
<td>15</td>
<td>2.5</td>
<td>203</td>
<td>110</td>
<td>3.4</td>
<td>246</td>
</tr>
<tr>
<td>CsLa/MCM-41</td>
<td>190</td>
<td>3.7</td>
<td>166</td>
<td>540</td>
<td>0.8</td>
<td>170</td>
</tr>
<tr>
<td>CsLa/Na-MCM-41</td>
<td>160</td>
<td>4.9</td>
<td>163</td>
<td>330</td>
<td>2.3</td>
<td>169</td>
</tr>
<tr>
<td>CsLa/HMS</td>
<td>190</td>
<td>3.5</td>
<td>205</td>
<td>1001</td>
<td>0.7</td>
<td>197</td>
</tr>
<tr>
<td>CsLa/Na-HMS</td>
<td>170</td>
<td>4.2</td>
<td>184</td>
<td>180</td>
<td>0.2</td>
<td>197</td>
</tr>
<tr>
<td>CsLa/ASA1</td>
<td>160</td>
<td>4.5</td>
<td>202</td>
<td>150</td>
<td>5.6</td>
<td>225</td>
</tr>
<tr>
<td>CsLa/ASA2</td>
<td>190</td>
<td>3.1</td>
<td>203</td>
<td>730</td>
<td>0.8</td>
<td>178</td>
</tr>
<tr>
<td>CsLa/Al₂O₃</td>
<td>220</td>
<td>2.8</td>
<td>174</td>
<td>310</td>
<td>2.0</td>
<td>202</td>
</tr>
</tbody>
</table>

ᵃ Amount of desorbed CO₂ measured by TPD; b) the number of metal atoms per the number of CO₂ molecules; c) temperature corresponding to the maximum of the CO₂ TPD plot; d) amount of desorbed NH₃ measured by TPD; e) the number of metal atoms per the number of NH₃ molecules; f) temperature corresponding to the maximum of the NH₃ TPD plot.

It can be concluded that the structure of these materials is retained during preparation.

The strength and the amount of basic sites were analyzed by CO₂ temperature-programmed desorption (TPD). The number of basic sites is expressed by the metal atoms per CO₂-ratio of the catalysts, tabulated in Table 5.6. In the ideal case this ratio should be 2 for Cs₂O and CsLaO₂ if the catalysts contain a perfect monolayer of metal oxide. The low ratios obtained for the studied catalysts indicate that the Cs and CsLa-oxides show a good accessibility for CO₂ and are reasonably well homogeneously dispersed in a thin (2 layers averaged) layer of metal oxide. The basicity of a material is related by Tₘₐₓ and any desorption of CO₂ in the high temperature region would reflect strong basicity. As can be seen in Figure 5.5 and 5.6, Cs/MCM-41 and Cs/HMS material show almost the same TPD plot of CO₂ in the low temperature as well as the higher temperature region. This indicates that Cs/MCM-41 and Cs/HMS are comparable in strength.
Na\(^+\) ion-exchange of HMS results eventually in a strong increase of the amount of basic sites but in a decrease in their strength (Figure 5.6). Cs/Na-MCM-41 however, gave neither an improvement of the basicity nor of

Figure 5.5. TPD plots of CO\(_2\) on Cs/MCM-41 (1), CsLa/MCM-41 (2), Cs/Na-MCM-41 (3) and CsLa/Na-MCM-41 (4).

Figure 5.6. TPD plots of CO\(_2\) on Cs/HMS (1), CsLa/HMS (2), Cs/Na-HMS (3) and CsLa/Na-HMS (4).
Chapter 5

the amount of basic sites. Interestingly, Na⁺ ion-exchange of the MCM-41 and HMS support reduces the width of the desorption-peak of the cesium oxide containing materials (Figure 5.5 and 5.6). Ammonia TPD (Table 5.6) shows for both Na⁺ ion-exchanged mesoporous supports a decrease in the acidity. In contrast to Cs/Na-MCM-41 a clear reduction of the amount of acid sites is observed for the Cs/Na-HMS material. Figure 5.7 illustrates that the alumina and ASA2 supported cesium oxide systems, and to a lesser extent the ASA1 systems, are the strongest basic materials of the studied series which is reflected by the desorption in the high-temperature region, though no distinct peaks are seen. Here the >300 °C area should be compared with the lines 3 and 4 in Figure 5.5 and 5.6.

![Desorbed CO₂ (a.u.)](image)

**Temperature (°C)**

Figure 5.7. TPD plots of CO₂ on Cs/ASA1 (1), CsLa/ASA1 (2), Cs/ASA2 (3), CsLa/ASA1 (4) Cs/Al₂O₃ (5) and CsLa/Al₂O₃ (6).

The amount of desorbed CO₂ for the CsLa-oxide containing materials is larger than that of the Cs-oxide materials which is caused by the occluded 5 wt% La metal. This is actually a matter of weight which is underlined by the calculated metal-to-CO₂-ratio which is comparable with these of the Cs-oxide containing materials. The basicity of the supported CsLa-oxides is somewhat lower than that of their Cs-oxide analogues.
which is reflected by a larger CO₂ desorption in the high temperature region. This was, however, not observed for the ASA1, ASA2 and alumina systems (Figure 5.7). Na⁺ ion-exchange of the MCM-41 and HMS support gave also for the CsLa-oxide containing materials a narrowing of the desorption peak. The amount of acid sites, measured by ammonia TPD, is in general higher than that of the La-omitted materials which is in agreement with the stronger Lewis acidic character of lanthanum.

Table 5.7 shows the specific surface area and the pore size of the mesoporous MCM-41 and HMS catalysts. Generally the HMS materials possess smaller mesopores than the MCM-41 materials which is in agreement with literature data.¹¹,¹² The decrease in BET surface area for the metal oxide-loaded materials is caused by the presence of the intraporous Cs- and CsLa-oxide particles, giving only an increase in weight. The presence of these particles inside the pores is consistent with the decrease in the pore diameter, \( d_p \).¹³

<table>
<thead>
<tr>
<th>sample</th>
<th>BET area ((m^2/g))</th>
<th>( d_p ) ((Å))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>758</td>
<td>36</td>
</tr>
<tr>
<td>Cs/MCM-41</td>
<td>700</td>
<td>29</td>
</tr>
<tr>
<td>CsLa/MCM-41</td>
<td>660</td>
<td>35</td>
</tr>
<tr>
<td>HMS</td>
<td>1100</td>
<td>29</td>
</tr>
<tr>
<td>Cs/HMS</td>
<td>1040</td>
<td>26</td>
</tr>
<tr>
<td>CsLa/HMS</td>
<td>860</td>
<td>26</td>
</tr>
</tbody>
</table>

a) Corrected pore diameter according to Broekhoff and De Boer.¹³

5.4. Discussion

Aldol condensation of aldehydes over basic catalysts is a common reaction. That beside this reaction also rearrangement occurs of the aromatic aldehydes towards alkyl phenyl ketones is surprising. The presence of Cs in the catalysts is thereby probably a prerequisite. The reported aldol condensation of butyraldehyde over alkali oxide containing basic catalysts showed beside this also the Tishchenko reaction giving the dimeric ester.¹⁴ The presence of acid sites at the surface of the catalyst are held responsible for this reaction. The Tishchenko reaction is generally catalyzed by Al Lewis centers (e.g. AlOEt₂). The authors¹⁴ reported also that the sodium-, potassium- and rubidium oxide-loaded alumina are very active basic catalysts in the self-condensation of butyraldehyde at 50 °C giving 2-ethyl-3-hydroxyhexanal, its corresponding dehydrated
product and the trimeric glycol ester, a Tishchenko-type cross esterification product. The alkali oxide-loaded zeolite X catalysts required, however, a significantly longer reaction time to achieve the same conversion.

The isomerization of phenylacetaldehyde to acetophenone can, in accordance with the work of other researchers, at first sight be explained by a phenyl-shift.\textsuperscript{1,2} This mechanism can, however, not explain the rearrangement of 3-phenylpropionaldehyde and 4-phenylbutyaldehyde to propiophenone and butyrophenone, respectively. Moreover, in this case basic catalysts are used instead of mildly Bronsted and Lewis acidic zeolites like B-MFI and Fe-MFI.\textsuperscript{1,2} Therefore a general mechanism has to be proposed in which the reaction is base catalyzed which results eventually in the rearrangement of the aryl alkyl aldehyde into the corresponding phenyl alkyl ketone.

When accepting a basic mechanism the first step in the rearrangement is probably abstraction of the $\alpha$-proton giving a carbanion. Bond breaking between the carbonyl carbon and the $\alpha$-carbon as the second step is not very obvious, though, other researchers have used this mechanism to explain the product formation in the base-catalyzed aldol condensation of acetone.\textsuperscript{15} Bond breaking is also proposed in the photo-rearrangement of aromatic ketones over alkali ion-exchanged zeolites but here radical formation is involved.\textsuperscript{16,17}

Considering the type of products formed it is plausible to propose a mechanism in which the carbonyl group attacks the phenyl ring via a cyclic intermediate. The 1- or 2-position of the ring are candidates to play a role in this process. The exclusive formation of 4-methoxyacetophenone from (4-methoxyphenyl)acetaldehyde, the inactivity of (3-methoxyphenyl)acetaldehyde and the aldolization of (2-methoxyphenyl)acetaldehyde favours the idea that the rearrangement involves a nucleophilic attack at the 1-position of the phenyl group. In general methoxy-substituents have an activating ability at the corresponding ortho and para positions for aromatic electrophilic substitution. As to nucleophilic substitution the reverse is expected to hold. The lower rate of the reaction of (4-methoxyphenyl)acetaldehyde is therefore in agreement with the deactivating power of the $p$-methoxy-substituent for nucleophilic substitutions. The virtual inactivity of (3-methoxyphenyl)acetaldehyde remains to be explained, though it is not in contradiction with the proposed mechanism.

It is plausible that the methoxy-substituent at the $\alpha$-position hinders the (nucleophilic) attack giving a three-membered ring intermediate (Figure 5.8). Aldol condensation is therefore the most reasonable option in this reaction system. When both ortho-positions are occupied by chloro atoms again aldolization followed by dehydration is observed. It should be mentioned that the ring-type intermediate for 3-phenylpropionalde-
Novel isomerization of \( \omega \)-phenylalkanals to phenyl alkyl ketones over cesium (lanthanum) oxide on...

![Chemical structure](image)

**Figure 5.8.** General mechanism for the rearrangement of an \( \omega \)-phenylalkanal to a phenyl alkyl ketone. Curved line represents 1, 2 or 3 carbon bonds.

Hyde and 4-phenylbutyraldehyde is four and five-membered, respectively. Figure 5.8 illustrates such ring-type intermediates by changing the corrugated bond by two or three bonds, respectively.

![Chemical structure](image)

**Figure 5.9.** Schematic presentation of the interaction of phenylacetaldehyde with cesium oxide and cesium-lanthanum oxide \((M = Cs\) and La, respectively). The oxygen and metal ions are the basic and acid sites, respectively.

As visualized in Figure 5.9 the presence of Cs\(^+\) cations in all the catalysts can lower the electron density of the phenyl group by \( \pi \)-coordination.\(^{10,22}\) This interaction stimulates the nucleophilic substitution at the phenolic ring. Interaction of the carbonyl-oxygen with Cs\(^+\) or La\(^{3+}\) ions results in an increase in the acidity of the \( \alpha \)-proton which is therefore activated for substitution by the negative charged oxygen ions of the metal oxide. Interaction of toluene and formaldehyde with Lewis acidic Cs\(^+\) ions and basic oxygen sites in Cs\(^+\) ion-exchanged or cesium oxide loaded zeolites has been proposed in the side-chain alkylation of toluene.\(^{18,19}\) Quantumchemical studies demonstrate that interactions of carbonyl-oxygens with Lewis acid alkali cations lead to a transfer of electron density from the carbonyl compound to the alkali containing zeolite.\(^{10,21}\) This results in a weakening of the \( \alpha \)-C-H bonds. Comparable results are achieved by infra red studies on ketone loaded zeolites.\(^{22}\) The Lewis acid sites in the Cs- and CsLa-oxide containing materials are
also held responsible for the dehydration of the aldol products giving the α,β-unsaturated aldehydes.

Strongly basic sites present in cesium oxide loaded MCM-41 and HMS materials are affective for the rearrangement and aldol condensation. In general the HMS systems produces more of the phenyl alkyl ketone than the larger- sized α,β-unsaturated aldehyde. Considering the equal basicity the higher affinity in producing the smaller molecule is probably caused by the smaller mesopores of HMS compared to those of MCM-41. The lower activity of Cs/HMS in the other reactions in which even larger molecules are involved, may also result from the smaller pores of the catalyst. In contrast to the very high activity of the strongly basic alumina and ASA2 systems in the conversion of phenylacetaldehyde these systems show activities comparable with the MCM-41 and HMS catalysts in the conversion of 3-phenylpropionaldehyde and 4-phenylbutyraldehyde. This is tentatively assigned to the large size of the molecules and the corresponding products. Beside the fact that Cs/ASA2 and Cs/Al₂O₃ are strongly basic and very active catalysts, at least in the conversion of phenylacetaldehyde, they both produce substantial amounts of ethylbenzene. The formation of this product is still unclear and therefore further investigations are required to get more insight in this side-reaction.

The Na⁺ extraframework ions in the mixed cations systems studied show no enhanced effect on either the activity or basicity. A weaker interaction of the oxides adjacent to the aluminum of the support might be a result. Considering the supported CsLa-oxide materials it can be noticed that, in spite of their lower basicity, these systems are quite active and selective to the phenyl alkyl ketones. The reason for this is that lanthanum activates the α-proton via coordination of the carbonyl oxygen. It is noteworthy that the Tishchenko reaction is not observed over the Lewis acidic lanthanum containing catalysts and the other materials. It has been reported that the alkali oxide-loaded alumina and zeolite X produces a significant amount of the trimeric glycol ester, a product from the Tishchenko reaction of butyraldehyde and its aldol dimer.¹⁴

5-5. Conclusions

Aluminosilicate MCM-41 and HMS, amorphous silica-alumina and alumina containing Cs and CsLa-oxide are effective catalysts for the rearrangement of aromatic aldehydes to phenyl alkyl ketones in the liquid phase. The mechanism of this hitherto unknown isomerization is proposed to go via an intramolecular aromatic nucleophilic substitution at the one-position involving a cyclic transition state. The presence of cesium ions is playing probably a key role in this process. The product ratio can be influenced by factors like the basicity of the catalyst and the size of the mesopores.
Novel isomerization of α-phenylalkanals to phenyl alkyl ketones over cesium (lanthanum) oxide on...

References

Catalysis of the tetrahydropyranylation of alcohols and phenols by H-MCM-41*

6-1. Introduction

Various classes of ion-exchange resins and porous materials have been used as heterogeneous acid catalysts for the tetrahydropyranylation of alcohols and phenols (Figure 6.1). Until now only two systems, which show catalysis inside microporous channels and cavities of the catalyst, were published, namely H-Y zeolite and K-10 clay. With respect to the efficiency of the H-Y zeolite, the pores (7.5 Å) are too small to allow large organic molecules to enter. Also the reaction times are rather long which is probably caused by diffusion limitations in the micropores. Most of the used catalysts have limitations when complex molecules are converted which possess acid-sensitive functionalities. To overcome these problems a material with mild acidity inside mesoporous channels should be used. A mildly acidic catalyst suffices here, because the double bond is activated by the neighbouring oxygen atom. Upon protonation the relatively stable oxocarbenium ion is formed. This also explains the high regioselectivity of the addition. The mesoporous H-MCM-41 molecular sieve, as mentioned in chapter 1, seems to be the perfect candidate for this purpose. MCM-41 with a pore diameter around 35 Å would be large enough to allow diffusion of large molecules like cholesterol and naphthol and the tetrahydropyranylated products derived from them.

\[ \text{ROH} + \begin{array}{c} \text{1} \\ \text{2} \end{array} \rightarrow \begin{array}{c} \text{RO} \\ \text{3} \end{array} \]

Figure 6.1. Tetrahydropyranylation of ROH (R = alkyl or aryl) with 3,4-dihydro-2H-pyran (2).

Tetrahydropyranyl ethers (THP-ethers) are synthetically useful derivatives for the protection of hydroxy groups, because they show an outstanding stability under a variety of reaction conditions such as oxidative, alkylating and acylating conditions, the presence of Grignard reagents, alkaline media, reduction

with hydride and lithium alkyls. The versatility of 3,4-dihydro-2H-pyran (DHP) as a hydroxy group protector has been proven in peptide, nucleotide, carbohydrate and steroid chemistry.2

In this chapter it is reported that the mildly acidic H-MCM-41 molecular sieve (with different Si/Al ratios) is an excellent catalyst for the tetrahydropyranylation of primary, secondary and tertiary alcohols including bulky systems such as cholesterol and two phenolic compounds.

6-2. Experimental

Catalysts

The MCM-41 materials were synthesized according to a modification of example 11 of ref. 10. A typical synthesis procedure is as follows: a solution of 0.49 g of NaAlO₂ (Riedel-de Haén; 54 wt% Al₂O₃ and 41 wt% Na₂O) in 1.1 g of water was mixed with 7.6 g of 20 wt% tetraethylammonium hydroxide (ACROS) and 9.6 g of colloidal silica (Ludox HS-40; 40 wt% solution). The gel was stirred vigorously for 0.5 h and mixed with an equal volume of 25 wt% cetyltrimethylammonium chloride (Aldrich). Then the gel was heated statically at 100 °C for 2 days, cooled to room temperature, filtrated, washed to neutral and dried at 80 °C under vacuum. Finally, the material was calcined at 540 °C in dry air for 10 h. Si/Al ratios, determined by ICP-AES/AAS analysis, were 18 and 26, respectively. The quality of the MCM-41 materials was checked by powder X-ray diffraction on a Philips PW 1877 diffractometer using CuKα radiation and was found to be in agreement with literature data.8 Benzene adsorption measurements were performed at atmospheric pressure in a N₂ flow on a home-made TGA microbalance and indicated that all used MCM-41 materials possess the common adsorption capacity of -60 g benzene/100 g MCM-41.8,10 According to ²⁷Al MAS NMR data most of the aluminium (~ 80%) was tetrahedrally incorporated.11 The calcined aluminosilicate MCM-41 samples were ion-exchanged with an excess of a refluxing 1M NH₄NO₃ solution to form NH₄-MCM-41 samples. The H⁺ form of MCM-41 was obtained by heating the dried NH₄-MCM-41 samples at 450 °C in an air flow. Prior to use, the H-MCM-41 materials were activated at 400 °C in the presence of air.

HA-HPV (High Alumina-High Pore Volume; specifications: 25.0 wt% Al₂O₃, a surface area of 540 m²/g and a pore volume of 0.76 ml/g), is a commercial silica-alumina cracking catalyst and was kindly donated by Akzo Nobel Chemicals bv, Amsterdam.

Reagents

The alcohols 1-octanol [CH₃(CH₂)₇OH], cyclooctanol [C₈H₁₇OH] 1-adamantanol [C₁₀H₁₇OH] and cholesterol [C₂₇H₄₅OH], phenol [C₆H₅OH], 2-naphthol [C₁₀H₇OH] and 3,4-dihydro-2H-pyran were purchased from ACROS except neopentyl glycol [HOCH₂C(CH₃)₂CH₂OH] which was supplied from Aldrich.
Catalysis of the tetrahydropyranylation of alcohols and phenols by H-MCM-41

General reaction procedure

To a solution of the hydroxy compound (30 mmol) in hexane (50 mL) were added successively, the H-MCM-41 material (0.5 g) and 3,4-dihydro-2\(^H\)-pyran (3.11 g, 37 mmol), and the mixture was refluxed with stirring for the specified period of time (Table 6.1). The progress of the reaction was monitored by GLC (CP sil 5CB column). Quantification was done with 1,3,5-tri-isopropylbenzene as the internal standard which was added prior to the reaction mixture. It is observed that the internal standard is not adsorbed significantly by the catalyst under the present conditions. The products were identified by GLC-MS (VG70-250S/SE instrument). In the case of the tetrahydropyranylation of neopentyl glycol a double amount of DHP was used.

Deprotection of the THP-ethers can be done in two ways. Method I: add the activated H-MCM-41 to a refluxing solution of 20 g hexane, 10 mmol THP-ether of 1-octanol and 20 mmol of methanol (Baker). Method II: add the activated H-MCM-41 to a refluxing methanolic (30 g) solution containing the THP-ether (20 mmol).

6-3. Results and discussion

When an alcohol or a phenolic compound 1 (Figure 6.2) is treated with a small excess of DHP 2 in the presence of H-MCM-41 material in hexane it is selectively converted in the corresponding THP-ether 3 within short reaction times. Even at room temperature, cf. 1-octanol, fast and essentially complete conversion was achieved with a high selectivity to the product. In some cases completion of the reaction could not be

![Molecular structures](image)

**Figure 6.2.** Molecular structures of 1-octanol (a), cyclooctanol (b), 1-adamantanol (c), phenol (d), 2-naphthol (e) and cholesterol (f).
Table 6.1. Tetrahydropyranylation of alcohols and phenols over H-MCM-41.

<table>
<thead>
<tr>
<th>ROH</th>
<th>Reaction time (min)</th>
<th>Si/Al ratio of cat.</th>
<th>Temp. (°C)</th>
<th>Conversion of 1 (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Selectivity to 3 (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octanol</td>
<td>15</td>
<td>26</td>
<td>69</td>
<td>92</td>
<td>95</td>
</tr>
<tr>
<td>1-octanol</td>
<td>35</td>
<td>26</td>
<td>25</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>1-octanol</td>
<td>150</td>
<td>26</td>
<td>0</td>
<td>82</td>
<td>99</td>
</tr>
<tr>
<td>cyclooctanol</td>
<td>15</td>
<td>26</td>
<td>69</td>
<td>87</td>
<td>99</td>
</tr>
<tr>
<td>1-adamantanol</td>
<td>30</td>
<td>18</td>
<td>69</td>
<td>67</td>
<td>99</td>
</tr>
<tr>
<td>phenol</td>
<td>5</td>
<td>26</td>
<td>69</td>
<td>64</td>
<td>98</td>
</tr>
<tr>
<td>2-naphthol</td>
<td>120</td>
<td>26</td>
<td>69</td>
<td>67</td>
<td>46</td>
</tr>
<tr>
<td>2-naphthol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>210</td>
<td>26</td>
<td>69</td>
<td>92</td>
<td>73</td>
</tr>
<tr>
<td>cholesterol</td>
<td>360</td>
<td>18</td>
<td>69</td>
<td>44</td>
<td>98</td>
</tr>
<tr>
<td>cholesterol&lt;sup&gt;b&lt;/sup&gt;</td>
<td>360</td>
<td>26</td>
<td>69</td>
<td>69</td>
<td>99</td>
</tr>
</tbody>
</table>

<sup>a</sup> determined by GLC (CP sil 5CB column); b) DHP was added dropwise within 90 min.

obtained (Table 6.1). The relatively low reactivity of these alcohols caused longer reaction times, which induced DHP to oligomerize. Improvement of the alcohol conversion and the selectivity to the THP-ether could be obtained when DHP was added dropwise to the reaction mixture.

