Catalysis Letters 33 (1995) 157–163

MCM-41 type materials with low Si/Al ratios

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Received 26 September 1994; accepted 19 April 1995

The synthesis of MCM-41 type materials with high amounts of tetrahedral aluminum is reported. Transmission electron microscopy with EDX elemental analysis shows that when using a tetraalkylammonium base in the synthesis of MCM-41 materials Si/Al ratios as low as 12 are possible. In all cases the MCM-41 materials contain an aluminum-rich dense phase in which the aluminum is also tetrahedrally coordinated. This dense phase consumes most of the aluminum of the synthesis mixture.

Keywords: MCM-41; dense phase; tetrahedral aluminum; crystallinity

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 Brønsted and Lewis acidity of these materials.

The synthesis of MCM-41 materials with high levels of tetrahedral aluminum was recently reported [4,5]. 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. We report here the synthesis of MCM-41 type materials with high amounts of tetrahedrally coordinated aluminum. Transmission electron microscopy shows that beside MCM-41 an aluminum-rich dense phase exists, which accounts for the high amounts of bulk tetrahedral aluminum in the synthesized material.

2. Experimental

2.1. 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 Haen, 54% Al_2O_3, 41% Na_2O) varying between 3.22 and 1.90 g, and 119.5 g of $C_{16}H_{33}(CH_3)_3NCl$ (Aldrich, 25 wt% in water) were stirred for 1 h. A proper amount of sodium hydroxide (Baker, 98.5%) varying between 1.15 and 1.37 g such that $2 < Na_2O/Al_2O_3 < 3$, 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 Chimica). 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/min from room temperature to 540°C.

2.2. TECHNIQUES

2.2.1. X-ray diffraction

The calcined samples were characterized by X-ray powder diffraction on a Philips PW 1840 diffractometer using monochromated Cu Kα 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.

2.2.2. ^{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).

2.2.3. 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 in vacuum at 350°C prior to use.

2.2.4. 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 micro-grid carbon polymer was loaded with a few droplets of this suspension.

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_2O/Al_2O_3 ratio of the gel should be kept between 3 and 2 going from Si/Al = 10 down to 6. The lowest Si/Al ratio of calcined grey-coloured MCM-41 products synthesized, determined by elemental analysis, containing a high level of tetrahedrally coordinated aluminum, was 5. In the case of MCM-41 with even lower Si/Al ratios (down to 3) a slight increase in the amounts of amorphous material was determined. 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. [6]. These workers found that the incorporation of tetrahedral aluminum requires charge balancing cations, like sodium ions beside the cationic head groups of the surfactant, which can contribute in compensating the additional anionic charge introduced by the aluminum.

The calcined MCM-41 materials show XRD patterns (fig. 1) with broad not well-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 [10]. The relatively poor crystallinity of all the samples is probably a result of distortion of the mesophase before forming of the MCM-41 structure.

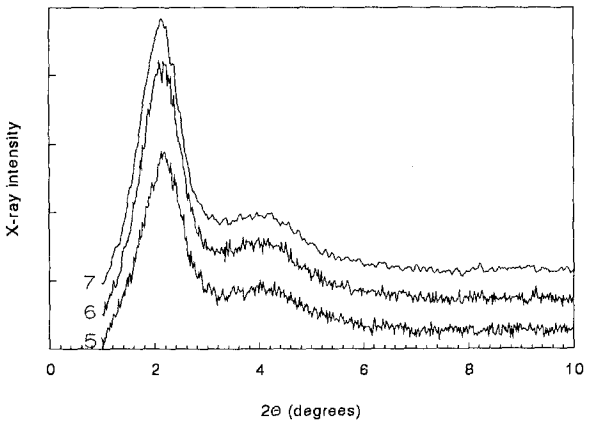

Fig. 1. Powder X-ray diffraction spectra of calcined MCM-41 samples 5, 6 and 7.

TEM examination of the calcined specimens shows that beside MCM-41 a dense phase is present (fig. 2). Sometimes a mixed phase appears in which MCM-41 is mixed up with an aluminum-rich dense phase. Most of the MCM-41 material in each specimen has a chaotic morphology. The fraction of crystalline hexagonal MCM-41 was smaller than 10% of the MCM-41 fraction for all studied samples. The chaotic morphology can be explained by spaghetti-like arrangements of the tubes resulting in a spongy material. Table 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 at% (Si/Al = 30). A more aluminum-rich MCM-41 could be provided when the tetraalkylammonium bases were used in the synthesis mixture (~5–8 at% or Si/Al = 20–12). The dense phase contains a much higher amount of aluminum (~15–20 at% or Si/Al = 6–5). It can be suggested that this aluminum-rich matter is responsible for the low overall Si/Al ratios of the bulk material measured by elemental analysis and thus consumes most of the aluminum. Also MCM-41 sample 8 prepared according to a literature procedure [6] contained parts of this aluminum-rich dense phase (table 1).

