

Mesopore Molecular Sieve MCM-41 Containing Framework Aluminum

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A range of mesoporous aluminosilicate molecular sieves with the MCM-41 structure has been synthesized using different sources of aluminum and characterized in detail by powder X-ray diffraction (XRD), ^{29}Si and ^{27}Al magic-angle-spinning (MAS) NMR, and transmission electron microscopy (TEM). NMR clearly shows that, when Catapal alumina or sodium aluminate is used, virtually all Al in the solid is 6-coordinate. On the other hand, by using aluminum sulfate, MCM-41 can be easily prepared with all aluminum in 4-coordination and a framework Si/Al ratio as low as 10. Resolution of the XRD pattern of aluminosilicate MCM-41 rapidly deteriorates as the aluminum content of the solid increases, and TEM shows that the mesopore system is no longer strictly hexagonal. On the other hand, the resolution of the XRD patterns improves upon calcination of the samples at 550 °C for 24 h, indicating that heat treatment enhances the formation of the mesopores. The walls of the mesopores are essentially amorphous, and the local atomic arrangement is similar to that in amorphous aluminosilicates.

Introduction

Microporous (pore diameter $\leq 20 \text{ \AA}$) and mesoporous (20–100 Å) inorganic materials admit molecules below a certain critical size into their extensive internal space, which makes them of considerable interest as heterogeneous catalysts and sorbents.¹ Zeolites are by far the best known (and the most useful) family of crystalline microporous solids containing regular arrays of uniformly-sized channels.^{2,3} Considerable effort has recently been devoted to synthesizing mesoporous materials for chemical processing of large molecules,^{4–7} but so far none of them have found practical applications.

A new family of mesoporous molecular sieves with pore diameters in the 15–100 Å range, designated as M41S, has been synthesized by the Mobil scientists^{8,9} using liquid crystal templates. These materials allow faster diffusion of large organic molecules than the zeolithic and aluminum phosphate-based microporous sieves. Their high thermal and hydrothermal stability, the uniform size and shape of the pores over micrometer length scales, and the prospect of “tuning” the pore aperture by selecting a suitable template make these materials potentially useful as catalysts for fluidized catalytic cracking (FCC)^{10,11} and for the manufacture of fine chemicals.¹² MCM-41, a member of this family of solids, lacks strict crystallographic order on the atomic level, and its powder XRD patterns consist of a handful of peaks reflecting the quasi-regular arrangement of the mesopores.

The Brønsted acidity of aluminosilicate catalysts arises from the presence of accessible hydroxyl groups associated with 4-coordinate framework aluminum (“structural hydroxyls”) created by calcining their ammonium-exchanged forms. Purely siliceous materials have electrically neutral frameworks and consequently no Brønsted acidity. Much effort has therefore been devoted to the introduction of 4-coordinate Al into silicate frameworks. While some work has been published on MCM-41,^{13–16} we are not aware of any study of the chemical status of aluminum. We have found that in the material prepared using Catapal alumina as the source of aluminum (as described by

TABLE 1: Elemental Composition of the Gel Mixture and Samples of Aluminosilicate MCM-41

gel mixture products (by XRF)	10	20	30	40	60			
	10.4	21.5	34.1	43.0	71.0			
(c) from Cab – O – Sil + Catapal alumina	100	110	200	210				
(b) from Cab – O – Sil								
(a) from sodium silicate								
Intensity (arbitrary units)	100	110	200	210				
2 θ (degrees)	0.0	2.5	5.0	7.5	10.0	12.5	15.0	17.5

Figure 1. XRD patterns of purely siliceous MCM-41 prepared using (a) sodium silicate and (b) Cab-O-Sil M-5 as the source of silicon. (c) Aluminosilicate MCM-41 made with Catapal alumina as the source of aluminum.

the Mobil scientists) virtually all Al is 6-coordinate, report new routes for the synthesis of MCM-41 containing only 4-coordinate framework aluminum, and consider the effect of the introduction of Al on the structure.

