

Influence of Template Extraction on Structure, Activity, and Stability of MCM-41 Catalysts

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Up to 73% of the template in MCM-41 can be removed by extraction with solutions of an acid or salt in ethanol. When extracting with acidic ethanol, ion exchange of the sodium ions for protons is achieved simultaneously. After calcination to remove the residual template, the resulting catalysts show high activity for the acetylation of 2-methoxynaphthalene. The activity depends on the sodium content and on the Si/Al ratio of the catalyst. MCM-41 materials which had not been extracted, but directly calcined to remove all template ions and subsequently ion exchanged, had a mesoporous structure that deteriorated with repeated calcinations. The acid extracted catalysts, on the other hand, retained their highly ordered pore structure throughout several thermal treatments. This stabilization results from the precondensation of silanol groups previously associated with template ions during the extraction. The extraction in acidic medium produced a MCM-41 catalyst with more Brønsted acid sites than the not extracted material. ^{27}Al -NMR measurements showed that the observed increase in octahedral aluminium upon calcination usually ascribed to dealumination can also be explained by a change of coordination number depending on chemical environment as previously reported for zeolite β . © 1997

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range. It cannot only be used for the cracking of heavy oil feedstocks, but also for the processing of fine chemicals in liquid phase reactions because fast diffusion of molecules in the mesopores enables good conversions (6).

Before MCM-41 can be used as a catalyst, large amounts of organic surfactant template must be removed from the pores to make them accessible. Usually the template is burnt during calcination at 540°C but part of it can be extracted from the silicate framework (7–9). The calcined materials are usually ion exchanged in NH_4NO_3 solution to remove the residual sodium ions (7, 10, 11), and after another calcination the active H-MCM-41 catalyst is obtained.

In this paper we compare different extraction media for their efficiency in template removal. The obtained MCM-41 samples are characterized by TG/DTA, XRD, nitrogen adsorption, and MAS-NMR to gain information about structural changes caused by the extraction. These extracted materials are compared with directly calcined and ion-exchanged samples not only for their catalytic performance in the Friedel–Crafts acetylation of 2-methoxynaphthalene, but also for structural differences.

INTRODUCTION

Zeolites are widely used as catalysts for acid-catalyzed reactions (1). Their tunable acid strength and well-defined pore diameters make them very valuable for selective reactions, but limit their use for the conversion of bulky molecules because they can only react on the external surface. The need to process heavier refinery feedstocks and the prospect of synthesizing fine chemicals has led to the production of large pore molecular sieves such as VPI-5 (2) and cloverite (3). The practical use of these materials, however, is still limited. Recently a new family of mesoporous materials has been discovered (4, 5). One member of this family, MCM-41, shows a regular hexagonal array of uniform pores with diameters in the range of 20–100 Å. These materials are synthesized using micellar arrays of templating agents and aluminium can be introduced into their frameworks in tetrahedral coordination. MCM-41 is an acid catalyst and its Si/Al ratio can be varied in a wide

EXPERIMENTAL

Materials

Parent MCM-41 material with a Si/Al ratio of 25 was prepared according to standard procedures (5, 12). Sodium aluminate (3.8 g) was dissolved under stirring in 298 g of a 25% hexadecyltrimethylammonium chloride solution (CTMA) and 10 g of deionized water. This solution was added to a homogenous gel prepared from 53.5 g sodium waterglass, 45 g Cabosil M-5, 16.1 g tetramethylammonium hydroxide pentahydrate (TMAOH), and 130 g deionized water. The molar composition of the gel was 1.0 SiO_2 : 0.0205 Al_2O_3 : 0.096 Na_2O : 0.214 $(\text{CTMA})_2\text{O}$: 0.045 $(\text{TMA})_2\text{O}$: 19.75 H_2O . The reaction mixture was stirred vigorously for another 30 min, loaded into Teflon bottles, and statically heated at 70°C for 40 h. The resulting solid was recovered by filtration, washed extensively with deionized water, and dried at room temperature. For comparison of the catalytic activity, a sample

with a Si/Al ratio of 40 was prepared in the same way varying only the amount of sodium aluminate in the synthesis mixture.

Extracted samples were obtained as follows: 3 g of the dried parent material were stirred in 150 ml of the extraction medium for 1 h at 78°C followed by filtration and washing. This procedure was repeated twice. After drying at room temperature, samples were obtained which will be referred to as dry samples. All dry samples were calcined to remove the residual template (1 h at 120°C; 6 h at 540°C; heating rate, 1°/min, flowing air). Three categories of extraction media were used: (a) solvents only: ethanol (EtOH), 2-propanol (iPOH), and an ethanol–heptane azeotropic mixture (EtOH + C₇); (b) acids or cationic proton donors in ethanol: 0.1 M acetic acid (EtOH/HOAc), 0.1 M NH₄NO₃ (EtOH/NH₄NO₃), 0.05 M sulfuric acid (EtOH/H₂SO₄); (c) neutral salts in ethanol: 0.1 M NaNO₃ (EtOH/NaNO₃), 0.1 M KNO₃ (EtOH/KNO₃), 0.1 M tetraethylammonium bromide (EtOH/TEABr) (see Table 1).

Directly calcined and ion-exchanged samples (no extraction) were obtained by the following procedure: 3 g of calcined MCM-41 parent material were ion exchanged with 150 ml of an aqueous solution of 0.1 M exchanging agent at 60°C for 1 h. After threefold ion exchange the samples were dried (dry samples) and calcined again at 540°C for 6 h (calcined samples). They were named after the exchanging agent used (0.1 M concentration): HOAc, NH₄NO₃, H₂SO₄ (0.5 M only), NaNO₃, KNO₃, TEABr, *n*Bu₂NH₂Cl (di-*n*-butylammonium chloride), CsNO₃, and Ca(NO₃)₂ (see Table 2).

An amorphous silica/alumina (13% Al₂O₃) was used as received from GRACE GmbH, Worms.

Characterization

Powder X-ray diffraction patterns from 1° to 10° 2θ were obtained on a Siemens D5000 diffractometer using CuKα radiation at a step size of 0.02° with a count time of 10 s. Nitrogen adsorption/desorption isotherms were recorded at –196°C on a Micromeritics ASAP 2010 instrument using a conventional volumetric technique. Freshly calcined samples were outgassed at 400°C for additional 4 h at pressures below 10 μm Hg prior to analysis. Samples were dissolved in hydrofluoric acid before measuring atomic absorption on a Varian SpectrAA-10 spectrometer. TG/DTA analyses were performed on a Polymer Laboratories STA 1500H instrument in flowing air using a heating rate of 5°C/min.

Solid-state MAS-NMR spectra were recorded on a Bruker AMX400 spectrometer. Chemical shifts are given relative to tetramethylsilane (²⁹Si), hexafluoroisopropanol (¹H), or ammonium aluminium sulfate (²⁷Al). Conventional acquisition procedures were used, except for ²⁹Si-MAS-NMR spectra which were recorded at a repetition time of 60 s to allow complete relaxation. In the ²⁷Al-MAS-

NMR spectra narrow pulses of 1.3 μs ensured quantitative measurements. ¹H-MAS-NMR samples were dehydrated under vacuum at 350°C and sealed under vacuum in zirconia rotors prior to data acquisition. The rotors have been tested for tightness over several weeks: The ¹H spectra of hydrophilic zeolites did not change over time.

Catalytic test reactions were carried out at 100°C in stirred batch reactors equipped with a reflux condenser strictly avoiding water entering the experimental setup. 2-Methoxynaphthalene (50.0 mmol) was dissolved in 25 ml sulfolane. When the reaction temperature was reached 25.0 mmol acetic anhydride, 0.5 g freshly calcined catalyst, and 1.0 ml nitrobenzene (internal standard) were added. Samples were taken regularly and analyzed by gas chromatography (HP 5890, 25 m × 0.32 mm × 0.52 μm HP-1 column). Products were identified by comparison with reference compounds or by GC/MS.

