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Metastability of MCM-41 and Al-MCM-41

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The apparent stability of MCM-41 and Al-MCM-41 in water was appraised in a series of solubility experiments. MCM-41 is a siliceous, mesoporous material of hexagonal symmetry and exceptionally high surface area first synthesized in 1992. The dissolution experiments were carried out at several solid/water ratios: 1/200, 1/100, and 1/75. Results indicated that MCM-41 and Al-MCM-41 are more soluble than amorphous silica at ambient temperatures. Using standard thermodynamic data, a minimum Gibbs free energy of formation of −847.9 kJ/mol for MCM-41 was calculated compared to −848.85 kJ/mol for amorphous silica and −856.3 kJ/mol for quartz. X-ray diffraction (XRD) analyses of recovered solids indicated a progressive loss of crystallinity in MCM-41 and Al-MCM-41 over the 79 day dissolution experiment. BET nitrogen surface area analyses of recovered solids revealed no appreciable change in the surface area of either material after 79 days of reaction in water. Field emission scanning electron microscope (SEM) images taken of the 79 day MCM-41 sample showed some degradation of the initial structure—fine, worm-like particles.

Introduction

MCM-41 was first developed by Mobil Corporation researchers in 1992 as a subset of the M41S family of mesoporous materials.[1] The material presents itself as a loose white powder with several interesting properties at the subnanometer scale. Particles of the material are composed of agglomerations of hexagonally arranged siliceous mesopores with radii ranging between 2 and 10 nm depending on the reagents and procedure used in its synthesis.[1,2] Perhaps the most notable characteristic of MCM-41 with regards to its potential use as a metal catalyst support in environmental catalysis applications is an exceptionally high surface area, exceeding 1000 m^2/g in well-formed samples.[3−6]

The purpose of this study was to determine the stability of MCM-41 with respect to other forms of silica (SiO_2) in water at ambient temperature and pressure. There are several forms of silica: trydimite, cristobalite, stishovite, coesite, and amorphous silica. All have higher free energies compared to that of quartz and thus are less stable than quartz at ambient temperature and pressure. Free energies of polymorphs can be determined through solubility measurements. The dissolution reaction of any form of silica can be represented at pH < 8 by

$$2H_2O_{(l)} + SiO_{2(s)} \leftrightarrow H_4SiO^0_{4(aq)}$$

Since the solubility of a particular form of silica is directly proportional to its free energy of formation ($\Delta G^\circ_{(SiO_{2(s)})}$), as seen through the following two relations

$$\Delta G^\circ_R = \Delta G^\circ_{f(H_4SiO_4^0)} - 2\Delta G^\circ_{f(H_2O)} - \Delta G^\circ_{f(SiO_{2(s)})}$$

$$\ln K_{sp} = -\Delta G^\circ_R/RT$$

a solubility determination of a particular polymorph can be performed to determine its ΔG°_f and thus its relative stability compared to other polymorphs. This is the approach used to determine the stability of MCM-41 in this study. The effect of aluminum substitution for silica on the stability of MCM-41 was also investigated. This aspect was prompted by a previous study which proposed that MCM-41's resistance to degradation by hydrothermal treatment varied with Al content.[7]

Experimental Section

Synthesis of MCM-41. MCM-41 was synthesized using a procedure published by Cheng et al.[3,4] Tetramethylammonium hydroxide pentahydrate (TMAOH, 97%) and fumed silica (SiO_2, 99.8%) were obtained from Sigma-Aldrich. Hexadecyltrimethylammonium bromide (CTABr, technical) was obtained from Fisher Scientific. Briefly, TMAOH and CTABr were dissolved in Nanopure deionized water under gentle stirring at 300 K. Fumed silica powder was added once the opaque solution turned clear, and the resulting mixture was stirred and heated for 3 h. The final relative molar composition of the gel was 1 SiO_2, 0.19 TMAOH, 0.27 CTABr, 40 H_2O. The required masses of the reagents were calculated on a basis of 200 g of water. After aging for 24 h at room temperature, the mixture was transferred to an autoclave and heated for 68 h at 400 K. The reaction was stopped by quenching the autoclave under cold water for 30 min. The contents of the autoclave were transferred to plastic centrifuge bottles and washed with deionoized water, centrifuged, and decanted until the conductance of the supernatant rinsate was less than 1 mS/cm. Finally, the solid material was calcined for 8 h at 923 K to ensure complete removal of the organic template.

