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Boron-Modified MCM-41 Mesoporous Molecular Sieves

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Since the discovery of the crystalline mesoporous M41S materials by Mobil's researchers,[1] this area has attracted many scientists. Among these materials the so-called MCM-41 family which shows a hexagonal array of uniform mesopores has been the focus of most workers. Major contributions, particularly in the field of synthesis of such materials have been reported.[2-4] Incorporation of aluminum,[1,4,5] titanium,[6] and vanadium[7] in the framework of silica-based MCM-41 has been evidenced. Stucky et al.[3] described the synthesis of a large number of crystalline mesoporous materials based on oxides other than silica.

Recently, Gies et al.[8] reported on the synthesis of boron containing MCM-41. They found that in the as-synthesized noncalcined samples ^{11}B exhibits an NMR peak at −2 ppm indicative of a tetrahedral environment. However, upon calcination ^{11}B NMR spectra consisted mainly of a narrow signal at 19 ppm corresponding to a separate borate phase, thus indicating an extensive deboronation during either calcination or subsequent storage. In the present communication, we report on the preparation and characterization of stable boron modified MCM-41 molecular sieves.

A series of boron-containing MCM-41 samples were synthesized hydrothermally using gels with the following molar composition: $\mathrm{SiO_2 \cdot 63H_2O \cdot 0.085Na_2O \cdot 0.16CTAB \cdot \mathit{x}H_3BO_3}$, where CTAB stands for cetyl trimethylammonium bromide. The Si/B ratio (i.e., $1/x$) was varied from 6.25 to ∞. The following is an example of preparation of a sample with a Si/B ratio of 50. A mixture of 5.0 g of Cab-O-Sil M5 silica and 32.2 g of H_2O was prepared under vigorous stirring. After 10 min, a solution of 16.2 g of CTAB in 108.7 g of H_2O was added to the previous silica−water slurry. After another 10 min period, a third solution was added. It consisted of 14.36 g of tetramethylammonium silicate (10 wt % SiO_2) and 6.82 g of sodium silicate (28 wt % SiO_2; 10 wt % Na_2O). Subsequently, 0.170 g of H_3BO_3 was added, and the mixing continued for an additional 30 min. The gel thus obtained was transferred into a Teflon-lined au-

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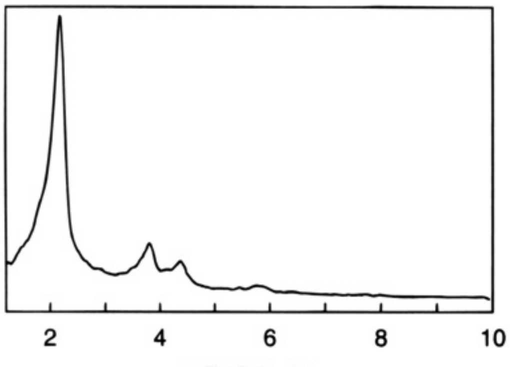

Figure 1. X-ray diffractogram of B-MCM-41-25.

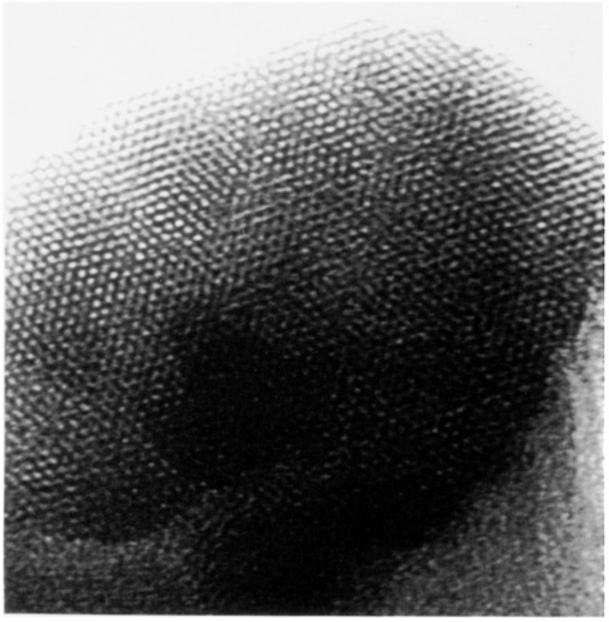

Figure 2. Transmission electron micrograph of B-MCM-41-25.

toclave and heated statically under autogenous pressure at 100 °C for 24 h. The sample was then filtered, thoroughly washed, dried in static air at 100 °C, and then calcined. Samples will be referred to as B-MCM-41-*r*, where *r* is the Si/B ratio in the gel.

