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Aluminum incorporation in MCM-41 mesoporous molecular sieves

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Abstract

Twelve MCM-41 samples with a Si/Al ratio varying from 12 to 200 were prepared by using sodium aluminate in a tetramethylammonium hydroxide solution as aluminum source and an unexchanged CTMAcI template solution. The thermogravimetric analysis (TGA) weight losses caused by thermal removal of the template cations, which are associated with the siloxy groups on the one hand and the aluminum sites on the other hand, correspond with these different Al contents. X-Ray diffraction (XRD) revealed that at Si/Al=5, in addition to MCM-41, a lamellar phase and a dense crystalline tridymite structure are formed. ^{27}Al Magic-angle spinning nuclear magnetic resonance (MAS NMR) indicates that upon calcination the tetrahedral aluminum sites are altered. Fourier transform infrared (FTIR) analysis of proton-exchanged MCM-41 with acetonitrile as probe molecule showed a very weak Brönsted and a rather strong Lewis acidity. The latter may be the result of the distortion of the aluminum sites by thermal treatment.

Keywords: MCM-41; Synthesis; Characterization; Acidity

1. Introduction

Aluminum incorporation in MCM-41 is essential for catalytic applications in hydrocarbon conversion such as cracking, alkylation and isomerization. Currently, these processes are carried out with catalysts based on zeolites. However, large molecules of non-distillable feeds cannot enter the micropores. Because of its hexagonal array of uniform one-dimensional mesopores, varying in size from 20 to 100 Å, MCM-41 is a potentially interesting catalyst for converting these residues to fuels and other products.

Unfortunately, the amount of Brönsted acid

sites in MCM-41 is lower than in USY zeolite as was shown by Corma et al. [1]. They used Catapal as aluminum source in the preparation of their samples. In this study we investigated the acid properties of MCM-41 synthesized with sodium aluminate, since this Al source can be better incorporated in the framework (checked with ^{27}Al MAS NMR) [2].

Instead of the often used pyridine, deuterated acetonitrile served as probe molecule in the FTIR analysis. Acetonitrile is a weak base, so no protons are abstracted and real hydroxyl groups can be observed. CD_3CN is more appropriate for these studies than CH_3CN , because the spectrum of the latter probe is complicated by resonances between CN, CC and CH_3 frequencies. The spectra are compared with those of zeolite Y.

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By TGA Beck et al. [3] and Schmidt et al. [4] observed that the alkyltrimethylammonium template cation is removed from the framework in two steps: the cations connected to the siloxy groups and the aluminum sites are decomposed at 250°C and 400°C, respectively. Under inert atmosphere this two-stage decomposition can be attributed to a base-catalyzed Hoffmann elimination and subsequent pyrolysis. In order to verify whether the ratio of these two weight losses is proportional to the Si/Al ratio or not, we prepared MCM-41 samples with a Si/Al ratio varying from 5 to 200 and studied their behaviour during thermal treatment. A deviation from this correlation forms additional evidence for the existence of extra-framework aluminum.

2. Experimental

2.1. Materials

Two different silica sources were used: sodium silicate, 27 wt.-% silica, 8 wt.-% Na₂O, Merck; Ludox HS-40 colloidal silica, 40 wt.-%, Du Pont. The hexadecyltrimethylammonium surfactants were obtained from Aldrich (25 wt.-% C₁₆H₃₃(CH₃)₃NCl solution) and Janssen Chimica (as a solid bromide salt). Sources of aluminum were: sodium aluminate, Strem Chemicals; aluminum sulfate (Al₂(SO₄)₃·18H₂O), Merck. Sulfuric acid (95–97 wt.-%, Merck) and tetramethylammonium hydroxide (TMAOH, 40 wt.-%, Fluka) served to dissolve aluminum sulfate and sodium aluminate, respectively.