The mesoporosity and hexagonal structure of the material were verified by low-angle X-ray diffraction analysis (XRD) between 1 and 10° 2θ using a Bruker AXS D8 Advance X-ray diffractometer with a 1.5418 Å X-ray source. The surface area was determined using a Micromeritics Gemini III 3275 surface area analyzer following the Brunauer−Emmet−Teller isotherm (BET) nitrogen adsorption surface area technique.[8] The morphology of the material was examined using a Leo 1530 field emission scanning electron microscope (SEM).

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Synthesis of Al-MCM-41. Sodium hydroxide (NaOH, ACS) was obtained from J. T. Baker. Hexadecyltrimethylammonium chloride (CTMACl, 25% by mass in water) was obtained from Sigma-Aldrich. Sodium aluminum oxide ($Al_2O_3 \cdot Na_2O$, technical) was obtained from Alfa-Aesar. The Al-MCM-41 synthesis procedure involved slowly adding 100 g of a TMAOH and silica solution to 100 g of a NaOH, CTMACl, and $Al_2O_3 \cdot Na_2O$ solution.[9,10] The mixing of the two solutions at room temperature produced a gel, which was stirred for an additional 15 min. The final relative molar composition of the mix was 1 SiO_2, 0.05 Al_2O_3, 0.23 CTMACl, 0.11 Na_2O, 0.089 TMAOH, and 125 H_2O. The required masses of the reagents were calculated on a basis of 200 g of water. The gel was transferred to an autoclave and heated for 48 h at 373 K, after which the reaction was stopped by quenching with cold water for 30 min. The gel was transferred to plastic centrifuge bottles and washed with deionized water, centrifuged, and decanted until the conductance of the supernatant rinsate was less than 1 mS/cm. The recovered solid was dried overnight at 323 K and calcined under air for 10 h at 833 K to remove any remnant of the organic template. The relevant physical properties of the material were examined via XRD and BET analyses in the same manner as that described for MCM-41.

MCM-41 Dissolution Experiment. Duplicate samples of MCM-41 in deionized water were prepared in 60 mL high-density polyethylene (HDPE) bottles. The masses of MCM-41 were added to sample bottles to obtain solid/liquid ratios of 1/200 and 1/100. Control samples (i.e., without solid) were prepared and analyzed to ensure that there were no sources of silica contamination. For the Al-MCM-41 solubility experiments, an additional run at a 1/75 solid/water ratio was performed. Sample bottles were mounted horizontally on a carousel and continuously rotated in an isotemperature bath maintained at 298.15 ± 0.1 K. The supernatant was sampled for Si analyses periodically during the 79 day experiment and filtered through 0.2 μm Acrodisc membrane filters. Si was analyzed using a Pharmacia LKB Novaspec II spectrophotometer using the Molybdosilicate method.[11] The spectrophotometer was calibrated using external standards prepared by dilution of gravimetrically prepared concentrated sodium metasilicate stock solution and a blank. The minimum detectable concentration of silica for the technique was 1 ppm. The method detection limit (MDL) for the procedure was determined by analyzing seven samples spiked with stock solution to produce concentrations of 5 ppm silica. The standard deviation of the spiked sample concentration results was 0.266, and the MDL was 0.835. The pH of several samples was measured with a Hanna Instruments 8417 pH meter and Corning probe. The pH probe was calibrated using 7.00 and 10.00 NIST SRM-traceable buffers. Some MCM-41 material was recovered from the bottles on days 28 and 79 and dried under vacuum over a saturated KCl solution (80% relative humidity). Solid material was recovered from the Al-MCM-41 experiment only on day 79. All recovered solid samples were examined using XRD and BET analyses and compared to those of freshly prepared material.

