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Synthesis of MCM-48 by a Phase Transformation Process

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M41S materials are ordered, highly porous silicates and aluminosilicates with pore sizes in the range 20−100 Å.[1] Although these materials may exist in a variety of hexagonal, cubic, and other forms,[1−4] the majority of publications in this area have been concentrated on the first reported hexagonal phase, MCM-41. This may be due to the difficulty in synthesizing the other phases. For example, the synthesis of the cubic MCM-48 phase can require extended heating times[1] compared to MCM-41, which may be formed by stirring overnight at room temperature. Although the surfactant “22-12-22”[2,5] has been shown to produce MCM-48 at room temperature, its synthesis is tedious and low yield; further, there is no established method to characterize this surfactant due to its large size and involatility. MCM-48 is a more attractive candidate as an adsorbent or catalyst support than MCM-41, since its highly interwoven and branched structure provides many places where reactant molecules can avoid pore blockages that may occur. Thus, finding a method of synthesizing this material quickly and easily would lend a significant advantage to the use of M41S materials in applications similar to those in which zeolites are now used.

It is possible to synthesize M41S materials under a variety of concentrations and conditions.[1,6−9] At high concentrations of surfactant, it has been proposed that micellar aggregates are formed in solution, around which the silicate source polymerizes.[1] The fact that these materials may also be formed in mixtures with as little as 0.5 wt % of surfactant, however, indicates that at these low concentrations a cooperative templating process[2−4,6,10] is in operation. This self-assembly process is sensitive to factors such as temperature and the presence of cosolvents in the solution. Thus in syntheses using low concentrations of surfactants and short reaction times, when the silicate is only partially polymerized and still flexible, it should be possible to transform the organic−inorganic composite material from one M41S phase to another. In this report, we describe the use of temperature modification to transform MCM-41 into MCM-48. The process takes less than a day and produces a material which is sufficiently polymerized to be stable to calcination.

Table 1. Results of Experiments Using Several Combinations of Stirring/Heating Times To Determine Optimum Conditions for Transformation of MCM-41 to MCM-48[a]

stirring time (h)	heating time (hr)	result
1	5	MCM−48
2	4	well-ordered MCM−48
3	3	well-ordered MCM−48
4	2	MCM−41
5	1	poorly ordered MCM−41 + single diffraction peak

[a] Stirring was performed at room temperature in 150 mL beakers; heating was performed at 150 °C in stainless steel Parr bombs.

Table 2. Peak Indices, Peak Positions, and Unit Cell Parameters for Samples in Figures 1, 3, 4, and 5[a]

	hexagonal patterns		
(*hkl*)	Figure 1a	Figure 3a	Figure 4
(100)	38.05	38.92	40.50
(110)	21.97	22.67	23.15
(200)	19.17	19.79	20.15
(210)	14.49	14.94	15.13
a	44.10 Å	45.41 Å	46.46 Å

	cubic patterns			
(*hkl*)	Figure 1b	Figure 3b	Figure 5b	Figure 5c
(211)	36.01	37.01	38.15	37.89
(220)	31.05	31.99	32.69	32.54
(321)	23.63	24.24	24.93	24.53
(400)	22.20	22.74	23.35	23.01
(420)	19.76	20.30	20.93	20.46
(332)	18.92	19.36	19.93	19.54
(422)		18.48	19.11	18.72
(510)	18.01	17.83	18.41	17.96
a	88.89 Å	90.73 Å	93.40 Å	91.89 Å

[a] Curve fitting was performed using Scintag DMSNT software; the unit cell parameter, *a*, is an average of unit cell parameters calculated from each peak in the pattern.

To synthesize these materials, CTAB (cetyltrimethylammonium bromide) was dissolved in water and 2 M NaOH. After heating slightly (35−40 °C) to dissolve the surfactant, the silicate source TEOS (tetraethyl orthosilicate) was added. The ratios of the reactants SiO_2:Na_2O:CTAB:H_2O were 8.4:2.1:1.0:1108.9. Precipitation occurred after approximately 5 min, and the resulting mixture was stirred rapidly at room temperature. Heating at 150 °C was performed in stainless steel Parr bombs which were allowed to cool to room temperature afterward. Several stirring/heating times were used, which are summarized in Table 1. Samples were then collected by filtration, washed with 50 mL of water, and

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(1) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710. (b) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.−W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(2) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(3) (a) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176. (b) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

(4) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.

(5) (a) “22-12-22” = $CH_3(CH_2)_{21}N^+(CH_3)_2(CH_2)_{12}N^+(CH_3)_2(CH_2)_{21}CH_3$.