RESULTS AND DISCUSSION

Thermal Analysis

Figure 1 shows weight losses and heat flows for the parent material and two of the extracted samples. Most of the samples showed a plateau between 100 and 150°C which was taken as the end of solvent/water desorption and the beginning of template decomposition and desorption. For the samples with high template content such as the parent sample and the solvent-only extracted samples these two steps could only be separated by differentiation of the weight curve. The template loss can be divided into several steps (5, 7, 8): Base-catalyzed Hofmann elimination and subsequent trimethylamine desorption occurs from 120 to

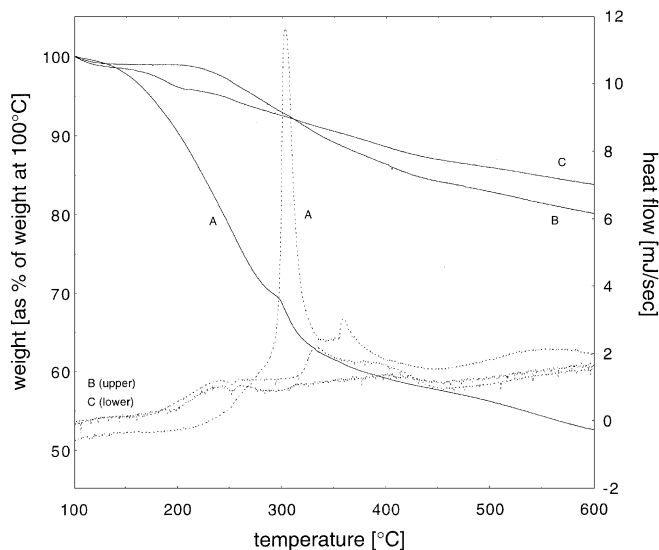


FIG. 1. Thermogrammes of parent material (A) and two solvent extracted materials: EtOH/HOAc (B) and EtOH/NH₄NO₃ (C). Solid lines, sample weight; dotted lines, heat flow.

250°C, while at higher temperatures hexadecene and its decomposition products are desorbed and subsequently oxidized exothermally. The DTA curve of the parent material shows a broad endothermic signal for the desorption of trimethylamine followed by a very intense exothermic signal at 302°C and a smaller signal at 359°C. The DTA signals of the extracted samples are more difficult to evaluate because of the smaller intensity of the broader signals.

The template content was calculated from the weight loss between the beginning of the trimethylamine desorption and the weight at 500°C. All values were related to 100% dry sample and are compiled in Table 1. The further weight loss above 500°C is most likely due to water produced by thermal condensation of silanol groups and is comparable for all our samples.

The extraction with EtOH/HOAc removes a large amount of template. The removal of the residual template in TG/DTA followed a similar mechanism as for the parent material. The weight loss caused by trimethylamine desorption starts at higher temperatures, the DTA signal is smaller and the peak maximum is shifted toward higher temperature. This implies that the remaining template is bound strongly by ionic interactions between tetraalkylammonium ions and Brønsted acid sites. An extraction in EtOH/NH₄NO₃ yields a slightly different material. More template could be removed and it is difficult to assign distinct steps for the decomposition of the residual template. The weight loss between 150 and 200°C for the EtOH/NH₄NO₃ sample could be assigned to the decomposition of the ammonium ions. Deamination occurs at low temperatures indicating that this ammonium form is not very stable (see interpretation of ²⁹Si-NMR).

TABLE 1

Characterization of Samples Obtained by Extraction Methods

Sample name	% of template extracted ^a	Na/Al ratio ^b	<i>d</i> spacing of dry sample ^c (Å)	BET surface area ^d (m ² /g)
Parent material ^e	0	0.059	41.7	990
EtOH/NH ₄ NO ₃	71	0.009	40.3	973
EtOH/HOAc	63	0.031	41.3	968
EtOH/H ₂ SO ₄	68	0.004	40.2	960
EtOH/TEABr	59	0.083	41.7	872
EtOH/NaNO ₃	73	1.53	40.6	520
EtOH/KNO ₃	19	0.008 ^f	41.8	77
EtOH	23	0.058	41.4	997
EtOH + C ₇	17	0.065	41.8	992
iPOH	4	0.062	41.3	994

^a Estimated error of TGA, 2%.

^b Estimated error of AAS analysis, 10%.

^c Estimated error of *d* spacings, 1%.

^d Estimated error of BET analysis, 3%.

^e Contained 44% template.

^f K/Al = 0.82.

Using 2-propanol as extraction medium, only 4% of the template could be extracted, while the more polar ethanol proved to be a more efficient solvent for the template ions. An azeotropic mixture of ethanol and heptane was less efficient, probably due to its lower polarity.

Using strong acids (EtOH/H₂SO₄) or small cations (EtOH/NaNO₃, EtOH/NH₄NO₃), about 70% of the template could be extracted. EtOH/HOAc with a low acid dissociation constant is slightly less efficient. Equal amounts of KNO₃ are not as efficient as NaNO₃, and also TEABr is less suitable for extraction of template. This suggests that the size and therefore the mobility of the cation in the close packed micellar aggregates is one of the factors determining the amount of template that can be removed by extraction in ethanol.

Hofmann elimination is the dominant mechanism for template decomposition when MCM-41 is heated during calcination or thermogravimetry (5, 7, 8, 13). However, decomposition of CTMA⁺ cannot be an important route for the removal of template in acidic or neutral alkali nitrate medium. Therefore, an ion-exchange mechanism instead of a decomposition of the template ion is operative during extraction. The different formation mechanisms of MCM-41 postulated by several authors (4, 5, 12, 14) always include interactions of the cationic CTMA template with silicate anions that are preferred over small Cl⁻ or OH⁻ anions. Since the template remains in the void volume of the silicate framework after synthesis, its positive charge must be compensated by framework aluminium sites or siloxy groups. Due to the low aluminium concentration in the framework of a material with a Si/Al ratio of 24, charge compensation of the template cations is impossible exclusively by aluminium. A substantial amount of siloxy groups must be present to compensate the charge of the residual template ions. These siloxy groups must either be protonated or other charge compensating cations must be added in order to extract template ions from the material.

A simple calculation shows that our parent material consisting of 44 wt% CTMA⁺ and 56 wt% SiO₂ contains 1 CTMA cation for every 6 SiO₂. Assuming a Si/Al ratio of 24 and an extraction efficiency of 73% one calculates a ratio of 1.1 CTMA cation for every AlO₂⁻ after extraction. This supports the findings by other authors (5, 8, 15) that mainly the template associated with the siloxy groups can be removed by extraction, while the more strongly bonded template associated with the framework aluminium remains in the material.

With an average wall thickness of three tetrahedrons (9–10 Å) there should be four surface silicate species per template molecule. Therefore one-quarter of the surface silicons are siloxy species compensating template charges, while the remaining silanol groups interact with the template ion by ionic–dipolar interactions. The negative charge of tetrahedrally coordinated framework aluminium also

compensates a positive template charge and therefore allows a higher degree of condensation of the silicate framework by avoiding the presence of another siloxy group. In our material with a Si/Al ratio of 24, one-quarter of the template molecules are associated with framework aluminium sites. Their strong interaction is supported by the small Na/Al ratio of the parent material.

Chemical Composition

The Na/Al ratios of the parent material and extracted samples are given in Table 1. The Si/Al ratio of the parent material is close to the gel composition, but the Na/Al ratio is below 0.1. Even though a large excess of sodium ions per aluminium is present in the gel (Na/Al = 4.7), they are not incorporated into the MCM-41 material. This shows that preferentially CTMA⁺ and TMA⁺ templating cations are charge compensating for framework aluminium. Therefore, a sodium form of MCM-41 can only be obtained by ion exchange. Even though several Na forms of MCM-41 have been described and characterized by various techniques, their sodium content has not been specified (10, 16, 17) making it difficult to compare our results with the literature.