Results and Discussion

Characterization of MCM-41. The XRD trace of the original MCM-41 (labeled "as-prepared" in Figure 1) shows three principal peaks, labeled according to its hexagonal unit cell. The 100 peak indicates that the sample is mesoporous, while peaks 100, 110, and 200 indicate a well-ordered arrangement of hexagonal pores. The "*a*" unit cell length is given by the position of the 100 peak, which, from Bragg's Law, equals 4.6 nm. This corresponds to the center-to-center distance of the hexagonal pores of the sample.[1]

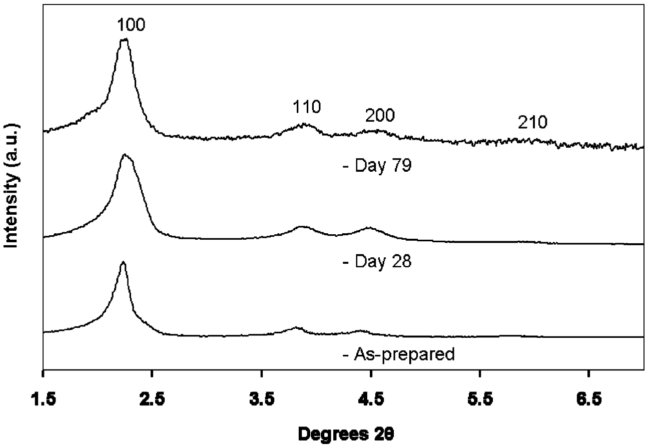

Figure 1. Comparative XRD trace exhibiting "as-prepared" MCM-41 compared to materials recovered at 28 and 79 days of the dissolution experiment.

BET nitrogen adsorption surface area analysis yielded a value of 1090 m^2/g. The reproducibility of the BET analysis is on the order of 5−10%. A SEM image of the MCM-41 sample is presented in the upper left panel of Figure 2. The morphology is similar to material described in the literature as "wormy" MCM-41.[12] SEM images revealed elongated particles with an average width of 3.5 μm and length of 7.3 μm. In many cases, these individual particles were agglomerated, forming a massive morphology with the wormy texture mentioned above.

Characterization of Al-MCM-41. The XRD trace of the original Al-MCM-41 (labeled "as-prepared" in Figure 3) shows only one identifiable peak, 100. The 110 and 200 peaks typically seen for MCM-41 samples are likely represented by the broad shoulder to the right of the 100 peak. The broad 100 peak and higher background reflect a lower degree of crystallinity in Al-MCM-41. This is consistent with characterizations by other researchers.[13−15] BET analysis of this material indicated a surface area of 1300 m^2/g.

MCM-41 Dissolution Experiments. Figure 4 shows concentration versus time results for Al-free MCM-41 at solid to liquid ratios of 1/100 and 1/200. The SiO_2 concentration increases sharply at both solid to liquid ratios, indicating rapid dissolution of MCM-41. The 1/200 sample approached a maximum concentration of approximately 128 ppm within 7 days, while the 1/100 sample approached a maximum of 175 ppm. The long-term concentration value of 115−122 ppm corresponds to that predicted for amorphous silica in pure water using the solubility product (K_{sp}) of $10^{-2.7}$.[16] The attainment of a maximum concentration and the subsequent decrease reflects competitive kinetics between the dissolution of MCM-41 and nucleation and precipitation of amorphous silica. Therefore, when MCM-41 is added to water, it dissolves and becomes supersaturated to and precipitates amorphous silica. This process should continue until all of the MCM-41 has been converted to amorphous silica. The 1/100 water/solid shows a more substantial maximum than the 1/200 sample. This is likely due to the lower flux of Si into the solution for the 1/200 sample. This indicates that the dissolution reaction is surface-controlled, and the flux of SiO_2 from the solid to solution is purely a function of the solid to liquid ratio. Note that the solution near the solid surfaces will likely attain supersaturation with respect to amorphous silica before the bulk solution. Therefore, amorphous silica precipitation can be occurring before the bulk solution

