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Observation of Adsorption of Water in MCM-41 with Neutron Diffraction

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Adsorption/desorption of water in the mesoporous material MCM-41 was observed with neutron diffraction. Results obtained with a $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture contrast-matched to the host material unambiguously show that the pores are fully hydrated in the presence of excess water. During desorption carried out by air-drying a saturated sample, water in the partially filled pores redistributes and the statistical distribution of water within each pore is characterized by a smooth function that decreases from a maximum around the edge to a minimum at the center.

1. Introduction

The objective of experiments involving porous materials is usually to study the sorption process or to study a foreign material confined within the pores of the host material. An important question is, To what degree and how uniformly is the available pore space filled?, during adsorption, at saturation, and during desorption. Estimating the filling ratio from measured pore volume and weight gain of a filled sample may not be reliable since part of the gain could be due to the foreign material coating the exterior surface of the sample. Neutron (or X-ray) diffraction is potentially a better technique since it is a bulk probe that directly measures the change of contrast at the interface between the host material and the pores.

MCM-41 is an extensively studied molecular sieve whose properties and potential applications are recently reviewed by Ying, Mehnert, and Wong.¹ To first order, its pores are long, straight cylinders packed on a 2D hexagonal lattice. Neutron studies have been reported on MCM-41, with the aim of studying pore formation² and the dynamics of water already incorporated.³ In addition, by contrast matching the water (by mixing H_2O and D_2O) to the silicate material, it has been shown^{4,5} that pores in MCM-41 are fully accessible to aqueous and organic solvents. Since most foreign materials of interest contain hydrogen (hydrocarbons and polymers), H/D contrast matching is a broadly applicable technique. This, combined with the neutron's ability to penetrate various sample environments, makes it a particularly powerful probe to study sorption processes. Tun and Mason⁶ have recently shown that even a single-layer coating on the inside walls of

MCM-41 by a relatively small molecule (e.g., water) could lead to measurable changes in a neutron diffraction experiment.

In this letter, we report observation by neutron diffraction of the saturation and desorption of contrast-matched water in the pores of MCM-41. During desorption, facilitated by air-drying the sample, we obtained a diffraction pattern that is *qualitatively* different from that of dry or fully water saturated powder. This observation allows us to infer the statistical distribution of water within the partially filled pores.

2. Experimental Section

2.1. Synthesis of MCM-41 Powder. Fumed Silica powder (99.8%, metal free, particle size of 0.07 microns) and tetramethylammonium hydroxide pentahydrate (TMAOH, 97%) were obtained from Sigma. Cetyltrimethyl ammonium bromide (CTABR, 99%) was obtained from Aldrich. TMAOH and CTABR were dissolved in distilled deionized water in a 250-mL beaker while stirring with a magnetic stirrer (500 rpm) at 30 °C until a clear solution was obtained. The silica powder was then added, and the mixture was stirred for 3 h at 30 °C. The final molar composition of the materials was 1.0 SiO_2 , 0.19 TMAOH, 0.27 CTABR, and 40 H_2O and contained 200 g of water. The mixture was aged for 24 h at room temperature and transferred into a stainless steel Viton-lined autoclave. The mixture was allowed to react in a furnace at 125 °C for 68 h, after which the autoclave was cooled under running water. The solid material was recovered by filtration, washed extensively in distilled deionized water, and dried at 45 °C overnight. Finally, calcining the sample at 650 °C for 8 h removed the organic template material, giving the powder we label the "dry sample". All the samples used for this study were drawn from this single batch of preparation.

2.2. Neutron Diffraction. Measurements were carried out at the NRU reactor, Chalk River, using the C5 spectrometer. The spectrometer was set up with a vertically focused pyrolytic graphite (PG) monochromator and a flat PG analyzer set for elastic scattering. The instrument thus measured $S(Q, \omega)$ with $\omega = 0$. Since the energy resolution of the analyzer ($\Delta E/E = 0.032$ full width at half-maximum (fwhm)) is much wider than the energy spread of the incident beam (0.012 fwhm or $\Delta\lambda/\lambda = 0.006$), the measured signal is essentially the same as the energy-integrated diffraction pattern $S(Q)$. The advantage of this setup over the conventional two-axis setup (i.e., without the analyzer) is that the background due to epithermal neutrons propagating mainly along beam channels is greatly reduced, resulting in a higher signal-to-noise ratio. The neutron wavelength λ was 2.37

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Figure 1. Neutron diffraction pattern of the dry MCM-41 powder sample (filled circles) and the instrument background measured with no sample (open circles). The background arises from air-scattering and, at very low Q , from the straight-through beam.