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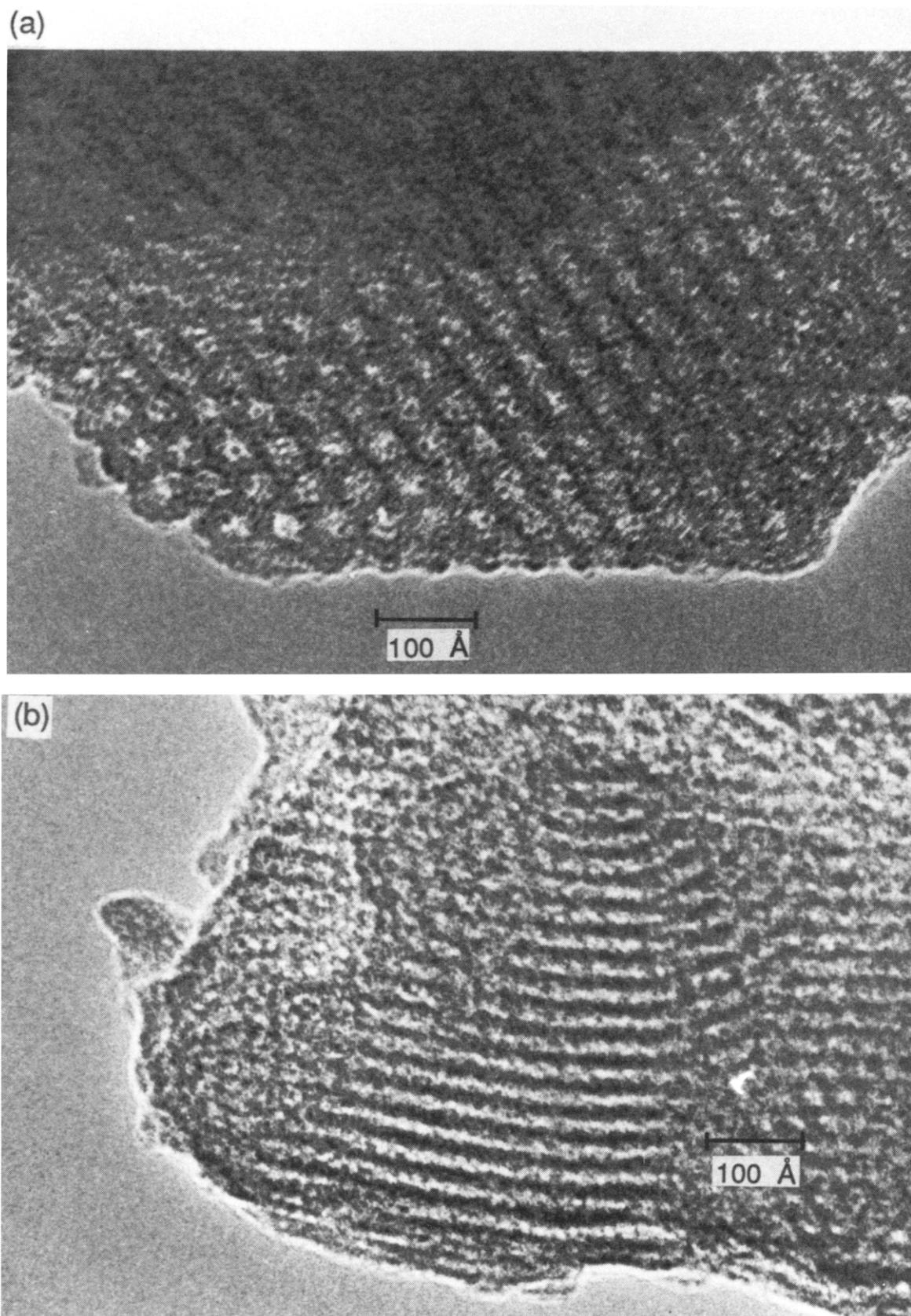


Figure 2. TEM micrographs of purely siliceous MCM-41 (a) in the direction of the pore axis and (b) in the direction perpendicular to the pore axis.

Experimental Section

Synthesis. The sources of silicon were Cab-O-Sil M-5 fused silica (BDH) and sodium silicate solution (30% silica, East Anglia Chemicals). A solution of cetyltrimethylammonium hydroxide was prepared by batch exchange of a 25 wt %

aqueous solution of $C_{16}H_{33}(CH_3)_3NCl$ using the IRA-420(OH) ion-exchange resin (both from Aldrich). The sources of aluminum were aluminum sulfate (Fluka-Garamtie), Catapal alumina (Vista), sodium aluminate (BDH) aluminum orthophosphate (Aldrich), aluminum acetylacetone (Aldrich), aluminum isopropylate (Aldrich), and aluminum hydroxide hydrate