The advantage of the mesoporous channels of H-MCM-41 is manifested by the reaction with cholesterol, which compound is converted within a rather short reaction time. The selectivity is hereby not negatively effected, which also indicates the mildness of the molecular sieve. An example of a tertiary alcohol was used to investigate whether less reactive hydroxy groups could be also converted within reasonable reaction time. It appeared that 1-adamantanol could be easily converted with a 99% selectivity. In the case of neo-

![Figure 6.3. Tetrahydropyranylation of neopentyl glycol.](image-url)
pentyl glycol, which contains two neopentyl-type hydroxy groups, the second hydroxy group is converted less easily than the first one, which is almost completely tetrahydropyranolated within 30 min in refluxing hexane allowing selective mono-THP formation (Figure 6.3).

As with other heterogeneous acid catalysts, the work-up is reduced to a simple filtration with no need for acid removal or troublesome neutralization. The H-MCM-41 material is recovered unchanged and can be reactivated for re-use by heating it at 400 °C in the presence of air or it can be re-used as such. Though the reaction temperature is slightly higher, in Figure 6.4 it is shown that the directly re-used H-MCM-41 is still active.

An amorphous aluminosilicate, HA-HPV, a commercial fluid cracking catalyst, was compared with H-MCM-41. The reaction of 1-octanol with DHP was catalyzed by HA-HPV; after 15 minutes reaction time in refluxing hexane 70% of 3 at 76% alcohol conversion was obtained. An improvement of the yield of 4% could be observed after 30 minutes, but this was accompanied by the formation of a substantial amount of by-products. It may be concluded that the performance of the amorphous silica-alumina is substantially lower than that of H-MCM-41 (cf. Table 6.1, first row). The former catalyst is also more sensitive for deactivation during this reaction.

H-MCM-41 turned out to be able to deprotect the THP-ether of 1-octanol in hexane at reflux temperatures with a small excess (2 equivalents) of methanol or in a methanolic solution. In the latter case

![Graph showing conversion and selectivity over reaction time](image)

**Figure 6.4.** Catalysis by a fresh (1st cycle) and a re-used as such H-MCM-41 (Si/Al = 26; 2nd cycle) in the tetrahydropyranylation of 1-octanol (1); (+) selectivity to 3 and (o) conversion of 1-octanol of 1st cycle; (□) selectivity to 3 and (□) conversion of 1-octanol of 2nd cycle. The 1st and 2nd cycle were performed at 0 °C and 25 °C, respectively.
the reaction will run faster, but in both cases completion required more than ten hours.

6-4. Conclusions

The mesoporous molecular sieve H-MCM-41 is a mild and efficient catalyst for the tetrahydropyranylation of alcohols and phenols. The reaction can be carried out in a simple way and provides high selectivities within short reaction times. The catalyst can be re-used as such without reactivation at high temperature. Deprotection of the dehydropyryanyl ethers can be done by the same H-MCM-41 catalyst.

References

MCM-41 type materials with low Si/Al ratios*

7-1. Introduction

The recently developed mesoporous molecular sieve MCM-41\(^1\)\(^2\) opens many new possibilities in the catalytic conversion of large molecules.\(^3\) For acid-type catalysts it is often advantageous to incorporate aluminum in the framework, because this allows tuning Bronsted and Lewis acidity of these materials. Considering ZSM-5 the acidity and catalytic activity is correlated with the amount of tetrahedral framework-aluminum.\(^4\)

The synthesis of MCM-41 materials with high levels of tetrahedral aluminum was recently reported.\(^5\)\(^6\) Although the resolution of the \(^{27}\)Al MAS NMR spectra of the calcined MCM-41 materials was moderate in contrast to the as-synthesized MCM-41, the authors concluded that no octahedral aluminum was present. Similar results were reported by other workers also using sodium aluminate as the aluminum source.\(^7\) These authors claimed that aluminosilicate MCM-41 materials with Si/Al ratios as low as 2 were possible. In this case only \(^{27}\)Al MAS NMR spectra of as-synthesized MCM-41 were included, however poorly resolved X-ray diffraction patterns indicate ill-defined materials.

Here the synthesis of MCM-41 type materials with high amounts of tetrahedrally coordinated aluminum is reported. Transmission electron microscopy (TEM) reveals that beside MCM-41 an aluminum-rich dense phase exists, which accounts for the high amounts of bulk tetrahedral aluminum in the synthesized materials.

7-2. Experimental

Synthesis

MCM-41 materials with bulk Si/Al ratios of 10 down to 6 were prepared according to the following general procedure. Amounts of sodium aluminate (Riedel-de Haën, 54% Al\(_2\)O\(_3\), 41% Na\(_2\)O) varying between 3.22 g and 1.90 g, and 119.5 g of C\(_{10}\)H\(_{35}\)(CH\(_3\))\(_3\)NCl (Aldrich, 25 wt% in water) were stirred for 1 h. A proper

amount of sodium hydroxide (Baker, 98.5%) varying between 1.15 g and 1.37 g such that $2 < \text{Na}_2\text{O}/\text{Al}_2\text{O}_3 < 3$, and 120 g of distilled water were added. When all the sodium hydroxide pellets were dissolved, 12.3 g of fumed silica (HiSil 233 of PPG Industries) was added. In two samples the sodium hydroxide was replaced by 8.63 g of 25 wt% aqueous tetramethylammonium hydroxide (Aldrich) or 28.45 g of 20 wt% aqueous tetraethylammonium hydroxide (ACROS). In all cases the pH was around 13. The gel formed was stirred for 2 h and subsequently heated in an autoclave at 120 °C for 24 h. After cooling to room temperature, the solids were collected by filtration and washed with distilled water. The product was stirred for 2 h in ethanol, to remove part of the template, centrifugated and dried in air at 100 °C. The residual template was removed by calcining the samples for 10 h in air with a heating rate of 1 °C per min from room temperature to 540 °C.

**X-ray diffraction**

The calcined samples were characterized by X-ray powder diffraction on a Philips PW 1840 diffractometer using monochromated CuKα radiation. Patterns were recorded from 1° to 10° (2θ) with a resolution of 0.02° and a count time of 10 s at each point.

**$^{27}$Al NMR spectroscopy**

Solid-state $^{27}$Al MAS NMR spectra were recorded at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe. A resonance frequency of 104.21 MHz, a recycle delay of 0.1 s, and short 3 μs pulses (45° pulses of 3 μs), a spectral width of 50 kHz and a spin rate of 6.2 kHz were applied. The lines were referenced to Al(NO$_3$)$_3$ (0 ppm).

**Nitrogen physisorption measurements**

Multipoint BET surface areas, pore volumes and pore size distributions of the MCM-41 materials were calculated from N$_2$ adsorption/desorption isotherms at -196 °C using a Quantachrome Autosorb 6 instrument. The samples were outgassed for 1 h in vacuum at 550 °C prior to use.

**Transmission electron microscopy**

Transmission electron microscopy (TEM) was performed with a Philips CM 30 ST electron microscope with a field emission gun operated at 300 kV and equipped with an energy dispersive X-ray (EDX) element analysis system. The Si/Al ratio of the Al and Si peaks in the EDX spectrum was calibrated with zeolites with known Si/Al ratios (NaY and NaA). The samples were prepared as follows. The ground MCM-41 samples were suspended in ethanol. A copper grid coated with a microgrid carbon polymer was loaded with a few droplets of this suspension.
7-3. Results and discussion

Powder X-ray diffraction, $^{27}$Al MAS NMR, elemental analysis and transmission electron microscopy (TEM) were applied to investigate the incorporation of aluminum in the MCM-41 framework. From a systematic synthesis study by only using the three former techniques it could be concluded that with fixed amounts of sodium aluminate the amount of sodium hydroxide should be varied to minimize the level of octahedral aluminum. Then the Na$_2$O/Al$_2$O$_3$ ratio of the gel should be kept between 3 and 2 going from Si/Al = 10 down to 6. The calcined grey-coloured MCM-41 products synthesized, containing a high level of tetrahedrally coordinated aluminum, showed Si/Al ratios determined by elemental analysis, as low as 5. In the case of MCM-41 materials with even lower Si/Al ratios (down to 3) a slight increase in the amounts of amorphous material was observed. The influence of the sodium hydroxide on the synthesis of MCM-41 with tetrahedral aluminum agrees reasonably well with the results of Janicke et al. The workers found that beside the cationic head groups of the surfactant the incorporation of tetrahedral aluminum requires charge balancing sodium cations, which contribute in compensating the additional anionic charge introduced by the aluminum.

![Figure 7.1. Powder X-ray diffraction patterns of the calcined MCM-41 samples 5, 6 and 7.](image)

The calcined MCM-41 materials show X-ray diffraction patterns (Figure 7.1) with broad weakly defined peaks in the 3 to 5° 2θ-range, indicating a distortion of the long range ordering of the mesoporous structure and/or badly built hexagonal arrays. No improvement of the crystallinity of these materials was
obtained by using cetyltrimethylammonium bromide instead of the chloride. The relatively poor crystallinity of all the samples is probably a result of distortion of the mesophase before forming of the MCM-41 structure. Decrease of the resolution of X-ray diffraction patterns of aluminosilicate MCM-41 materials as the aluminum content increases was observed by other workers. TEM examination of the calcined specimens shows that beside MCM-41 a dense phase is present (Figure 7.2). Sometimes a phase appears in which MCM-41 is mixed up with an aluminum rich dense phase. Most of the MCM-41 materials in each specimen have a chaotic morphology. The fraction of crystalline hexagonal MCM-41 was smaller than 10% of the studied samples. The chaotic morphology can be explained by spaghetti-like arrangements of the tubes resulting in a spongy material. Table 7.1 shows elemental dispersive X-ray (EDX) data of the MCM-41 samples. These EDX measurements show that the amounts of aluminum of the MCM-41 phases synthesized without the use of a tetraalkylammonium base of every sample are around 3 atom% (Si/Al = 30). A more aluminum-rich MCM-41 could be achieved when the tetraalkylammonium bases were used in the synthesis mixture (= 5-8 atom% Al or Si/Al = 20-12). The dense phase contains a much higher amount of aluminum (= 15-20 atom% or Si/Al = 6-5).

![Figure 7.2. TEM micrograph of a representative calcined MCM-41 sample showing two different phases, namely: the aluminum-rich dense phase and the chaotic phase of MCM-41.](image)

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It can be suggested that this aluminum-rich material is responsible for the low overall Si/Al ratio of the bulk material measured by elemental analysis. Thus most of the aluminum is consumed by this dense phase. Also MCM-41 sample 8, prepared according to a literature procedure, contained parts of this aluminum-rich dense phase (Table 7.1).

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Al (atom%)</th>
<th>aluminum content (atom%)</th>
<th>( d_{100} ) spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.5</td>
<td>0-3</td>
<td>43</td>
</tr>
<tr>
<td>2</td>
<td>7.5</td>
<td>1-3</td>
<td>46</td>
</tr>
<tr>
<td>3</td>
<td>7.5^a</td>
<td>5-6</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>7.5^c</td>
<td>5-8</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>1-3</td>
<td>40</td>
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<td>41</td>
</tr>
<tr>
<td>7</td>
<td>10.0</td>
<td>2-5</td>
<td>43</td>
</tr>
<tr>
<td>8</td>
<td>14^d</td>
<td>0-3</td>
<td>42</td>
</tr>
</tbody>
</table>

a) According to EDX analysis of the calcined materials; b) tetramethylammonium hydroxide applied in synthesis mixture; c) tetraethylammonium hydroxide applied in synthesis mixture. d) synthesized according to reference 7.

The \(^{27}\)Al MAS NMR spectra of all calcined MCM-41 samples exhibit a peak at 56 ppm, which can be assigned to tetrahedrally coordinated aluminum.\(^{5,7,11,12}\) Figure 7.3 shows two \(^{27}\)Al MAS NMR spectra which are representative for all materials. In some cases the spectra reflect the presence of a very small amount of octahedral aluminum. The broad MAS line width is expected to be caused by second-order quadrupole interaction of the aluminum species,\(^{11}\) which is in the case of high amounts of aluminum the most reasonable explanation. The presence of aluminum in a highly distorted environment and/or in a low symmetry (due to the large range of T-O-T bond angles, where T represents an individual \( \text{SiO}_4 \) or \( \text{AlO}_4^- \) tetrahedron) might also be responsible for the peak broadening.\(^{7,8,11,12}\) A distinction between framework and non-framework aluminum could not be made by use of the one-pulse MAS technique. This is also the case with aluminum incorporated in MCM-41 and in the aluminum rich dense phase observed by TEM.

Apparently the addition of tetraalkyammonium bases does effect the way of incorporation of the aluminum species. By using these quaternary ammonium bases the aluminum content can at least be doubled in MCM-41. Probably these tetraalkylammonium bases are acting as an aluminum directing agent for MCM-41. It is found\(^{12}\) that tetramethylammonium has a stabilizing function in the preparation of MCM-41 with
the cubic aluminosilicate precursor \( \text{Al}_x\text{Si}_y(\text{OH})_z\text{O}_{12} \). By using these precursors MCM-41 can be prepared with Si/Al ratios as low as 1. Our results confirm actually that sodium aluminate is very suitable as the aluminum precursor for synthesizing MCM-41 materials with a high tetrahedral aluminum content, as was suggested by Chen et al., but only for MCM-41 materials with Si/Al ratios down to 12. Large amounts of Na⁺ ions are necessary to govern the incorporation of large amounts of aluminum. The number of moles of \( \text{Na}_2\text{O} \) used here is twice the molar amount of \( \text{Al}_2\text{O}_3 \), however, the amount of incorporated aluminum is still quite low. The exact reason for the formation of a dense phase beside the low-aluminum containing MCM-41 is therefore not clear.

Table 7.2 shows a selection of the MCM-41 samples, which were subjected to nitrogen physisorption. We note that these data are representative for all the MCM-41 materials synthesized. From these data it is observed that the MCM-41 materials possess surface areas of \(-500\ \text{m}^2/\text{g}\) and mesopore volumes of \(-0.58\ \text{cm}^3/\text{g}\), characteristic for MCM-41 materials, although larger values (about 1200 \( \text{m}^2/\text{g} \) and 0.79 \( \text{cm}^3/\text{g} \), respectively) have been reported. It should be noted that the pore volumes and surface areas of Table 7.2 are negatively influenced by the dense phase. The MCM-41 materials possess a high thermal stability which is nicely illustrated by the constant pore diameter (39 Å) and pore volume of sample 4 calcined once and calcined for a second time.

A study of aluminum incorporation in MCM-41 by using sodium aluminate reported recently, showed that at Si/Al = 5, beside MCM-41, a lamellar phase and a dense crystalline tridymite structure were formed. In contrast to our work, the \(^{27}\text{Al}\) MAS NMR spectrum of this as-synthesized sample contains a
**MCM-41 type materials with low Si/Al ratios**

<table>
<thead>
<tr>
<th>sample</th>
<th>pore diameter (Å)</th>
<th>mesopore volume (cm³/g)</th>
<th>BET area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>39</td>
<td>0.570</td>
<td>724</td>
</tr>
<tr>
<td>2</td>
<td>39</td>
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<td>692</td>
</tr>
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<td>3</td>
<td>39</td>
<td>0.580</td>
<td>632</td>
</tr>
<tr>
<td>4</td>
<td>39</td>
<td>0.570</td>
<td>695</td>
</tr>
<tr>
<td>4c</td>
<td>39</td>
<td>0.562</td>
<td>693</td>
</tr>
<tr>
<td>8d</td>
<td>36</td>
<td>0.703</td>
<td>926</td>
</tr>
</tbody>
</table>

a) Calculated with the corrected Kelvin equation for cylindrical pores of de Boer.19 b) cumulative volume. c) sample 4 calcined twice. d) synthesized according to reference 8.

A large fraction of octahedral aluminum and is this aluminum-rich dense phase X-ray visible.16,17 Several workers have reported about the incorporation of tetrahedral aluminum by using aluminum sulfate.10,18 By using this aluminum source MCM-41 can be synthesized with a Si/Al ratio as low as 10 without losing the characteristic mesoporous features of MCM-41.

7-4. Conclusions

TEM examination shows that when sodium aluminate is used as the aluminum source, calcined mesoporous aluminosilicate MCM-41 materials can be synthesized with Si/Al ratios as low as 12, of which the incorporated framework aluminum is almost completely tetrahedrally coordinated. The use of tetraalkylammonium bases in the MCM-41 synthesis has a positive influence on the incorporation of aluminum in the MCM-41 framework. When applying MCM-41 with Si/Al < 15 in the synthesis mixture an aluminum-rich dense phase is formed in all samples. In this dense phase the aluminum is also tetrahedrally coordinated. This indicates that one-dimensional 27Al NMR does not distinguish between framework and nonframework aluminum. This aluminum-rich phase is not easily observed by X-ray diffraction, which underlines the importance of electron microscopy in the characterization.

In spite of the rather decreased crystallinity, these thermally stable MCM-41 type materials possess the characteristic mesoporous features.
References

Study of catalysts comprising heteropoly acid \( H_3PW_{12}O_{40} \) supported on MCM-41 molecular sieve and amorphous silica*

8-1. Introduction

Keggin-type heteropoly acids (HPAs), \( H_{x+}XM_{12}O_{40} \), where \( X \) is the central atom (Si\(^{4+}\), P\(^{5+}\), etc.), \( x \) its oxidation state and \( M \) the metal ion (Mo\(^{6+}\), W\(^{6+}\)), are widely used as acid catalysts due to their very strong Bronsted acidity and special structural properties.\(^1\,^6\) Usually, tungsten HPAs are preferred over molybdenum HPAs as acid catalysts because of their stronger acidity, higher thermal stability and lower oxidation potential.\(^6\) \( H_3PW_{12}O_{40} \) (PW), the strongest acid in the HPA series, is particularly recommended.\(^6\) So far most HPA applications concern homogeneous or biphasic (L/L) systems. When heterogeneous HPA catalysis is considered supported HPA catalysts are an obvious option, as bulk HPAs have a relatively low specific surface (<10 m\(^2\)/g). Note here that sometimes reactions on HPAs also take place on sub-surface sites. Acidic or neutral substances such as SiO\(_2\), active carbon, acidic ion-exchange resin, etc., are all suitable as supports, but SiO\(_2\) which is relatively inert towards HPAs, is the most often used.\(^1\) Recently, HPAs supported on the all-silica mesoporous molecular sieve MCM-41 have attracted interest as promising solid strong acid catalysts for conversion and formation of large organic molecules.\(^7\,^8\) The PW/MCM-41 compositions, having uniformly sized mesopores of around 30 Å, were shown to exhibit a high catalytic activity and shape selectivity in liquid-phase phenol alkylation with isobutene and the bulky styrene.\(^7\)

The state of HPAs on the SiO\(_2\) surface has been reviewed recently.\(^1\) According to earlier infra red and X-ray diffraction studies, PW retains the Keggin structure when supported on SiO\(_2\). However, recent investigations with \(^31\)P MAS NMR, which is the most useful and accurate probe of the state of heteropolyphosphates so far,\(^9\) showed that the state of PW on SiO\(_2\) is more complex, and that a chemical interaction between HPA and SiO\(_2\) takes place. Supporting PW on SiO\(_2\) was found to result in a shift as well as a line-broadening in the \(^31\)P NMR spectrum, indicating a distortion of the HPA structure compared with that in bulk HPA.\(^10\)\(^1\)\(^1\)H MAS NMR\(^10\) and microcalometry\(^11\) also showed the reaction of PW with SiO\(_2\) and the formation of a new type of proton sites on the silica surface, resulting in a decrease of the HPA acid

strength. Protonation of surface Si-OH groups followed by dehydration was suggested \((1 \leq m \leq 3)\):\(^{10}\)

\[
H_3PW_{12}O_{40} + m (= \text{Si-OH}) \rightarrow (= \text{Si}_(m)(H_3PW_{12}O_{40})^{m-} + m H_2O
\]  (1)

In a subsequent \(^{31}\)P NMR study\(^{12}\) of a series of PW/SiO\(_2\) catalysts, with HPA loading ranging from 13 to 87 wt\%, two partially resolved peaks were detected, one at -15.1 ppm and the other at -14.5 ppm from external 85 % H\(_3\)PO\(_4\). These were assigned to the bulk crystalline PW and to the 'interacting' form, \((\text{Si-OH}_2)_1(H_3PW_{12}O_{40})\), respectively, the relative amount of the latter increasing as HPA loading decreases. The interacting species may be formed by proton transfer according to (2):

\[
H_3PW_{12}O_{40} + \text{Si-OH} \rightarrow (\text{Si-OH}_2)_1(H_3PW_{12}O_{40})^{-}
\]  (2)

Two species resonating at -15.2 and +3.2 ppm, were found by \(^{31}\)P NMR in SiO\(_2\)-supported PW calcined at 300 °C.\(^{13}\) In PW/MCM-41, HPA retains the Keggin structure at HPA loadings above 20 wt\%, but at lower loadings two forms were also observed by \(^{31}\)P NMR with well-resolved signals at -15.3 ppm and -13.3 ppm.\(^3\)

The first one was attributed to finely dispersed HPA molecules, retaining the Keggin structure, and the second to a lacunary or unsaturated species, such as PW\(_{11}\) and dimeric species as P\(_2\)W\(_{17}\) or P\(_2\)W\(_{18}\) and P\(_2\)W\(_{21}\), which have similar lines in \(^{31}\)P NMR solution spectra.\(^9\) Therefore, at least two species originating from PW were detected on the SiO\(_2\) surface; their amount depends on the HPA loading and probably on the preparation conditions.