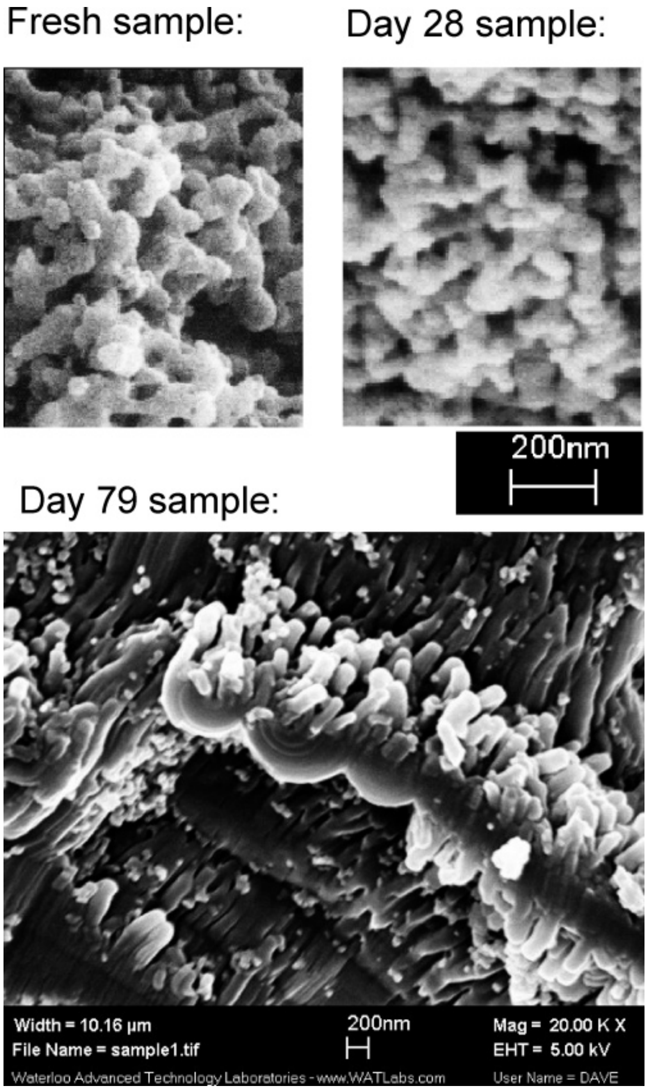

Figure 2. Comparison of SEM image of “as-prepared” MCM-41 to images taken of materials recovered on days 28 and 79 of the dissolution experiment.

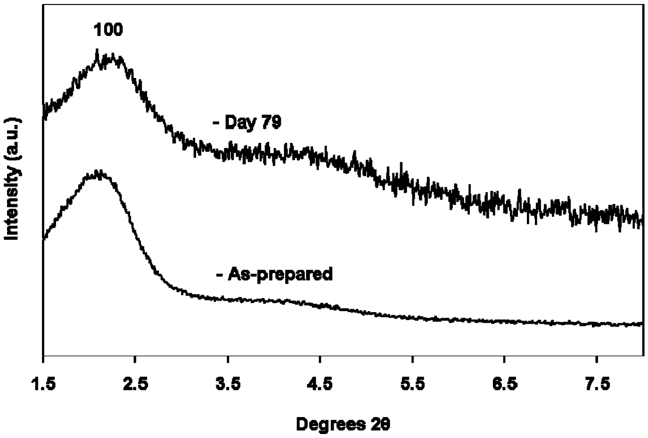

Figure 3. XRD trace of calcined Al-MCM-41 and Al-MCM-41 recovered on day 79 of the dissolution experiment.

actually exhibits supersaturation. Thus, SiO_2 concentrations higher than amorphous silica saturation may only be observed for MCM-41 at high solid/water ratios.