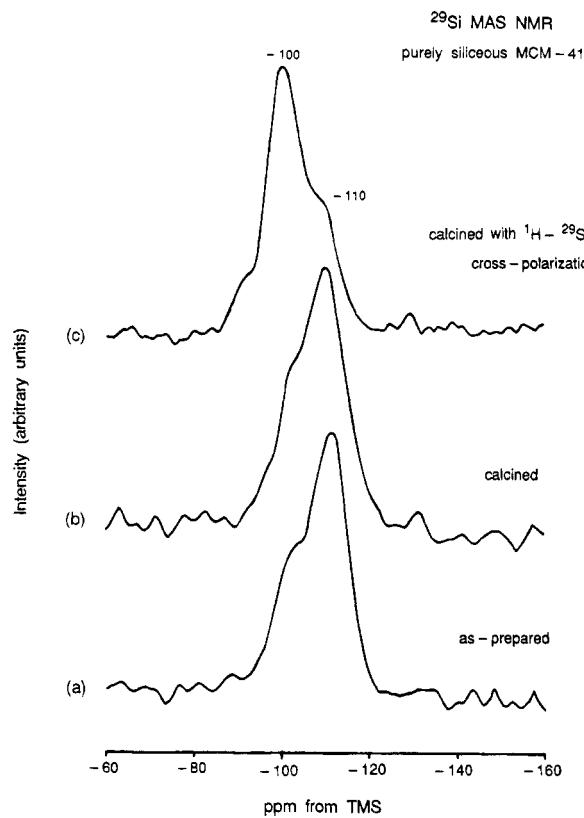


Figure 3. ^{29}Si MAS NMR spectra of purely siliceous MCM-41 prepared using sodium silicate as the source of silicon: (a) as-synthesized, (b) calcined, and (c) ^1H - ^{29}Si CP/MAS NMR spectra of the calcined sample.

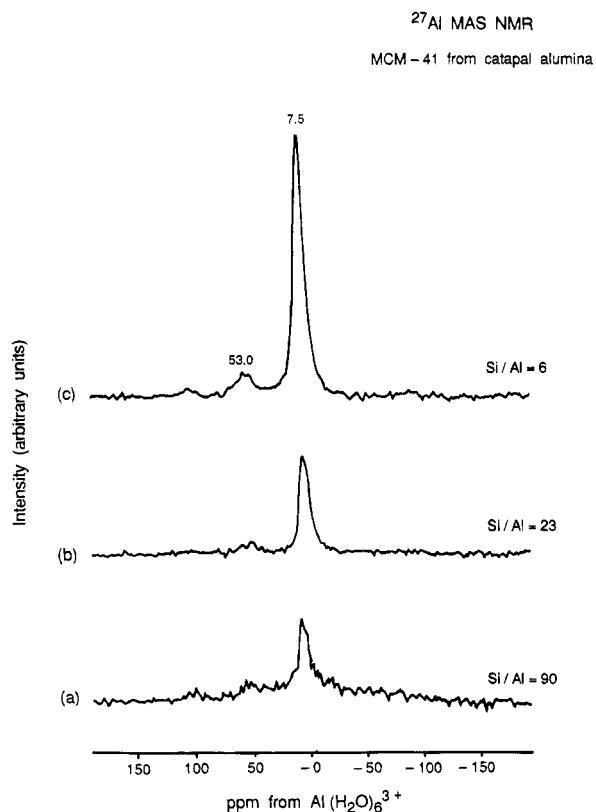


Figure 4. ^{27}Al MAS NMR spectra of aluminosilicate MCM-41 prepared using Catapal alumina. The bulk Si/Al ratio is (a) 90, (b) 23, and (c) 6.

(BDH). A 25% aqueous solution of tetramethylammonium hydroxide was obtained from Aldrich.

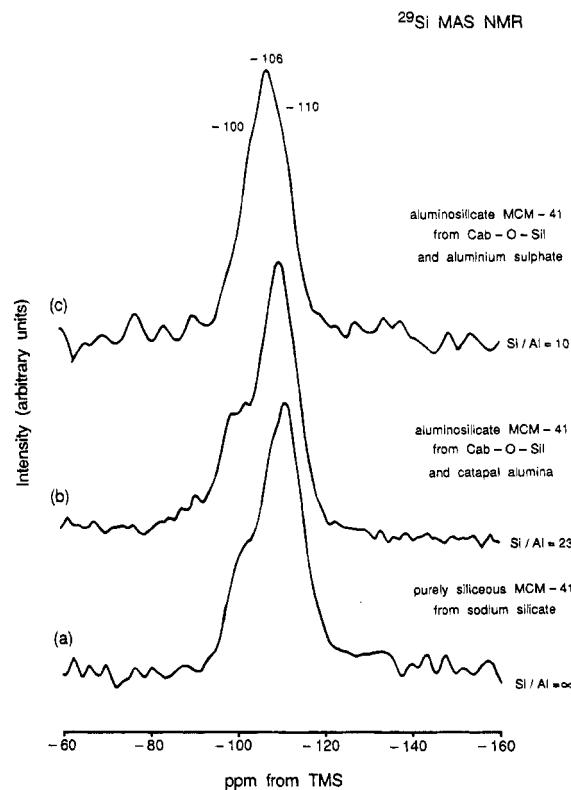


Figure 5. ^{29}Si MAS NMR spectra of (a) purely siliceous MCM-41, (b) aluminosilicate MCM-41 ($\text{Si}/\text{Al} = 23$) prepared using Catapal alumina, and (c) aluminosilicate MCM-41 ($\text{Si}/\text{Al} = 10$) prepared using aluminum sulfate.