Considering the interaction of PW protons with Si-OH groups, it has been suggested that the cesium salt of HPA (CsPW), C\(_3\)H\(_3\)PW\(_{12}O_{40}\) \((0 \leq y \leq 3)\),\(^{14,15}\) would have a weaker interaction with silica-type surfaces compared to H\(_3\)PW\(_{12}O_{40}\) due to the large Cs\(^+\) cations.

In this chapter, the preparation of HPA catalysts comprising PW supported on a mesoporous all-silica molecular sieve MCM-41 and on an amorphous SiO\(_2\) has been studied, with the aim of obtaining certain HPA forms on the siliceous surface. The preparation of MCM-41-supported CsPW was investigated to get more insight in the interaction of heteropoly acid with the siliceous surface, particularly with MCM-41. The HPA containing catalysts were characterized by \(^{31}\)P and\(^{29}\) Si MAS NMR, powder X-ray diffraction and transmission electron microscopy and tested in the liquid-phase trans-de- tert-butylolation of 2,6-di-tert-butyl-4-methylphenol using o-xylene as acceptor molecule.
Study of catalysts comprising heteropoly acid $H_3PW_{12}O_{40}$ supported on MCM-41 molecular sieve...

8-2. Experimental

Materials

$H_3PW_{12}O_{40} \cdot 24H_2O$ from ACROS, containing >99 mol% Keggin HPA (from $^{31}$P NMR), was used. $H_2P_2W_{18}O_{62}$ ($\alpha/\beta$ 4:1) ($P_2W_{18}$) was synthesized by a known procedure\(^{16}\) and purified by multiple extraction with diethyl ether; $^{31}$P NMR in aqueous solution for $\alpha$-$P_2W_{18}$: -13.0 ppm (lit. -12.7 ppm),\(^9\) for $\beta$-$P_2W_{18}$: -11.5 ppm and -12.2 ppm (lit. -11.0 and -11.6 ppm).\(^9\) $H_6P_2W_{21}O_{71}$ ($P_2W_{21}$) was prepared by an electromembrane method;\(^{17}\) $^{31}$P NMR in aqueous solution: -13.5 ppm (lit. -13.3 ppm).\(^9\) $Cs_2xH_{x5}PW_{12}O_{40}$ was quantitatively prepared by titrating $H_3PW_{12}O_{40}$ with $Cs_2CO_3$ (ACROS).\(^{14}\) Aerosil 380 (Degussa) was used as the amorphous silica support. All-silica mesoporous molecular sieve MCM-41 was synthesized according to a literature procedure.\(^{18}\) The material showed a typical X-ray diffraction pattern (Figure 8.1) with a $d_{100}$, $d_{110}$- and $d_{200}$-spacing of 38, 22 and 19 Å, respectively, and from nitrogen physisorption, had a multipoint BET surface area of 1250 m$^2$/g, a pore volume of 0.93 cm$^3$/g and uniform pores 32 Å in size.

The catalysts comprising of 10 to 50 wt% HPA on a siliceous support were prepared by shaking a suspension of Aerosil 380 or MCM-41 (0.5 - 1 g) in an aqueous (3 - 5 ml) or methanol (around 30 ml) solution, containing a certain amount of HPA, in a glass vessel for 1 to ca. 20 h (overnight) at room temperature. The pH of the impregnating aqueous solution was varied from 1 to 2 depending on the HPA

![Figure 8.1. X-ray diffraction patterns for 1) parent MCM-41 and 2) 10 wt% PW on MCM-41 (from MeOH, 20 h).](image-url)
loading. Evaporation of the suspension was carried out below 60 °C using a rotary evaporator. Unless otherwise stated, the catalysts were mildly calcined at 130 °C/0.3 mmHg for 1.5 h and stored in a desiccator over P₂O₅.

CsPW/MCM-41 materials were prepared via two routes. Route I: 30 wt% PW/MCM-41 (prepared as mentioned above) was allowed to react with 2.5 equivalents of Cs₂CO₃ with respect to the PW loading, in methanol. Route II: MCM-41 was impregnated in methanol with the same amount of Cs₂CO₃ as in route I. Then Cs₂CO₃/MCM-41 was loaded with 0.75 equivalents of HPA in methanol. In all cases the solvent was removed as mentioned earlier.

**Techniques**

**³¹P NMR spectroscopy**

161.90 MHz ³¹P MAS NMR spectra were measured at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe as described elsewhere. ³¹P in D₂O was used as an external reference. Special care was taken to protect solid samples from moisture. The accuracy of the chemical shift determination was within ± 0.4 ppm.

**²⁹Si NMR spectroscopy**

Solid-state ²⁹Si MAS NMR spectra were recorded in a similar way as above. Applying a resonance frequency of 79.450 MHz, a recycle delay of 20.0 s, short 3.0 μs pulses, a spectral width of 15 kHz and a spinning rate of 7 kHz. The lines were referenced to tetramethylsilane (0 ppm).

**X-ray diffraction**

Powder X-ray diffraction measurements were carried out on a Philips PW 1840 diffractometer using monochromated CuKα radiation. Patterns were recorded over the range from 1 to 40° (2Θ) in steps of 0.02° with a count time of 2 s at each point.

**Transmission electron microscopy**

Transmission electron microscopy (TEM) was performed with a Philips CM 30 ST electron microscope with a field emission gun operated at 300 kV and equipped with an energy dispersive X-ray (EDX) element analysis system. The ground PW/MCM-41 and PW/SiO₂ samples were suspended in n-hexane. A copper grid coated with a microgrid carbon polymer was loaded with a few drops of this suspension.
Study of catalysts comprising heteropoly acid H₃PW₁₂O₄₀ supported on MCM-41 molecular sieve...

Reactions

Liquid phase trans-de-tert-butylation of 2,6-di-tert-butyl-4-methylphenol (DBMP) with o-xylene as tert-butyl group acceptor and suspended solid HPA catalysts was carried out as follows. A round-bottomed flask containing 0.95 mmol of DBMP (0.209 g; ACROS), 1.8 mmol of o-xylene (1.9 g; ACROS) and an appropriate amount of n-undecane (internal standard) was brought to 70 °C. The reaction was started by adding the HPA containing catalyst (5 wt% with respect to the total amount of reactants). The products 2-tert-butyl-4-methylphenol, p-cresol and 1,2-dimethyl-4-tert-butylbenzene formed during the reaction were analyzed by GLC (a Varian Star 3400 CX instrument with 25 m x 0.32 mm CP sil 5CB column) at suitable time intervals.

8-3. Results

Having observed different HPA forms in PW/MCM-41 and also in PW/C, we supposed that PW could partially decompose to form lacunary and/or unsaturated HPA species when preparing the catalysts. In particular, this is likely at low HPA loadings, i.e. at a low PW concentration in the impregnating solutions. In aqueous solution, Keggin HPAs are known to decompose as the pH increases to lacunary PW₁₁O₃₇ (PW₁₁) species at pH ≥ 2, which is close to the pH in our impregnating solutions. This process may be promoted by a solid support, especially if the latter includes basic impurities. On the other hand, Keggin HPAs are more stable in polar organic solvents than in aqueous solutions, which could be used for the preparation of supported HPA catalysts to prevent the decomposition of the Keggin-type species. Methanol is a particularly useful organic solvent due to its high stability towards acids and the high solubility of PW therein. It is also easily removed from the catalysts.

The conditions of catalyst preparation and pretreatment may also influence the stability of supported HPA. In this work, we used milder conditions than those in the publications mentioned above.

PW supported on SiO₂

Figure 8.2 shows the ³¹P MAS NMR spectra for bulk crystalline PW and PW/SiO₂ catalysts at PW loadings ranging from 10 to 50 wt%, obtained by impregnating in water. The spectrum (1) of the bulk PW shows a well-known resonance at around -15 ppm and ca. 50 Hz linewidth, depending on the amount of water of crystallization in the sample. In the spectra of PW/SiO₂, generally two lines are present: one (A) at around -15 ppm from the PW species with intact Keggin structure and the other (B) at around -14 ppm which reflects the presence of a species with a different structure. The relative amounts of the species depend on the HPA loading. Form A is dominating: at higher loadings (30 - 50 wt%), form A is practically the only one.
Figure 8.2. $^{31}$P MAS NMR spectra of PW (1) and PW/SiO$_2$ (from H$_2$O) at various loadings and impregnation times: (2) 50 wt%, 3 h; (3) 40 wt%, 20 h; (4) 25 wt%, 20 h; (5) 20 wt%, 3 h; (6) same sample calcined at 350 °C/0.3 mmHg for 0.5 h; (7) 10 wt%, 3 h.

present on the SiO$_2$ surface. At lower loadings, both forms exist, the amount of B increasing as the HPA loading decreases, in agreement with data.$^{12}$

In aqueous systems, no decomposition of the HPA Keggin structure was observed during shaking SiO$_2$ with HPA aqueous solution (PW/SiO$_2$ 1:4 w/w t) at room temperature for 1 to 20 h, as evidenced by $^{31}$P solution NMR after removing SiO$_2$ from the system. Thus, the transformation of the Keggin units possibly takes place during the drying of the SiO$_2$ + PW + H$_2$O mixture at an elevated temperature and the calcination of wet catalysts. Probably as a result of this, a rather poor reproducibility of the A/B ratio was observed in parallel preparations.

Treating SiO$_2$ with 0.1 M HCl aqueous solution, followed by washing until neutral, did not affect the state of the HPA species on the silica surface. The same occurred with MCM-41 (vida infra). This means that either basic impurities were absent in our supports or they did not affect HPA.

Figure 8.3 shows the $^{31}$P MAS NMR spectra of 10-20 wt% PW/SiO$_2$ catalysts obtained by
impregnating PW onto silica from methanol (MeOH) for 20 h. In these catalysts, only form A was observed even at a HPA loading as low as 10 wt%, in contrast to the impregnation from aqueous systems.

![Figure 8.3](image)

**Figure 8.3.** $^{31}$P MAS NMR spectra for PW/SiO$_2$ (from MeOH, 20 h) at two PW loadings: (1) 20%; (2) 10%.

To examine the influence of the calcination temperature, two catalysts 20 wt% PW/SiO$_2$, one prepared in methanol and containing only form A (Figure 8.3, spectrum 1), the other prepared in water and containing 40 mol% form B (Figure 8.2, spectrum 5), were additionally calcined at 350 °C/0.3 mmHg for 0.5 h. After the calcination, both catalysts, initially white, turned blue, and the intensity of their $^{31}$P resonances was somewhat reduced. However, the first one did not change its NMR spectrum, while in the second the signal of the form B decreased and a new signal appeared at -11.6 ppm, whereas the signal of form A remained unchanged (Figure 8.2, spectrum 6). This may indicate the decomposition of form B upon calcination at 350 °C.

The X-ray diffraction patterns for 10 and 20 wt% PW/SiO$_2$ catalysts prepared in H$_2$O and MeOH as well as for a PW + SiO$_2$ (1:9 wt) mixture are shown in Figure 8.4. Neither of the PW/SiO$_2$ catalysts shows
Figure 8.4. X-ray diffraction patterns for: (1) PW + SiO₂ 1:9 wt mixture; (2) 20 wt% PW/SiO₂ (from H₂O, 3 h); (3) 10 wt% PW/SiO₂ (from MeOH, 20 h); (4) 10 wt% PW/SiO₂ (from H₂O, 3 h).

Figure 8.5. ³¹P MAS NMR spectra of PW/MCM-41 (from H₂O, 20 h) at various PW loadings: (1) 50 wt%; (2) 40 wt%; (3) 30 wt%; (4) 20 wt%.

a HPA crystallinity regardless of the state of HPA therein. This is in agreement with the literature data²⁰,²¹
that the HPA crystal phase on the SiO₂ surface (Sₚₑₑ 200 - 300 m²/g) appears at HPA loadings above 20 wt%.

**PW supported on MCM-41**

Figure 8.5 shows the ³¹P MAS NMR spectra for 20 - 50 wt% PW/MCM-41 catalysts prepared in H₂O (20 h) which have already been discussed elsewhere. Like PW/SiQ, the PW/MCM-41 catalysts at higher loadings, 30 - 50 wt%, consist of practically pure form A, while at lower loadings form B is also present.

The ³¹P MAS NMR spectra for 10 - 40 wt% PW/MCM-41 prepared in MeOH (20 h) are presented in Figure 8.6. As is clearly seen, only form A is present in the catalyst over the whole range of PW loading, as with PW/SiO₂.

As shown earlier by X-ray diffraction, no HPA crystal phase exists in the PW/MCM-41 catalysts obtained in water at the HPA loading as high as 50 wt% due to the large surface area of MCM-41. Therefore a complete monolayer would mean a loading of 50 wt% HPA. Figure 8.1 shows the X-ray diffraction pattern for the 10 wt% PW/MCM-41 prepared from MeOH (20 h). As expected, there is no HPA crystallinity either.

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**Figure 8.6.** ³¹P MAS NMR spectra of PW/MCM-41 (from MeOH, 20 h) at various PW loadings: (1) 40 wt%; (2) 30 wt%; (3) 20 wt%; (4) 10 wt%. 

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Apparently during the solvent vaporization the molecules prefer to enter the MCM-41 system and to coat the wall. In addition, the hexagonal morphology of the MCM-41 support remained intact while the unit cell dimension was decreased from 44 to 42 Å, probably as a result of acid catalyzed condensation of silanol groups.\textsuperscript{24}

Transmission electron microscopy (TEM) analysis was performed on some PW/MCM-41 and PW/SiO\textsubscript{2} samples to determine the location and the size of the PW species which can be distinguished as dark dots in TEM images (Figure 8.7 and 8.8). The TEM image of the MCM-41 structure is rather dominant, which makes it difficult to detect the supported PW species. For this reason the MCM-41 lattice was subjected to amorphization using the electron beam. The TEM image (Figure 8.7b) of a thinner part of the 40 wt% PW/MCM-41 sample (from MEOH, 20 h) shows that in this catalyst there is practically no PW species on the edges of the MCM-41 particles. The PW species range from 10 to 15 Å close to the molecular size of HPA (12 Å). It should be noted that this is only a rough estimate because of the difficulty in size determination due to the blurring by the amorphous matrix. In contrast, in 35 wt% PW/SiO\textsubscript{2} (from MeOH, 6 h) (Figure 8.7a), there are many PW species on the edge of the SiO\textsubscript{2} particles, indicating that PW is situated on the outer surface of the non-porous support. Figure 8.8a and 8.8b show the micrographs of the same area of the 40 wt% PW/MCM-41 before and after amorphization, respectively. The sample before amorphization exhibits a TEM image with strong contrast dark lines indicative of the regular crystal lattice of MCM-41. Remarkably, after amorphization, the similar structure although with less contrast is observed. In this case, the dark lines originate from the PW species which were in the MCM-41 channels before the amorphization. No indication of PW clustering during amorphization was obtained. In addition, no PW species are observed on the edges of the MCM-41 particles. This is a clear indication that the PW species are mainly located inside the MCM-41 pores, which is supported by EDX elemental analysis. Thin parts of a given MCM-41 particle showed the same W/Si ratio as the much thicker parts. If PW species were mainly located on the surface, the W/Si ratio of the thick parts would be much smaller.

$^{29}$Si MAS NMR on activated (150 °C/3 mmHg) 40 wt% PW/MCM-41 and on the original MCM-41 support showed a difference in the spectra considering the Q4 environment and Q3 (Q4 and Q5 represent incompletely condensed and fully condensed silicon atoms, respectively).\textsuperscript{24,25} Upon impregnation of MCM-41 with PW, the Q4/Q5 ratio decreases from 0.8 to 0.5.

The preparation of CsPW/MCM-41 was followed by X-ray diffraction. Interestingly, both routes (see experimental section) gave the same X-ray diffraction pattern which is shown by bulk crystalline cesium salt of PW.\textsuperscript{1} In spite of the insolubility of CsPW in water and organic solvents,\textsuperscript{14,15,26} it appeared that formation of these X-ray visible species could not be suppressed by varying the impregnation conditions. Evaporation of methanol immediately after addition of one of the active components (Cs\textsubscript{2}CO\textsubscript{3} or PW) did not
Figure 8.7. TEM images: (a) 35% PW/SiO$_2$ (from H$_2$O, 6 h) and (b) 40% PW/MCM-41 (from MeOH, 20 h) after amorphization.

Figure 8.8. TEM images of the same area of 40% PW/MCM-41 (from MeOH, 20 h): (a) before and (b) after amorphization.
result in vanishing of these diffraction patterns.

Catalyst testing

The catalysts were tested in the trans-de-tert-butylation of 2,6-di-tert-butyl-4-methylphenol (DBMP) with o-xylene (Figure 8.9) as a model reaction. This reaction is of potential interest as a step in the synthesis of stabilizers; it was studied in detail earlier by one of the present authors with both bulk and SiO₂-supported PW.¹⁹

Table 8.1 shows the testing results for the authentic specimen 20 wt% P₂W₁₈/SiO₂ (from MeOH) and two catalysts with the same loading 20 wt% PW/SiO₂ obtained from methanol or water, one containing the pure form A (see Figure 8.3, spectrum 1), and the other containing the maximum amount of form B, A/B

![Chemical structure](https://example.com/chemical_structure.png)

**Figure 8.9.** Trans-de-tert-butylation of DBMP with o-xylene.

60/40 mol% based on phosphorous (Figure 8.2, spectrum 5). The catalytic activity was characterized as the time corresponding to a 30 % DBMP conversion, the selectivity to 2-tert-butyl-4-methylphenol being 100 %; at higher conversions, p-cresol was also formed as a result of the de-tert-butylation of 2-tert-butyl-4-methylphenol. The 60/40 mol% A/B catalyst (from H₂O) appeared to be twice as active as the 100 % A catalyst (from MeOH) per catalyst weight, and P₂W₁₈/SiO₂ was the most active in the series. It should be noted that 20 wt% P₂W₂₁/SiO₂, which might be expected to be nearly as active as the P₂W₁₈/SiO₂ catalyst, showed about two times lower activity than P₂W₁₈/SiO₂. This may be due to incomplete exchange of Na⁺ by H⁺ in the electromembrane synthesis of P₂W₂₁.¹⁷

Interestingly, 10 wt% PW/MCM-41 (100 % A, from MeOH) is about 6 times more active than the higher loaded 20 wt% PW/SiO₂ though both preparations contain pure A. MCM-41 loaded with 10 wt% pure A shows also a higher activity than 10 wt% PW/MCM-41 (100 % B, from H₂O). The high activity of 10 wt% PW/MCM-41 (100 % A, MeOH) is probably due to a high accessibility of the highly dispersed PW particles on the MCM-41 support (high BET surface area and pore volume). The difference in activity between MCM-41
Table 8.1. Trans-de-tert-butylation of DBMP with HPA catalysts.\textsuperscript{a}

<table>
<thead>
<tr>
<th>catalyst</th>
<th>time (min)\textsuperscript{b}</th>
<th>relative activity per 1 mol HPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 wt%PW/SiO\textsubscript{2} (100% A, from MeOH)</td>
<td>64</td>
<td>1</td>
</tr>
<tr>
<td>20 wt%PW/SiO\textsubscript{2} (60/40 A/B, from H\textsubscript{2}O)</td>
<td>27</td>
<td>8\textsuperscript{c}</td>
</tr>
<tr>
<td>20 wt% P\textsubscript{2}W\textsubscript{18}/SiO\textsubscript{2} (from MeOH)</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>10 wt% PW/MCM-41 (100% A, from MeOH)</td>
<td>21</td>
<td>6</td>
</tr>
<tr>
<td>10 wt% PW/MCM-41 (100% B, from H\textsubscript{2}O)\textsuperscript{d}</td>
<td>54</td>
<td>4\textsuperscript{e}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Conditions: 70 °C, [o-xylene]/[DBMP] = 20 mol/mol, 4.5 wt% catalyst (with respect to the total amount of reactants; selectivity to 2-tert-butyl-4-methylphenol is 100 mol%). \textsuperscript{b} Corresponding to a 30% DBMP conversion. \textsuperscript{c} Activity of form B per P\textsubscript{2} entity. \textsuperscript{d} Reaction at 100 °C, for more details about the catalyst see ref. 7.

supported form A and B might be the result of partial pore blocking for the relatively large DBMP due to the much bulkier B (radius of P\textsubscript{2}W\textsubscript{18} is about 25 Å and the pore size of MCM-41 is 32 Å). The poor accessibility is also reflected by the required higher reaction temperature.

8.4. Discussion

Despite the relative inertness of the silica towards tungsten HPAs, the catalysts, comprising PW supported on pure siliceous supports, amorphous SiO\textsubscript{2} or mesoporous molecular sieve MCM-41, prepared by conventional impregnation with an aqueous PW solution include at least two HPA forms, which can well be discriminated by \textsuperscript{31}P MAS NMR.\textsuperscript{12} One (A) with intact Keggin structure and the other (B) with a different structure. The relative amount of the two forms depends on the HPA loading and the preparation method. Under the reported conditions, form A is the dominating one, the amount of B is increasing with decreasing HPA loading. Maximally about 40 mol% form B has been observed in 20 wt% PW/SiO\textsubscript{2} (Figure 8.2, spectrum 5), which is somewhat less than that found in reference 12. This may be explained by the difference in preparation conditions. It is worth noting that the pure Keggin-type PW species on SiO\textsubscript{2} or MCM-41 surface can be prepared from water at higher loadings, 30 - 50 wt%.

With the less stable molybdenum HPAs, the decomposition of the Keggin units on the SiO\textsubscript{2} surface, depending on the HPA loading, was shown elsewhere\textsuperscript{26} (for a review see reference 1). Thus PMo, SiMo and PMo\textsubscript{10}V\textsubscript{2} retain the Keggin structure at high loadings, like PW, but decompose to form MoO\textsubscript{3} and practically lose their acidity at a very low loading, due to their strong interactions with surface silanol groups. On the other hand, thermally decomposed Keggin structures of molybdenum HPAs on the silica surface may be
generated on exposure to water vapor.\textsuperscript{26}

The important result of this work is the preparation of the catalysts, comprising the purely Keggin-type PW species on the siliceous surface over a wide range of PW loading. This is conveniently done by PW impregnation from an organic solution, viz. methanol. The major reason why it succeeds is thought to be the greater stability of the Keggin units towards hydrolysis in organic solvents compared to aqueous solutions\textsuperscript{6} in combination with the strong affinity to adsorb at the siliceous surface. Both SiO\textsubscript{2}- and MCM-41-supported PW catalysts can be prepared in this way.