The Si/Al ratio of most samples was not significantly affected by the extraction procedure. Within the experimental error all extracted samples in Table 1 have the same Si/Al ratio as the parent material (Si/Al = 24 ± 1), except for EtOH/H₂SO₄ which had a Si/Al ratio of 28. For samples extracted with solvents only (EtOH, EtOH + C₇, and iPOH) the Na/Al ratio remained constant. The difference in dissociation constants between H₂SO₄ and HOAc influences the ion exchange which occurs simultaneously with the template extraction. The hydroxonium ion of the fully dissociated sulfuric acid substitutes even more sodium ions than the ammonium cation. Treatment with the not fully dissociated acetic acid replaces only half of the sodium cations present in the parent material. The high sodium content of the EtOH/TEABr sample can be explained by impurities in this batch of TEABr: Elemental analysis gave a sodium content of 124 ppm.

The Na/Al ratio of the EtOH/NaNO₃ sample is much higher than expected if sodium were only compensating the framework charges induced by tetrahedrally coordinated aluminium. Some of the sodium cations are most likely associated with negative siloxy groups, or they must form small Na₂O particles inside MCM-41. During the extraction in EtOH/NaNO₃, Na-siloxo groups can be formed because only small amounts of proton donors such as water are present which would transform the siloxy anions into the more stable silanol groups. Furthermore, under the conditions applied the template ions do not decompose to form substantial amounts of protons. The same must be true for potassium ions: Even though the ion exchange for potassium was not as high as for sodium, the large amount of

TABLE 2
Characterization of MCM-41 Samples Which Had Been Ion Exchanged after Direct Calcination

Exchanging agent	Na/Al ratio	M ⁺ /Al ratio ^a	BET surface area (m ² /g)
Parent	0.059	—	990
NH ₄ NO ₃	0.007	—	861
HOAc	0.006	—	960
H ₂ SO ₄	0.004	—	921
TEABr	0.007	—	883
<i>n</i> Bu ₂ NH ₂ Cl	0.005	—	870
NaNO ₃	0.95	—	903
KNO ₃	0.002	0.28	700
CsNO ₃	0.007	0.74	762
Ca(NO ₃) ₂	0.009	0.32	831

^a M⁺ stands for K⁺, Cs⁺, or Ca²⁺.

residual template implies that potassium-siloxo species or small K₂O particles are present.

The chemical compositions of the directly calcined and ion-exchanged samples are given in Table 2. While the Si/Al ratio compared to the parent material remained constant (except for the sample exchanged with H₂SO₄ (Si/Al = 189)), the Na/Al ratios were considerably lower except for the sample which was sodium exchanged. The total amount of cations exchanged varied with the cation used. The total capacity for sodium ions was close to one cation per aluminium. This means that a minimum of 95% of the aluminium is negatively charged framework aluminium and is accessible for ion exchange. These findings are further confirmed by the Al-NMR spectra shown later. An ion exchange with potassium or cesium ions was less complete and resulted in a material which showed the typical MCM-41 powder pattern, but a lower surface area and a poor pore ordering as proved by nitrogen adsorption data.

X-Ray Diffraction

Powder X-ray diffraction is a major tool for MCM-41 structure determination. It has been shown (10, 18–20) that even materials with low pore ordering, mainly caused by the number of heteroatoms in the framework, exhibit the typical low angle diffraction peak around 2.2° 2θ, whereas only highly ordered, superior quality material exhibits the higher order reflections such as (110), (200), and (210). With a pure silicon oxide MCM-41 material the higher order reflections can be observed, but their intensities usually decrease with the amount of other metals incorporated into the framework. Even though a Si/Al ratio of 25 is quite low for a pure MCM-41 phase (15, 17), all our dry samples obtained by extraction methods as well as the parent material show three to four peaks in their powder patterns. Therefore, we conclude that our material is a highly ordered MCM-41 sample.

TABLE 3

Wall Thickness of Extracted and Subsequently Calcined Samples

Sample	<i>d</i> value XRD	Pore diameter BJH	Wall thickness ^a
Parent	37.7	28.2	9.5
EtOH	38.0	28.5	9.5
EtOH + C ₇	38.0	28.4	9.6
iPOH	38.0	28.3	9.7
EtOH/NH ₄ NO ₃	37.3	28.8	8.5
EtOH/H ₂ SO ₄	37.4	28.9	8.5
EtOH/HOAc	37.5	29.1	8.4
EtOH/TEABr	37.9	29.0	9.1
EtOH/NaNO ₃	36.0	≈26	≈10

Note. All values in Å.

^a Estimated error of wall thickness, 3%.

Since the experimental error of a diffraction instrument is considerably high for very low angle peaks, more accurate values for the *d*-spacing and lattice parameters of MCM-41 materials can only be obtained if the (110), (200), and (210) reflections are well enough resolved in the powder pattern to be used for *d*-value determination. All *d*-values given in Table 1 have been calculated by using the higher order reflexes as well as the dominant low angle (100) peak. No significant loss of crystallinity was observed for any of the extracted samples even after treatment with strong acid.

Lattice contractions in MCM-41 are usually around 10% but can be as high as 25% (7, 21, 22). Our parent material showed a lattice contraction of 9.5% upon calcination (Tables 1 and 3). Only small lattice contractions caused by the extraction procedure are observed (Table 1). Even though they are significant and related to the amount of template, they are lower than the lattice contractions observed upon calcination of MCM-41. This shows that the amount of template in the pores of MCM-41 is of less influence on the lattice parameters than the effects of the heat treatment during calcination.

After calcination of the extracted samples most XRD patterns showed the initial MCM-41 peaks. Only the pattern of EtOH/KNO₃ was featureless in the range of 1° to 10° 2θ indicating a collapse of the structure upon calcination. Also the directly calcined and ion-exchanged samples showed the typical powder pattern for MCM-41 before and after calcination with no significant loss of crystallinity.

Nitrogen Adsorption

A typical MCM-41 sample with 25–30 Å pore diameter exhibits a reversible, hysteresis free type IV isotherm. The sharp inflection at relative pressures >0.3 is characteristic of capillary condensation within uniform mesopores. The sharpness of the step reflects the uniformity of the pores (23–25). The second step in the isotherm at relative pressures >0.9, which is observed for all our samples, is at-

tributed to the condensation of nitrogen in the depressions of rough surfaces or between small MCM-41 particles. Small particles are preferred for catalytical applications and are typical for the low Si/Al samples obtained under our high pH synthesis conditions. SEM revealed a primary particle size of 0.3 μm aggregated into 5-μm-diameter secondary particles. The very rough surface of the fractal particles results in a larger surface area than estimated from particle size only: The parent material has a BET surface area (26) of 990 m²/g, while the inner mesopore surface area estimated by the *t* plot method (27) is 865 m²/g. The mesopore area therefore contributes 87% to the total surface area and the external surface area is 13%.

Figure 2 shows clearly that even a material such as EtOH/NaNO₃ which has a well-structured XRD pattern can have a low surface area and a low mesopore volume. This indicates that a sample with a well-established periodicity as detected by XRD must not necessarily show the characteristically high surface area. Therefore, both techniques should be used to judge the overall quality of the sample. However, nitrogen adsorption has proved to be more sensitive on structural changes in our samples. As an example Fig. 3 gives the nitrogen adsorption isotherms of the parent material and two representative extracted samples (EtOH/NH₄NO₃ and EtOH/HOAc).