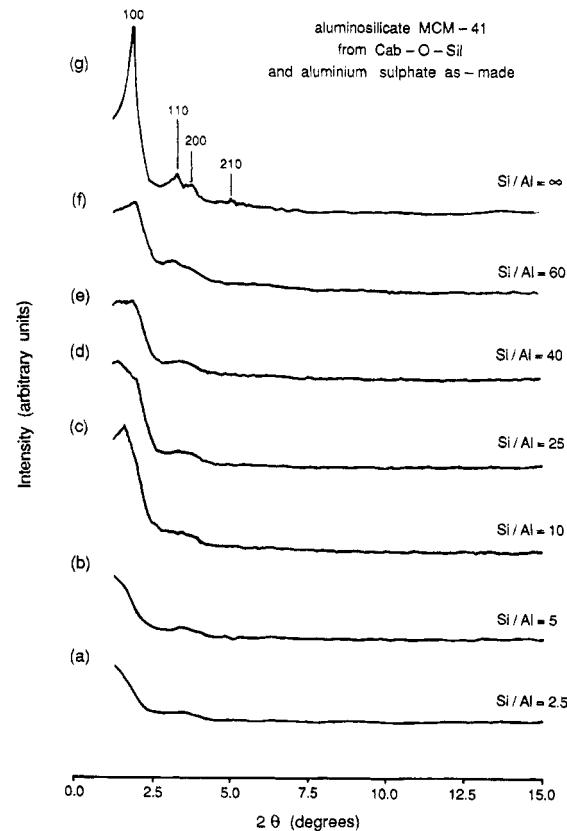


Figure 6. XRD patterns of as-synthesized aluminosilicate MCM-41 with bulk Si/Al ratios of (a) 2.5, (b) 5, (c) 10, (d) 25, (e) 40, and (f) 60 prepared with aluminum sulfate. (g) XRD pattern of purely siliceous MCM-41.

Aluminosilicate MCM-41 was prepared using Cab-O-Sil M-5 fused silica as the source of silicon. A typical synthesis

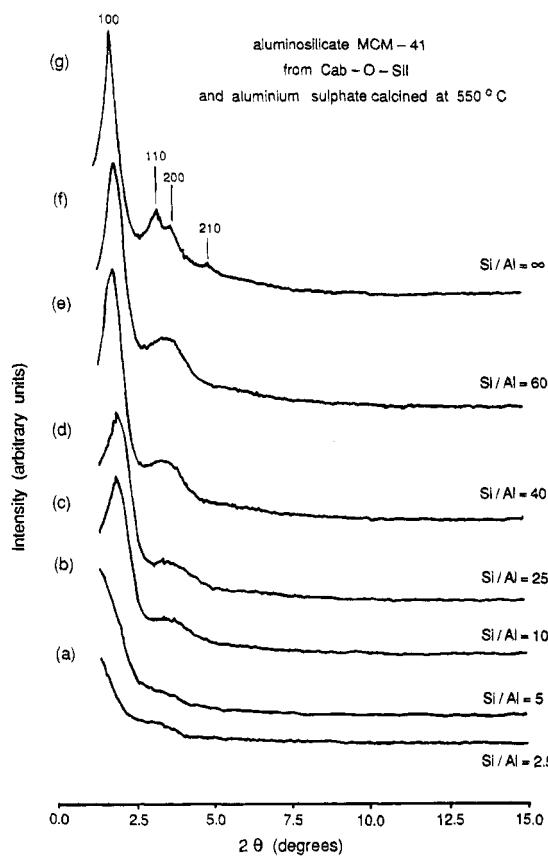


Figure 7. XRD patterns of calcined aluminosilicate MCM-41 with bulk Si/Al ratios of (a) 2.5, (b) 5, (c) 10, (d) 15, (e) 25, (f) 40, and (g) 60 prepared with aluminum sulfate. (g) XRD pattern of purely siliceous MCM-41.