Let us now consider the nature of species A and B. Earlier in the study of PW/SiO\textsubscript{2} catalysts with higher PW loadings (up to 87 wt\%), form A was assigned to the bulk crystalline PW on the SiO\textsubscript{2} surface, as based on the \textsuperscript{31}P NMR together with X-ray diffraction data; the latter indeed indicated the presence of the PW crystal phase on the surface.\textsuperscript{12} In the case reported here, as shown by X-ray diffraction, and regardless of the solvent used, no PW crystal phase is present in PW/MCM-41 at loadings in the range of 10 - 50 wt\%;\textsuperscript{7} nor is there PW crystallinity in PW/SiO\textsubscript{2} at the loadings below 20 wt\%. As found by TEM, these catalysts include finely dispersed species, mainly discrete PW molecules on the surface of siliceous support. In the case of PW/MCM-41, the PW species are mostly situated inside the channels rather than on the outer surface of the molecular sieve and are interacting with the MCM-41 support via the silanol groups by proton transfer (equation 2) as indicated by \textsuperscript{29}Si MAS NMR. Therefore, not only can form A be assigned to the bulk PW species on the silica surface, as in the PW/SiO\textsubscript{2} catalysts with higher PW loadings but also to the discrete surface of HPA molecules with intact Keggin structure, as observed in this work. These two species have \textsuperscript{31}P NMR spectra similar to those of crystalline PW and PW in solution.\textsuperscript{9}

Less certain is the nature of form B. This species was supposed to be the 'interacting' Keggin-type HPA formed via reaction (2)\textsuperscript{12} or the product of a partial decomposition and transformation of the Keggin structure, e.g. the lacunary species, like PW\textsubscript{11} or P\textsubscript{2}W\textsubscript{17}, or unsaturated HPAs P\textsubscript{2}W\textsubscript{8} or P\textsubscript{2}W\textsubscript{21}, having \textsuperscript{31}P NMR solution resonances in the same region.\textsuperscript{9} The latter seems to be more likely for the following reasons:

(i) Form B is not present in the catalyst prepared from MeOH, as expected from the greater stability of the Keggin HPAs in MeOH compared to water.\textsuperscript{6} On the other hand, reactions (1) and (2) could proceed without any solvent on the catalyst surface and, therefore, would not be affected by solvent.

(2) Given form A for both bulk PW and discrete PW molecules on the surface, from the chemical point of view, there is hardly any difference between the surface PW molecule and the 'interacting' species like (\textsuperscript{= Si-OH})\textsuperscript{2}(H\textsubscript{2}PW\textsubscript{12}O\textsubscript{40}).

(3) The \textsuperscript{31}P MAS NMR spectra of the species (\textsuperscript{= Si-OH})\textsuperscript{2}(H\textsubscript{2}PW\textsubscript{12}O\textsubscript{40}) and bulk PW are unlikely to be different, because PW in aqueous solution, where it is completely deprotonated,\textsuperscript{6} and the solid bulk PW with the protons localized thereon exhibit \textsuperscript{31}P resonances at the same positions.
The lacunary species are possibly not stable enough to sustain evaporation and calcination. More likely these species, if formed in the SiO₂ + PW + H₂O system, transform to dimeric HPAs like P₂W₁₈ and P₂W₂₁ and undefined W(VI) species. Mechanisms of such transformations are quite complex and scarcely understood. The α-P₂W₁₉O₆₂⁻ and P₂W₂₁O₇₁⁻ heteropolyanions exhibit in the solution ³¹P NMR spectra the signals at -12.7 and -13.3 ppm, respectively. As found in this work, ³¹P MAS NMR spectra of 20 wt% P₂W₁₉/SiO₂ and 20 wt% P₂W₂₁/SiO₂ (from MeOH, 20 h) also give rise to the lines at -13.0 and -13.5 ppm, respectively (Figure 8.10), which is in agreement with the spectrum B (Figure 8.2 and 8.5). P₂W₁₈ and P₂W₂₁ are thermally less stable than PW. Thus they were found to decompose at 350 °C and showed no activity in the cracking of n-hexane at this temperature, while PW was intact and active. The products of decomposition of bulk and SiO₂-supported P₂W₁₈ and P₂W₂₁ exhibited broad signals in ³¹P NMR spectra in the range from -10 to -12 ppm similar to what is observed after calcining 20 wt% PW/SiO₂, containing 40 mol% form B, at 350 °C (Figure 8.2, spectrum 6).

**Figure 8.10.** ³¹P MAS NMR spectra for 20 wt% HPA/SiO₂ (from MeOH, 20 h): (1) P₂W₂₁/SiO₂ and (2) P₂W₁₉/SiO₂. In the spectrum of 20 wt% P₂W₁₈/SiO₂, the signals at -13.0 and around -11 ppm are from α-P₂W₁₈ and β-P₂W₂₁, respectively.

Interaction of the surface PW species with Si-OH is likely considering the ²⁹Si MAS NMR data of the parent MCM-41 and PW/MCM-41. The Q₃/Q₄ ratio decreases from 0.8 to 0.5 after impregnation which
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reflects an increase in the number of fully coordinated silicon and a decrease in the number of free silanol groups. This strengthens the proposed interaction according to equation (2). The interaction according to equation (1) is unlikely, because this would give a new type of Si-resonance instead of a decrease in the intensity of $Q_3$ in the $^{29}$Si MAS NMR spectrum of PW/MCM-41.

Table 8.1 shows the relative molar catalytic activities of A, B and P$_2$W$_{18}$ species on a SiO$_2$ surface in the de-tert-butylation of DBMP. The activity of B is in good agreement with that of P$_2$W$_{18}$. Unexpectedly, B species is around 8 times more active than A despite the fact that P$_2$W$_{18}$ and P$_2$W$_{21}$ are nearly as strong acids as PW.$^{15,29,30}$ A possible explanation of this is that the acid strength of the surface dimeric species B decreases to a lesser extent compared to the Keggin species A due to the interaction with Si-OH groups, as illustrated schematically in Figure 8.11. However, in high-temperature reactions the catalysts containing form B may be less active than those with pure Keggin form A due to the possible decomposition of form B, as found in o-hexane cracking.$^{27}$

\[ A \quad B \]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{Si} \\
\text{OH} \\
\end{array}
\quad
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{Si} \\
\text{OH} \\
\end{array}
\]

Figure 8.11. The binding of A and B to the siliceous surface (schematic).

Considering dimeric PW supported onto the mesoporous MCM-41, the picture contrasts with the SiO$_2$ systems. Pore blocking due to the larger size of P$_2$W$_{18}$ and/or P$_2$W$_{21}$ influences the activity negatively. Actually, comparing all the activities of the subjected materials it can be suggested that the advantage of pure-Keggin type HPA for catalysis is clearly demonstrated by the MCM-41 systems.

Regarding the formation of crystalline cesium salt of HPA on impregnation of MCM-41 via both two-step procedures (see experimental section), the proposed interaction of HPA according to equation (2) is most reasonable. In principle the cesium salts of the type Cs$_x$H$_{3_y}$PW$_{12}$O$_{40}$ (2 ≤ y ≤ 3) are insoluble in methanol. The rapid formation of X-ray visible CsPW might be the result of supported-H$_3$PW$_{12}$O$_{40}$ partly exchanged by Cs$^+$ cations which are probably better soluble in methanol than completely Cs$^+$ ion-exchanged PW. The weak interaction of the HPA-protons with the support due to the large size of Cs$^+$ cations may result in a gradual migration of the better-soluble partly ion-exchanged CsPW species to the edge and/or outer surface of the MCM-41 particle. Migration of CsPW species immediately after addition of the active
components PW or Cs$_2$CO$_3$ and rapid-solvent evaporation seems unlikely. A comparable supported-CsPW preparation via precipitation/deposition of PW on Cs$_2$CO$_3$/SiO$_2$ appeared to be diffusion controlled and gave crystalline CsPW on silica at 40 wt% Cs$_2$H$_{10}$PW$_{12}$O$_{40}$ loading.$^{26}$

Imagine an interporous Cs$^+$ ion-exchange process in which Cs$_2$CO$_3$ is neutralizing adsorbed HPA in the proton form; during the course of the reaction the PW compound will grow in size till the pore size maximum of MCM-41 is reached. This will probably result in interporous CsPW which is anchored due to its large dimension. On the other hand, CsPW likes to form submicron particles or in other words has a preference to be situated on the outer surface of the support. Bulk particles of the cesium salt Cs$_y$H$_{3y}$PW$_{12}$O$_{40}$ (y is around 2.5) have a size between 70 and 100 Å, calculated from physisorption data.$^{14}$ A recent transmission electron microscopy study gave a size between 60 and 150 Å.$^{15}$ The precise interplay between the Cs$^+$ cations and the (supported)-HPA is thus quite complicated. Nevertheless, whatever the process is it can be concluded that the interaction of MCM-41 with CsPW is weaker than that with PW.

8.5. Conclusion

At low loadings active pure Keggin-type heteropoly acid (HPA) on MCM-41 and SiO$_2$ has been prepared. When water is avoided during the preparation, formation of dimeric structures is suppressed, even at low HPA loading. The interaction of HPA with the siliceous surface of the support occurs basically via proton transfer to silanol groups.

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Controlled recrystallization of MCM-41 and HMS to a composite mesoporous material with ZSM-5 nanostructures*

9-1. Introduction

Among various refining processes for upgrading heavier feedstocks to lighter products is the fluid catalytic cracking (FCC) process definitely indispensable.¹ Active zeolitic components in commercial FCC catalysts are Y and often ZSM-5.²,³ Unfortunately, selective cracking of the “bottom of the barrel” is limited due to pore size restrictions. H-MCM-41⁴ gives in the cracking of vacuum gas oil a higher yield of gasoline and less gaseous products compared to USY.⁵,⁶ Comparable results are found in the cracking of naphtha, whereby ZSM-5 gives more undesirable products, such as light gas and linear paraffins, than MCM-41 does.⁶ Other workers have found that MCM-41 is a suitable active component in cracking catalysts for “deeper” cracking of high boiling hydrocarbons.⁸ The benefit of the mesopores of MCM-41 is illustrated in a tenfold higher conversion in the cracking of 1,3,5-tri-tert.-butylbenzene compared to USY.⁵ However, the latter material contains much stronger Bronsted acid sites than MCM-41 which is reflected by a much higher activity of USY in n-heptane cracking.⁶ A small difference in catalytic activity between H-MCM-41 and H-Y is observed in the hydrocracking of cumene. The latter catalyst appeared to be about twice as active.⁵ The mesoporous molecular sieve HMS which is prepared via the neutral templating route¹⁰ is two times more active in cumene cracking than the related MCM-41 material.¹¹ The authors reported that HMS possesses a higher number of Bronsted acid sites than MCM-41. Nevertheless, it is apparent that for particular applications the acidity of both MCM-41 and HMS is too weak.

The framework of both MCM-41 and HMS has an amorphous character.¹²,¹³ This implies that framework aluminum is not tightly bonded, which is a useful tool for further modification of the mesoporous framework. The flexibility of incorporated aluminum¹⁴ therefore allows a transformation from an amorphous to a crystalline surrounding. From crystallization studies on ZSM-5 it is known that a synthesis gel is first converted into oligomers or monomers of double-five rings.¹⁵,¹⁶ ¹³C NMR on these X-ray amorphous ZSM-5

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precursor phases show that the tetrapropylammonium (TPA) cations are not randomly orientated, but are directed in a particular configuration.15 Creating such oligomers of double-five rings at the inner surface of the mesoporous framework of MCM-41 and HMS materials will most probably enhance the acidity of these materials. The approach reported in this chapter to prepare modified aluminosilicate mesoporous molecular sieves is by hydrothermal treatment of TPA-containing materials. The extracrystalline TPA-cations are positioned by ion-exchange of mesoporous material in the Na- or H-form with TPA bromide salt or TPA hydroxide.

Another strategy to increase the acidity and catalytic activity is to recrystallize MCM-41 and HMS into a composite consisting of the mesoporous host with very small interporous ZSM-5 aggregates. Actually, in this case the original material is partially transformed into an other material. Theoretically, a material with this composition possesses a bimodal pore size distribution, or even better, micropores which are only accessible via the mesoporous support. In FCC preparation today a combination of macropores frp 3xmacropores amorphous matrix with micropores of a zeolite is used.17 Controlled growth of macro-/mesopores ending up progressively in zeolitic micropores will probably enhance the accessibility of the various catalytic sites and thus the catalytic performance.17 In the field of zeolite synthesis such "cascade-type" pore configurations are aimed at by preparing mesopores interconnecting micropores. In microporous materials such pore configurations can be achieved in various ways. Firstly, by creating mesopores via dealumination of Y,18 mordenite19 or mazzite.20 Secondly, by pillaring of MCM-22.21 Finally, by overgrowth of MCM-41 on FAU.22

By combining the experience in the crystallization of ZSM-523 and in the synthesis of MCM-41,22,24 a new route might be opened in preparing composite materials with both mesopores and micropores. In this chapter a study of tetrapropylammonium hydroxide treatment of aluminosilicate mesoporous molecular sieve with formation of a composite molecular sieve containing both host and ZSM-5 structures is reported. Materials of this type could perhaps be of particular interest to refiners. In fact, additives containing an estimated ≤3 wt% of ZSM-5 have been in use worldwide to improve gasoline octane.25,26 Typically the zeolite-containing additive, consists of a matrix such as alumina or an aluminosilicate gel5 in which ZSM-5 crystallites are uniformly dispersed.

The approach chosen to synthesize the present composite molecular sieve is based on optimization of the ZSM-5 stoichiometry in for instance the MCM-41 phase. It is well-known that in as-synthesized ZSM-5 each tetrapropylammonium (TPA) is surrounded by 24 tetrahedrally coordinated silicon and/or aluminum atoms.27 Thus in MCM-41 with a Si/Al of 30 there are thirty one T-atoms neighbouring one TPA-cation in TPA-MCM-41. This ZSM-5 precursor-like situation is expected to accelerate ZSM-5 crystallization. Eventually, to obtain a mesoporous support with randomly distributed very small microporous ZSM-5 crystallites of a few unit cells it is necessary to control the ZSM-5 synthesis and suppress the complete
Controlled recrystallization of MCM-41 and HMS to a composite mesoporous material with...

consumption of the MCM-41 material by interrupting ZSM-5 crystallization.

This chapter deals first with the hydro-isomerization of n-heptane over Pt loaded large-scale synthesized MCM-41 and MCM-48. Thereby it will be shown that the acid strength and catalytic performance resemble that of commercially amorphous silica-aluminas and that ZSM-5 is actually a much stronger Bronsted acid catalyst. The surface-modified mesoporous aluminosilicates, the prepared composites and the original mesoporous hosts are tested in the catalytic cracking of n-hexane and cumene. Enhanced acidity and catalytic activity of the modified aluminosilicates will eventually result in an improved performance compared to the starting materials. Various characterization techniques are presented to study the recrystallization process and other related parameters.

9-2. Experimental

Synthesis

MCM-41 support

MCM-41 was prepared by mixing 16.5 g TMA-SiO₂ solution (TMA/SiO₂ = 0.5; 10 wt% SiO₂; tetramethylammonium hydroxide (TMAOH) was purchased from Aldrich and the silica source was Cab-o-sil M5 purchased from Fluka) with 6.35 g of sodium silicate (Aldrich; 27 wt% SiO₂). Subsequently 45 g of water and 4.7 g of silica (Cab-o-sil M5) were added to the mixture. Under vigorous stirring 4.9 g of cetyltrimethylammonium bromide (ACROS) in 100 g of water was poured in the mixture. Finally, the gel was enriched with 0.37 g of sodium aluminate (Riedel de Haën; 54% Al₂O₃). The resulting MCM-41 gel was put in a 250 mL polypropylene bottle and kept for 3 days at 100 °C. The solid was filtered and thoroughly washed, dried at 90 °C under vacuum and then calcined at 540 °C for 10 h under air. The Si/Al was 30 according to elemental analysis.

MCM-48 support

The aluminosilicate MCM-48 with Si/Al = 30 was prepared according to reference 28. The procedure is as follows: 14.9 g of cetyltrimethylammonium bromide (ACROS) was dissolved in 2.48 g of sodium hydroxide (Baker) and 180.2 g of water in a 250 mL polypropylene bottle. When the mixture had reached a temperature of around 36 °C 21.3 g of TEOS (Merck) was added under vigorous stirring (~500 rpm). After 5 min the gel was enriched with 1.1 g of Al₂(SO₄)₃.18H₂O (UCB) and stirred finally for 1 h. Then the gel was heated statically at 100 °C for 3 days. The working-up procedure is similar to that of MCM-41.
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HMS support

The aluminosilicate HMS was prepared according to an upscaling of reference 29. A typical procedure is: a mixture of 3.40 g of aluminumisopropoxide (ACROS), 68.3 g of isopropanol (Baker), 158 g of ethanol (Baker) and 104.2 g of TEOS (Merck) was heated at 70 °C. After 3 h this mixture was added to the template solution, which consists of 30.2 g of hexadecylamine (Fluka), 200 g of water and 237 g of ethanol, under vigorously stirring. After 3 days the white solid was worked up which included filtration, soxhlet extraction for template recovery with ethanol for 1 day and calcination at 540 °C under dry air for 10 h.

Large-scale synthesis of MCM-41

Batches of 50 g of aluminosilicate MCM-41 with an Si/Al ratio of 10 and 20 were prepared by using two different templates namely decyltrimethylammonium bromide (C10) and octadecyltrimethylammonium bromide (C18; Aldrich). A typical large-scale synthesis procedure for a small pore MCM-41 with Si/Al = 20 is: 38.3 g of sodium silicate (Aldrich; 27 % SiO₂) was put in a 2 L glass vessel equipped with a mechanical stirrer. A mixture of 26.0 g of 25 wt% TMAOH (Aldrich), 8.1 g of Cab o-sil M5 and 57.8 g of water was added, followed by 28.0 g of Cab o-sil M5. When all the silica was dissolved 70.0 g of decyltrimethylammonium bromide in 470 g of water was poured in the gel under vigorous stirring. After 5 min a suspension of 5.9 g of sodium aluminate (Riedel de-Haën) was added. The mixture was stirred for 2 h at room temperature and subsequently heated to 100 °C after the vessel had been sealed. After 1 day the mixture was cooled down to room temperature and the solids were collected by filtration and washed till the pH was neutral. The other batches were prepared by adding the appropriate amount of sodium aluminate and the same concentration of template.

The X-ray diffraction data indicated that the prepared materials possessed the usual MCM-41 features. 27Al MAS NMR showed that most of the aluminum was tetrahedrally incorporated. Nitrogen physiosorption gave a pore size of the MCM-41 materials prepared with C10 and C18 templates of 2.5 and 40 Å, respectively.

Large-scale synthesis of MCM-48

The procedure of the preparation of batches of 50 g of MCM-48 with Si/Al = 30 is similar to that of the preparation of MCM-48 mentioned earlier. However, in this case the amounts are substantially larger, namely 1470 g of water, 20.2 g of NaOH, 121.3 g of cetyltrimethylammonium bromide, 173.4 g of TEOS and 8.95 g of aluminum sulfate. The same setup was used as for the large-scale synthesis of MCM-41. The X-ray diffraction data indicated that the prepared material possessed the usual MCM-48 features. 27Al MAS
NMR showed that most of the aluminum was tetrahedrally incorporated. Elemental analysis gave a Si/Al ratio of 22.

TPAOH treatment/recrystallization

Method I

The calcined MCM-41 material (1.0 g) was allowed to equilibrate with TPAOH (CFZ; 40 wt% aqueous solution) and water under stirring at room temperature for 2 h in the following molar ratios: \(60 \text{SiO}_2 : \text{Al}_2\text{O}_3 : x \text{TPA}_2\text{O} : 1500 \text{H}_2\text{O} (x = 1, 2, 3 \text{ and } 4)\). The mixture was put in a 15 ml teflon lined autoclave and allowed to react in a conventional oven at 170 °C for appropriate times. The resulting materials were cooled quickly to room temperature, collected by filtration, washed with distilled water and dried at 90 °C under vacuum. Eventually, the materials were calcined at 500 °C for 5 h under air.

Method II

2 g of a calcined mesoporous material was ion-exchanged with 1.5 eq. of TPAOH with respect to the amount of framework aluminum (about 1.2 g of 40% TPAOH), in 1 L of water. After one night the material was filtrated, washed and dried at 90 °C under vacuum. The dry powder and 10 g of glycerol were loaded in a teflon-lined autoclave and heated at 120 °C for 1, 2 or 3 days and subsequently cooled down and washed with water.

Characterization

The calcined samples were characterized by powder X-ray diffraction on a Philips PW 1840 diffractometer using monochromated CuKα radiation. Patterns were recorded from 1° to 40° (2θ) with a resolution of 0.02° and a count time of 1 s at each point.

Solid-state \(^{27}\text{Al}\) MAS NMR spectra were recorded at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe. A resonance frequency of 104.21 MHz, a recycle delay of 0.1 s, short 3 \(\mu s\) pulses (45° pulses of 3 \(\mu s\) ), a spectral width of 50 kHz and a spinning rate of 6.2 kHz were applied. The lines were referenced to \(\text{Al(NO}_3\text{)}_3\) (0 ppm). The materials measured were hydrated by equilibrating them with air.

Multipoint BET surface areas and pore volumes were calculated from \(\text{N}_2\) adsorption/desorption isotherms at -196 °C using a Quantachrome Autosorb 6 instrument. The samples were outgassed for 16 h in vacuum at 350 °C prior to use. Argon adsorption measurements in the micropore as well as in the mesopore region were conducted on a Micromeritics ASAP 2000 apparatus reconstructed with very low-pressure equipment. The method of Horváth and Kawazoe\(^30\) was used to determine the pore size distribution.
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Transmission electron microscopy was performed with a Philips CM 30 ST electron microscope with a field emission gun operated at 300 kV and equipped with an energy dispersive X-ray (EDX) elemental analysis system. The ground samples were suspended in ethanol. A copper grid coated with a microgrid carbon polymer was loaded with a few droplets of this suspension.