2.2. Synthesis

The MCM-41 samples were prepared in the following way: varying amounts of sodium aluminate, up to a maximum of 2.1 g (bulk Si/Al=12), were dissolved in 22.8 g of TMAOH solution by heating to 50°C. This was combined with 45.75 g of Ludox under stirring and diluted with 14 g of water. Finally 97.30 g of a 25 wt.-% hexadecyltrimethylammonium chloride solution were added. Because the solubility of NaAlO₂ in TMAOH is about 10 wt.-%, another procedure was used to

lower the Si/Al ratio to 5. An aluminum sulfate solution was prepared by dissolving 6.2 g of Al₂(SO₄)₃·18H₂O and 1.2 g of sulfuric acid in 40 g of water. Then, this solution was mixed with 20.0 g of sodium silicate and 20 g of water. After 30 min the template solution, containing 15 g of hexadecyltrimethylammonium bromide in 45 g of water, was introduced. Precipitation of all mixtures took place in a static PTFE-coated autoclave at 110°C for seven days. After cooling to room temperature, the product was recovered by centrifugation. The template was removed by calcining 1 h in nitrogen and 6 h in air at a temperature of 540°C.

The calcined aluminosilicate MCM-41 samples were ion-exchanged with an excess of 1 M NH₄NO₃ solution at room temperature (at a liquid-to-solid ratio of 250 ml/g) to form NH₄-MCM-41 samples. The H-form of MCM-41 was obtained by heating the NH₄-MCM-41 samples at 650°C under a flow of helium.

2.3. Instrumentation

X-Ray powder diffraction data of the MCM-41 molecular sieves were collected on a Philips PW 7200 X-ray powder diffractometer using FeK α radiation. The XRD pattern was obtained between 2 θ =2° and 2 θ =45° with a scan speed of 1°/min. The samples were thermogravimetrically analysed on an electronic Cahn 2000 balance in helium at a heating rate of 1°C/min.

Solid-state ²⁷Al MAS NMR experiments were performed at room temperature on a Bruker MSL 400 NMR spectrometer with a magnetic field of 9.4 T. The spinning rate was 10 kHz and 4000 free induction decays were accumulated by using 30° pulses (0.6 μ s) with a repetition time of 1 s. The calcined sample for the NMR experiment was degassed on a vacuum line at 723 K for 2 h in high vacuum (10⁻⁵ mbar) and cooled to room temperature.

IR spectra were measured on a Bruker FTIR spectrometer (IFS 113 v) equipped with a vacuum cell. Self-supporting discs with a thickness of 8 mg cm⁻² were used. The spectra were recorded by co-adding 500 scans at room temperature with a resolution of 1 cm⁻¹. Activation of the samples was performed at 720 K in high vacuum for 1 h. After cooling down to room temperature, the

spectrum of the unloaded sample was taken, followed by contacting the sample with deuterated acetonitrile for 30 min at a pressure of 1.14 mbar. Then another spectrum was recorded. After this, the loading of the samples was reduced stepwise by lowering the equilibrium pressure to 0.05 mbar and desorption at 295, 353 and 573 K. Under these three conditions spectra were collected again.

3. Results and discussion

The calcined samples with a Si/Al ratio of 12 and higher showed the characteristic MCM-41 XRD pattern with peaks corresponding to d -spacings of 40, 23, 20 and 15 Å [3]. However, in case of the as-synthesized material with Si/Al=5 additional peaks appeared (Fig. 1). The peaks M1 and M2 belong to the above-mentioned MCM-41 reflections. L1, L2, L3 and L4 can be assigned to a lamellar structure with a d -spacing of 25.7 Å (Table 1). The space between the layers must be filled with template, since the structure is completely destroyed upon calcination. Disappearance of the peaks M1 and M2 after this treatment indicates that the hexagonal and layered structure

Table 1
Peaks and corresponding d -spacings of as-synthesized MCM-41 with Si/Al=5

Peak	d -spacing (Å)	Index
M1	40.93	1 0 0
M2	21.88	1 1 0
L1	25.74	1 0 0
L2	12.94	2 0 0
L3	8.64	3 0 0
L4	6.49	4 0 0
T1	4.53	0 0 18
T2	4.27	2 0 2
T3	4.00	1 0 18
T4	3.88	1 0 19
T5	3.80	2 0 10

are connected. We are sure that this is not the lamellar material which is formed at surfactant/silicate ratios higher than 1.5 described by Stucky and co-workers [5–7]. The layers of that structure have a d -spacing between 38 and 39 Å and their reflections have never been recognized in combination with MCM-41 in one XRD pattern but only in transmission electron microscopy (TEM) photographs. A third structure, with diffraction angles indicated as T1–T5, can be iden-