The calcination procedure is of crucial importance to avoid deboronation. Our procedure was as follows: a sample was deposited in a refractory boat and calcined under flowing dry nitrogen while its temperature was raised to 500 °C at a rate of 1 °C min^{-1}. The temperature was kept at 500 °C for 2 h before switching slowly from N_2 to dry air. After an additional 4 h at 500 °C, the sample was cooled to room temperature under flowing air and stored under dry N_2.

All samples exhibited X-ray diffraction patterns similar to those reported for hexagonal mesoporous MCM-41 silica (Figure 1). They all had surface areas above 1000 m^2 g^{-1} and exhibited N_2 adsorption isotherms with the characteristic stepped shape.[1,9] Figure 2 shows a typical high-resolution electron micrograph. It is clear that our materials exhibit a pore system with a hexagonal pattern identical to that of silica MCM-41 molecular sieve.[1]

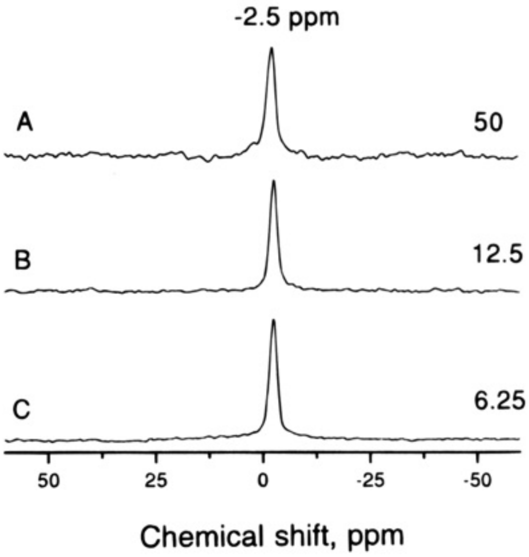

Figure 3. ^{11}B MAS NMR spectra of as-synthesized B-MCM-41-*r* samples; The numbers on the right-hand side indicate *r*, the Si to B ratio.

^{11}B NMR experiments were carried out at room temperature using a Bruker AMX-300 spectrometer at a static 7 T magnetic field (^{11}B Larmor frequency = 96.3 MHz). Magic angle spinning (MAS) spectra were recorded on a Doty Scientific double-bearing high-speed 7 mm probe. Special O-ring sealed rotors were used to prevent the samples from exposure to air. Loading of the rotors with calcined samples was performed in a glovebox under argon atmosphere. All the spectra were obtained with one pulse sequence and high power proton decoupling. The lengths of RF-pulse and repetition time were 2 μs ($\pi/4$ in selective excitation limit) and 1−3 s (depending on the sample), respectively. Depending on boron content, between 200 and 40 000 scans were acquired for sufficient signal-to-noise ratios. The spinning rate of the sample was 7 kHz. Chemical shifts were measured relative to 15% solution of $BF_3{\cdot}(C_2H_5)_2O$ in $CHCl_3$ as an external reference ($\delta = 0$). Simulations of the spectra were performed using the program WINFIT from Bruker.

Figure 3 shows typical ^{11}B MAS NMR spectra for noncalcined B-MCM-41 samples. All the as-synthesized samples exhibited only one narrow peak with a chemical shift at −2.5 ppm. This peak attributed to B in framework tetrahedral position[10−15] indicates complete incorporation of B in the MCM-41 framework, even for Si to B ratios as low as 6.25 (i.e., B/Si = 16%). Moreover, the relative integral intensity of this peak follows very closely the boron content of the synthesis gel,[16] thus providing additional evidence for quantitative incorporation of boron.

Upon calcination, samples with Si/B ratios down to 12.5 show a mixture of two B species (Figure 4), (i) a

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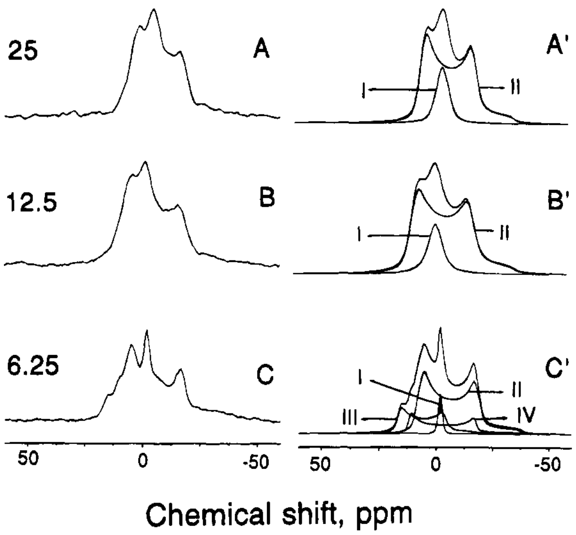