(6) Stucky, G. D.; Monnier, A.; Schüth, F.; Huo, Q.; Margolese, D. I.; Kumar, D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Mol. Cryst. Liq. Cryst.* **1994**, *240*, 187.

(7) (a) Chen, C.-Y.; Xiao, S.-Q.; Davis, M. E. *Microporous Mater.* **1995**, *4*, 1. (b) Chen, C.-Y.; Burkett, S. L.; Li, H.-X.; Davis, M. E. *Microporous Mater.* **1993**, *2*, 27.

(8) Cheng, C.-F.; Luan, Z.; Klinowski, J. *Langmuir* **1995**, *11*, 2815.

(9) (a) Inagaki, S.; Fukushima, Y.; Kuroda, K. *J. Chem. Soc., Chem. Commun.* **1993**, 680. (b) Inagaki, S.; Koiwai, A.; Suzuki, N.; Fukushima, Y.; Kuroda, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1449.

(10) (a) Firouzi, A.; Kumar, D.; Bull, L. M.; Besier, T.; Sieger, P.; Huo, Q.; Walker, S. A.; Zasadzinski, J. A.; Glinka, C.; Nicol, J.; Margolese, D. I.; Stucky, G. D.; Chmelka, B. F. *Science* **1995**, *267*, 1138. (b) Firouzi, A.; Atef, F.; Oertli, A. G.; Stucky, G. D.; Chmelka, B. F. *J. Am. Chem. Soc.* **1997**, *119*, 3596.

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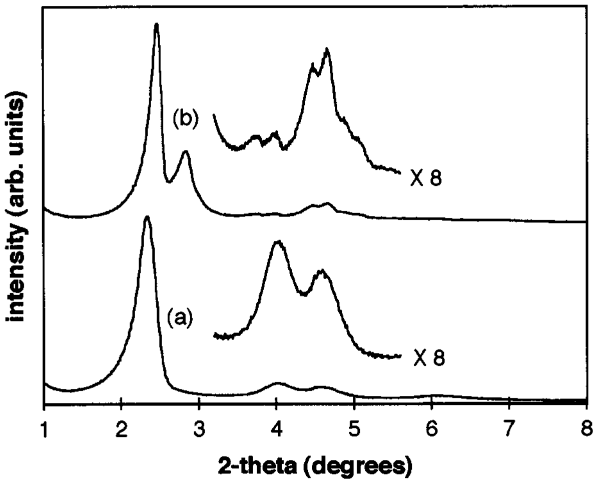

Figure 1. Powder X-ray diffraction spectra of (a) a sample from a surfactant/silicate mixture stirred for 2 h at room temperature and (b) an identical sample stirred for 2 h at room temperature and then heated at 150 °C for 4 h. The silicate source in these experiments was tetraethyl orthosilicate (TEOS).

air-dried before powder X-ray diffraction (XRD) analysis.[11]

Figure 1a shows the XRD spectrum of a sample produced by stirring the reaction mixture at room temperature for 2 h. Although the peaks are slightly more broad than would be expected if the mixture had been stirred for a longer time, this sample is clearly the hexagonal MCM-41 phase. In contrast, a sample that was produced by stirring the reaction mixture for 2 h followed by heating for 4 h at 150 °C (Figure 1b) has an XRD spectrum matching that of MCM-48. Assuming that the phases of both samples are identical after 2 h of stirring, we can conclude that the heating step for the second sample has caused a phase transformation from MCM-41 to MCM-48. This transformation is dependent upon the combination of stirring and heating times, as indicated in Figure 2. Shorter stirring times combined with longer heating times resulted in MCM-48 with XRD peaks which were broad and of lower intensity, indicating a less ordered structure, while longer stirring/shorter heating times produced either MCM-41 or a layered phase. We have found that the optimum degree of silicate polymerization required for transformation to a well-ordered phase is obtained after 2−3 h of stirring at room temperature. At this degree of polymerization, the mesophase shows a definite structure from XRD but is still flexible enough to undergo structural distortions.