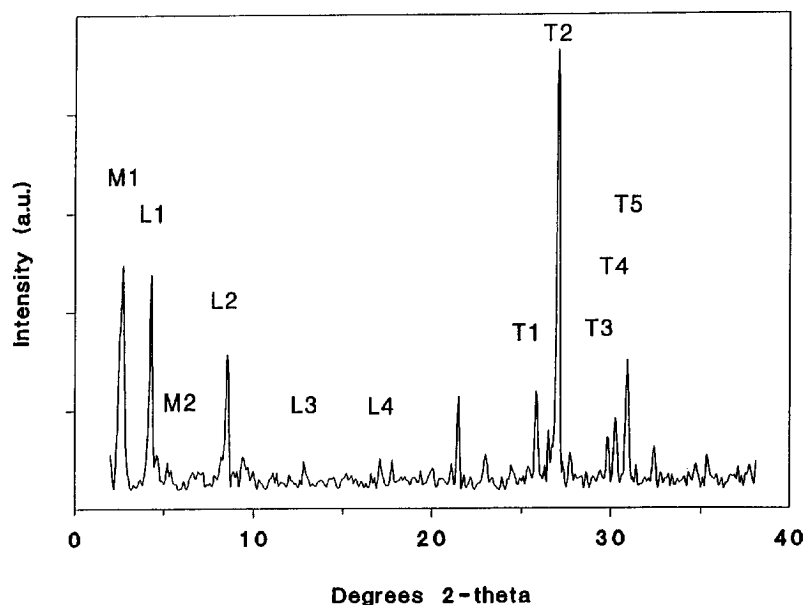


Fig. 1. Powder X-ray diffraction pattern of as-synthesized MCM-41 with Si/Al=5.

tified as a dense tridymite-like material. The large amount of aluminum sulfate must be the cause of the formation of these two by-products, since a perfect MCM-41 can be synthesized from an analogous all-silica mixture.

Samples with bulk Si/Al ratios of 12, 15, 18, 21, 25, 31, 36, 40, 63, 100 and 200 were thermogravimetrically analysed. Atomic absorption

measurements confirmed that the Si/Al ratios in the samples are practically equal to those in the synthesis gels. In order to be certain that the weight loss between 125°C and 450°C can be ascribed completely to the removal of template, the elemental composition was determined. The amounts of nitrogen, hydrogen and carbon for two samples are given in Table 2. There is only a

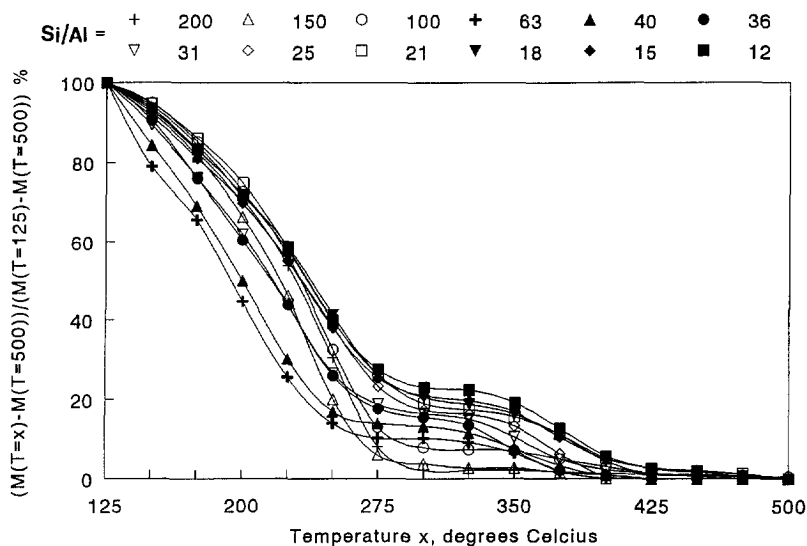


Fig. 2. Thermogravimetric analysis of as-synthesized MCM-41 samples with different Si/Al ratios in helium. Heating rate: 1°C/min.