Figure 4. ^{11}B MAS NMR spectra of calcined B-MCM-41-*r* samples; (A, B, C) experimental spectra; (A′, B′, C′) simulated spectra. The numbers on the left-hand side indicate *r*, the Si to B ratio.

species (I) with a signal at −2.5 ppm, identical to the species found in noncalcined samples, i.e., B in framework tetrahedral sites, and (ii) a species (II) with a signal characteristic of strong quadrupolar interaction. Simulation of this signal gave the following magnetic resonance parameters: the isotropic chemical shift corrected for the second-order quadrupolar interaction is 12.5 ppm, the quadrupolar coupling constant C_Q = 2.6 MHz, and the asymmetry parameter is $\eta = 0.12$. Such parameters correspond to trigonally coordinated boron in the silicate framework. Similar data were reported for borosilicate minerals[10,11] and boron modified zeolites.[13-15] This indicates that as long as calcined samples are not exposed to water vapor, they exhibit complete retention of boron in their framework up to a B/Si ratio of at least 8%.

For higher B contents (e.g., Si/B = 6.25, Figure 4C,C′), in addition to species I and II, two other species (III and IV) were generated upon calcination. Species III had a chemical shift of 20.6 ppm and C_Q = 2.52 MHz, $\eta = 0$. All these parameters are very close to those of pure boric acid (δ_{iso} = 23.0 ppm, C_Q = 2.51 MHz, $\eta = 0$). Therefore line III was assigned to extraframework, highly dispersed H_3BO_3. Species IV had a signal at 18.8 ppm with C_Q = 3.0 MHz and $\eta = 0$, which is indicative of three-coordinated boron. A more precise assignment of species IV is difficult. As its isotropic chemical shift was close to that of boric acid, this line may also be attributed to an extraframework species. Notice however, that the value of the quadrupolar constant for this line is noticeably out of the range 2.3−2.7 MHz, normally observed for trigonally coordinated boron in its compounds.[10,12] Full determination of the structure details of species (IV) requires further work.

The relative concentration of boron in different sites can be obtained by integration of simulated patterns. Caution should be taken to avoid errors in the determination of peak intensities because of possible differences in excitation properties of boron in different sites.[13,17] First, we should ensure a linear excitation of the spin system, which can be tested in experiments with very short radio frequency pulses. We carried out such experiments using the sample with Si/B = 12.5 and found no difference in the relative intensities of the lines in experiments with pulses of $\pi/4$ and $\pi/16$. Then, the intensities of the lines affected by strong quadrupolar interactions (i.e., trigonal boron) must be corrected, because only the central transition is excited. This transition represents 40% of the intensity of all transitions for $I = {}^3/_2$. In addition, only a certain fraction of the intensity of the MAS centerband of the quadrupolar lines appears.[17] Taking these facts into consideration, the relative amounts of boron species were estimated. For samples with Si/B ≤ 12.5, the relative populations of site I and site II obtained from the corrected intgral intensities were constant at 5% and 95%, respectively. For the calcined B-MCM-41-6.25 (Figure 4C,C′), the corrected relative intensities were 1, 55, 18, and 25% for species I, II, III, and IV, respectively.

Exposure of calcined samples to ambient air leads ultimately to the hydrolysis of a fraction of the framework boron into hydrated extraframework boric acid with an isotropic narrow signal at 19.5 ppm (spectrum not shown). The hydrolysis process is relatively slow, and changes in the spectra end only after 20−30 h of exposure to water vapor saturated air. The amount of boron leaving the lattice depends on its initial concentration and can be as high as 50% for B-MCM-41-6.25 and is about only 15% for B-MCM-41-50. Detailed analysis of ^{1}H, ^{29}Si, and ^{11}B NMR data, as well as the steps involved in the hydrolysis of framework boron will be published in a forthcoming paper.[16]

In conclusion, boron containing MCM-41 molecular sieves were prepared and characterized by X-ray diffraction, N_2 adsorption, and ^{11}B NMR techniques. NMR data confirm the incorporation of boron into the lattice and show the coexistence of several B sites in calcined samples. The stability of such systems is relatively low, and part of the boron can be removed from the lattice by hydrolysis with water vapor at room temperature.

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