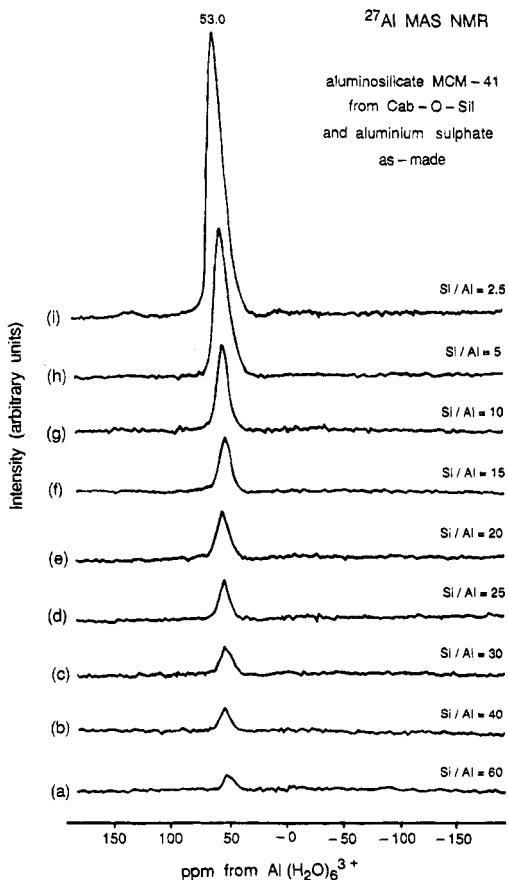


Figure 8. Absolute intensity scale ^{27}Al MAS NMR spectra of as-synthesized aluminosilicate MCM-41 prepared using aluminum sulfate. Bulk Si/Al ratios are (a) 60, (b) 40, (c) 30, (d) 25, (e) 20, (f) 15, (g) 10, (h) 5, and (i) 2.5.

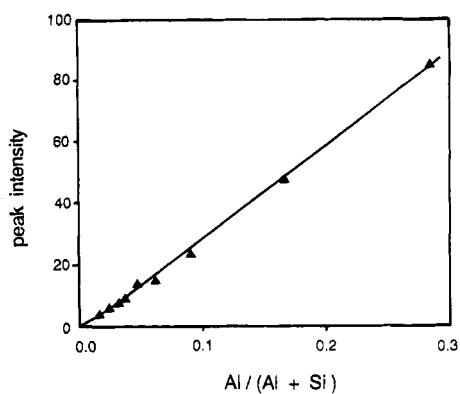


Figure 9. Spectral intensity of the ^{27}Al line at 53.0 ppm in Figure 8 versus the Al/(Al + Si) ratio.

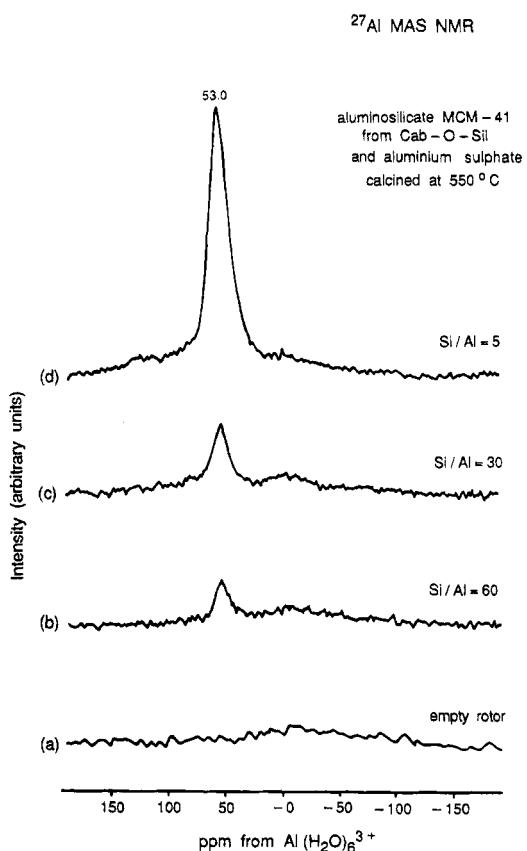


Figure 10. Absolute intensity scale ^{27}Al MAS NMR spectra. (a) Empty MAS rotor. Calcined aluminosilicate MCM-41 prepared using aluminum sulfate and with bulk Si/Al ratios of (b) 60, (c) 30, and (d) 5.

procedure was as follows.⁸ (1) A 10 g sample of solution of tetramethylammonium hydroxide (TMAOH) was combined with 5.9 g of sodium silicate dispersed in 50 g of water with stirring, and 34.2 g of $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NCl}/\text{OH}$ (CTACl/OH) solution and 4.52 g of silica were added and stirred for 2 h. (2) A required amount of the desired source of aluminum was dissolved or dispersed in water and then slowly added to the gel. (3) The pH was adjusted with dilute sulfuric acid to 11.5, and the mixture was transferred into a Teflon-lined autoclave and heated to 150 °C for 48 h. The molar composition of the final gel mixtures was SiO_2 :0.27CTACl/OH:0.13 Na₂O:0.26TMAOH:60H₂O:(0–0.5)Al₂O₃. (4) The solid product was centrifuged, filtered, washed with distilled water, dried in air at 100 °C and finally calcined at 550 °C for 24 h. Purely siliceous MCM-41 was made by mixing 9.3 g of sodium silicate with 20 g of water and 34 g of CTACl/OH solution with stirring. The pH of the