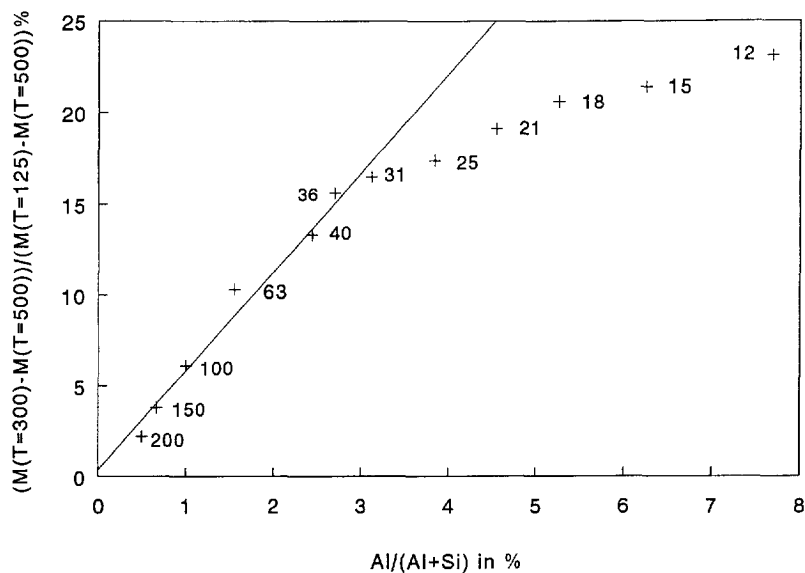


Fig. 3. High-temperature weight loss as a function of the aluminum weight percentage in the samples.

Table 2
Elemental analysis of two as-synthesized MCM-41 samples

Si/Al	H (wt.-%)	C (wt.-%)	N (wt.-%)	Total organic content (wt.-%)	Weight loss 125–150°C (wt.-%)
100	8.79	43.83	2.75	55.37	56.24
40	7.75	37.86	2.40	48.01	49.20