We found these results interesting in light of a recent publication by Beck et al.[12] These researchers found no transformation at 150 °C when CTAB was used as the surfactant, only improvement of the original MCM-41 structure, as determined by XRD. In addition to using 2 wt % surfactant (versus 11 wt % used in ref 12), our synthesis uses the silicate source TEOS, which produces 4 equiv of ethanol/mol of SiO_2 as the reaction progresses. To examine the role of ethanol in our transformation process, sodium silicate and fumed silica were used in place of NaOH and TEOS. Molar ratios identical with those in the first sets of experiments were used. Repeating the 2 h stir/4 h heat sequence produced only MCM-41 (Figure 3). However, the addition of 3 mol equiv (with respect to SiO_2) of 100% EtOH just prior to heating caused a clean transformation to MCM-48. This shows that ethanol is required for the transformation to occur. Interestingly, the addition of 4 mol equiv of ethanol, the amount that would be produced from TEOS, yielded a material with only a single broad peak in the diffraction pattern. Indeed, altering reaction parameters such as stirring rate and beaker size was found to drastically affect the phases produced. Unlike experiments using TEOS, which consistently gave MCM-48 under appropriate conditions of heating and stirring, the samples produced in these experiments varied

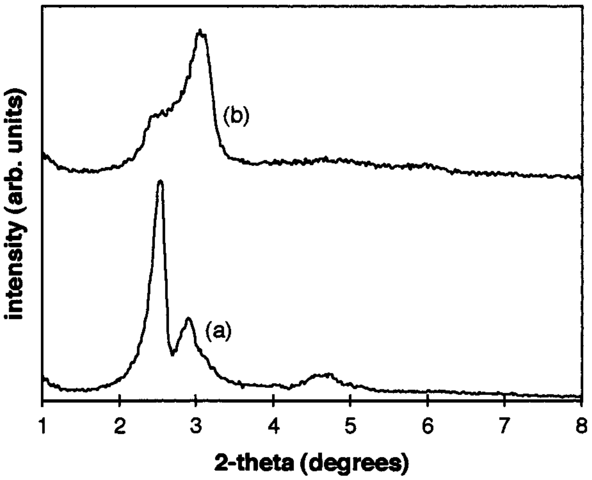

Figure 2. Powder X-ray diffraction spectra of (a) a sample from a surfactant/silicate mixture stirred for 1 h at room temperature and then heated at 150 °C for 5 h and (b) an identical sample, stirred for 5 h, and then heated for 1 h. The silicate source was TEOS.

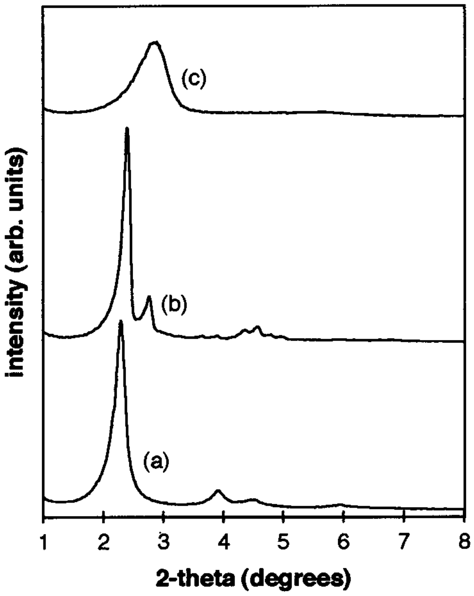

Figure 3. Powder X-ray diffraction spectra of samples from a surfactant/silicate mixture using sodium silicate and fumed silica, which were stirred for 2 h and heated at 150 °C for 4 h: (a) no ethanol added: (b) 3 equiv of ethanol added just prior to the heating step; (c) 4 equiv of ethanol added.

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(11) Powder X-ray diffraction experiments were performed on a Scintag X1 $\theta-\theta$ diffractometer equipped with a Peltier (thermoelectrically cooled) detector and using Cu Kα radiation. Scans were performed between 1° and 8° 2θ, with step sizes of either 0.02° or 0.01° and count times of either 1.5, 5, or 7 s/point depending upon the sample.

(12) Beck, J. S.; Vartuli, J. C.; Kennedy, G. J.; Kresge, C. T.; Roth, W. J.; Schramm, S. E. *Chem. Mater.* **1994**, *6*, 1816.

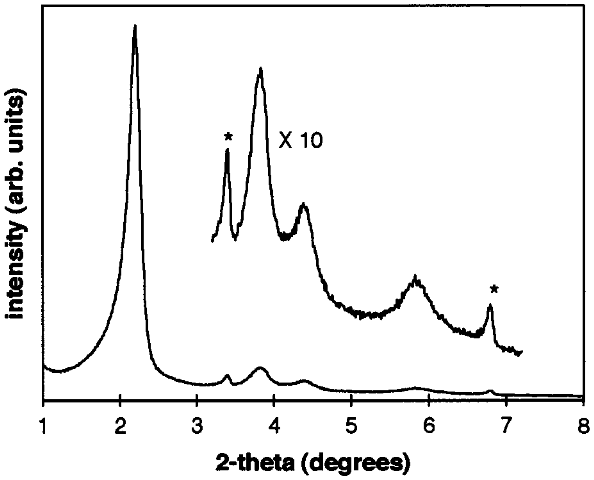

Figure 4. Powder X-ray diffraction spectrum of a sample from a silicate/surfactant mixture using TEOS as the silicate source. The sample is identical with that in Figure 1b except that the reaction mixture was heated at 40−50 °C during the 2 h stirring time to volatilize the ethanol being produced, and then heated at 150 °C for 4 h. Peaks marked with an asterisk are due to the surfactant cetyltrimethylammonium bromide (CTAB).