Ammonia temperature programmed desorption (TPD) was performed on a Micromeritics 2900 TPD/TPR instrument. First the materials were calcined at 600 °C for 5 h under a stream of dry air and subsequently cooled down to 110 °C under a helium flow. The activated samples were saturated at this temperature with ammonia during 0.5 h followed by purging under a helium flow till all the physisorbed ammonia was removed. The TPD was performed in a helium flow of 10 mL/min by heating from 110 to 600 °C with a heating rate of 10 °C/min.

Fitr spectroscopy was performed on an IFS 66 Bruker Spectrometer using the KBr pellet technique.

Activity tests

Hydro-isomerization of n-heptane

The experiments were performed in a test unit at the Shell Research and Technology Centre, Amsterdam. The 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 mol/mol ratio. The temperature during the reactions was successively increased and decreased between 160 and 400 °C, respectively, by using a heating rate of 0.22 °C/min. The gas hourly space velocity (GHSV) in all cases was 1120 mol(stp)/g.h. The products were analyzed by GC. The activity of the catalysts is denoted as the temperature at which the conversion was 40%.

The MCM-41 and MCM-48 materials were prepared according to the large-scale procedures described above. All were NH₄⁺ ion-exchanged and subsequently calcined at 450 °C for 4 h to obtain the extraframework H⁺ cation for charge compensation. A sieve fraction of 40-80 mesh has been used and was impregnated with 0.4 % Pt. The tests were done with extrudates containing 50 % alumina as a binder. Before each reaction the catalysts were in situ reduced at 400 °C for 2 h. Measurements on a commercial amorphous silica-alumina (ASA) catalyst and H-ZSM-5 (both loaded with 0.4 % Pt) have been included. For confidential reasons more details can not be given.

Cracking of n-hexane

Samples of the starting aluminosilicates and the TPAOH treated samples were tested in a hexane cracking test. The ammonia exchanged materials were carefully pelletized, crushed and sieved; the fraction with a diameter between 0.7 and 1.0 mm was collected. Cracking was performed at 450 °C and atmospheric pressure with 0.5 g of material stored under ambient, downflow, in a borosilicate glass tube (i.d. 7 mm) heated
by a fluidized bed oven. The catalysts were pretreated under a nitrogen stream at 450 °C to accomplish the calcination of the \( \text{NH}_4 \)-form to the H-form. The feed gas (400 \( \mu \text{l}\text{N}_2 / \text{s} \)) contained 24.4 vol % hexane. Quantitative analysis was performed by on-line GC (cp sil5 column).

**Cracking of cumene**

Cracking of cumene was carried out using an automated bench-top reactor system of Autoclave Engineers BTRS-900 in a conventional fixed bed set-up with 1.0 g of catalyst pellets (\( d_p = 0.7 \) to 1.0 mm) in a stainless steel tube reactor (i.d. 7 mm). Prior to the reaction the catalysts were activated for 5 h at 500 °C under a stream of dry air and subsequently the furnace was cooled down to the reaction temperature under a stream of nitrogen. The carrier gas (25 mL N\(_2\)/min) was saturated constantly with 14.4 \( \mu \text{mol} \) cumene/min (ACROS). The progress of the reactions were monitored by an on-line GC (cp sil5 column).

**9-3. Results and discussion**

**Structural acidity of MCM-41**

Hydro-isomerisation of \( n \)-heptane is an often used test reaction to establish the Bronsted acidity of an acid catalyst. The experiments, which are performed at in a test unit at the Shell Research and Technology Centre at Amsterdam, require the use of large amounts of catalyst. A combination of different factors such as choice of ingredients and equipment resulted in the large-scale syntheses of a number of batches at a 50 g scale. The details about the synthesis are presented in the experimental section. The characterization data of these batches are almost identical to those of the materials prepared on a small-scale.

**Table 9.1** Temperature at 40 % conversion in the hydro-isomerization of \( n \)-heptane\(^a\) over aluminosilicate catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41(^b)</td>
<td>330</td>
</tr>
<tr>
<td>MCM-48(^c)</td>
<td>331</td>
</tr>
<tr>
<td>ASA</td>
<td>340</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>210</td>
</tr>
</tbody>
</table>

\(^a\) Conditions see experimental part; \(^b\) H-MCM-41 with Si/Al = 10 and 20; \(^c\) H-MCM-48 with Si/Al = 30.

Table 9.1 shows the activity of the parent catalysts which is expressed as the temperature at 40 % conversion. The observed behaviour of MCM-41 and MCM-48 is comparable with that of ASA, a
commercial amorphous silica-alumina catalyst. ZSM-5, however, gave the same conversion at about 210 °C which can be explained by the higher Bronsted acidity. These data confirm that the Bronsted acidity of MCM-41 is rather low compared to that of zeolites. MCM-41 behaves like an amorphous aluminosilicate which is in agreement with the results of other workers. Nevertheless, there is no doubt that the catalytic activity of MCM-41 type materials might be improved to expand the number of potential applications.

Recrystallization study of MCM-41 upon treatment with TPAOH

Results concerning the partial recrystallization of MCM-41 will be presented first, followed by the modification of the surface of the framework of MCM-41 and HMS. Studying the TPAOH treatment of MCM-41 by X-ray powder diffraction some interesting aspects are observed. Figure 9.1 shows the X-ray diffractograms of the parent MCM-41 (Si/Al = 30) and the TPAOH-treated MCM-41 samples (calcined at 500 °C) at reaction times varying from 90 min to 1080 min (samples A to D, x = TPA/Al = 4) by using method I (aqueous medium). It can be observed that the high order reflections of the parent MCM-41 (d_{110} = 22 Å and d_{200} = 19 Å) have disappeared within 90 min. The intensity of the d_{100}-spacing (38 Å) of MCM-41 is moderately present in samples A and B. Surprisingly, a new peak with a 63 Å d-spacing can be observed in sample A. Sample B shows also a peak in the very low angle region related to a d-spacing of 67 Å. ZSM-5 peaks appear when the reaction time is around 135 min. Further increase of the reaction time leads to complete formation of ZSM-5 (sample D). In other words MCM-41 has been recrystallized into ZSM-5. The strong decrease of the diffraction peaks of the original MCM-41 suggests that the features of MCM-41 have disappeared and the framework is destroyed and becomes amorphous. Sample A shows that the original phase is partly converted into another phase as indicated by the presence of a new peak with a spacing of 63 Å in the X-ray powder diffractogram and by TEM (vida infra), showing non-crystalline areas (indicated by arrows in Figure 9.3). Further quantification of these observations is too speculative however, this phase transformation is tentatively assigned to the development of ZSM-5 precursors. The gradual increase of the ZSM-5 X-ray diffraction peaks of the samples B and C indicates growing of ZSM-5 aggregates. Actually, the recrystallization of ZSM-5 is interrupted in these samples. The TPA-containing sample D (uncalcined) shows an X-ray diffraction pattern (not shown) with a low intensity of the 2θ peaks at 7.8° and 8.7° compared to the 23.1° 2θ peak. This pattern differs from that shown in Figure 9.1 and that of ZSM-5 prepared in a homogeneous solution. 31

FTi.r. spectroscopy reveals that going from sample A to D the vibration at 550 cm⁻¹ is gradually growing, indicating development of ZSM-5 skeleton structures. 32 Though sample A shows a weak skeleton bending vibration at 550 cm⁻¹ it does not possess an X-ray diffraction pattern. This suggests that this material contains very small ZSM-5 structures of a size of at most one unit cell. Differences between X-ray diffraction
Figure 9.1. X-ray diffraction patterns of calcined TPAOH-treated MCM-41 materials (170 °C; x = TPA:Al = 4) with different recrystallization times: A = 90 min, B = 135 min, C = 180 min and D = 1080 min and parent MCM-41 (lower pattern).

and i.r. crystallinity for ZSM-5 on an amorphous matrix have already been reported by other workers. It was already mentioned that the disappearance of the X-ray diffraction pattern of the original MCM-41 suggests at first sight a very fast consumption of MCM-41. However, when applying x = 1 and 90 min reaction time the consumption of MCM-41 could be controlled much better and the disappearance of the d-spacings is retarded.

Transmission electron microscopy (TEM) examination of sample A revealed the presence of 3 types of MCM-41 like particles (Figure 9.3). The first type, the primary phase, showed only barely the $d_{100}$ spacing of MCM-41 in some areas, whereas this spacing was absent in other areas of the crystal. The second type showed the $d_{001}$ spacings of MCM-41 rather dominantly, but with some patches in which these spacings were (almost) absent. Figure 9.3 illustrates the MCM-41 framework which is severely affected by the hydrothermal
Figure 9.2. FTR absorption spectra of the samples A to D (cf. Figure 9.1) and MCM-41. The increase in intensity of the 550 cm\(^{-1}\) band can be observed.

treatment. Also voids and/or amorphous material (a few domains are indicated by arrows) can be observed. The third MCM-41 type material observed is crystalline with continuous \(d_{001}\) spacings. The two latter types were minor phases. Only the first type of MCM-41 particles were observed in samples B and C. These observations suggest that, within one batch several stages of the transformation of MCM-41 into another phase occur. The TEM experiments also show that patches in which MCM-41 \(d_{001}\)-spacings were absent, do occur in a random manner in the whole volume representing the MCM-41 crystal.

The importance of the TPA/Al ratio of MCM-41 is reflected by the difficulty in converting MCM-41 with a Si/Al = 20 into ZSM-5. In contrast to the MCM-41 sample described above (Si/Al=30) only a very small amount of X-ray crystalline ZSM-5 could be observed after TPAOH loading and reaction overnight at 170 °C \((x = 4)\). TEM analysis of these materials reveals just slightly affected MCM-41 particles. This also indicates that the first step is apparently not just amorphisation of MCM-41. Analogously, a thermally treated aluminosilicate gel (sodium free) with a comparable Si/Al ratio is crystallized with difficulty towards ZSM-5 and leads to ZSM-5 of a poor crystallinity.\(^{33}\)

Nitrogen physisorption on sample A differs substantially from that found for MCM-41 (Figure 9.4). MCM-41 shows the typical Type IV isotherm with the presence of hysteresis.\(^{34}\) The effect of the thermal TPAOH-treatment for 90 min on the pore aperture of MCM-41 is illustrated by the nitrogen isotherm of sample A. The sharp inflection at \(p/p_0 = 0.3 - 0.4\), characteristic of capillary condensation within uniform
cylindrical pores, has disappeared. The desorption isotherm inflects to the adsorption isotherm at p/p₀ = 0.45. This isotherm can be classified as a Type I isotherm with a hysteresis loop of the Type H4 of the IUPAC classification. The combination of this type of isotherm and the hysteresis loop is indicative of microporosity with large holes or slit-like pores. TEM data do not allow distinction between these two possibilities. The BET area of sample A has decreased by a factor 3 compared to MCM-41 (Table 9.2). The high C-value for the BET equation for sample A is normally associated with micropore filling. Micropore filling into cavities of molecular size can not be excluded, neither can secondary micropore filling which involves quasi-multilayer formation.

Horváth-Kawazoe analysis on the parent MCM-41 and sample A shows again the drastic influence of the TPAOH treatment on the pore size distribution of MCM-41 (Figure 9.5). The Horváth-Kawazoe plot

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET area (m²/g)</th>
<th>Cumulative pore volume (cm³/g)</th>
<th>C-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>1079</td>
<td>0.802</td>
<td>70.6</td>
</tr>
<tr>
<td>A</td>
<td>335</td>
<td>0.171</td>
<td>451.5</td>
</tr>
</tbody>
</table>

Figure 9.3. TEM image of sample A. Voids or amorphous areas are indicated by arrows.
Chapter 9

of MCM-41 shows two peaks. The peak at 10 Å results from monolayer adsorption and the pore filling peak

Figure 9.4. Nitrogen adsorption/desorption isotherms of the parent MCM-41 material and sample A.

Figure 9.5. Horváth-Kawazoe plots of the parent MCM-41 and sample A.
Controlled recrystallization of MCM-41 and HMS to a composite mesoporous material with...

is situated at 40 Å. It is observed that sample A possesses micropores, with a maximum at 5.5 Å which is in harmony with ZSM-5 formation. The distribution extends to the mesopore region indicating the presence of a broad distribution of mesopores.

Figure 9.6 shows the $^{27}$Al MAS NMR spectra of the parent MCM-41 and of samples A to D. Deconvolution of the $^{27}$Al NMR spectrum of MCM-41, assuming Lorentzian profiles for each component, reveals a splitting of the octahedral peak into two peaks at 30 ppm and -2 ppm. The former peak is tentatively assigned to extra-framework aluminum and the latter peak to octahedral aluminum. Compared to the original MCM-41 a large reduction in extraframework aluminum is observed in samples A, B and C. Although effects of the aluminum quadrupole moment and the quadrupole coupling constant cannot be excluded, the decrease of the broad peak is attributed to extraframework aluminum conversion during ZSM-5 formation. Sample D shows only one peak at 53 ppm which can be assigned to tetrahedral aluminum. Line-narrowing of the tetrahedral aluminum peak in the samples A to D is noticed (Figure 9.6-right). This indicates that the local symmetry of the framework AlO$_4$ species in the TPAOH treated samples has increased indicating a smaller T-O-T angle distribution (T represents a SiO$_4$ or AlO$_4$ tetrahedron) due to formation or arrangement of monomers or oligomers of five-membered rings, the building blocks of ZSM-5.

![Figure 9.6 $^{27}$Al MAS NMR spectra of the parent MCM-41 and of the samples A to D (left) and MCM-41 and sample A (right).](image)

Hexane cracking is an often used reaction to investigate the strength of the Bronsted acid sites of a catalyst or the crystallinity of ZSM-5. Generally, only strong Bronsted acid sites are capable of cracking
hexane at mild conditions (350 °C - 450 °C). Table 9.3 illustrates the performance of the samples studied in cracking hexane at 450 °C in a continuous flow reactor. The samples A, B and C appeared to be active in cracking hexane, though the conversions are rather low compared to ZSM-5 (sample D). It is noteworthy, that a commercial aluminosilicate catalyst containing 20 wt% of alumina (HA-HPV) tested under the same conditions showed no hexane cracking activity. Neither did the parent MCM-41 material which contains relatively weak acid sites.38

Table 9.3. Hexane cracking activity of tested samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion (μmol hexane/g.min)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>354.5</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>3.9</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>1.4</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>2.4</td>
<td>335</td>
</tr>
<tr>
<td>MCM-41</td>
<td>0</td>
<td>1079</td>
</tr>
<tr>
<td>HA-HPV*</td>
<td>0</td>
<td>433</td>
</tr>
</tbody>
</table>

a) amorphous aluminosilicate containing 20 wt% alumina and a pore volume of 0.87 ml/g, provided by Akzo-Nobel Chemicals BV.

Interestingly, HMS material (Si/Al = 30) showed a cracking activity which was a little bit lower than that of sample A. This is in agreement with the higher activity of Brønsted acidity of HMS compared to MCM-41 observed in the cracking of cumene11 and indicates that the Brønsted acidity of A is higher than that of the MCM-41 host. The activity of sample A compared to that of sample B and C which both contain small ZSM-5 aggregates suggests that this cracking activity of sample A is caused by the small amount (about 10%) of affected MCM-41 material (Figure 9.2). The affected framework of MCM-41 contains strong acid sites presumably from very small interporous ZSM-5-type aggregates with a size less than one unit cell. The activity of sample A might be improved substantially if the other 90% of the material would also be accessible for catalysis. All the samples showed rapid deactivation by coke formation. The observed activities are consistent with the reported activity for ZSM-5 particles with a size of a few unit cells on an amorphous matrix.33 The low activity of samples B and C, possessing X-ray crystalline ZSM-5, indicates a poor accessibility of the ZSM-5 aggregates which are surrounded by unconverted amorphous material. A low accessibility of silica-supported ZSM-5 crystals in cracking reactions is also found by Landau et al.45 Sample A shows most of the features of the desired composite MCM-41/ZSM-5 molecular sieve, but the amount of
amorphous material has to be decreased by controlling the consumption of MCM-41. This will be rather
difficult to achieve, because the fast vanishing of the X-ray diffraction patterns of the MCM-41 host indicates
that the first step in the recrystallization process is amorphization of the framework.

The approach to synthesize the MCM-41/ZSM-5 composite is actually the opposite of the procedure
of the reported amorphous mesoporous silica-alumina preparation of Bellussi et al.33 These authors
interrupted the ZSM-5 synthesis and obtained ZSM-5 precursors which possessed a mesoporous size
distribution. However, these systems were achieved within a small crystallization-time window and showed
never an X-ray diffraction crystallinity of ZSM-5. Therefore, the system of Bellussi et al. might be more
difficult to control. Recently a transformation of the layered silicate kanemite46 and the aluminum-substituted
magadiite47 to pure-silica ZSM-5 (Silicalite-1) and ZSM-5, respectively, was reported. The authors used a
similar procedure as presented here. It is worth to mention that all-silica MCM-41 is recrystallized into
Silicalite-1 much more easier than aluminosilicate MCM-41 with Si/Al = 30 into ZSM-5 which is in
agreement with the much faster recrystallization of kanemite compared to magadiite.46,47 The easy
transformation of all-silica MCM-41 is also reflected by the hydrothermal alumination into zeolite Na-A.48
The recrystallization process first involves destruction or amorphization of the framework followed by
crystallization into Na-A.

**Controlled recrystallization of MCM-41**

In order to control the recrystallization of MCM-41 more adequately it was thought to be better to
position the TPA-cations at the surface of the framework of MCM-41 which suppresses the diffusion of the
TPA template. Such a thermally controlled recrystallized TPA/MCM-41 sample might result eventually in
a mesoporous molecular sieve with interporous crystalline ZSM-5 nanostructures, called a porous
nanocrystalline aluminosilicate (PNA). The general procedure hereby to prepare the TPA/MCM-41 or
TPA/HMS materials involved ion-exchange in a very diluted TPAOH aqueous solution to avoid the
dissolution of MCM-41 and HMS, respectively (method II in experimental section). Theoretically, a TPA/Al
ratio of 1 would be obtained which agrees with the decrease in Na/Al ratio from 0.8 to 0.1 meaning
substitution of extraframework Na⁺ ions for TPA cations. Table 9.4 illustrates the X-ray diffraction data of
the hydrothermal treatment of TPA/MCM-41 samples in water at 120 °C. Compared to the parent MCM-41
material the intensity of the main diffraction peak of the PNA-1 samples, Iₙ, has decreased substantially. The
Iₙ of the calcined PNA-1 samples are at least similar to the as-synthesized samples, containing the TPA-
template. Complete conversion of MCM-41 into ZSM-5 is not observed by this procedure. Nevertheless, in
all cases the MCM-41 framework is retained more or less which indicates that the transformation of MCM-41
is controlled better than with the previous procedure (method I). Considering ZSM-5 crystallization it is


known that glycerol retards the crystallization of ZSM-5 due to an increase in viscosity.\(^\text{49}\) It was reported that glycerol plays a role in the formation of alkoxy silanes (silicon-glycerol complexes) and \(\equiv SiO\) \(\rightarrow\) cleavage of siloxane bonds and prevents the precipitation of amorphous aluminosilicates.\(^\text{49}\) It seemed therefore worthwhile to investigate the influence of glycerol instead of water on the thermal process of TPA/MCM-41. Interestingly, the \(I_w\) of the samples reacted in glycerol (Table 9.5) appeared to be higher compared to the samples reacted in water which indicates that the mesoporous framework is essentially preserved.

Table 9.4. X-ray diffraction data of the MCM-41 host and the hydrothermally treated TPA/MCM-41 samples giving PNA-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>reaction time(^a) (hours)</th>
<th>(d_{100})-spacing (Å)</th>
<th>(I_w)-as-synthesized(^b) (%)</th>
<th>(I_w)-calcined(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCM-41</td>
<td>-</td>
<td>41</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>41</td>
<td>30</td>
<td>39</td>
</tr>
<tr>
<td>F</td>
<td>4</td>
<td>40</td>
<td>35</td>
<td>40</td>
</tr>
<tr>
<td>G</td>
<td>6</td>
<td>41</td>
<td>25</td>
<td>39</td>
</tr>
</tbody>
</table>

a) Reaction time at 120 °C; b) intensity of the \(d_{100}\)-spacing compared to the original MCM-41.

HMS, which is proposed to be thermally and mechanically more stable than MCM-41 due to the thicker pore walls of HMS,\(^\text{13}\) was subjected to the same procedure. The original HMS material (Si/Al = 30) exhibit a single \(d_{100}\) reflection at \(2\theta = 2.5^\circ\) corresponding with a spacing of 36 Å (Figure 9.7).\(^\text{29}\) The absence of high order Bragg reflections does not necessarily imply a mesoporous material with an ill-defined hexagonal structure.\(^\text{10,13}\) The X-ray diffraction pattern of a thermally treated TPA/HMS sample (PNA-2) in glycerol at 120 °C shows the original \(d_{100}\)-spacing which is a little less intense than that of the parent HMS. In general HMS withstands the thermal procedure better than MCM-41 does, probably due to the thicker pore wall of the former material.

Table 9.5. X-ray diffraction data of the thermally treated TPA/MCM-41 samples in glycerol giving PNA-1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>reaction time(^a) (hours)</th>
<th>(d_{100})-spacing (Å)</th>
<th>(I_w)-as-synthesized(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>3</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>I</td>
<td>5</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>J</td>
<td>23</td>
<td>40</td>
<td>60</td>
</tr>
</tbody>
</table>

a) Reaction time at 120 °C; b) intensity of the \(d_{100}\)-spacing compared to the original MCM-41.
Figure 9.7. X-ray diffraction patterns of calcined (500 °C for 5 h) PNA-1 (sample J) and PNA-2 prepared from MCM-41 and HMS, respectively.

Ft.r. spectroscopy on the original MCM-41 and HMS and the corresponding PNA samples, depicted in Figure 9.8, shows the development of a weak absorption band at 550-560 cm⁻¹. This indicates creation of ZSM-5 nanostructures. The combination of X-ray invisible ZSM-5 structures and the preservation of the mesoporous framework suggests therefore that the surface of the framework is modified to such an extent that interporous double-five rings are formed. It should be noted that the small size of the nanostructures makes detection of the 1260 cm⁻¹ band impossible.