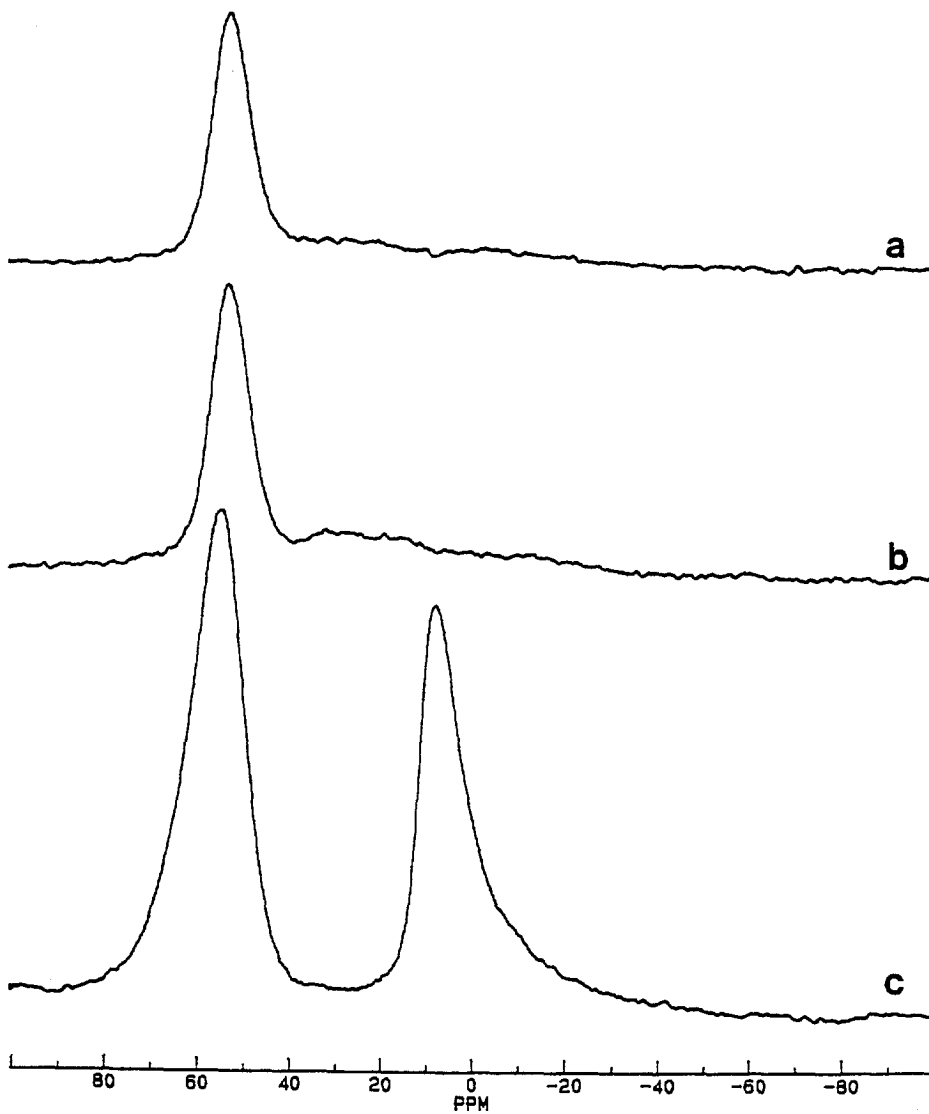


Fig. 4. ^{27}Al MAS NMR spectra of as-synthesized MCM-41 samples with Si/Al-ratios of 40 (a), 25 (b) and 5 (c).

small difference between the sum of these three weight percentages and the TGA weight loss above 125°C. This justifies the assumption that the water is removed below that temperature. The total decrease in weight in the temperature interval 125–450°C is adjusted to 100% and the resulting TGA curves are shown in Fig. 2. For all twelve samples there is a clear distinction at about 300°C between high- and low-temperature template removal. When the aluminum content increases, a larger part of the template is removed at high temperature. In Fig. 3 the high-temperature weight loss is plotted versus the weight percentage of aluminum in the sample. Impurities in the silica sources made it impossible to obtain a Si/Al ratio higher than 200. The first six data points can be correlated by a linear regression curve (with a correlation coefficient of 0.99). Extrapolation to all-silica MCM-41 provides a nearly negligible high-temperature weight loss. This is in agreement with the explanation of Beck et al. [3] that template cations bonded to siloxy groups decompose at low temperature and those associated with aluminum sites at high temperature. However, if there are more than 3 wt.-% of aluminum in the sample, a deviation from linearity occurs. This can be

explained by the existence of extra-framework aluminum which is not associated with template cations and causes the convex shape of the curve.

Fig. 4 shows the ^{27}Al MAS NMR spectra of the samples with Si/Al=5, 25 and 40 in the as-synthesized state. At a Si/Al ratio of 40 a peak with a chemical shift of 52.7 ppm is observed, which is characteristic for tetrahedral aluminum. When the aluminum content increases to Si/Al=25, the appearance of a peak at about 20 ppm points out that some extra-framework aluminum is formed. This is in agreement with the results of the TGA experiments. In case of a Si/Al ratio of 5, about 40% of the total amount of aluminum in the sample is extra-framework and the position of this peak is characteristic for an octahedral coordination. However, care should be taken when applying the intensity of ^{27}Al MAS NMR signals for quantitative use because of quadrupole moment and quadrupole coupling constant influences. Schmidt et al. [8] managed to reach a Si/Al ratio of 9 without octahedrally coordinated aluminum which is the lower limit up till now. After calcination, the peak of tetrahedral aluminum is shifted to 37 ppm, probably caused by the distortion of the aluminum site in the MCM-41 framework