widely among MCM-41, MCM-48, layered materials, samples with single diffraction peaks, and mixtures of all of the above. It appears that when ethanol is added externally to the reaction mixture rather than being intimately involved at the silicate−surfactant interface, the transformation is much more dependent on macroscopic parameters such as particle size which are in turn tied to the stirring rate and beaker size. This indicates that the ethanol must be present at the interface region for transformation to happen.

We also examined preparations in which TEOS was used as the silicate source, but the mixture was heated at 40−50 °C during the 2 h stirring time, to volatilize the ethanol being produced. Figure 4 shows that no transformation occurred under these conditions; MCM-41 was the product even after heating for 4 h at 150 °C.

The results shown here confirm that ethanol plays an important role in the transformation process. Previous research has shown that the self-assembly of the organic−inorganic structure can be modeled by the surfactant packing parameter $g = (V)/(a_0)(l)$,[2,13] where V is the total volume of the surfactant chain plus any cosolvent molecules between the chains, a_0 is the effective headgroup area at the organic−inorganic interface, and l is the surfactant chain length. Small values of g stabilize more curved surfaces such as MCM-41 ($^1/_3 < g < ^1/_2$), while larger values stabilize structures with less curvature such as MCM-48 ($^1/_2 < g < ^2/_3$) and layers ($g = 1$). As has been shown by Stucky et al., alcohol molecules with shorter alkyl chains (<4 carbons) tend to reside primarily in the outer shell of the surfactant micelle.[2,4,14] Thus, the addition of alcohols as cosolvents increases the effective surfactant volume, raising the value of g and causing transformation to a different phase. Adding ethanol to the hexagonal phase is thus expected to cause a transformation to the cubic phase under appropriate conditions.

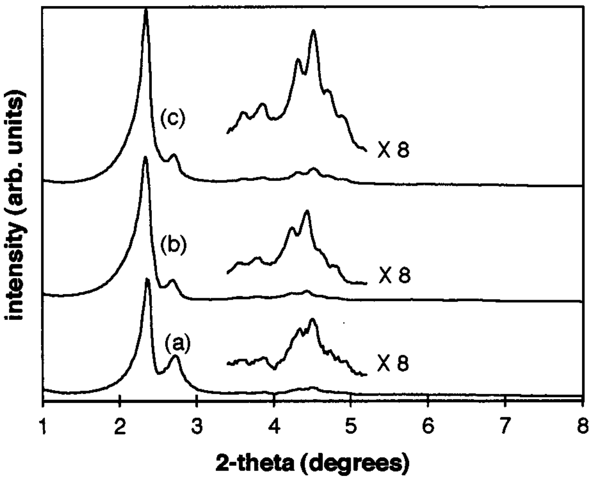

Figure 5. Powder X-ray diffraction spectra of (a) a "transformed" sample, (b) the same sample after being resuspended in water at pH = 7 and 100 °C for 7 days, and (c) the sample from (b) after calcination in air.

We theorize that during the time in which our reaction mixture is stirred at room temperature, ethanol is produced in the vicinity of the organic−inorganic interface. Upon heating, the ethanol is driven further into the organic region, increasing the surfactant packing parameter and causing the system to transform from MCM-41 into MCM-48.[15] Of course, this process is also dependent upon the flexibility of the silicate framework, since it must be able to accommodate the structural changes in the organic region. Thus, the transformation of MCM-41 to MCM-48 is an example of cooperative effects across the organic−inorganic interface. The process is optimized at particular combinations of (1) degree of silicate polymerization, (2) concentrations of ethanol and surfactant, and (3) system temperature.