Figure 10.9 illustrates the N₂ adsorption-desorption isotherms of HMS and PNA-2. The adsorption step in the P/P₀ = 0.15 to 0.4 region of HMS is indicative of the existence of framework-confined mesopores. The PNA-2 material shows a less steep adsorption step indicating a reduction in the uniformity of the mesopores. In contrast to HMS PNA-2 shows clearly textural mesoporosity which is verified by the hysteresis loop in the P/P₀ = 0.5 to 1.0 region. The reduction in specific surface area of HMS from 1267 to 796 m²/g for PNA-2 is the result of the increased framework density (2.2 to 2.1 g/cm³) and plugging of a number of pores with amorphous aluminosilicate. Figure 9.10 shows the Horváth-Kawazoe plots by using the cylindrical model of Saito and Foley. The pore size of HMS is calculated to be 27 Å corresponding to a porewall thickness of 15 Å (subtracting the pore size from 4, the repeat distance between pore centers, \( a = 2d_{(100)}/\sqrt{3} \)). The distribution around 10 Å is the result of monolayer adsorption (cf. MCM-41 in the previous
Figure 10.8. F.t.r. absorption spectra of 1) MCM-41, 2) PNA-1, 3) HMS and 4) PNA-2.

paragraph). PNA-2 shows also two pore size distributions, at 10 and 20-25 Å, whereby the former is assigned

Figure 9.9. Nitrogen adsorption-desorption isotherms for HMS and PNA-2.

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Figure 9.10. Horváth-Kawazoe plots (using the cylindrical model of Saito and Foley) of HMS and PNA-2.

to monolayer adsorption. The average pore diameter of PNA-2 may be set to 23 Å. This indicates a calculated wall thickness of around 19 Å.

Ammonia TPD data of H-MCM-41 and of sample J (PNA-1) are illustrated in Figure 9.11. The acidity of MCM-41, which resembles that of amorphous aluminosilicates, is quite weak. It is clear that the aluminosilicate sample J possesses more strong acid sites than the original H-MCM-41 which is illustrated by an increase in NH₃-desorption in the high-temperature region. The acidity is still small compared to crystalline H-ZSM-5 (Si/Al = 26). Nevertheless, the increased acidity of sample J, with respect to MCM-41, is reflected by the cumene and initial n-hexane-cracking activity of sample J (vida infra).

Cumene cracking

An appropriate reaction to make a distinction between Lewis and Bronsted acidity is the conversion of cumene. Cumene is cracked preferentially to benzene and propene over Bronsted acid sites as opposed to mainly dehydrogenation to α-methylstyrene over Lewis acid sites. Both type of acid sites can be responsible for other catalytic process. Dehydrogenation of cumene to α-methylstyrene is mainly observed over (pillared) clays. Table 9.6 summarizes the results of cumene conversion over various samples (observed to be a first order reaction). Considering the two original supports it is observed that HMS is about equally active as H-
Figure 9.11. Ammonia TPD of MCM-41, sample J (TPA/MCM-41: dotted line) and H-ZSM-5 (Si/Al = 26).

MCM-41 which is in agreement with literature data.\textsuperscript{11} The PNA-1 and PNA-2 materials show both a significantly higher cumene conversion than the parent hosts. The four mesoporous aluminosilicates produce only propene and benzene beside traces of α-methylstyrene. The increase in activity of PNA s, the TPA-modified materials, is therefore attributed to an increase in Bronsted acidity. Interestingly, the initial \( n \)-hexane cracking activity of the PNAs is about 4 times higher than that of MCM-41 and HMS. It was observed that when the flow rate was doubled at the same reactant concentration the conversion of cumene over the four

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion (%) at time on stream</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 min</td>
</tr>
<tr>
<td>H-MCM-41</td>
<td>14.7</td>
</tr>
<tr>
<td>PNA-1 (J)</td>
<td>41.3</td>
</tr>
<tr>
<td>HMS</td>
<td>24.8</td>
</tr>
<tr>
<td>PNA-2</td>
<td>47.6</td>
</tr>
<tr>
<td>H-ZSM-5\textsuperscript{a}</td>
<td>95.1</td>
</tr>
</tbody>
</table>

a) Si/Al = 78.
mesoporous aluminosilicates was decreased by a factor two. ZSM-5 however, gave again a high conversion (84 %) which indicates that diffusion limitations play a role in this microporous system.

---

It may be concluded that thermally-treated TPA-MCM-41 and TPA-HMS recrystallize, assisted by glycerol, the amorphous aluminosilicate framework partly to such an extent that infra red-detectable ZSM-5 structures are created. Due to the attachment of the TPA cations at the interporous framework the recrystallization process is forced to nucleate heterogeneously. The advantage of this process is the formation of embryonal ZSM-5 in a controlled way. The shape of these structures is probably a chain of double-five rings, the building units of ZSM-5,\textsuperscript{23,25} corresponding to the size of a clathrated TPA molecule which is about 10 nm.\textsuperscript{59} Schematic presentation of the composite configuration; a) tubular geometry of MCM-41 and HMS material, pore diameters of 4.0 and 2.7 nm, respectively, pore length of a few tenth of nm with an framework wall-thickness of about 1.0 and 1.5 nm, respectively. b) The pore wall composition of the TPA ion-exchanged host with a Si/Al ratio of 30 is close to the ideal composition of (TPA)\textsubscript{d}(AlO\textsubscript{2})\textsubscript{d}(SiO\textsubscript{2})\textsubscript{92} of ZSM-5. As the composition of the host as well as that of ZSM-5 are comparable, Ostwald's rule of successive transformations\textsuperscript{37} may be applicable here. c) As already noticed by the groups of Davis\textsuperscript{58} and of Van Santen\textsuperscript{59} short-range interaction of the TPA-hydrogen atoms with the oxygen atoms of aluminosilicate can result in the embryonal formation of ZSM-5 framework. In this conceptual impression the most ideal configuration comprising 1 TPA surrounded by 24 T-atoms is depicted.
1 nm (Figure 9.12). Interestingly, static and MAS $^{27}$Al NMR measurements, depicted in Figure 9.13 show a transformation of strongly anisotropic aluminum into a quasi isotropic tetrahedral environment going from HMS to PNA-2. This implies an increase in symmetry around the framework aluminum which is in agreement with the FTr.r. data and the enhanced Bronsted acidity. Calcination of the as-prepared PNA materials results in the formation of protons which are necessary to balance the framework charge.

![Figure 9.12. $^{27}$Al MAS NMR spectra of HMS (A) and PNA-2 (B).](image)

The importance of the TPA/T-atom ratio in MCM-41 and HMS materials is reflected by the production of only X-ray amorphous material when TPA/Al = 1 and Si/Al = 15 instead of 30. However, when the same mesoporous aluminosilicate is ion-exchanged to a TPA/Al ratio of 0.5 and subsequently thermally processed, the X-ray diffraction pattern was retained much better and nanocrystalline ZSM-5 structures were observed, as indicated by the 550 cm$^{-1}$ band. The higher amount of framework aluminum and therefore the increase in interattached TPA causes disturbances of the recrystallization of the framework. When the pre-positioning of TPA is omitted and a homogeneous mixture of TPAOH and MCM-41 is heated the MCM-41 is recrystallized overnight into aggregates of ZSM-5. This process goes even faster when purely siliceous MCM-41 is used, resulting in Siicaelite-1, which all-silica ZSM-5 member is not useful in catalytic processes.

Thus the need to pre-position TPA at the aluminum sites is a prerequisite to induce the recrystallization at the aluminum sites. The diffusivity of TPA is suppressed in this way. Preparation of PNA by interrupting the ZSM-5 crystallization appeared to be very difficult and not reproducible.

In conclusion, the synthetic approach to apply a viscous medium and to position the TPA-cations controls the recrystallization and can lead to new opportunities in the design of catalysts. Modification of the surface of an aluminosilicate material has a large impact on its catalytic behaviour. Moreover, upgrading of the catalytic properties of MCM-41 and related materials might lead to more valuable components in commercial cracking catalysts used in oil refining of heavy feedstocks. 

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9-4. Conclusions

An explorative study on mild tetrapropylammonium hydroxide treatment of MCM-41 shows that a porous aluminosilicate MCM-41 material with ZSM-5 structures is obtained. The phase transformation occurs randomly, via several stages, in the whole MCM-41 material. The recrystallization of MCM-41 into ZSM-5 is stimulated by applying the optimized stoichiometry of ZSM-5 in TPA-MCM-41, leading to short crystallization times.

Positioning of TPA at the framework of MCM-41 and HMS together with the application of glycerol as a medium leads to a controlled partial recrystallization of the surface of the framework giving PNA. The PNA materials show a higher activity in cracking of cumene and of hexane than the parent MCM-41 and HMS materials, indicating the generation of strong Bronsted acid sites.

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Controlled recrystallization of MCM-41 and HMS to a composite mesoporous material with...
10-1. Introduction

In the course of our work on MCM-41 materials\(^1\)\(^2\) with relatively large amounts of tetrahedral aluminum\(^3\) we encountered an interesting phenomenon. Thermal treatment of a synthesis gel containing the conventional MCM-41 ingredients with a relatively large amount of sodium oxide and alumina gave a fascinating composite material consisting of zeolite Y with overgrowth of MCM-41. Actually, this material is a molecular sieve with a bimodal pore size distribution, combining meso- and micropores. This bimodal molecular sieve might have potential applications in adsorption and catalysis. From a catalytic point of view it would be especially interesting to investigate the influence of such an MCM-41 coating on USY in cracking of heavy petroleum fractions, because the architecture of cracking catalysts involves a transition from mesopores to micropores.\(^4\)

We report here the synthetic deposition of MCM-41 on FAU-type zeolites. The influence of the mesoporous MCM-41 layer on USY crystals on catalytic performance was tested by cracking of vacuum gasoil (VGO).

10-2. Experimental

*Successive in situ synthesis of FAU and MCM-41*

A series of hydrogels with the following molar composition were prepared: 15 SiO\(_2\); Al\(_2\)O\(_3\); x Na\(_2\)O; 5.7 C\(_{16}\)TMACl; 720 H\(_2\)O.

Sodium aluminate (Riedel de Häen, 54 % Al\(_2\)O\(_3\), 41 % Na\(_2\)O) and 25 wt% cetyltrimethylammonium chloride (Aldrich) were stirred until a clear solution was obtained. Sodium hydroxide (Baker, 98.5 %) and distilled water were added and the mixture was stirred again prior to the addition of the fumed silica (HiSil 233 of PPG Industries). The gel formed, was stirred for 2 h and subsequently heated in a teflon-lined stainless steel autoclave at 120 °C for 24 h. After cooling to room temperature, the solid was collected by filtration.

washed with distilled water and dried under vacuum at 90 °C. The template was removed by calcining the samples for 10 h in dry air with a heating rate of 1 °C per min from room temperature to 540 °C.

Synthesis of MCM-41 on pre-added NaY, NaX or USY crystals

MCM-41 was prepared by mixing 2.8 g TMA-SiO2 solution (TMA/SiO2 = 0.5; 10 wt% SiO2; tetramethylammonium hydroxide (25 wt% solution of TMAOH; Aldrich) purchased from Aldrich and the silica source was Cab-osil M5 purchased from Fluka) with 1.10 g of sodium silicate (Aldrich; 27 wt% SiO2). Subsequently 14.65 g of water and 0.76 g of silica (Cab-osil M5) were added to the mixture. Under vigorous stirring 10.20 g of 25 wt% cetyltrimethylammonium chloride was poured in the mixture. Finally, the gel was enriched with 0.13 g of sodium aluminate. Cetyltrimethylammonium (CTA+) ion-exchanged Y was prepared by ion-exchanging 2 g of NaY (Akzo Nobel Chemicals; Si/Al = 2.4) or NaX (Union Carbide; Si/Al = 1.4) with 3 g of 25 wt% aqueous cetyltrimethylammonium chloride and 7 g of water. This material was subsequently added to the freshly prepared MCM-41 gel. The resulting MCM-41 gel/Y mixture was put in a 55 mL teflon-lined stainless steel autoclave and kept for 24 h at 110 °C. The solid was filtered and thoroughly washed, dried at 90 °C under vacuum and then calcined at 540 °C for 10 h.

The preparation of MCM-41 (Si/Al = 20.8) on USY (Akzo Nobel Chemicals; Si/Al = 2.5), weight ratio MCM-41:USY is 1:1.6) was done in the same way as described above. However there are a few deviations. One difference is the titration of the surfactant-USY mixture with a 33 wt% solution of NaOH to pH = 11. The calcined product was finally ion-exchanged by shaking for 2 days in an aqueous solution of 1M NH3NO3 at room temperature and subsequently washed and dried at 90 °C.

Characterization

The calcined samples were characterized by powder X-ray diffraction on a Philips PW 1840 diffractometer using monochromated CuKα radiation. Patterns were recorded from 1° to 70° (2θ) with a resolution of 0.02° and a count time of 1 s at each point.

Transmission electron microscopy was performed with a Philips CM 30 ST electron microscope with a field emission gun operated at 300 kV and equipped with an energy dispersive X-ray (EDX) element analysis system. The ground samples were suspended in ethanol. A copper grid coated with a microgrid carbon polymer was loaded with a few droplets of this suspension.

Solid-state 13C CP MAS NMR spectra were recorded at room temperature on a Varian VXR-400S spectrometer, equipped with a Doty Scientific 5 mm Solids MAS Probe. A resonance frequency of 100.6 MHz, a contact time of 0.2 ms, a recycle delay of 2 s, short 5.9 μs pulses (90° pulses of 5.9 μs), and a spinning rate of 4.6 kHz were applied. The lines were referenced to external solid hexamethyldisilazane (17.3
Overgrowth of mesoporous MCM-41 on faujasite

ppm) with the substitution method.

The size of the crystals was determined using a Jeol JXA 50A scanning electron microscope.

Catalyst testing

Samples of the parent USY and the MCM-41 coated USY were tested in a VGO pulse monofunctional cracking test at the Akzo Nobel Central Research Laboratory, Arnhem, the Netherlands. A small amount of the materials was heated to a relevant temperature, after which a small pulse of VGO was administered. The products of the cracking reaction were examined gas-chromatographically allowing to determine both conversion levels and selectivity of the cracking reaction.

10-3. Results and discussion

In situ synthesis

The Na₂O content (x) of the gel (see Experimental) was found to have a strong effect on the formation of MCM-41 with Si/Al = 7.5. An x-value lower than 5 leads to a product of the MCM-41 type which shows a powder X-ray pattern with only the 100 reflection. Amorphous material was formed when the molar amount of Na₂O was around 6. However, when x exceeds 9 mainly FAU zeolite crystallized. The powder X-ray diffraction of this material (Figure 10.1) shows FAU and a contamination of another zeolite which appeared to be zeolite P (vide infra).

![X-ray powder diffraction pattern](image)

**Figure 10.1.** X-ray powder diffraction pattern of a successively prepared MCM-41/FAU composite.
Transmission electron microscopy (TEM) examination of the MCM-41/FAU material (x = 9) revealed beside a separated MCM-41 phase, overgrowth of a thin layer of a mesoporous material with the structural features of MCM-41 on the outer surface of the FAU crystals. The MCM-41 layer, covering most of the FAU surface, had a thickness of only a few nanometers.

The Si/Al ratio of the bulk material, determined by elemental analysis, is 2.2. Therefore the material is, considering also the presence of the small amount of MCM-41, rather zeolite Y than zeolite X. The Na/Al ratio of the calcined material is 0.97. This indicates the presence of other counter ions than sodium in the material. A blank synthesis without the presence of cetyltrimethylammonium chloride provided crystalline Y with a small contamination of zeolite P, but without any MCM-41 phase. Elemental analysis showed that the Si/Al and Na/Al ratios were 2.4 and 1.00, respectively.

Apparently the large amount of sodium cations in the synthesis gel is responsible for the fact that first NaY crystallized; at a particular stage the sodium cation concentration is lowered to a level at which the mixture reaches the synthesis conditions from which MCM-41 is able to form. That MCM-41 is deposited on Y suggests that first sodium cations on the outer surface of Y are exchanged for cetyltrimethylammonium cations (CTA). Secondly, monolayers of CTA-cations on Y self-assemble with the free surfactant in solution and the inorganic species to form the MCM-41 coating. $^{13}$C CP/NMR study on this material showed an NMR spectrum (Figure 10.2) consistent with long-chain surfactant molecules occluded in the mesoporous channels of MCM-41 material. These data compared with the TEM results suggest that the surfactant serves only as a template for the formation of the mesoporous MCM-41 layer and not as a structure directing agent for Y. Recently Mobil workers claimed on the basis of $^{13}$C CP/NMR data that

![Figure 10.2. $^{13}$C CP/NMR spectrum of an as-synthesized successively prepared MCM-41/Y material.](image)

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quaternary ammonium surfactants with short alkyl chains can serve as a structure directing agent for the formation of zeolitic materials like ZSM-5.⁶

Scanning electron microscopy (SEM) on the composite and the blank material illustrated that both samples were contaminated with a very small fraction of cauliflower-like crystals, which are typical spherulitic aggregates and can be assigned to zeolite P (Figure 10.3).⁷ SEM illustrated that the Y crystals synthesized in the presence of surfactant are smaller in size (approximately 1 μm) than the blank Y crystals (approximately 8 μm). The influence of surfactants on the crystallization of zeolite NaA was recently reported.⁸ It was found that the presence of surfactant can lead to crystals with a reduced size and a narrower crystal size distribution.

![Figure 10.3. SEM micrograph of zeolite-P (cauliflower-like aggregate) surrounded by zeolite-Y crystals.](image)

**NaY, NaX and USY crystals applied as seed material**

From the described process of successive crystallization of Y and deposition of MCM-41 on Y it can be deduced that an important driving force is the exchange of Na-cations for CTA-cations. This creates a situation which stimulates the synthesis of MCM-41 and in particular the nucleation on the Y crystal surface. Adsorption of cationic surfactants on alkaline silica and mica (contains aluminate) shows that the adhesion isotherm is almost identical for both materials.⁹ However untreated silica shows a very low adsorption
capacity. Obviously, surface charge stimulates the cation exchange process. Zeolite X has a higher outer surface cation exchange capacity.\textsuperscript{10} It might be expected that after CTA-exchange the crystal surface of X is more densely packed with CTA than that of Y. Studies on reduced charge montmorillonites show that the amount of hexadecylammonium ions can even exceed the cation exchange capacity of montmorillonite.\textsuperscript{11} Overgrowth of zeolite X on A can be stimulated by adding seeds of X in the synthesis gel.\textsuperscript{12} A mixture of CTA-cation exchanged Y zeolite and a freshly prepared MCM-41 gel aged at 110 °C overnight, gave indeed MCM-41 overgrowth on Y. When using zeolite NaX instead of NaY, more pronounced MCM-41 overgrowth was observed. Probably the larger cation-exchange capacity of X is responsible for this. When cetyltrimethylammonium bromide (CTAB) was used as the template instead of the chloride form, only independent MCM-41 was formed and hardly any overgrowth was observed by TEM. In contrast, when applying in a conventional MCM-41 synthesis surfactants containing bromide counterions, MCM-41 is easier formed\textsuperscript{13} and better ordered MCM-41\textsuperscript{3} than when chloride counterions are applied.

The overgrowth phenomena are schematically shown in Figure 10.4. Figure 10.4a illustrates the most desired and ideal situation in which the MCM-41 tubes are oriented perpendicular on the crystal surface. However from a chemical point of view this situation is improbable to obtain by using CTAB. Surfactants are generally bound perpendicular to the crystal surface. Thus during the self assembly of the silicate/surfactant mixture we would expect to get the situation shown in Figure 10.4b. However, CTAB seems to prefer to form independent surfactant-silicate mesophases and not to nucleate at the CTA-FAU surface, as mentioned earlier. Figure 10.4c illustrates the MCM-41 coating, short mesoporous channels interconnected in a three-dimensional network, obtained when using CTACl as the surfactant source which is probably the result of the less easier formation of the silicate-CTACl mesophase.

![Figure 10.4. Schematic drawing of orientations of MCM-41 tubes on a zeolite crystal surface.](image)

Both X and Y possess rather smooth crystal surfaces, which can give a rather continuous monolayer of surfactant on top of the crystals. Mesoporous cavities on the crystal surface of a steamed ultrastable HY

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Figure 10.5. TEM images of MCM-41 coated USY. A: USY surrounded by MCM-41. B: Overgrowth of disordered MCM-41 on USY crystal.
Chapter 10

(USY) can disturb this monolayer formation and eventually, the overgrowth of MCM-41. Also the H-counter ions are an unfavourable factor. The pH of a USY-CTACl mixture and of a NaY-CTACl mixture appeared to be around 7 and 11, respectively. Before mixing USY-CTACl with the MCM-41 gel, the USY-CTACl mixture was titrated with diluted sodium hydroxide to adjust the pH to 11 to stimulate the CTA-exchange process. TEM examination of the hydrothermally treated material showed that MCM-41 was indeed situated on the USY crystals. Beside this, a part of the MCM-41 is present as an independent phase which surrounds the USY crystals (Figure 10.5a). Figure 10.5b illustrates that the USY crystals are coated with a few nanometers thick layer of MCM-41. Some pieces are covered by a 10 nm or more thick layer and other parts with only 4 nm (monolayer of MCM-41). The TEM images indicate that the MCM-41 layer consists of channels which are parallel to the FAU surface without any ordering (Figure 10.4c). It is noteworthy, that when the USY-CTACl mixture was not titrated with NaOH hardly any MCM-41 overgrowth on USY was observed.

Composite materials with progressively smaller pores may have interesting applications in refinery conversion processes. Although other materials with combinations of mesopores and micropores have been reported, the present material is actually the first reported composite consisting of two different types of large pore molecular sieves, namely MCM-41 and FAU. The applicability of MCM-41 in acid and basic catalysis of fine organic chemicals or catalytic hydrocarbon conversions has recently been demonstrated. USY has proved to be a superior catalyst in catalytic cracking applications.