Samples that had been extracted with alkali metal salts (see also Fig. 2) or TEABr had a lower surface area and

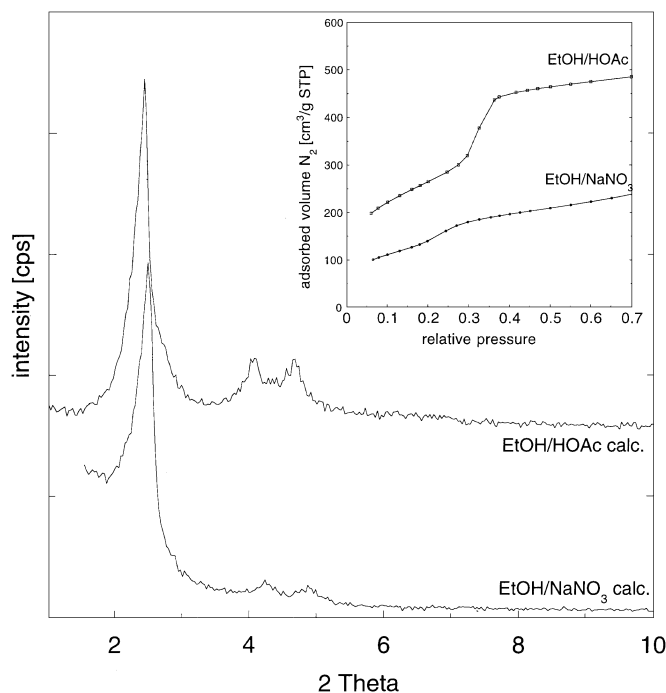


FIG. 2. XRD spectra of samples extracted with EtOH/HOAc and EtOH/NaNO₃ and subsequently calcined. The inset shows nitrogen adsorption isotherms of the same samples.

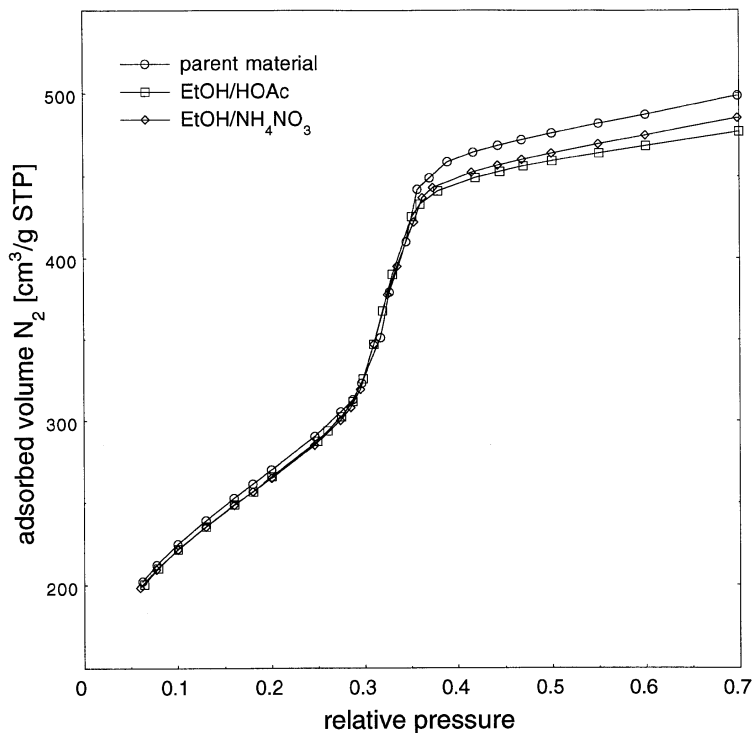


FIG. 3. Nitrogen adsorption isotherms of parent material, EtOH/NH₄NO₃, and EtOH/HOAc.

lower mesopore volume than samples that had been extracted with either pure solvents or with acid-containing solutions. From our results of the nitrogen adsorption it is evident that the combination of a reduced template amount and a high alkali metal content not associated with framework aluminium makes MCM-41 very unstable toward the following calcination step. The effect is more pronounced for large alkali metal cations and for higher loadings. These findings are supported by experimental results with a MCM-41 sample of higher Si/Al ratio where a crystalline sodium silicate phase was detected after calcination of an EtOH/NaNO₃ sample with high sodium content. Therefore, we conclude that the formation of amorphous or even crystalline alkali metal-silicate phases is favored over the formation of the sodium form of MCM-41 if excess alkali cations are present during calcination and major amounts of template have been removed before calcination.

The wall thickness of MCM-41 is given by the difference between the d -value obtained from powder diffraction and the pore diameter obtained from nitrogen adsorption. The pore diameters were calculated based on the BJH model (28) which is more appropriate for cylindrical MCM-41 pores and nitrogen as the adsorptive than the Horvath-Kawazoe model (29). In Table 3 only the wall thicknesses of extracted samples are given. The step in the isotherms of directly calcined and ion-exchanged samples was less pronounced resulting in a broader distribution of pore sizes and

therefore an inaccurate determination of the wall thickness. Numerical values of wall thicknesses in MCM-41 should be judged carefully, because the choice of the model for pore diameter analysis might lead to systematic errors. However, such errors are equal for all samples and therefore the general trend observed is real.

The wall thickness of samples that had been extracted in an acidic medium is lower than for the parent material or for samples extracted in solvents only. It has been shown that the wall thickness of MCM-41 depends on the pH value during the synthesis (30). Our results show that a postsynthesis treatment in an acidic medium also reduces the wall thickness. The thinner walls can be explained by the controlled precondensation of silanol groups during the extraction procedure (see results of Si-NMR). Our results on the structure of recycled catalysts support that the acidic extracted samples are more stable than untreated material. We therefore conclude that not only the thickness of the walls but also the degree of condensation of the constituting silicate units influence the thermal stability of a MCM-41 sample.

Solid State NMR

The ²⁹Si-MAS-NMR spectra of our samples can be deconvoluted into three gaussian lines, as shown in Fig. 4. The results of the deconvolution for all samples are given in Table 4. The peak around 107 ppm is attributed to Q⁴ atoms (four T-atom neighbors). The majority of the silicon

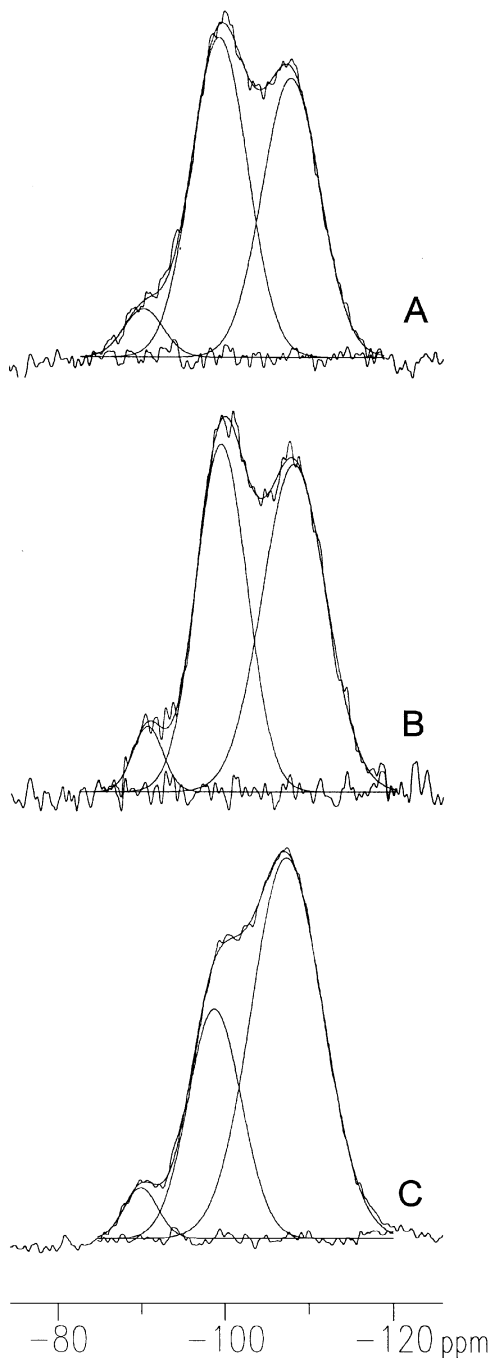


FIG. 4. ^{29}Si -MAS-NMR spectra of parent material, dry (A), EtOH/HOAc (B), and parent material, calc. (C).

atoms with a chemical shift of 98–100 ppm must be due to Q^3 silanol or siloxy species, since a small contribution of $\text{Q}^4(1\text{Al})$ Si atoms is to be expected, because of the Si/Al ratio of 24. Similarly, the signal around 90 ppm is assigned to Q^2 species which are known to exist on a silica surface even after treatment at 800°C (31), although some of the intensity may be due to $\text{Q}^3(1\text{Al})$ species. In the quantitative comparison of the deconvoluted spectra (Table 4)

we have disregarded a significant contribution of $\text{Q}^4(1\text{Al})$ and $\text{Q}^3(1\text{Al})$ species since their influence on the spectra must be small and comparable for all the investigated samples.