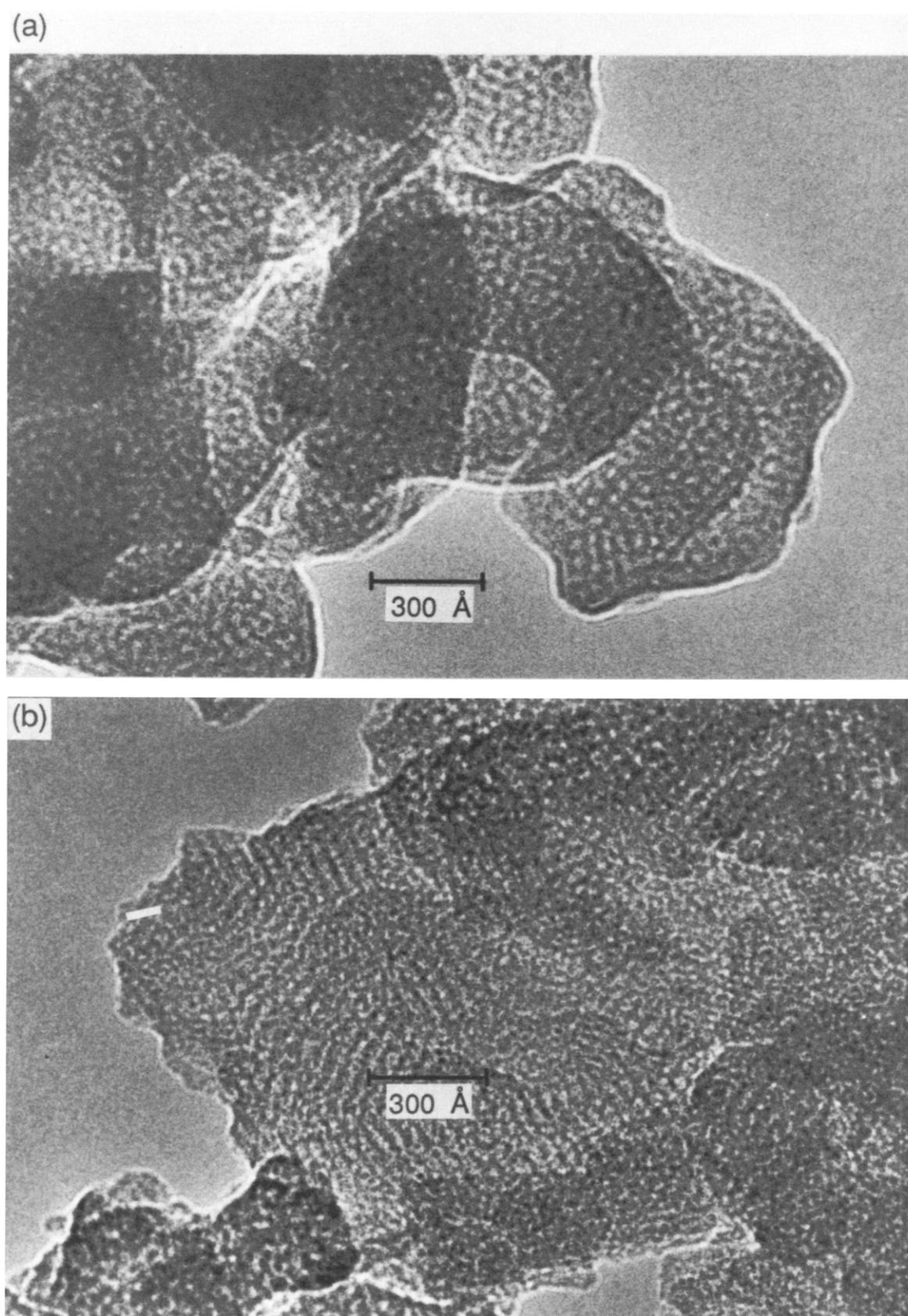


Figure 11. TEM photographs of aluminosilicate MCM-41 with Si/Al = 60 (a) in the direction of the pore axis and (b) in the direction perpendicular to the pore axis.

mixture was adjusted with sulfuric acid to 11.5. The gel was treated as described above.

Sample Characterization. Composition. Table 1 shows that the Si/Al molar ratios of the samples as determined by X-ray fluorescence (XRF) are in close agreement with the composition of gel mixtures showing that aluminum and silicon in the gel are incorporated into the solid in equal proportions.