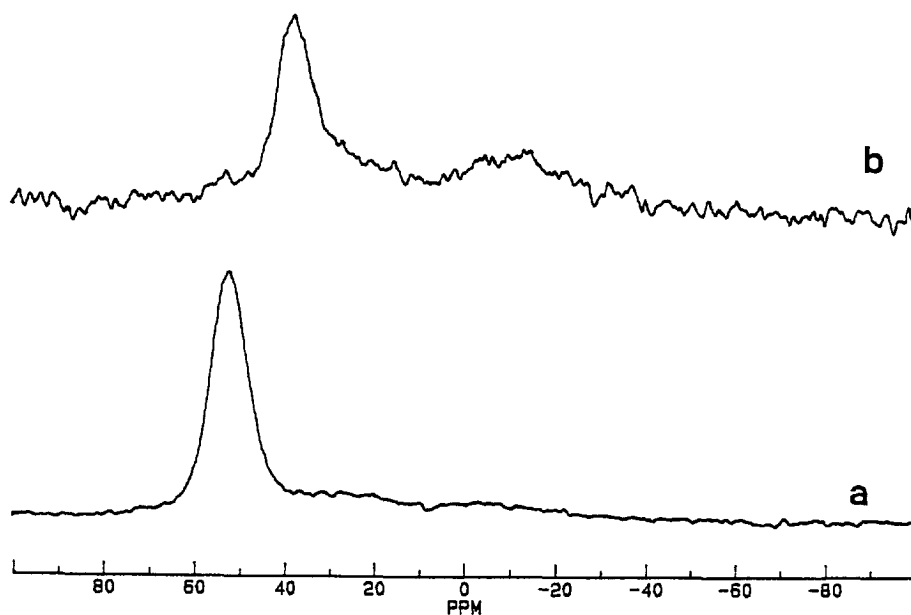
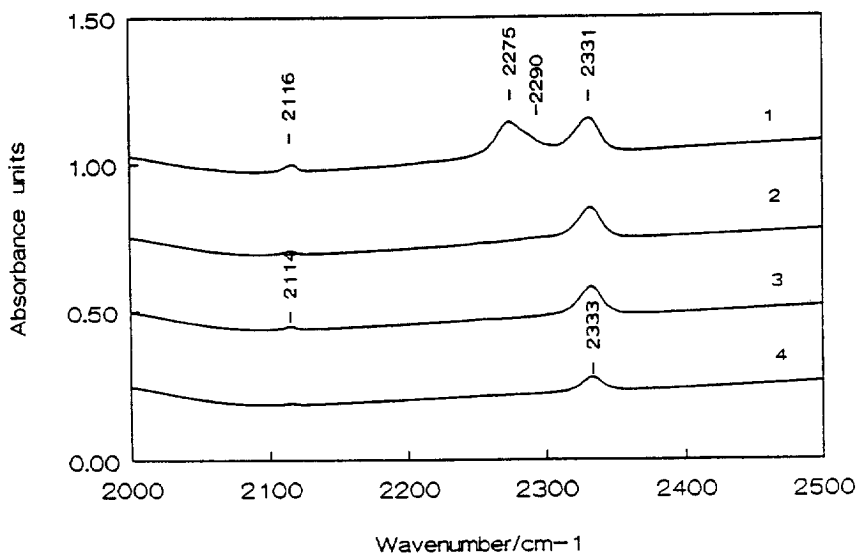
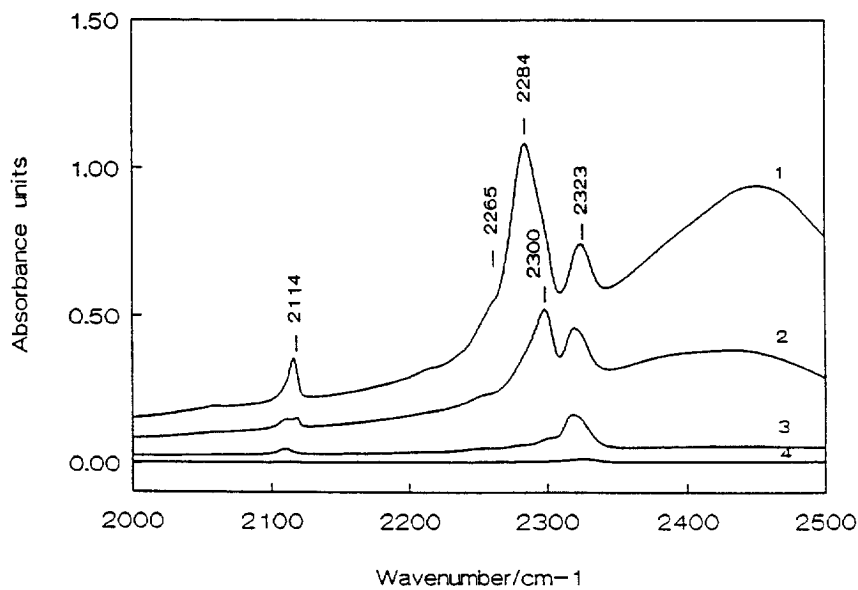


Fig. 5. ^{27}Al MAS NMR spectra of a MCM-41 sample with Si/Al=40 before (a) and after (b) calcination.