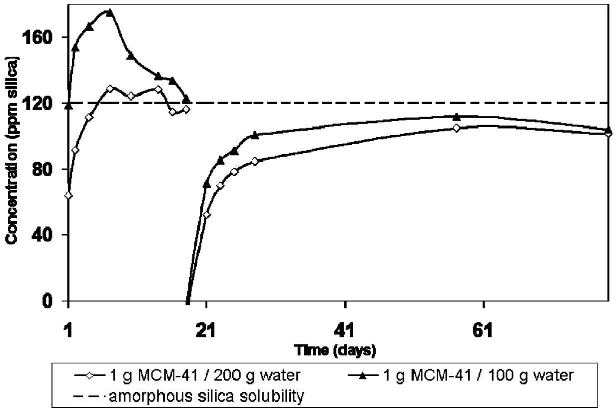

Figure 4. Silica concentration results of the MCM-41 solubility experiment showing the effect of decanting and replacing supernatant solution.

The only other explanation for the high solubility of MCM-41 is the development of pHs in the solutions above 9.0 because silica solubility is enhanced due to the formation of $H_3SiO_4^-$, the first hydrolysis product of silicic acid ($H_4SiO_4^\circ \Rightarrow H^+ + H_3SiO_4^-$; $K = 10^{-9.8}$). Because all pure silica-saturated water systems are slightly acidic, high pHs could only occur as a result of some caustic contaminant in the MCM-41. To rule out this possibility, we measured sample pHs at 4, 7, and 14 days, and they were between 5 and 6, consistent with predicted silica/water system pHs and too low for any solubility enhancement. Therefore, solution Si concentrations higher than amorphous silica at early time are a reflection of the intrinsically higher solubility, and thus lower stability, of MCM-41 compared to amorphous silica rather than an artifact of high pH development in solutions containing MCM-41.

The effect of decanting and replacing the solution with fresh deionized water on day 18 of the experiment is shown in Figure 4. Both samples again exhibit a rapid increase in SiO_2 concentration toward amorphous silica saturation. Interestingly, amorphous silica supersaturation is not attained in these recycled samples. This is likely due to shrouding of the MCM-41 particles by amorphous silica precipitates formed during the initial period of reaction. Consequently, no induction period or supersaturation is required before precipitation can occur since amorphous silica is already present on the surface of the recycled material. Therefore, precipitation of amorphous silica is faster than dissolution of MCM-41. An alternate explanation is that the high silica concentrations observed at the beginning of the experiment were due to the rapid dissolution of a small amount of ultrafine silica of higher solubility than MCM-41, perhaps present in the material after its synthesis. This alternate explanation was disproved by the following experiment. Duplicate 0.12 g samples of MCM-41 were added to 1 L of water. This mass of MCM-41 is just sufficient to reach saturation with respect to amorphous silica (120 ppm as SiO_2). If MCM-41 is intrinsically less stable than amorphous silica, then the added MCM-41 should dissolve completely, and the silica concentration in the solution would trend toward 120 ppm. The first attempt at this experiment failed because with such small amounts of MCM-41 in the solution, the dissolution rates were too slow to attain complete dissolution in a reasonable time. A study by Hanton,[17] however, showed that the presence of a neutral salt markedly enhanced the dissolution rate of silica compared to that with deionized water. On the basis of these reported observations, we chose to repeat the experiment in a 0.5 M K_2SO_4 solution. After 11 days of reaction, the concentrations in the duplicate samples were 114 and 96 ppm. This represents dissolution of 95 and 80% of the initial MCM-41 mass added to the solutions. Although complete dissolution of MCM-41 apparently did not occur in the time frame of this experiment, the results are sufficient to conclude that the observed high solubility of MCM-41 is a property of the material, not a result of a small amount of ultrafine particles initially present in the material.