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 [4–6,8,9]. Fig. 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 [8], which is in the case of

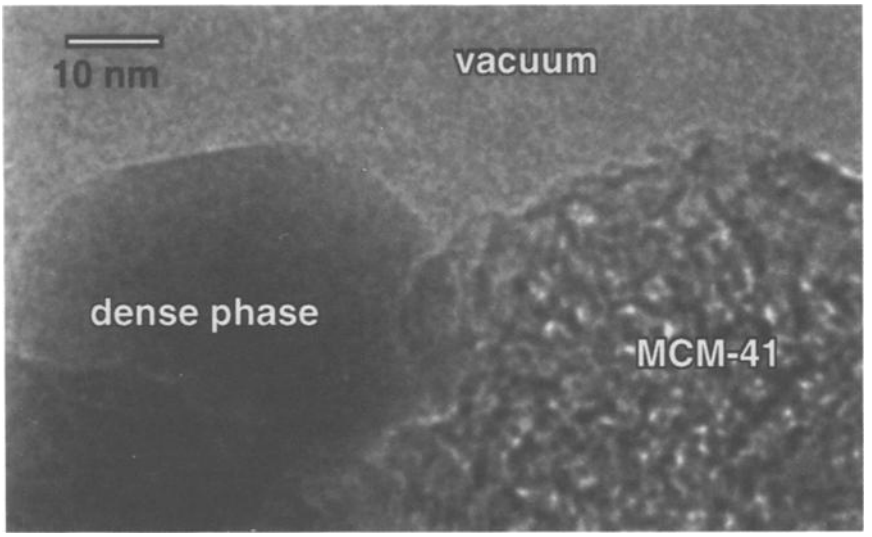

Fig. 2. TEM micrograph of a representative calcined MCM-41 sample showing two different phases, namely: the aluminum-rich dense phase and the chaotic phase of MCM-41.

Table 1
Aluminosilicate MCM-41 samples with low Si/Al ratios

Sample	Si/Al gel	Aluminum content [a] (at%)	d_{100} spacing calcined (Å)
1	7.5	0–3	43
2	7.5	1–3	46
3	7.5 [b]	5–6	45
4	7.5 [c]	5–8	44
5	6.0	1–3	40
6	8.0	1–3	41
7	10.0	2–5	43
8	14 [d]	0–3	42

[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 ref. [6].

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 SiO_4 or AlO_4 tetrahedron) might also be responsible for the peak broadening [5,6,8,9]. 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 tetraalkylammonium 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. Our results confirm that sodium aluminate is very suitable as the aluminum precursor for synthesizing MCM-41 materials with a high tetrahedral aluminum con-

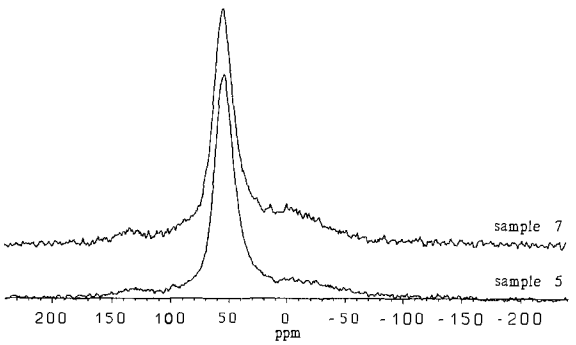

Fig. 3. ^{27}Al MAS NMR spectra of calcined MCM-41 samples 5 and 7.

tent, as was recently suggested by Chen et al. [9], but only for MCM-41 materials with Si/Al ratios down to 12.

Table 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 can be seen that the MCM-41 materials possess surface areas of $\sim 690\ m^2/g$ and mesopore volumes of $\sim 0.58\ cm^3/g$, characteristic for MCM-41 materials [10], although larger values (about 1200 and 0.79 cm^3/g, respectively) have been reported [1,4,5,9]. It should be noted that the pore volumes and surface areas of table 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 (table 2).

4. Conclusions

TEM examination shows that, when using sodium aluminate 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 specimens. In this dense phase the aluminum is also tetrahedrally coordinated. This aluminum-rich phase is not easily observed by X-ray, which indicates the importance of electron microscopy in this characterization.

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

Table 2
Nitrogen physisorption data of some MCM-41 samples

Sample	Pore diameter [a] (Å)	Mesopore volume [b] (cm^3/g)	BET area (m^2/g)
1	39	0.570	724
2	39	0.575	692
3	39	0.580	632
4	39	0.570	695
4 [c]	39	0.562	693
8 [d]	36	0.703	926

[a] Calculated with the corrected Kelvin equation for cylindrical pores of De Boer [11].
[b] Cumulative volume.
[c] Sample 4 calcined twice.
[d] Synthesized according to ref. [6].

Acknowledgement

We thank the Dutch School of Catalysis for financial support.

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