The MCM-41 coated USY was tested in hydrocracking of vacuum gasoil (VGO) and compared to the original USY. For a true comparison of both samples, the Na-content of the parent USY zeolite was adjusted to that of the MCM-41 coated USY. Elemental analysis showed that the Na₂O contents were 0.86 and 1.05 wt%, respectively. The MCM-41 coated USY sample shows a lower conversion than the uncoated material. The difference is about 10%. When the absolute selectivities at equal conversion (interpolated) are compared, it is observed that the coated material has a 3% higher gasoline selectivity, and a 1.5% higher LCO (Light Cycle Oil) selectivity. In contrast, the selectivity towards the heavier fraction (High Cycle Oil, HCO) in the product is 1.5% lower for the coated sample, and the coke-selectivity is about 2% lower. Therefore, it can be concluded that the coated material has a slightly higher selectivity towards cracking heavier fractions. Further investigations to study the influence of the MCM-41 coating on the catalytic performance are in progress.

10-4. Conclusions

Overgrowth of MCM-41 on FAU has been observed by TEM. The MCM-14 layer is disordered
Overgrowth of mesoporous MCM-41 on faujasite

which causes a random orientation of the mesopores and a good accessibility of the zeolitic micropores. These composites can be prepared by a one step successive synthesis of FAU followed by MCM-41 on FAU, or by adding FAU crystals to a MCM-41 synthesis gel. In both cases there is also formation of an independent MCM-41 phase. An MCM-41 coated USY has been tested in the cracking of vacuum gasoil and showed a higher selectivity towards the lighter fractions and a total conversion of about 10 % lower compared to the parent USY.

Acknowledgment

We thank Dr. Eelco Vogt of Akzo Nobel Chemicals for his kind mediation with the pulse cracking tests.

References

Thermoporometry as a new tool in analyzing mesoporous MCM-41 materials*

11-1. Introduction

The sorption of gases is a widely used standard technique for characterization of mesoporous solids. Thus, by measuring the adsorption isotherm of nitrogen at low temperature, the specific surface area, pore volume and pore size distribution are calculated.1-3 During the adsorption process, nitrogen condenses in the pores to form a metastable liquid phase in a process known as capillary condensation. The condensation pressure is an increasing function of the pore size, and is given by the Kelvin equation.

Physisorption of nitrogen, cyclopentane and alcohols (methanol, ethanol, 1-propanol and 1-butanol) onto MCM-41 material, a member of the mesoporous M41S molecular sieve family,4,5 with pore sizes less than 43 Å showed isotherms of the unusual reversible Type IV.6-12 On the other hand, MCM-41 with an average pore diameter of 45 Å showed hysteresis.11,12 For the adsorption of argon and oxygen, a significant hysteresis has been observed.7,10,12 Some authors describe this to a transition from "secondary micropores" to mesopores.11 A Type V isotherm with hysteresis has been found by using water vapour as the adsorbate.13,14 This indicates an initial repulsive character for the water adsorbate followed by a capillary condensation step. The low adsorption affinity can be attributed to the weak adsorbent-adsorbate interactions due to the 'hydrophobic' surface of MCM-41.13,14 Freezing phenomena in water-saturated MCM-41 systems with various pore dimensions were studied with 1H NMR spectroscopy and for MCM-41 materials with pore sizes less than 40 Å it was found that intraporous water showed a phase transition at low temperature and no hysteresis effect.12,15-19

In this chapter we report on the use of thermoporometry for analyzing mesoporous molecular sieves. Thermoporometry20 is based on the fact that conditions of the equilibrium of the solid, liquid and gaseous phases of a pure substance depend on the curvature of the solid-liquid interphase. In the case of a liquid occluded in a porous material the solid-liquid interphase curvature is closely related to the dimensions of the pore. By measu-

ring a solidification thermogram of a pure condensate inside a porous material the pore size can be determined from the temperature at which the condensate solidifies and the pore volume can be determined from the amount of energy involved. An important advantage of this method is that information is obtained about the internal size of the pores and not of their entrances.\textsuperscript{20,21} The theory of thermoporometry will be summarized in section 12.3. A full description is given by Brun et al.\textsuperscript{20}

We have applied thermoporometry to a series of mesoporous materials of the MCM-41 type with various pore diameters\textsuperscript{5} for measuring their pore size and volume, surface area, wall thickness and the so-called shape factor. The results obtained are compared with nitrogen physisorption data.

11-2. Experimental

\textit{Materials}

MCM-41 samples 1 to 5 with various pore sizes were synthesized by applying dodecyl-, myristyl-, cetyl-, and octadecyltrimethylammonium bromide, respectively (purchased from Aldrich and ACROS) as the template. In each case the surfactant concentration was kept constant at 16 wt\% by adjusting the amount of water.\textsuperscript{5} The molar ratio of the synthesis gels is: 32 SiO\textsubscript{2} : 2026 H\textsubscript{2}O : 1.4 (TMA\textsubscript{x})\textsubscript{2}O : 5 (C\textsubscript{x}TMA\textsubscript{y})\textsubscript{2}O : y Al\textsubscript{2}O\textsubscript{3}, where x = 12, 14, 16 or 18 and y = 28, 40 or 0. A typical preparation procedure is as follows. 6.66 g of a TMA-silicate solution (TMA = tetramethylammonium, purchased as TMAOH from Aldrich) was added to 3.14 g of sodium silicate (Aldrich; 27 \% SiO\textsubscript{2}). This solution was combined under vigorous stirring with 14.8 g of water, 2.30 g of silica (Cab o-sil M5) and a solution of 7.44 g of C\textsubscript{16}TMABr in 50 g of water. Aluminum was then added to the synthesis mixture in varying amounts in the form of sodium aluminate (Riedel-de Haën; 54 \% Al\textsubscript{2}O\textsubscript{3} and 41 \% Na\textsubscript{2}O). After two hours stirring at room temperature the mixture was heated statically at 100 °C. After two days the product was washed and dried at 90 °C under vacuum. Finally, the material was calcined at 540 °C for 10 h under dry air with a heating rate of 1 °C per min from room temperature. Cetyltrimethylammonium bromide (C\textsubscript{16}H\textsubscript{33}(CH\textsubscript{3})\textsubscript{3}NBr) with addition of the expander compound mesitylene (MES = 1,3,5-trimethylbenzene; ACROS) was used to prepare MCM-41 material 6 with the largest pore size studied (MES/C\textsubscript{16}H\textsubscript{33}(CH\textsubscript{3})\textsubscript{3}NBr = 1.0).\textsuperscript{5}

\textit{X-ray diffraction}

The calcined samples were characterized by X-ray powder diffraction on a Philips PW 1840 diffractometer using monochromated Cu K\textsubscript{α} radiation. Patterns were recorded from 1° to 10° (2θ) with a
resolution of 0.02° and a count time of 10 s at each point.

**Nitrogen physisorption measurements**

Multipoint BET surface areas, pore volumes and pore size distributions of the MCM-41 materials were calculated from N$_2$ adsorption/desorption isotherms at -196 °C using a Quantachrome Autosorb 6 instrument. The samples were outgassed for 16 h under vacuum at 350 °C prior to use.

**Thermoporometry measurements**

Thermoporometry measurements were carried out on a DSC Gold apparatus of Polymer Laboratories. First the DSC apparatus was calibrated with a sapphire and adamantane run and by melting experiments with indium, mercury and water.$^{23}$ A small amount of a dehydrated sample (15 mg) was put in a small aluminum-pan. After adding a few drops of distilled water (30 mg), the pan was sealed with an aluminum-lid. The DSC-probe, containing the crimped aluminum-pan, was cooled from 10 °C till -80 °C with a rate of 1 °C/min, which is slow enough to maintain equilibrium, and subsequently heated to 10 °C.

**Transmission electron microscopy**

Electron microscopy was performed with a Philips CM30ST electron microscope with a field emission gun operated at 300 kV. Through-focus exit wave reconstruction$^{24,25}$ was applied to obtain more detailed information on the walls of MCM-41. In this reconstruction one combines the information of a set of images (through focus series) recorded at various focus values to correct for the image distortion by the aberrations of the electron microscope optics. The reconstructed image represents the exit wave function, which describes the electron wave at the exit plane of the specimen. To calculate the exit wave a software program developed by Coene and Thust$^{26}$ was used. The parameters required as input for the exit wave reconstruction are: the spherical aberration: 1.35 mm, the defocus step: 8.6 nm, and the starting focus, which was estimated from minimum contrast in the image. Images were recorded with a magnification of 200.000. The through focus high resolution images were recorded using a Tietz software package and a 1024x1024 pixel Photometrix slow-scan CCD camera having a dynamic range of 12 bits. The images were binned resulting in 512x512 pixel images. The samples were prepared as follows: the grinded MCM-41 samples were suspended in alcohol and a copper grid coated with a microgrid carbon polymer was loaded with a few droplets of this suspension.
11-3. Results and discussion

Thermoporometry theory

The relation between the triple point temperature of a condensate inside a porous material and the curvature of the solid-liquid interphase is given by

$$\Delta S_i \, dT + \gamma_1 \frac{d\gamma_1}{d\gamma} = 0,$$

(1)

where $\Delta S_i$ is the solidification entropy of the condensate, $T$ is the temperature, $\gamma_1$ is the specific volume of the condensate and $d(\gamma_1 \, dA_1 / dV_1)$ is the curvature of the solid-liquid interphase. Here $\gamma$ is the surface of the curvature of the interphase $s$ and $V_1$ the volume of the liquid, and $\gamma$ is the free liquid-solid surface extension energy.\(^{20}\)

The most likely solidification process\(^{20}\) is freezing of the condensate by nucleation inside the pores. This process can only occur if no supercooling of the condensate takes place, which is unlikely in the case of a highly divided fluid inside a porous material. The curvature of the solid-liquid interphase is in this case equal to the pore radius $R_p$, but molecular layers which are in contact with the pore wall will not solidify. These non-solidifying layers are for water and benzene, 2.5 molecules (8.0 Å) and 3.5 molecules (13.3 Å) thick, respectively.\(^{21-29}\) It is noteworthy, that the non-freezing layers of adsorbed water agree very well with recent data obtained by NMR spectroscopy, which showed a value between 2.5 and 3.0 molecules.\(^{30}\) Somewhat comparable values were estimated by using DSC. A thickness of 1 to 3 molecules of water, or more accurately, a thickness of 5 to 8 Å was calculated using a cylindrical model and of 3 to 6 Å for a spherical model.\(^{31}\) A recent $^1$H NMR study on the low-temperature phase transition of water confined in mesopores gave a thickness of the water interface of $5.4 \pm 1.0$ Å and $7.3 \pm 1.3$ Å for cylindrical and spherical pores, respectively.\(^{19}\) Therefore, more correctly, the curvature radius of the solid-liquid interphase will equal $R_n$, which is $R_p$ minus the non-solidifying layer. Assuming the form of the initial model to be spherical from $\Delta T$ to $T_p$ eq. (2) is obtained:

$$\frac{1}{R_n} = \frac{1}{2 \gamma_1} \int_{T_0}^{T_p} \frac{\Delta S_i}{\gamma_1} \, dT,$$

(2)

where $T_0$ is the triple point temperature. This equation allows for each temperature $T$ to determine the radius of
the pores. Brun et al. measured the free surface extension energy for water and benzene by measuring the freezing point depression ($\Delta T$) of various alumina porous plugs with known texture and different pore radii. Assuming $\gamma_n$ to vary linearly with the temperature the resulting relation for water is:

$$\gamma_n = (40.9 + 0.39 \Delta T) \times 10^{-3}. \quad (3)$$

Substituting eq. (3) in the integrated eq. (2) leads to a relationship between the freezing temperature depression of a capillary condensate of water saturating a porous material and the pore radius $R_n$:

$$R_x = -64.67 / \Delta T + 0.57. \quad (4)$$

The pore volume represented by pores of a particular size can be calculated from the amount of energy involved in solidification of the condensate at a specific $\Delta T$. The signal $y$ of the calorimeter is proportional to the amount of energy involved:

$$\frac{dV}{dR_p} = v_i \Delta T^2 \frac{y}{(W_s \, mkC)}, \quad (5)$$

where $m$ is the weight of the sample, $k$ is the rate of heating, $C$ is a constant ($64.67$ for water) and $W_s$ is the apparent solidification energy of a capillary condensate. The relation between triple point temperature depression and $W_s$ of solidification is

$$W_s = -5.56 \times 10^{-2} \Delta T^2 - 7.43 \Delta T - 332 \quad (6)$$

and the melting energy is

$$W_m = -0.155 \Delta T^2 - 11.39 \Delta T - 332. \quad (7)$$

Brun et al showed that the numerical relations for solidification for water are certainly valid in the temperature range $0 > T > -40$°C. However, the extrapolated curve for the triple point depression in porous materials shows that the relations can also be used at lower temperatures.

Thermoporometry discerns two pore shapes, namely cylindrical and spherical. In the case of spherical
pores the solid-liquid interphase during solidification is the same as the interphase during melting, and the solidification temperature of the liquid inside the pores is the same as their melting temperature. Cylindrical pores show hysteresis between the solidification and the fusion thermogram. Materials with an 'intermediate' pore shape can be classified by calculating a dimensionless thermodynamic shape factor $f_i$, which is 1.0 in the case of pure spheres and 2.0 for pure cylinders,

$$f_i = 1 - [(1 - R_{pc} / R_p) / (1 - t / R_p)]$$

where $t$ is the thickness of the non-solidifying layer, $R_{pc}$ is the pore radius calculated from the melting thermogram assuming that the pores are cylindrical and $R_p$ is the real pore radius as calculated from the solidification thermogram. This method was applied to experimental and simulated thermoporometry data of γ-alumina and nickel fluoride. A good correlation was obtained between both sets of data.

**Measurements**

Powder X-ray diffraction data concerning the studied MCM-41 materials with various pore sizes are summarized in Table 11.1. The MCM-41 materials with increasing surfactant chain length show an increase in the $d_{100}$ spacing which is in agreement with literature data. The quality of the MCM-41 materials is improving going to larger surfactant templates, which is reflected by the increase and improvement of the intensity of the

<table>
<thead>
<tr>
<th>sample</th>
<th>Si/Al gel</th>
<th>surfactant chain length$^a$</th>
<th>$d_{100}$ spacing (Å)</th>
<th>$a_0$ (Å)$^b$</th>
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<tr>
<td>1</td>
<td>14</td>
<td>12</td>
<td>35</td>
<td>40</td>
</tr>
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<td>14</td>
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<td>14</td>
<td>18</td>
<td>46</td>
<td>53</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>16+MES$^c$</td>
<td>56</td>
<td>65</td>
</tr>
</tbody>
</table>

a) Number of carbon atoms in surfactant C$_n$H$_{2n-1}$(Me)$_2$N$^+$; b) unit cell dimension, $a_0 = 2d_{100}/\sqrt{3}$; c) addition of mesitylene (MES) as expander.
high order 'peak' in the region of the $d_{110}$ and $d_{200}$ reflections (Figure 11.1), which are characteristic for hexagonal mesopores. This can be better observed in the X-ray diffraction pattern of the all silica MCM-41 sample 4 showing clearly a well-defined pattern which can be indexed on a hexagonal lattice. The $d_{100}$-spacings of the calcined MCM-41 materials did not increase linearly going from the smaller C$_{12}$-surfactant to the larger C$_{18}$-surfactant, which is in contrast with literature data. This might be due to differences in the synthesis procedure such as the use of TMAOH and the silicate source.

The pore size distribution, pore volume and surface area of the synthesized MCM-41 materials were measured by thermoporometry. Figure 11.2 shows a typical solidification and melting thermogram of MCM-41 sample 5 with a pore size of around 40 Å going from 10 °C to -60 °C and reverse provided by the DSC apparatus. The two small peaks at -45 °C and -39 °C reflect solidification and melting of the water inside the pores, respectively. The two large peaks represent the bulk water outside the pores. Table 11.2 shows data derived from thermoporometry on the six MCM-41 samples. To investigate the validity of thermoporometry a comparison was made with nitrogen physisorption data (Table 11.3), which are in harmony with literature data. Adsorption isotherms of nitrogen on three MCM-41 samples are shown in Figure 11.3. Only MCM-41 sample 6 shows an isotherm of the Type IV of the IUPAC classification. A reversible type IV isotherm is shown by samples 3, 4 and 5. The isotherms of the MCM-41 samples 1 and 2 seem to be both of the type I. The mesopore volumes were
calculated in two ways namely, assuming it is the difference between total volume and micropore volume calculated by the De Boer &-plot\textsuperscript{23} (denoted as $v_{\text{p,h}}$) or by calculating the cumulative volume in the narrow pores.

Table 11.2. Thermoporometry data of the synthesized MCM-41 samples

<table>
<thead>
<tr>
<th>sample</th>
<th>$D_p$ (Å)</th>
<th>pore volume (cm(^3)/g)</th>
<th>surface area(^a) (m(^2)/g)</th>
<th>$f_t$(^b)</th>
<th>$D_p$-range (Å)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>30</td>
<td>0.720</td>
<td>884</td>
<td>1.15</td>
<td>27-67</td>
</tr>
<tr>
<td>2</td>
<td>34</td>
<td>0.676</td>
<td>785</td>
<td>1.10</td>
<td>28-57</td>
</tr>
<tr>
<td>3</td>
<td>39</td>
<td>0.731</td>
<td>755</td>
<td>1.10</td>
<td>31-63</td>
</tr>
<tr>
<td>4</td>
<td>37</td>
<td>0.436</td>
<td>478</td>
<td>1.09</td>
<td>32-45</td>
</tr>
<tr>
<td>5</td>
<td>41</td>
<td>0.619</td>
<td>596</td>
<td>1.17</td>
<td>35-57</td>
</tr>
<tr>
<td>6</td>
<td>52</td>
<td>0.642</td>
<td>534</td>
<td>1.50</td>
<td>35-92</td>
</tr>
<tr>
<td>6(^c)</td>
<td>49</td>
<td>0.826</td>
<td>722</td>
<td>1.37</td>
<td>37-67</td>
</tr>
</tbody>
</table>

\(^a\) Assuming cylindrical pores; \(^b\) thermodynamic shape factor; \(^c\) benzene as adsorbate.
Table 11.3. Nitrogen physisorption data of some MCM-41 samples

<table>
<thead>
<tr>
<th>sample</th>
<th>( D_p^a )</th>
<th>( D_p^b )</th>
<th>volume(_{cum}^c )</th>
<th>volume(_{t-plot}^d )</th>
<th>BET area</th>
<th>( D_p^b )-range( ^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Å)</td>
<td>(Å)</td>
<td>(cm(^3)/g)</td>
<td>(cm(^3)/g)</td>
<td>(m(^2)/g)</td>
<td>(Å)</td>
</tr>
<tr>
<td>1</td>
<td>22</td>
<td>29</td>
<td>0.527</td>
<td>0.960</td>
<td>916</td>
<td>22-60</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>33</td>
<td>0.680</td>
<td>1.661</td>
<td>1016</td>
<td>23-63</td>
</tr>
<tr>
<td>3</td>
<td>27</td>
<td>36</td>
<td>0.847</td>
<td>2.180</td>
<td>1091</td>
<td>22-50</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>33</td>
<td>0.756</td>
<td>1.002</td>
<td>1119</td>
<td>22-37</td>
</tr>
<tr>
<td>5</td>
<td>31</td>
<td>41</td>
<td>0.800</td>
<td>1.885</td>
<td>1035</td>
<td>23-55</td>
</tr>
<tr>
<td>6</td>
<td>39</td>
<td>50</td>
<td>0.820</td>
<td>1.393</td>
<td>893</td>
<td>28-66</td>
</tr>
</tbody>
</table>

a) Classical Kelvin equation; b) according to corrected Kelvin equation for cylindrical pores of De Boer;\(^{31}\) c) cumulative volume; d) calculated by the De Boer t-plot.\(^{31}\)

range of mesopores (denoted as volume\(_{cum}^c\)). In case of the former method it was assumed that the interparticle voids are negligibly small. All the studied MCM-41 materials showed the typical t-plot curve for mesopores with \( t = 0 \) intercepting the origin, which is typical for mesopores. It may be noted that the suggestion that the latter

![Figure 11.3. Adsorption isotherms of nitrogen on MCM-41 samples 1, 4 and 6 at -196 °C. Filled symbols denote adsorption and open symbols denote desorption.](image)

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property is an indication of non-detectable micropores is a misinterpretation of the t-plot. The micropore volume is calculated by the intercept of the back-extrapolated plateau. A comparison of the two methods shows that the mesopore volumes and surface areas give a fairly good agreement, except the volume \( v_{t-plot} \) values which are too large. Considering mesopores it can be suggested that the De Boer t-plot method gives too large pore volumes. Also the surface area provided by thermoporometry and the nitrogen multipoint BET area show a good correspondence, though the latter are significantly larger. The pore diameters of the MCM-41 samples provided by thermoporometry are also larger than the nitrogen pore sizes \( D_p \). However, a very good correlation is obtained with the thermoporometry data when the corrected Kelvin equation for cylindrical pores of De Boer is applied. Other workers have reported that the De Boer t-plot method gives reliable results and does not overestimate the pore diameter.

The pore size ranges of the synthesized MCM-41 products, calculated from the pore size distribution diagram where \( dP/dR_p = 0 \) intercepts the \( dR_p \) axis, are summarized in Table 11.2. These pore size ranges \( (L_p, \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \hfill 170
Figure 11.4. (a) TEM image of sample 4 showing two morphologies of MCM-41: i) a large hexagonal crystal and ii) two small chaotic MCM-41 particles on top of this crystal. (b) The amplitude image of the exit wave of MCM-41 with a hexagonal structure and with a \( d \)-axis of about 60 Å. The inset shows the Fourier transform of this image with reflections up to \( d_{20} \). Thin or partly absent walls are indicated by white arrows. The distance of the various 100 reflections is not the same, probably due to a tilt of the crystal.
2 might be a result of effects like pore-blocking and/or the presence of amorphous material inside the pores (vida infra), which effect the melting curve.

TEM was performed on the samples 1, 4 and 6. Two types of morphologies were observed: i) well ordered hexagonal and ii) chaotic. Both morphologies are shown in Figure 11.4. Morphology ii can be explained by assuming spaghetti-like arrangements of the tubes such that a particle is like a 'bowl of spaghetti' or by short tubes which are considerably shorter than the diameter of the particle; in both cases no ordering between the tubes occurs. Sample 1 contains only the chaotic morphology. Samples 4 and 6 contain a mixture of both morphologies with about 50% and 70% parts of ordered hexagonal material, respectively (Figure 11.4a and b).