MCM-41 Free-Energy Calculations. A minimum estimate of the Gibbs free energy of formation for MCM-41 ($\Delta G^\circ_{f(MCM-41)}$) can be determined from the maximum silica concentration observed in the dissolution experiment (175 ppm = 2.91×10^{-3} mol/kg). ΔG°_f values for $H_4SiO_4^0$ and H_2O used in the calculation were −1308.00 and −237.141 kJ/mol, respectively.[18] The activity of $H_4SiO_4^0$ in solution was assumed equal to its molality (i.e., activity coefficient equal to 1.0), and the activity of water and MCM-41 were equal to 1.0.[19] From the dissolution reaction of MCM-41

$$2H_2O_{(l)} + SiO_{2(s)} \leftrightarrow H_4SiO^0_{4(aq)}$$

the solubility product expression is formulated

$$K_{sp} = [H_4SiO^0_{4(aq)}]/[H_2O_{(l)}]^2[SiO_{2(s)}] = 2.91 \times 10^{-3} = 10^{-2.54}$$

The free energy of reaction is then

$$\Delta G^\circ_R = -RT \ln K = -5.606 \log K = 14.215 \text{ kJ/mol}$$

and $\Delta G^\circ_{f(MCM-41)}$ can be calculated

$$\Delta G^\circ_R = \Delta G^\circ_{f(H_4SiO_4^0)} - 2\Delta G^\circ_{f(H_2O)} - \Delta G^\circ_{f(MCM-41)}$$

$$\Delta G^\circ_{f(MCM-41)} = -847.9 \text{ kJ/mol}$$

A value of −847.9 kJ/mol for $\Delta G^\circ_{f(MCM-41)}$ can be compared to −856.3 kJ/mol for quartz and −848.85 kJ/mol for amorphous silica.[18] This relatively high free energy of formation for MCM-41 is a reflection of its intrinsic instability in water at ambient temperatures with respect to other forms of silica. Most importantly, however, MCM-41 is metastable with respect to amorphous silica. This is because a metastable polymorph like MCM-41 may persist indefinitely in water if it is only metastable with respect to crystalline polymorphs where kinetic restraints may prevent their formation. However, if a polymorph is metastable with respect to its amorphous counterpart, where no kinetic restraints prevent its precipitation, the transformation and disappearance of the metastable polymorph is inevitable.

In an attempt to get a better estimate of the intrinsic solubility and free energy of MCM-41, a separate dissolution experiment (not shown) was tried using as-prepared MCM-41 at solid to liquid ratios of 1/200 and 1/100 in a 120 ppm silica solution instead of deionized water. It was thought that with the starting solution already saturated with amorphous silica, the initial dissolution of MCM-41 would generate an even higher silica maximum and thus be closer to the actual solubility of MCM-41. However, samples from these solutions only attained a maximum silica concentration of 150 ppm. It appears that once amorphous silica supersaturation is attained, there is very little hindrance to its precipitation

Physical Characterization Results. XRD results on the "as-prepared" 28 and 79 day MCM-41 samples are compared in Figure 1. A progressive increase in background noise with time is clear in the comparative plots. This likely reflects an increasing proportion of amorphous silica precipitated as the MCM-41 particles dissolved. The relative positions of the 100, 110, and 200 peaks on the XRD trace do not change, indicating that the mesoporosity and hexagonal character of the material is not affected by contact with water.