The dried parent material shows a large number of not fully condensed silicate species: 61% of the silicon atoms can be assigned to Q^3 and Q^2 species. If the sample is extracted in EtOH/HOAc or EtOH/ NH_4NO_3 the relative amount of Q^3 and Q^2 decreases and the Q^3 line narrows significantly. An increase in Q^4 species was also observed when acetic acid was added during synthesis (22). After calcination the parent and the extracted EtOH/HOAc sample show comparable amounts of Q^3 silanol groups. The extracted material shows a slightly narrower peak for the Q^3 species. The directly calcined and ion-exchanged HOAc dry sample shows a higher amount of Q^3 species than the calcined parent material. Both Q^4 and Q^3 signals are narrower than in the calcined parent material indicating a more uniform environment for these species. These findings and their relation to the condensation of silanol groups are consistent with the findings of Chen *et al.* for a HCl-EtOH extracted sample (7).

The lattice contraction of 3.5 Å and the Si-NMR indicate that large amounts of silanol and siloxy species condense upon calcination to siloxane bonds. The term siloxane is used here for Si–O–Si bonds as in silica literature and should not be confused with $-\text{Si}(\text{R}_2)\text{O}-$ species referred as siloxane in other fields of chemistry. These thermally condensed siloxane bonds are known to be strained (31). It is obvious that a completely connected siloxane surface of MCM-41 is impossible. The surface of a calcined material will always contain silanol groups, as well as relaxed and strained siloxane bonds. The wider range of Si–O bond angles of the siloxane groups is reflected in the considerably larger line width for the Q^4 silicon atoms in calcined materials compared to dry material containing only relaxed siloxane bonds.

The lines for the Q^3 signal are narrower for the dried extracted samples than for the dry parent material, implying that the range of species contributing to this line is smaller.

TABLE 4

^{29}Si -MAS-NMR Deconvolution Results^a

Sample	% Q^4	% Q^3	% Q^2	% $(\text{Q}^3 + \text{Q}^2)$	FWHM Q^4 (ppm)	FWHM Q^3 (ppm)
Parent, dry	39	56	5	61	7.2	8.3
Parent, calc.	63	33	4	37	8.2	6.7
EtOH/ NH_4NO_3 dry	47	42	11	53	7.1	6.0
EtOH/HOAc dry	47	45	8	53	7.3	6.3
EtOH/HOAc calc.	63	29	8	37	8.4	6.2
HOAc dry	56	37	7	44	7.2	5.8

^a Estimated error of deconvolution data: for Q^4 , 3%; for Q^3 , 6%; for Q^2 , 20%; for $(\text{Q}^3 + \text{Q}^2)$, 2%.

From steric considerations it seems reasonable that vicinal silanol groups condense to form stable siloxane bonds while other types of silanol groups remain unchanged in acidic medium. Single silanol groups cannot react and silanol groups neighboring Brønsted acid sites are more difficult to condense because they stabilize or are stabilized by the Brønsted site by hydrogen bonding.

The higher Q^3/Q^4 ratio of the directly calcined and ion-exchanged dried HOAc sample shows that a certain amount of siloxane bonds present in the calcined parent material are not stable in acidic solution. It is known that the thermally condensed siloxane bridges of silica can be easily rehydrated in air (31). In an acidic solution the rehydration process is even faster and a large amount of silanol groups are formed. Since the condensation–rehydration process is reversible these groups condense again when the material is calcined. The stress on the framework induced by the repetition of this process weakens the structure of the pore walls of MCM-41 considerably.

When extracting 70% of the cationic template from MCM-41 by EtOH/HOAc or EtOH/ NH_4NO_3 an equal amount of charged surface siloxy groups must be compensated. If acetic acid is present, these siloxy groups will be protonated to silanol groups. A similar process occurs in EtOH/ NH_4NO_3 : The $SiO^-NH_4^+$ ion pairs hydrolyze to surface silanol groups and ammonia. The physisorbed ammonia desorbs at low temperatures as shown by TG (Fig. 1). In a suitable acidic extraction medium some of these newly formed silanol groups condense to unstrained and therefore more stable siloxane bridges. From the results in Table 4 one calculates that 13% of the original amount of not fully condensed species of the dry parent material (61% $Q^3 + Q^2$) were condensed during the extraction (53% $Q^3 + Q^2$ in EtOH/HOAc dry). This is 50% of the total amount of silanol groups that can be condensed (37% $Q^3 + Q^2$ in EtOH/HOAc calc.). This precondensation during extraction must be one of the reasons for the lattice contraction observed for extracted samples. Even though large amounts of silanol groups have been condensed, the influence of the extraction on the lattice contraction is smaller than the influence of the calcination.

The ^{27}Al -NMR spectra showed the typical broad lines caused by distributions of different environment of the Al nuclei in MCM-41. Some aluminium nuclei might have large quadrupolar coupling constants resulting in a peak broadening rendering them invisible. To minimize this effect, very short pulses have been used in our spectra. The spectra of the two dry samples (EtOH/HOAc and parent material) are quite similar (Fig. 5). Most of the aluminium is in tetrahedral coordination (signal at 55 ppm). The signal around 25 ppm which is usually attributed to pentacoordinated aluminium vanishes after extraction in the acidic medium. The amount of Al removed from the sample during extraction in EtOH/HOAc is too small to be detected

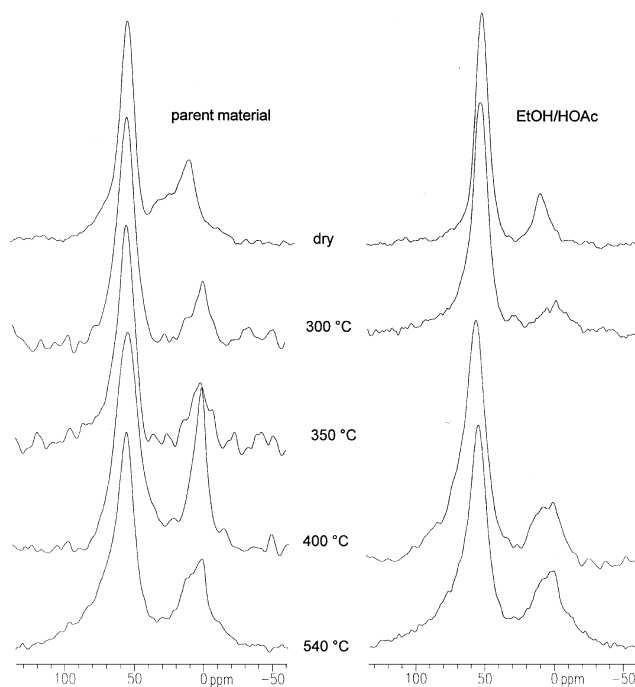


FIG. 5. ^{27}Al -MAS-NMR spectra of parent material and EtOH/HOAc calcined at different temperatures.

by AAS. Therefore, it is more likely that the coordination of the aluminium was changed during extraction. The high relative amount of octahedrally coordinated aluminium is typical for low sodium content materials (21) even before calcination. The intensities of the signals at 55 ppm and at 0 ppm (octahedrally coordinated aluminium) of the calcined materials (540 °C) are comparable. No significant influence of the amount of template which is decomposed and burnt during the calcination on the state of the aluminium can be observed. The relative intensity of the signal at 0 ppm decreases up to 300 °C (350 °C for the parent material). After calcination at 400 °C and subsequent rehydration a large amount of regularly octahedrally coordinated Al nuclei can be detected which vanishes after treatment at 540 °C. The increase in the amount of octahedrally coordinated aluminium is usually explained by the formation of extraframework aluminium (7, 8, 10, 16, 18).