It is also interesting to note that the MCM-48 produced by this process is stable to postsynthetic treatments, presumably due to the rapid polymerization of the silicate at advanced temperatures. Specifically, improvements in the degree of ordering of the MCM-48 structure in samples produced by our method can be yielded by "heat-treating" the sample.[2] Resuspending a "transformed" sample at pH = 7 and 100 °C for 1 week significantly increased peak intensities in its XRD pattern, allowing resolution of the secondary peaks between 3° and 5°. Calcination (removal of the surfactant by heating the sample in air at 500 °C)[16] caused similar changes in the diffraction pattern (Figure 5). The lack of any large shifts in the positions of the diffraction peaks upon these treatments indicates that the silicate structure is unusually stable; for example, heat treatments tend to induce increases in the pore sizes of silicate M41S materials,[2] while calcination can decrease

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(13) (a) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1525. (b) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *Biochim. Biophys. Acta* **1977**, *470*, 185. (c) Monnier, A.; Schüth, F.; Huo, Q.; Kumar, D.; Margolese, D. I.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.

(14) Huo, Q.; Feng, J.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1997**, *9*, 14.

(15) This is expected based on experiments involving the partitioning of aliphatic alcohols between water and octanol. For thermodynamic parameters see: Riebesehl, W.; Tomlinson, E. *J. Solut. Chem.* **1986**, *15*, 141.

(16) Calcination was performed in a Lindberg tube furnace at a heat rate of 1 °C/min to 400 °C, followed by a 4 h hold at that temperature. After this cycle, the sample was heated at 5 °C/min to 500 °C and held at that temperature for an additional 4 h. Air was used as the calcination gas.

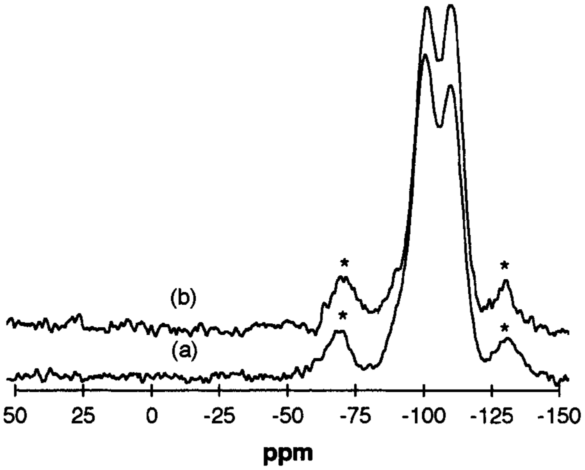

Figure 6. Solid-state ^{29}Si MAS NMR spectra of (a) a sample from a silicate/surfactant mixture which was stirred for 3 h at room temperature and (b) the same sample after heating for 3 h at 150 °C. Peaks marked with an asterisk are spinning sidebands.

pore sizes by collapsing the structure.[17] This indicates that the MCM-48 phase given by our transformation method is locked in place by rapid silicate polymerization at advanced temperatures. Further indication of the more highly polymerized nature of the mesoporous silicate after heating at advanced temperature is given by ^{29}Si MAS NMR (Figure 6).[18] Incompletely polymerized silicate species (Q^3) are indicated by a peak at approximately −100 ppm, while Q^4 silicate species (completely polymerized) are indicated by a peak at −110 ppm.[19] The Q^3/Q^4 ratio after stirring at room temperature for 3 h is greater than 1, while after heating an identical sample at 150 C for 3 h the ratio has decreased to approximately 1/1. The smaller ratio after heating indicates that during the 3 h heating time, the degree of polymerization and therefore rigidity has increased.

In conclusion, we have developed a method by which the mesoporous catalyst MCM-48 may be synthesized in 6 h, using a commercially available surfactant. This represents a significant advancement over previously established preparations. In addition, we have established that ethanol plays an important role in the transformation process, causing an increase in the surfactant packing parameter *g* and, provided that the silicate framework is still incompletely polymerized, inducing the transformation of the composite material from MCM-41 to MCM-48. The samples produced by this method are stable to postsynthetic treatments and to calcination. These studies provide information about the energetics and structural interactions surrounding organic−inorganic interfaces, and we anticipate reporting our findings in this and other related aspects of meso- and microporous silicate transformations in future publications.

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(17) Edler, K. J.; White, J. W. *Chem. Mater.* **1997**, *9*, 1226.

(18) ^{29}Si MAS NMR spectra were obtained on a Bruker AM500 spectrometer operating at 99.36 MHz. Samples were spun at 3.5 kHz; a pulse delay of 180 s and a dwell time of 16 μs were used. Between 300 and 400 acquisitions were used in the final Fourier transform.

(19) (a) Q^ynotation is used to indicate a silicate (SiO_4) tetrahedron which is connected to *y* silicon atoms through the bridging oxygen atoms. Thus a Q^3 species in a pure silicate mesoporous sample has one Si−O⁻ or Si−OH species through which it can continue to condense. (b) Engelhardt, G.; Michel, D. *High Resolution Solid-State NMR of Silicates and Zeolites*, Wiley: New York, 1987.