Through focus exit wave reconstruction was done on the hexagonal morphology of specimen 6. The resulting exit wave is shown in Figure 11.4b for which a series of 10 images was used. Subsequent series of 10 images showed a comparable result, indicating that the electron beam induced damage is rather small. The Fourier transform of the exit wave (see inset in Figure 11.4b) shows only the $d_{10}$, $d_{11}$, and $d_{20}$ reflections. This very limited number of reflections indicates that the projection of the walls of the tubes in the exit wave can be described with only three Fourier frequencies. This can be explained by assuming that the tube walls are not smooth but have some roughness. In projection this implies that moving from the centre of the wall to the centre of the tube the number of scattering atoms does not change suddenly from maximum to zero but shows a gradual change. In Figure 11.4b one can also see that some of the walls appear to be almost absent, which is probably due to a difference in approach of the surfactant-silicate aggregates during self-assembly of the mesophases. Another possibility might be an incomplete transformation of the surfactant-silicate system from lamellar to the hexagonal mesophase. There were also indications of the presence of amorphous material inside the pores. The observations of pore wall roughness and some amorphous material inside the pores applies for all the studied MCM-41 materials. The cause of the former is probably due to damage of the pore wall during calcination.

The shape factor $f_i$ can give information on the shape of the pore by studying the degree of hysteresis. It is assumed that absence of hysteresis is due to spherically shaped pores. The nitrogen isotherms of the samples 1 to 3 show no hysteresis. However, thermoporometry on the samples 1 to 3 showed a hysteresis of around 3.5 °C. A result of this might be the roughness of the pore wall, which causes a drastic influence on the melting process of the water inside the pores exhibiting spherically shaped nuclei. It should be noted that the constant shape factor of 1.1 can not only be a result of amorphous material inside the pores, otherwise this should indicate that all these samples had the same amount of it inside the pores. Considering the difference in degree of noncrystalline material in the studied materials and the constant hysteresis effect of the samples 1 to 5, then it can be concluded that the shape factor is not effected by these crystallinity effects. Also other workers remarked
that a decrease in the purity of the material can hardly affect the adsorption phenomena. The recently reported absence of hysteresis for MCM-41 materials with a pore diameter below 40 Å is in contrast with our results.

11-4. Conclusions

Thermoporometry is a promising technique for analyzing pore size distribution, pore volume and surface area of mesoporous molecular sieve materials. The small hysteresis effect of around 3.5 °C in MCM-41 materials with pore sizes below 40 Å is probably due to pore wall roughness effects observed by TEM. The shape factor of 1.5 deviates from the value expected for cylindrical pores, which might be caused by the presence of amorphous material inside the pores.

References

Chapter 11

Summary

Chemistry of mesoporous molecular sieves

The aim of this thesis is to explore the catalytic properties of MCM-41 materials in the liquid-phase and fits in the framework of the NIOK research program. This can be achieved by using MCM-41 as such, in its ion-exchanged form or as a support for catalytic active species. Generally, in the latter case improvement of the catalytic performance is often obtained. The very large surface area and mesopore volume of MCM-41 make it a perfect support for particular species for instance metal complexes and oxides. The interporous species are therefore easy accessible for reagents. The advantage of a large surface area is often reflected in a high dispersity of the species. The setup of this thesis is logical and is therefore beginning with liquid-phase acid catalysis by MCM-41 in its H⁺ form followed by improvements of the acidity of MCM-41 via various procedures. The second part of the thesis deals with the basic properties of MCM-41 in the liquid-phase. Increasing of the basicity is achieved by loading MCM-41 with strongly basic oxides. The last part of the thesis is dealing with novel applications of MCM-41 related materials. It has to be remembered that the objective of this thesis is not just the screening a couple of reactions, but to explore the basic properties of MCM-41 and to search for its optimum modification.

The introductory chapter 1 reviews the synthesis and the mechanism of formation and the characterization of (alumino)silicate MCM-41 and related materials. Potential applications, in particular catalytic ones, are briefly discussed.

The basic and acid properties of MCM-41 in the liquid-phase, in particular that of the sodium and cesium ion-exchanged MCM-41, are explored in chapter 2. It appeared that these materials are mild, selective, water-stable and recyclable catalysts for the base-catalyzed Knoevenagel condensation and the acid-catalyzed acetalization. The aldol condensation is however either acid or base-catalyzed by Na-MCM-41. The basicity of Na-MCM-41 and Cs-MCM-41 is investigated by carbon dioxide temperature programmed desorption (TPD). To get more insight in the coordination behaviour of the extraframework Na⁺ and Cs⁺ ions the Na-MCM-41 and Cs-MCM-41 materials are analyzed by ²³Na and ¹³³Cs MAS NMR in their hydrated and dehydrated state. The high mobility observed might explain the capability of these materials to catalyze the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate in aqueous media.

In spite of the low structural or intrinsic basicity of alkali ion-exchanged MCM-41 various large molecules can be converted, provided the pKₐ of the active C-H compounds is below 11. To react organic
molecules of a lower acidity it is therefore necessary to raise the basicity of MCM-41. Loading of MCM-41 with strongly basic metal oxides is a way to achieve this. In chapter 3 the preparation and characterization of cesium-oxide loaded MCM-41 are reported. These Cs/MCM-41 materials are prepared by impregnating MCM-41 with cesium acetate and subsequently calcination at high temperature. These materials are subjected to several characterization techniques, including CO₂ TPD, N₂ adsorption and ¹³³Cs MAS NMR, to elucidate the structure and the accessibility of interporous cesium oxide. Catalysis of the double Michael addition of neopentyl glycol diacylate with diethyl malonate by Cs/MCM-41 materials shows a regioselective formation of the mono-adduct, this in contrast to bulk and amorphous silica-alumina supported cesium oxide. This indicates that the presence of the cesium oxide particles inside the mesopores of MCM-41 has an influence on the product selectivity. Unfortunately the Cs/MCM-41 material showed a very poor regenerability which is reflected by a collapse of the framework structure of the MCM-41 support.

Chapter 4 reports on a binary cesium-lanthanum oxide supported on MCM-41: a new stable heterogeneous basic catalyst. These catalysts have been prepared by wet or solid-state impregnation of MCM-41 with cesium acetate and lanthanum nitrate (molar ratio 1:1) followed by thermal decomposition. ¹³³Cs MAS NMR data of CsLa/MCM-41 show an increase in the Cs-O bond length in the CsLa-mixed oxides compared with that in Cs oxides supported on MCM-41. A small difference in chemical shift between the hydrated and dehydrated state indicates a weak interaction of water with Cs⁺ ions. CO₂ TPD suggests that these materials possess small oxide clusters of mild basicity. These CsLa/MCM-41 materials appeared to be thermally very stable. Substitution of Cs⁺ for Na⁺, K⁺ or Rb⁺ leads to a thermally less stable material. The catalytic performance of CsLa/MCM-41 materials is demonstrated in the Knoevenagel condensation and the Michael addition. The CsLa/MCM-41 catalysts are re-usable after regeneration at high temperature without loss of activity and selectivity.

The liquid-phase conversion of aromatic aldehydes over CsLa/MCM-41 and Cs/MCM-41 and related mesoporous materials is discussed in chapter 5. The MCM-41 related mesoporous molecular sieve HMS is thereby also used as a support for the basic oxides. Particular ß-phenylalkanals gave beside aldol condensation a rearrangement to phenyl allyl ketones. A mechanism for this novel isomerization is proposed on the basis of the performance of the catalysts in various related reactions.

As an example of the use of H-MCM-41 in liquid-phase acid catalyzed reactions, the tetrahydropyranylation of alcohols and phenolic compounds is studied in chapter 6. The corresponding tetrahydropyranyl ethers were formed in high selectivities within short reaction times due to the mildness and efficiency of the catalyst. Large reactants such as cholesterol were used to demonstrate the benefit of the mesopores of MCM-41. Actually, the origin of this chapter is to give the reader an idea of the performance and re-usability of H-MCM-41 in an ordinary acid catalyzed reaction in the liquid phase.

The total acidity of MCM-41 is believed to be connected with the amount of tetrahedral aluminum
in the mesoporous framework. Chapter 7 deals with the preparation of MCM-41 materials with low Si/Al ratios i.e. high amounts of aluminum. A thorough transmission electron microscopy (TEM) study is carried out to examine the materials obtained. When using a tetraalkylammonium base in the synthesis mixture of MCM-41 it was observed that Si/Al ratios as low as 12 were possible. However in these cases the MCM-41 materials contained an aluminum-rich dense phase in which the aluminum was also tetrahedrally coordinated, as observed by $^{27}$Al MAS NMR. This dense phase consumes most of the aluminum of the synthesis mixture.

Keggin-type heteropoly acid (HPA) supported on MCM-41 has attracted interest as a promising solid acid catalyst and formation of large organic molecules. Chapter 8 reports the preparation of HPA catalysts, comprising of 10 to 50 wt% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW) supported on all-silica MCM-41 material and on an amorphous silica with the aim of obtaining pure Keggin-type heteropoly acid (HPA) species on siliceous surfaces. The state of HPA on the siliceous surface was characterized by $^{31}$P NMR, X-ray diffraction and TEM. Impregnating MCM-41 or amorphous $\text{SiO}_2$ with an aqueous solution of PW gave catalysts with, in general, two HPA species: one with intact Keggin structure (A) and the other with a different structure (B), supposedly, $\text{H}_3\text{P}_2\text{W}_{18}\text{O}_{62}$ ($\text{P}_2\text{W}_{18}$) and/or $\text{H}_6\text{P}_2\text{W}_{25}\text{O}_{71}$ ($\text{P}_2\text{W}_{25}$). The relative amount of species of A and B depends on HPA loading, with A dominating. At higher loadings, 30-50 wt%, A is practically the only one present on the surface; at lower loadings, both species exist, the amount of B increasing as the HPA loading decreases. In contrast, catalysts prepared by impregnation with a methanol solution of HPA contained exclusively Keggin-type A over the whole range of PW loading. In the PW/MCM-41 catalysts, as shown by TEM, the PW species are mainly located inside the MCM-41 pores. $^{29}$Si MAS NMR was used to study the interaction of HPA with the siliceous MCM-41 surface. The B species was about 8 times as active as A in the liquid-phase trans-tert-butylation of 2,6-di-tert-4-methylphenol and $\alpha$-xylene. In contrast to the impregnation of HPA onto MCM-41 that of its cesium salt failed. Here only X-ray visible crystalline cesium salt on the outer surface of the MCM-41 particles was obtained.

Chapter 9 reports the partial recrystallization of aluminosilicate MCM-41 into ZSM-5 by using tetrapropylammonium hydroxide (TPAOH). Suppressing of the complete recrystallization of MCM-41 is achieved by positioning the TPA cations at the framework of MCM-41 and by applying a viscous medium. Thereby a controlled conversion of the MCM-41 framework is observed giving nanocrystalline ZSM-5 structures. Similar results were achieved by the controlled recrystallization of aluminosilicate HMS. These porous nanocrystalline aluminosilicates (PNA) show a twofold increase of the conversion of cumene compared to the original MCM-41 and HMS materials.

The phenomenon of overgrowth of mesoporous MCM-41 on faujasite is described in chapter 10. Zeolite Y overgrown with a thin layer of MCM-41 has been prepared. TEM shows that a large part of the zeolite surface is covered with an MCM-41 layer of 5 to 20 nm thickness. The composite MCM-41/Y is formed by successive synthesis of Y and MCM-41. Also MCM-41 overgrowth on pre-added Y crystals is
investigated. The overgrowth of MCM-41 on X is stimulated by an increase in the external cation exchange capacity of X. This new biporous molecular sieve shows interesting catalytic properties. Cracking of vacuum gasoil by an MCM-41 coated USY shows a higher conversion of heavy products compared to USY.

Thermoporometry as a new tool in analyzing mesoporous MCM-41 materials is presented in the last chapter, number 11. Thermoporometry is a calorimetric procedure and is applied for measuring the pore size distribution, pore volume and surface area of mesoporous MCM-41 molecular sieves using water as the adsorbate. Minimum pore diameter for the method is 20 Å. A series of MCM-41 materials with various pore diameters was synthesized and subjected to the new method. The results are compared with N₂ physisorption. Both methods are complementary, whereby the former provides also information about the pore shape. MCM-41 materials with pores wider than 50 Å also allow the use of benzene as the adsorbate in thermoporometry.

The acidity and basicity of the various MCM-41 type materials is depicted schematically in the scheme below. It can be concluded that this thesis describes the development of MCM-41 as a multifunctional material for several potential applications in fine chemical as well as petroleum processes.

\[ \text{MCM-41} \]

HPA/MCM-41  PNA-1  H-MCM-41  Na-MCM-41  CsLa/MCM-41  Cs/MCM-41

acidity

basicity

K.R. Kloetstra

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Samenvatting

Chemie van mesoporeuze moleculaire zeven

Tegenwoordig hebben anorganische moleculaire zeven met een specifiek en geordend netwerk van poriën een belangrijke positie ingenomen in de industriële katalyse en in scheidingsprocessen. Een moleculaire zeef is een vaste stof die bestaat uit een gedefiniëerd raamwerk van poriën. Deze poriën hebben afmetingen van ongeveer 0,00000001 meter en daardoor kunnen alleen moleculen die kleiner zijn dan deze grootte het poriestelsel binnenkomen en door deze microporiën bewegen (zeef-effect).

De belangrijkste toepassing van kristallijne moleculaire zeven, zoals zeolieten, zien we in de aardolie raffinage en de petrochemische industrie. De ruwe aardolie wordt eerst gescheiden in verschillende kookpuntsfracties en bepaalde fracties worden vervolgens katalytisch omgezet m.b.v. zeolieten in bruikbare producten.

Zeolieten zijn kristallijne, vaste stoffen opgebouwd uit silicium (Si), aluminium (Al) en zuurstof (O). Si en Al zijn beide omringd door vier gemeenschappelijke O atomen (tetraëdrische coördinatie) waarbij moet worden opgemerkt dat een Al-O-Al eenheid nooit is waargenomen. Hierdoor kan geen lagere Si/Al verhouding dan 1 worden gehaald. Door alterneren Si, O en Al atomen te rangschikken, wordt een polymeernetwerk verkregen. Zo'n netwerk is in drie dimensies (3D) opgebouwd en de manier van opbouw bepaalt de structuur ofwel porieconfiguratie van de zeoliet. Voor elke zeoliet is een basiseenheid te vinden waaruit de hele zeoliet is opgebouwd en daardoor is een zeoliet dan ook kristallijn. De tegenhanger van de kristallijne moleculaire zeef is de amorphe moleculaire zeef. Een belangrijk verschil hierbij is dat er geen repeterende basiseenheid in het 3D netwerk te is vinden buiten de drie atomen Si, Al en O. Deze belangrijke eigenschap bepaalt of een moleculaire zeef kristallijn of amorf is te noemen. Zeolieten zijn in het algemeen thermisch en mechanisch stabiler dan amorphe moleculaire zeven.

Dit proefschrift beschrijft de bereiding en de chemie van de amorphe moleculaire zeef MCM-41 (Mobil's Collection of Materials nr. 41) en gerelateerde materialen. De structuur van MCM-41 is als volgt te beschrijven. Door een aantal cilinders te stapelen, ontstaat een zo dicht mogelijke hexagonale stapeling van parallele pijpen. De meest gebruikte MCM-41 materialen hebben poriediameters die ongeveer vier maal groter zijn dan die van de grootste zeoliet. Door de grootte van de poriën van MCM-41 wordt deze gerekend tot de mesoporeuze stoffen in tegenstelling tot zeolieten die bij de microporeuze stoffen horen. Er kunnen dus veel grotere moleculen in MCM-41 binnendringen dan in een zeoliet.
Schematische presentatie van MCM-41.

Het grote voordeel van het gebruik van poreuze vaste stoffen als katalysator in een organische reactie in de vloeistoffase is dat na afloop van de reactie de katalysator gescheiden kan worden van het produkt door middel van een simpele filtratie. De katalysator kan hierna gewoon weer gebruikt worden voor de volgende reactie. Deze vorm van katalyse wordt heterogene katalyse genoemd. In de classieke organische chemie wordt meestal gebruik gemaakt van een katalysator die net als de reactant in de vloeibare toestand is cq. opgelost is. Dit noemt men homogene katalyse. Het grootste probleem hiervan is de opwinst probleem hiervan is de opwinst van het produkt van de katalysator. Het promotieonderzoek richtte zich op het gebruik van MCM-41 materialen als heterogene katalysatoren in verschillende katalytische processen.

Dit promotieonderzoek is exploratief van karakter omdat de ontdekking van MCM-41 pas in 1992 is gerapporteerd. MCM-41 kan zowel als een zure katalysator en als een basische katalysator functioneren. Door de negatief geladen plaatsen in het MCM-41 raamwerk, die gecreëerd zijn door de aanwezigheid van aluminium, met een proton (H⁺ ion) te neutraliseren, wordt MCM-41 zuur gemaakt. Doordat zuur-base eigenschappen van oxides met elkaar verbonden zijn, bestaan naast de zure plaatsen ook basische plaatsen in het raamwerk. De sterkte van deze basische plaatsen is echter kleiner dan die van de zure plaatsen. Door de H⁺ ionen te vervangen door natrium ionen (Na⁺ ionen) wordt in principe de basiciteit van MCM-41 versterkt. De naamgeving van beide materialen is respectievelijk H-MCM-41 en Na-MCM-41. Gebleken is dat H-MCM-41 in de vloeistof fase zich gedraagt als een mild zure katalysator en daardoor zeer gunstig en selectief is voor zuurgevoelige producten. De bruikbaarheid van Na-MCM-41 als basische katalysator daarentegen beperkt zich niet alleen tot organische media, maar strekt zich ook uit tot waterige oplossingen. Afgezien van het feit dat water een zeer milieuvriendelijk oplosmiddel is, is het uniek voor een vaste basische katalysator om reacties te katalyseren in water.
In het algemeen kan gesteld worden dat de structurele, ofwel intrinsieke, zure en basische eigenschappen van MCM-41 in vergelijking tot zeolieten zwakker zijn en zeker voor verbetering vatbaar zijn. Een manier om dit te bewerkstelligen is om MCM-41 als drager te gebruiken voor katalytisch actieve deeltjes. Hierbij kan worden gedacht aan metaloxides en complexen. De bedoeling is dat deze deeltjes verankerd worden in de poriën van MCM-41 zoals die te zien zijn in de schematische presentatie. Het is natuurlijk wel essentieel dat deze deeltjes kleiner zijn dan de afmeting van de poriën van MCM-41.

Om de zuursterkte van MCM-41 indirect te verhogen worden heteropolyzuren in MCM-41 gebracht. Heteropolyzuren zijn anorganische complexen en bestaan bijvoorbeeld uit een centraal fosforatoom met daaromheen twaalf wolframatomaten die onderling met elkaar verbonden zijn door veertig zuurstofatomen. Een heteropolyzuur is een bolvormig molecuul en is ongeveer zo groot als één derde van de poriediameter van de meest gebruikte MCM-41 materialen. De zuursterkte van een heteropolyzuur is in het algemeen hoger dan die van zwavelzuur en zoutzuur. Uit ons onderzoek is gebleken dat MCM-41 beladen met heteropolyzuur zich gedraagt als een zeer sterk vast zuur. Verder is vastgesteld dat deze heteropolyzuren zeer homogeen verdeeld zijn in de poriën van MCM-41.

Om de structurele ofwel de intrinsieke zuursterkte van MCM-41 en gerelateerde materialen te verhogen is een totaal andere strategie gebruikt. Door de kristalliniteit aan de binnenkant van de poriën van deze materialen te verhogen wordt de zuursterkte verhoogd. Het is bekend dat zeolieten een veel sterker zuur zijn dan MCM-41 achtige materialen. Dit komt omdat de kristalliniteit van zeolieten vele malen groter is. Er kan geconstateerd worden dat de katalytische kraakactiviteit (kraken is een reactie waarbij een molecuul met veel molete wordt gesplitst in kleinere moleculen) van de semikristalline ‘MCM-41’ materialen ten minste verdubbeld is ten opzichte van de originele MCM-41 materialen en dit geldt ook voor de gerelateerde materialen van MCM-41. Hierdoor wordt de potentie van deze materialen om als actieve component in kraakatalysatoren te dienen in raffinageprocessen sterk verbeterd.

De structurele basiciteit van MCM-41 is duidelijk aanwezig, maar betrekkelijk zwak. Via een indirecte methode is ervoor gezorgd dat uiteindelijk sterk basische metaloxides in de poriën van MCM-41 worden gebracht. Het metaloxide dat uiteindelijk verkregen wordt is cesiumoxide. Cesiumoxide is één van de sterk basische metaloxides. Een nadeel is dat het hergebruik van deze cesiumoxide-MCM-41 systemen slecht is. Ook blijken deze materialen erg watergevoelig te zijn wat in bepaalde reacties nadelig kan zijn. Desondanks zijn ze in het algemeen zeer goed bruikbaar in base gekatalyseerde reacties in de vloeistoffase waarbij geen water vrijkomt. Het is dus mogelijk om een goede basische katalysator te maken op basis van cesiumoxide. Door een mengooxide van cesium en lanthaan in de molverhouding 1 : 1 aan te brengen op MCM-41 wordt een thermisch zeer stabiele basische heterogene katalysator verkregen. Verder blijkt dat door interactie van het mengooxide met de MCM-41 drager dit materiaal niet gevoelig is voor water wat zeer nuttig kan zijn voor katalytische toepassingen. Dit kunnen reacties zijn waarbij water wordt gegenereerd of waar
water zelfs als oplosmiddel dient. Dat de aanwezigheid van lanthaan verantwoordelijk is voor deze eigenschappen is zeer aannemelijk. Deze mengoxide systemen laten in de katalyse van bepaalde reacties zoals Michael-addities en aldolkondensaties zeer interessante selectiviteiten naar de producten zien. Bovendien werd een geheel nieuw type reactie met deze systemen teweeggebracht. Tenslotte verhoogt de extrabinnenlaag van het mengoxide van cesium en lanthaan de thermische stabiliteit van het MCM-41 materiaal aanzienlijk.

Er kan dus geconcludeerd worden dat MCM-41 zeer veel heeft te bieden om gebruikt te worden als katalysator dan wel als drager van katalytisch actieve materialen in fijnchemische en petrochemische processen.

K.R. Kloetstra
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Curriculum vitae