Our samples have been equilibrated in ambient air before NMR measurements. Therefore, we must consider the stage of rehydration for our samples (16). Figure 6 shows the spectra of the calcined parent material before and after addition of one drop of demineralized water. It is obvious that we must attribute the sharp peak around 0 ppm to well-ordered rehydrated octahedrally coordinated aluminium, while the underlying broad peak reflects the geometrically more stressed octahedrally coordinated aluminium. Both of them can be partially connected to the MCM-41 framework with a difference in the number of connections.

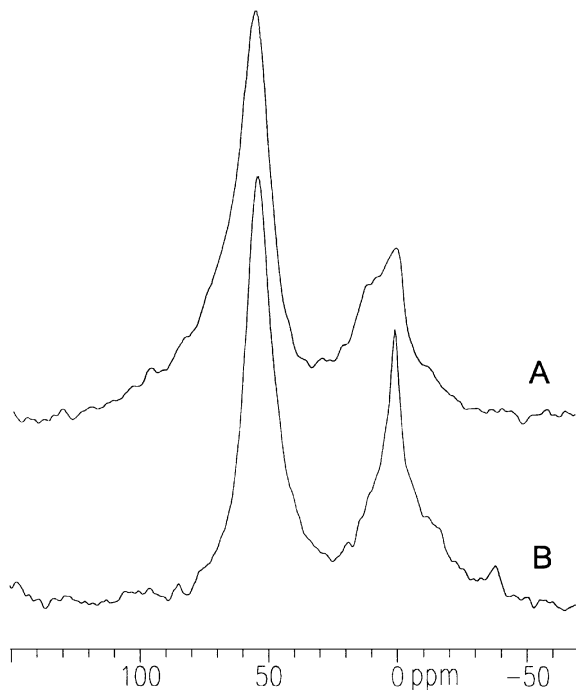


FIG. 6. ^{27}Al -MAS-NMR spectra of parent material calcined at 540°C before (A) and after (B) addition of one drop of water to sample in rotor.

It has been shown by different authors that the chemical environment can reversibly change the coordination sphere of aluminium in zeolite β . Calcination of this zeolite yields octahedral aluminium which cannot be washed out and is therefore still partially associated to the zeolite lattice (32). The tetrahedral coordination can be restored by either a treatment in NH_4NO_3 (33) or more efficiently in NaNO_3 (34). It is unlikely that extraframework aluminium can be reinserted into the framework by mere ion exchange. A more reasonable explanation is that the coordination sphere changes in dependence of the environment. The protons which are formed after calcination cause a distortion of the aluminium site geometry and therefore facilitate the addition of water to obtain the preferred octahedral coordination. Under mild treatment conditions the change in coordination number is reversible. This can be explained by the stacking faults in the β framework allowing a change in coordination geometry for the aluminium ions closely.

The same mechanisms can explain the higher amounts of octahedrally coordinated aluminium that are usually detected in calcined H-MCM-41. Especially MCM-41 material with a low Si/Al ratio can contain some octahedrally coordinated aluminium that is partially connected to the framework. The ill-defined amorphous wall structure of MCM-41 material and the therefore much larger flexibility of O-T-O angles might explain the presence of octahedrally coordinated aluminium partially connected to the silicon oxide framework. Except for very high pH val-

ues, aluminium prefers an octahedral coordination sphere. Therefore, it must be forced to take a tetrahedral coordination either by insertion into a stiff lattice as in zeolites or by chemical environment. Only during calcination the flexible Al sites of MCM-41 will be dehydrated to a tetrahedral coordination or a tricoordinated Lewis site (15) depending on the local structure. In humid air the preferred higher coordination can be attained by coordination of additional water molecules to these flexible Al atoms. This reversible rehydration has not only been shown for zeolite β (35) but also for the aluminium phosphate molecular sieve VPI-5 (36) and has been suggested for MCM-41 (21). In a different chemical environment, such as provided by sodium ions, the coordination changes and a tetrahedral coordination seems to be preferred, as seen in the ^{27}Al spectra of the ion-exchanged NaNO_3 and $\text{EtOH}/\text{NaNO}_3$ samples (Fig. 7). The spectra of the extracted sodium form must, however, be evaluated more carefully since the sample is of lower structural order. Furthermore, the dry sample contains still 27% template which partially forces an octahedral coordination of the aluminium associated to it (21). In the NaNO_3 sample with an exchange degree of 95% Na/Al we detected only negligible amounts of octahedrally coordinated aluminium species. The spectra of NH_4NO_3 dry (Fig. 8) shows smaller amounts of octahedrally coordinated aluminium than the calcined parent material (see Figs. 6 and 7). In the $\text{EtOH}/\text{NH}_4\text{NO}_3$ sample the residual amount of template causes more octahedrally coordinated aluminium. The effect of ammonium ions on aluminium coordination is less pronounced than that of sodium ions in MCM-41 materials. The calcination and following rehydration in air brings back the initial amount of octahedral coordination for both samples.

True extraframework aluminium can be extracted at low pH values because of its solubility at $\text{pH} < 3$. The octahedrally coordinated aluminium in our material, however, resists the severe treatment of extraction in 0.1 M sulfuric acid in ethanol with only small amounts of water present. Only a minor amount of aluminium is removed corresponding to

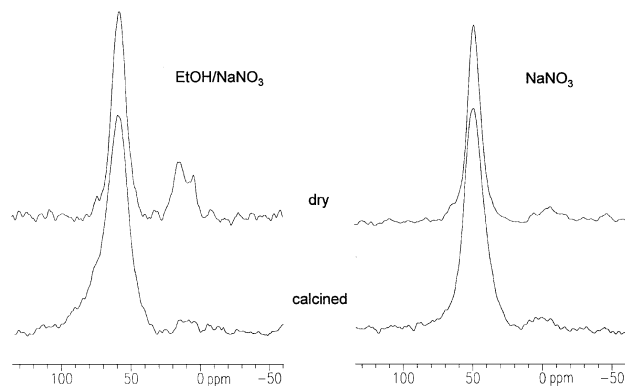


FIG. 7. ^{27}Al -MAS-NMR spectra of $\text{EtOH}/\text{NaNO}_3$ and NaNO_3 .

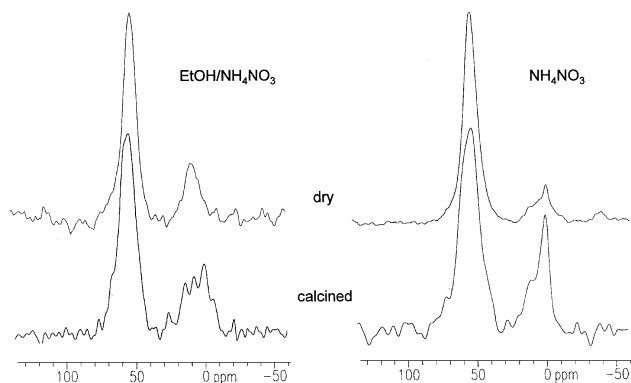


FIG. 8. ^{27}Al -MAS-NMR spectra of EtOH/ NH_4NO_3 and NH_4NO_3 .

the “real” extraframework aluminium detected in the ^{27}Al spectra of NaNO_3 . A treatment at pH 1 (0.05 M H_2SO_4 in water), however, removes large amounts of aluminium from the framework but the MCM-41 structure remains intact. This shows that MCM-41 can be dealuminated at pH 1 while a treatment in EtOH/ H_2SO_4 does not affect the aluminium content of the sample. At this low pH values also crystalline zeolite materials like mordenite can be dealuminated (37).