X-ray Diffraction. XRD patterns were recorded using Philips 1710 powder diffractometer with Cu K α radiation (40 kV, 40 mA), 0.025° step size, and 1 s step time.

Solid-State NMR. Magic-angle-spinning (MAS) NMR spectra were recorded at 9.4 T using a Chemagnetics CMX-400 spectrometer and rotors 4 mm in diameter spun at 8 kHz (for ^{27}Al) and 7 mm rotors spun at 3 kHz (for ^{29}Si). ^{29}Si spectra

were acquired at 79.4 MHz with 30° pulses and 180 s recycle time. ^1H - ^{29}Si cross-polarization (CP) MAS spectra were recorded with a single contact pulse sequence, 5 ms contact time, 8.5 μs ^1H 90° pulse, and 4 s recycle time. The Hartmann-Hahn condition was established using a sample of kaolinite,¹⁹ and the chemical shifts are given in ppm from external tetramethylsilane (TMS). ^{27}Al spectra were measured at 104.3 MHz with 0.3 s recycle delays. Short $\pi/20$ radio-frequency pulses were used to ensure that they are quantitatively reliable.¹⁸ External $\text{Al}(\text{H}_2\text{O})_6^{3+}$ was used as a reference.

Transmission Electron Microscopy. Calcined specimens of MCM-41 were preground and dried in an oven at 550 °C for 1 h. After being cooled to room temperature in a vacuum container, the dried powder was deposited on a grid with a holey carbon film and rapidly transferred to a Jeol JEM-200CX electron microscope operating at 200 kV. TEM images were recorded at a magnification of 35000 \times .

Results and Discussion

Purely Siliceous MCM-41. XRD patterns of purely siliceous samples made using sodium silicate and Cab-O-Sil M-5 fused silica are shown in Figure 1, a and b, respectively. The relatively well-defined patterns are typical of MCM-41 materials as described by Beck et al.⁹ All four XRD peaks can be indexed on a hexagonal lattice with pore diameter of ca. 43 Å (hexagonal with $a_0 = 2d_{100}/\sqrt{3}$).

Transmission electron micrographs (Figure 2a) reveal a regular hexagonal array of uniform channels ca. 40 Å in diameter. When viewed in the direction perpendicular to their axis (Figure 2b), the pores are seen to be arranged in patches composed of regular rows ca. 400 Å long. This is entirely consistent with the XRD results.

The broad ^{29}Si MAS NMR spectra of as-synthesized and calcined siliceous MCM-41 (Figure 3) are identical to those from amorphous silica, indicating that the local arrangement of Si—O—Si bonds in the pore walls is irregular and that a wide range of bond angles are present. The pore wall is therefore completely amorphous. ^1H - ^{29}Si CP/MAS spectra (Figure 3c) show that, as in amorphous silica, part of the silicon atoms exist as silanol groups.

Catapal Alumina as the Source of Aluminum. Aluminosilicate MCM-41 described by Beck et al.⁹ was made using Catapal alumina and sodium aluminate as sources of aluminum. Since the authors of ref 9 do not address the question of the coordination state of Al, we begin by examining MCM-41 with different contents of Catapal alumina. Figure 1 shows that a typical XRD pattern is identical to that from purely siliceous MCM-41, even though the alumina content varies in a wide range. Transmission electron micrographs (not shown) of these samples are identical to those of purely siliceous MCM-41.⁸

^{27}Al MAS NMR spectra (Figure 4) show that, over a wide range of Si/Al ratios (6–90), all “Catapal” samples give an intense line at ca. 7.5 ppm from 6-coordinate (nonframework) aluminum.¹⁷ A very low-intensity line from 4-coordinate Al (at 53.0 ppm) is only found in the most aluminous sample. ^{29}Si MAS NMR spectra (Figure 5b) are the same as those from purely siliceous samples (Figure 5a). It is clear that samples prepared with Catapal alumina contain virtually no 4-coordinate (framework) aluminum.

Aluminum Sulfate as the Source of Aluminum. Since aluminum is the origin of the Brøsted acidity of aluminosilicate molecular sieves, its quantity, location, and coordination state are of much interest. We will show that when aluminum sulfate is used as the source of aluminum for the synthesis of MCM-41, all Al is incorporated into the framework.