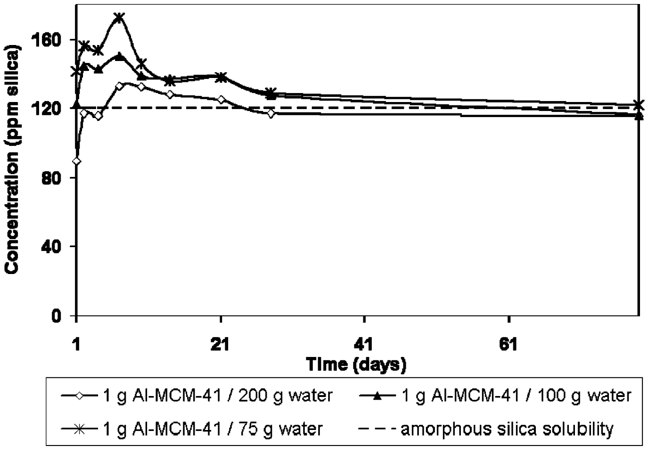

Figure 5. Silica concentration results of the Al-MCM-41 dissolution experiment.

The results of BET nitrogen adsorption analysis yield surface areas of 1040 and 1160 m^2/g for the 28 and 79 day samples, respectively. The surface area of the "as-prepared" material was 1090 m^2/g. This difference is likely not significant given the error inherent in the BET analysis technique.

SEM images taken of the "as-prepared" and 28 and 79 day samples are presented in Figure 2. There was no clear change in morphology between the "as-prepared" and the 28 day sample. In the 79 day sample, the worm-like structure appears clearer, and in the middle of the upper part of the photo, there is material with concentric banding. Such texture is characteristic of cryptocrystalline forms of quartz that are produced from the recrystallization of amorphous silica precipitates, agates and chalcedony.[20] This suggests that after 79 days in water, MCM-41 may be transforming to more stable amorphous silica, and the amorphous silica is transforming to a more stable silica phase.

Al-MCM-41 Results. Figure 5 presents the results of the Al-MCM-41 dissolution experiment as a plot of concentration in ppm of SiO_2 versus time at solid to liquid ratios of 1/200, 1/100, and 1/75. The results of the Al-MCM-41 dissolution experiment are analogous to those of the Al-free MCM-41 at similar solid/liquid ratios, indicating that incorporation of Al into the MCM-41 structure during synthesis has no effect on the material's stability in water. All three solid to liquid ratios achieved a maximum concentration within 7 days. Between 7 and 79 days, all three of the samples approached a long-term concentration of 120 ppm, representative of saturation with respect to amorphous silica.

XRD analysis of the 79 day Al-MCM-41 sample is presented in Figure 3 and can be compared to that of the "as-prepared" material. The general shape of both traces is similar. The 100 peak and the shoulder on its right-hand side are easily identified in both plots. The height of the shoulder in the 79 day sample is larger relative to the 100 peak than that in the as-prepared sample. There is also an increase in the amount of background noise in the 79 day sample plot. The change in these two features is likely related to an increase in the proportion of amorphous silica in the sample.

BET analysis yielded a surface area of 1180 m^2/g for the 79 day sample of Al-MCM-41. When compared to the "as-prepared" material (1300 m^2/g), this represents a percentage decrease in surface area of slightly less than 10%. As with regular MCM-41, this decrease is likely insignificant given the 5−10% reproducibility in the BET surface area analyses.

Conclusions

The results of this study indicate that MCM-41 is metastable with respect to amorphous silica in deionized water at ambient temperatures. Precipitation of amorphous silica on MCM-41 particles may produce a protective layer on the material's surface and slow down its transformation to amorphous silica. The maximum observed solubility of MCM-41 in water permitted an estimation of its minimum solubility product and a minimum Gibbs free energy of formation of −847.9 kJ/mol. Silica concentration versus time results for an aluminum-substituted MCM-41 in water revealed an analogous dissolution behavior as that of the pure silica form of MCM-41. The solubility results and physical characterization of the material indicate that incorporation of Al into the MCM-41 structure during sample synthesis does not improve the stability of MCM-41 in water.

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