The main signal at 1.8 ppm in the ^1H -NMR spectra given in Fig. 9 is assigned to silanol groups. The species causing the small peak or shoulder at higher field are still under discussion; they might be silanol groups. The protons from

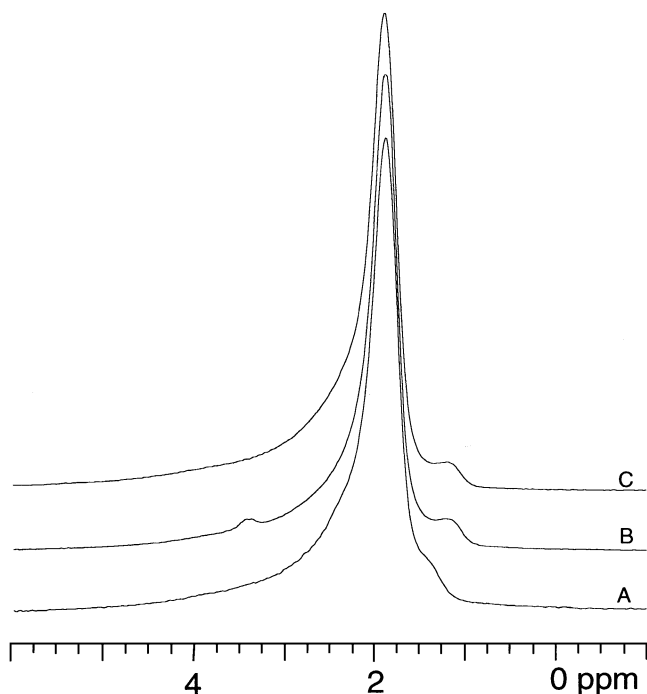


FIG. 9. ^1H -NMR spectra of parent material (A), EtOH/HOAc (B) and HOAc (C).

Brønsted acid sites are detected at 3.3 ppm. The high field shift of these protons compared to the bridging hydroxyls of most zeolites (38) indicates a lower Brønsted acid strength of MCM-41 materials as confirmed by other techniques (7, 18, 39). These Brønsted acid sites, however, can only be observed for the EtOH/HOAc calc. sample. Furthermore, the main silanol peak is narrower for this sample. We therefore conclude that the precondensation of silanol groups during acid extraction is the reason for the presence of Brønsted acid sites. In the calcined parent material and after an ion exchange and calcination no bridging hydroxyls are observed even though these catalysts are highly active in our catalytic test reaction. The active sites must therefore be Lewis acid sites which cannot be detected in ^1H -NMR. The presence of large amounts of Lewis acid sites has been confirmed by infrared measurements of adsorption of basic molecules on MCM-41 (15, 18, 39). These Lewis sites arise from a dehydration of the Brønsted site and a silanol group during calcination (or sample preparation for ^1H -NMR). The reduction of the amount of silanol groups by acidic extraction seems to prevent the dehydration of the acid site, therefore increasing the Brønsted/Lewis ratio of the acid sites.

Catalytic Activity

The acylation of 2-methoxynaphthalene (2-MN) has been extensively studied as a test reaction for zeolites β , USY, and ZSM-12 in our laboratory (40) and has recently been used with MCM-41 catalysts (11). Acetylation with acetic anhydride occurs at the 1-position yielding the kinetically favored 1-acetyl-2-methoxynaphthalene (1-Ac-2-MN). Although Friedel-Crafts acylation is usually irreversible, the main product 1-Ac-2-MN can undergo protodeacetylation (41) and reacylation then yields the thermodynamically more stable 2-acetyl-6-methoxynaphthalene (2-Ac-6-MN) which is also produced by migration of the acetyl group (42).

The conversions vs time obtained with the series of catalysts obtained by extraction methods after calcination are given in Fig. 10. The maximum possible conversion of 2-MN under our reaction conditions is 50% because it was used in twofold excess. Selectivities to 1-Ac-2-MN over large pore MCM-41 were 90% ($\pm 1\%$) in all reactions. Other acylated methoxynaphthalenes were detected as by-products in minor amounts only (less than 1%). The parent material and the catalysts which had been extracted with solvents only have equal activity. This proves the excellent reproducibility of the runs and confirms that the acetylation of 2-methoxynaphthalene is a suitable test reaction. However, the activity of the catalyst increased with the extraction in acidic medium. The activities of the catalysts obtained by extraction methods were compared to the catalysts obtained by direct calcination and ion exchange. The latter catalysts had activities similar to that of the extracted

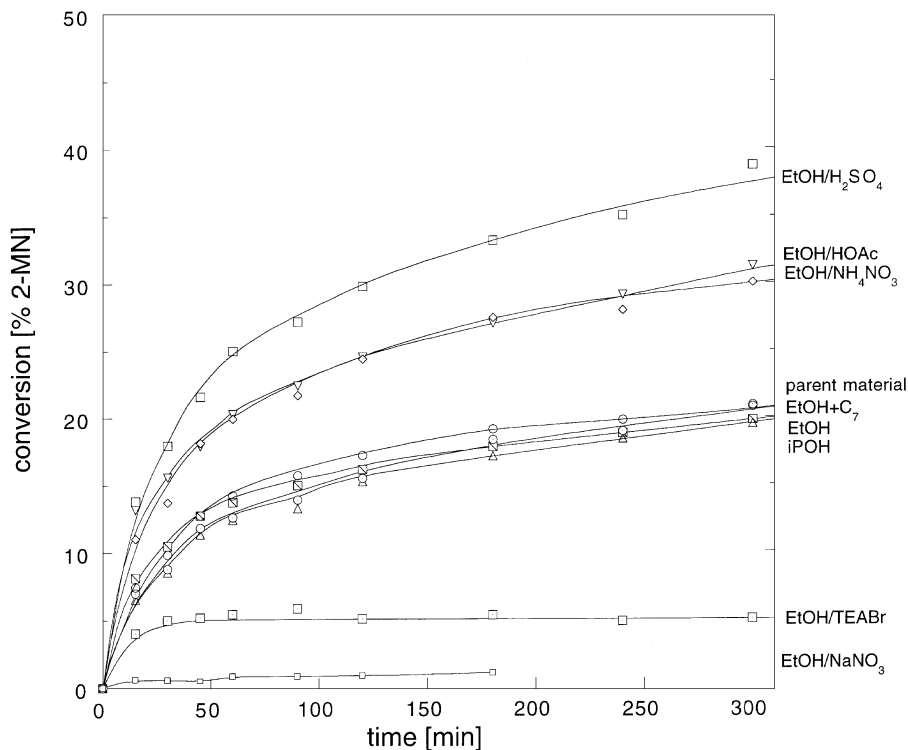


FIG. 10. Conversion of 2-methoxynaphthalene over extracted and calcined MCM-41 catalysts.

EtOH/NH₄NO₃ catalyst. This proves that the acid extracted and calcined catalysts are as active as the conventional calcined and ion-exchanged materials.