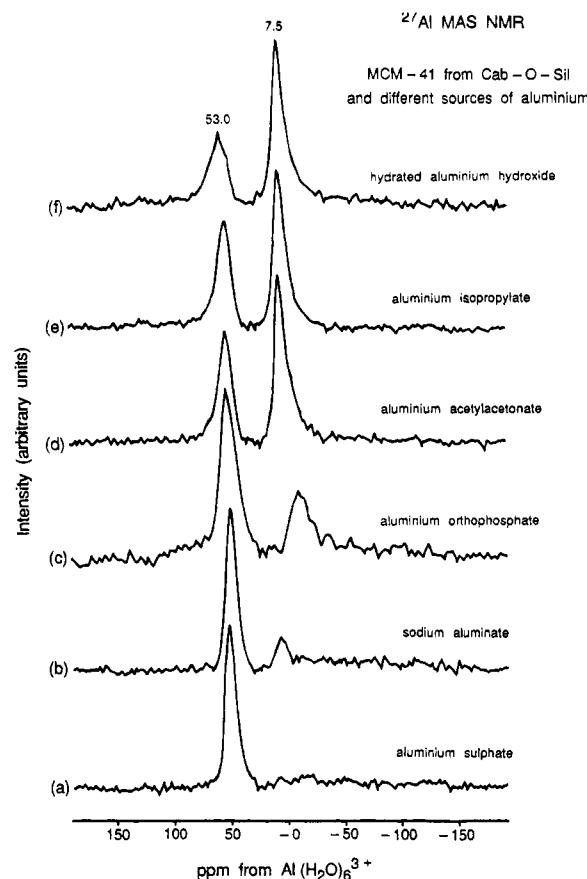


Figure 12. ^{27}Al MAS NMR spectra of aluminosilicate MCM-41 with Si/Al = 15 prepared using (a) aluminum sulfate, (b) sodium aluminate, (c) aluminum orthophosphate, (d) aluminum acetylacetone, (e) aluminum isopropylate, and (f) aluminum hydroxide.

The XRD diffraction patterns of as-prepared samples with Si/Al molar ratio from as low as 2.5 to 60 are given in Figure 6. Diffraction peaks at 2θ angles below 1.5° could not be measured accurately for instrumental reasons. All aluminosilicate samples give poorer quality XRD patterns than purely siliceous MCM-41. The intensity of the (100) peak decreases dramatically even at very low levels of aluminum incorporation (see Figure 6f). Other peaks overlap and greatly decrease in intensity. Figure 7 shows that the patterns from samples with Si/Al > 10 calcined at 550 °C (to remove the template molecules) are much better resolved than those from the as-prepared samples. The (100) peak becomes sharper and more intense upon calcination, although the (110) and (200) peaks are still ill-defined and overlap to give a single broad line.

^{27}Al MAS NMR spectra of as-prepared samples (Figure 8) give a single sharp resonance at 53.0 ppm from 4-coordinate Al. This means that, when aluminum sulfate is used as the source of aluminum, Al from the synthesis gel is incorporated exclusively into the framework. As expected, the intensity of the line at 53.0 ppm increases with increasing aluminum content, and the plot of its intensity versus the Al/(Si + Al) ratio is linear throughout the entire composition range (Figure 9). Upon calcination to remove the template, the sharp ^{27}Al peak broadens but does not decrease in absolute intensity (Figure 10). The broadening is a result of decreased symmetry of some aluminum sites in the anhydrous calcined sample.

^{29}Si MAS NMR spectra of aluminosilicate MCM-41 with Si/Al = 10 shown in Figure 5c contain three main features. The peak at ca. -110 ppm comes from Si(4Si) (Q₄) structural units and is also found in the spectrum of purely siliceous MCM-41 and that of MCM-41 with Si/Al = 23 (see Figure 5a,b). The well-developed peak at -106 ppm comes from Si(3Si,1Al) sites

and confirms the conclusion from ^{27}Al spectra that aluminum has been incorporated into the framework. The shoulder at ca. -100 ppm is due to Q₃ silicons on Si(OSi)₃OH sites. Spectra of samples with other framework Si/Al ratios (not shown) demonstrate that incremental addition of aluminum to the gel results in an increased intensity of the peak from the Si(3Si,1Al) structural units (i.e., at -106 ppm).

Transmission electron micrographs of aluminosilicate MCM-41 with Si/Al = 60 shown in Figure 11 reveal a somewhat irregular, yet essentially hexagonal, pore arrangement. This is in agreement with the XRD results. Rows of one-dimensional pores can still be observed. It is thus apparent that incorporation of aluminum into the framework of MCM-41 affects the long-range order of the mesopores without damaging the essentially mesoporous nature of the material.

Other Sources of Aluminum. We have synthesized aluminosilicate MCM-41 from a variety of aluminum sources. ^{27}Al MAS NMR spectra of the products (Figure 12) clearly show that not all sources of aluminum are equally suitable. The nature of the source of aluminum is therefore a critical factor in determining the location and coordination of Al in the MCM-41 framework.

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