A



B

Fig. 6. FTIR spectrum of activated HMCM-41 (A) and HY (B) induced by CD_3CN adsorption: (1) at 295 K and 1.14 mbar; after outgassing at 295 K for 15 min (2); at 353 K for 15 min (3); at 573 K for 1 h (4).

(Fig. 5). In addition, a broad peak, which can again be assigned to extra-framework aluminum, appeared at -15 ppm.

The FTIR spectra, obtained with deuterated acetonitrile as a probe molecule, are shown in

Fig. 6. Adsorption of CD_3CN results in the appearance of two bands in the CN frequency region at 2275 and 2331 cm^{-1} for the HMCM-41 sample with $\text{Si}/\text{Al}=40$. The first one can be attributed to the adsorption on the terminal SiOH and disap-

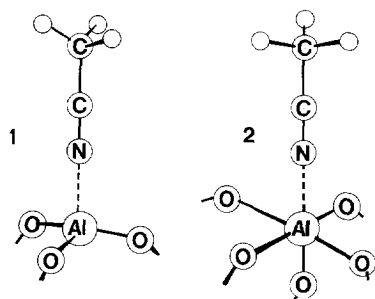


Fig. 7. Molecular models of the Lewis sites in HMCM-41 (1) and HY (2).

peared after desorption because of the low acidity of this group [9]. The peak is somewhat asymmetrical on the right-hand side due to a shoulder at 2290 cm^{-1} which can be ascribed to the Brönsted acid sites. This is supported by a small peak at 3080 cm^{-1} . However, the major part of the aluminum atoms is involved in Lewis sites. There are two possible positions for Lewis sites (Fig. 7): an aluminum atom bonded to three silicon atoms created by dehydration of a Brönsted site or one that has a five-fold coordination and originally had an extra-framework position. The CN frequencies of the acetonitrile bonded to these sites are 2332 and 2323 cm^{-1} , respectively. In our HMCM-41 sample the aluminum sites are of the former type as is indicated by the 2331 cm^{-1} band. The shift from 52.7 to 37 ppm in the ^{27}Al MAS NMR spectrum shows that these sites are formed during thermal treatment. The purpose of pyrolysis of the template during 1 h in nitrogen is to prevent dealumination (combustion in air causes formation of water that can extract aluminum from the framework). This is successful, since after calcination only a small extra-framework aluminum peak appears. However, this calcination procedure is not mild enough to maintain the Brönsted acid sites. Perhaps extraction of the template with organic solvents is a solution to this problem. [4]

For comparison the spectrum of dealuminated HY zeolite with $\text{Si}/\text{Al}=5$ is given in Fig. 6B. The 2300 cm^{-1} band shows that there are far more Brönsted sites than in HMCM-41, but the intensity of the band corresponding to the Lewis sites is almost equal. This does not mean that the amounts are equal too, since the Lewis sites in HY are of

type 2 (2323 cm^{-1}) in Fig. 7 and possibly have an extinction coefficient different from those of type 1.

4. Conclusion

It is possible to incorporate aluminum in the MCM-41 framework up to 3 wt.-% using sodium aluminate as Al source. At higher concentrations part of the aluminum remains outside the framework in an octahedral position. Two additional structures were formed when the Si/Al ratio was lowered to 5: a lamellar phase with a d -spacing of 25.7 \AA and a tridymite structure. Thermal treatment in inert atmosphere causes decomposition of the template in two stages, catalyzed by siloxy groups and tetrahedral aluminum sites. Under these conditions no dealumination takes place. However, a distortion of the tetrahedral (and potential Brönsted acid) aluminum sites cannot be prevented and finally Lewis sites are formed. This means that, in order to prepare a catalyst with Brönsted sites, a milder operation must be chosen to remove the template.

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