Turnover numbers for all catalysts are given in Table 5. The number of active sites was calculated from the catalyst mass and the Si/Al and Na/Al ratios, assuming that all aluminium atoms are active and that one sodium ion deactivates one site. The turnover number depends mainly on the sodium content of the catalyst which implies that a sodium ion seems to deactivate more than one active site, similar as in zeolites (43). The higher activity of the EtOH/H₂SO₄ sample can be explained by its higher Si/Al ratio and therefore stronger acid sites. This is proved by the higher activity of the sample with a Si/Al ratio of 40. Also a higher temperature causes a higher activity but lowers the selectivity toward the 1-acetylated product favoring migration of the acetyl group. Zeolite β is slightly more active than most of our MCM-41 catalysts. The shape selectivity of a narrow 12-ring zeolite causes a 1-Ac-2-MN/6-Ac-2-MN ratio of about 5 with an increase of 6-Ac-2-MN with time (40). No similar effect was observed for MCM-41. Even though the active sites of zeolite β are stronger than in MCM-41 the reaction rates are comparable. Diffusion rates are faster in the large pores of MCM-41 and seem to compensate its lower acidity. Furthermore, a stronger acidic catalyst deactivates faster by coke formation. Coking on MCM-41 was less than 8% for all catalysts as determined by TG/DTA.

No activity was observed for the EtOH/NaNO₃ catalyst. This demonstrates that no Friedel-Crafts acylation of 2-MN takes place either when the active sites of a catalyst are blocked by sodium ions or if no MCM-41 catalyst is present (11) in the reaction mixture.

The commercial silica/alumina catalyst had a very low activity for the acetylation of 2-MN. The conversion was 3.5% after 20 h.

TABLE 5
Activity^a for the Acetylation of 2-Methoxynaphthalene

Catalyst	TON at 1 h (h ⁻¹)	TON at 3 h (h ⁻¹)
Parent material	17	8
EtOH/NH ₄ NO ₃	25	11
EtOH/HOAc	24	11
EtOH/H ₂ SO ₄	35	16
EtOH/TEABr	7	2
EtOH	17	8
EtOH/C ₇	18	9
iPOH	18	8
NH ₄ NO ₃	26	12
HOAc	26	11
<i>n</i> Bu ₂ NH ₂ Cl	29	12
H- β (40)	≈37	15
EtOH/NH ₄ NO ₃ at 140°C	49	19
Si/Al = 40	68	27

^a Estimated error of GC analysis, 5%.

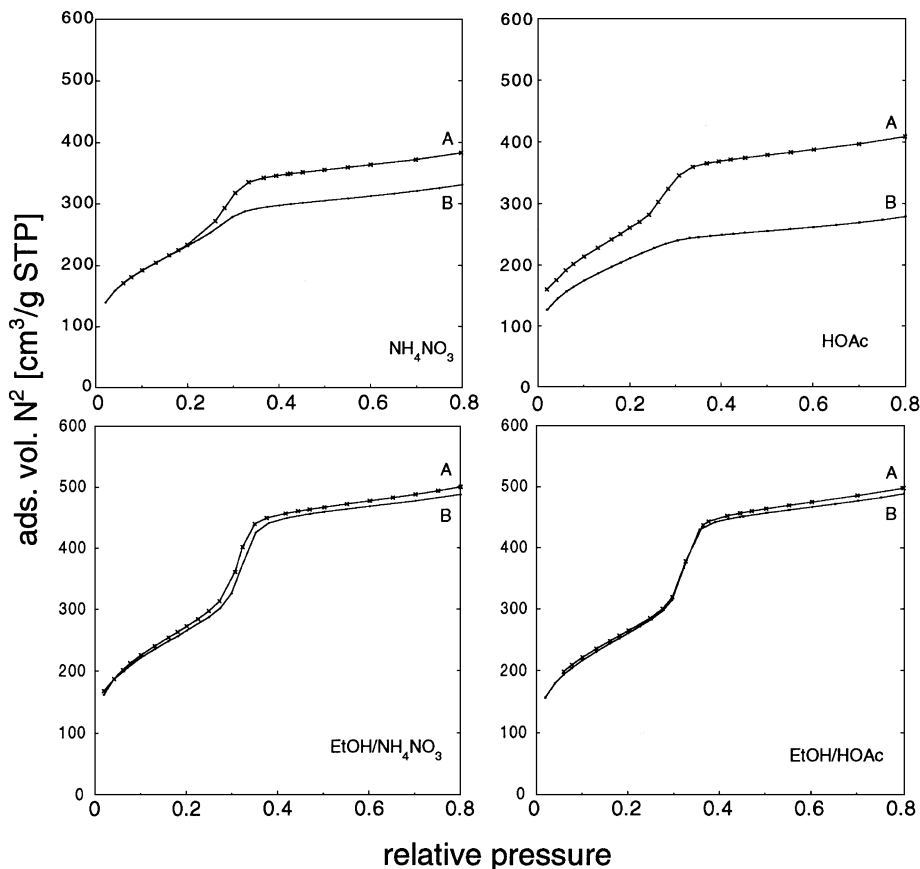


FIG. 11. Nitrogen adsorption isotherms of NH_4NO_3 , HOAc, EtOH/ NH_4NO_3 , and EtOH/HOAc (all calcined) before (A) and after reaction and repeated calcination (B).

All catalysts could be reactivated by calcination at 500°C . The activities of these recycled catalysts were comparable to the first runs ($\pm 2\%$).

Structure of Catalysts after Reaction

The structure of the reactivated catalysts was checked by nitrogen adsorption. Figure 11 demonstrates the striking difference between catalysts obtained by extraction in acidic medium and conventional catalysts obtained by direct calcination and ion exchange. The EtOH/ NH_4NO_3 and EtOH/HOAc samples (see Fig. 11) could be reactivated by calcination at 500°C without any loss in ordered mesoporous structure. The same stabilization effect was also observed for the solvent-only extracted samples but not for the parent material. The treatment in solvents removes water from the parent material, thereby stabilizing it toward thermal treatments by reducing the steaming effect during calcination. The conventional samples which had been calcined directly and ion-exchanged NH_4NO_3 and HOAc (Fig. 11) lost most of their ordered pore structure and the BET surface area decreased to three-quarters of its initial value. However, catalytic conversion of small molecules as used in our test reaction was not affected by the collapse

in mesoporous structure. This can be explained by the fact that substituted naphthalenes are much smaller than the collapsed mesopores. We expect, however, a decrease in activity if either larger molecules were converted or further calcination steps would be applied.

The improved stability of acid-extracted samples can be explained by the precondensation of silanol groups in the acidic medium. These stable siloxane bonds are not opened again. The thermally condensed SiOH groups of the HOAc sample (see ^{29}Si -NMR) are rehydrated during ion exchange and condense again when the catalyst is activated before the reaction. During the reaction they can be reopened by traces of water or acetic acid in the reaction mixture. The following third calcination cycle causes another deterioration step to the porous structure.

CONCLUSIONS

Large amounts of template can be removed from MCM-41 by extraction with solutions of acids or salt in ethanol. Extraction with alkali metal salts in ethanol yields thermally unstable materials. On the contrary, an extraction in acidic ethanol solution produces a thermally more stable material. At the same time, residual amounts of sodium

ions are removed. The removal of template ions from siloxy groups is followed by a precondensation of the silanol group. This precondensation stabilizes the lattice before the calcination. Furthermore, the Brønsted acid sites do not dehydrate to form Lewis sites if a large amount of silanol groups had been removed previously. Part of these Lewis sites and other-flexible aluminium sites partially connected to the framework are detected as octahedral aluminium in rehydrated ^{27}Al spectra because they fill their coordination sphere with water. In contrast to most zeolite structures (with the exception of zeolite β) the flexibility of the MCM-41 structure allows these changes without noticeable structural collapse. The activity of MCM-41 catalysts for 2-methoxynaphthalene acylation compares well with that of zeolite β .

The extraction in acidic medium provides a straightforward template removal and ion-exchange procedure. The one-step extraction is to be preferred over the conventional ion exchange because it is simpler, it produces an equally active catalyst, and this catalyst, can be recycled without loss in pore structure and catalytic activity.

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