$\text{\AA}$, with the higher order contamination suppressed with a PG filter. Scans were performed over a Q range with equal ΔQ steps, where $Q = 4\pi \sin(\theta)/\lambda$ and 2θ is the Bragg angle.

Airtight aluminum cuvettes were used to hold the powder sample. We had a provision of mounting the cuvettes on a scale so that the sample weight could be monitored during measurements or air-drying the powder. Prior tests showed that the scale was accurate to 2 mg for up to an hour after being zeroed. Diffraction measurements were carried out with two geometries. In the first case, the inside dimensions of the cuvette were larger than the neutron beam. The effective sample volume, limited in width and height by the beam, was 2 mm wide, 30 mm high, and 4 mm along the beam. In the second case, the inside dimensions of the cuvette, smaller than the selected beam size, were 3 mm wide, 35 mm high, and 3 mm along the beam. This geometry was used exclusively for observing changes in the diffraction pattern as an originally water-saturated sample was air-dried on the spectrometer. It has the advantage of keeping the effective sample volume constant even if the packing of the powder changes as it dries. For air-drying, the design of the cuvette incorporated a special feature: its face plate (the side perpendicular to the incident beam) that provides an airtight seal can be removed and resealed. Under the face plate is a fixed stainless steel screen that contains 0.15 mm diameter holes. With the face plate removed, the screen holds the powder in place and allows airing of the entire sample space.

We first measured the diffraction pattern of as-prepared MCM-41 powder sealed in a dry N_2 atmosphere. Subsequent measurements were on samples mixed with excess H_2O (natural isotopic abundance), 99.9% pure D_2O , and a mixture of H_2O and D_2O whose scattering amplitude was adjusted (see below) to match the host silicate. Finally, we did a series of scans while the sample containing the contrast-matched water was air-dried in stages on the spectrometer.

3. Results and Discussion

Figure 1 shows the diffraction pattern of the dry sample. The prominent peak at $Q \sim 0.17 \text{ \AA}^{-1}$ is the (1,0) peak of the 2D packing of cylindrical pores in a hexagonal array. Additional peaks at higher Q values are the (1,1) and (2,0) reflections which are much weaker because of the precipitous drop in the form factor of a finite-radius cylinder. The positions of the peaks correspond to the nearest-neighbor center-to-center pore distance of 42 $\text{\AA}$. The background beyond (2,0) is significantly higher than the instrument background (measured with no sample) but is relatively weak. Since the incoherent scattering cross section of hydrogen, 80 barns, is some 20 times larger than the cross section of any other elements relevant to our sample, the low background indicates there is not much H of any form in the dry sample.

Figure 2. Neutron diffraction patterns of MCM-41 powder soaked with excess H_2O (natural isotopic abundance), with excess 99.9% pure D_2O , and with 40:60 $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture.

Figure 2a shows the patterns obtained when the powder was mixed with excess distilled water (H_2O) and 99.9% pure heavy water (D_2O). Although the incident beam size and the size of the cuvette were the same as for the dry sample, reduced scattering from the sample was observed. This could be due to the presence of liquid water between grains which would reduce the volume of MCM-41 powder contributing to diffraction. On the basis of weight measurements, we estimate this reduction of effective sample volume could lead to a 10–20% decrease of peak intensities compared to the diffraction pattern of the dry sample (Figure 1).

Within this 10–20% accuracy, the diffraction pattern of the H_2O -saturated sample is similar to that of the dry sample except that the background is much higher. The background increases also in the D_2O -saturated sample but to a lesser extent. Above-background intensity of the (1,0) peak of the D_2O -saturated sample is $\sim 1/3$ of that of the dry sample, and the apparent lack of peaks at the expected positions of (1,1) and (2,0) is consistent with those peaks reduced by a similar factor. The changes in the peak intensities and the background can be explained separately:

Background. The liquid water between powder grains causes most of the increased background. The scattering functions $S(Q)$ for both H_2O and D_2O contain short-range order (i.e., broad) peaks, but they lie well beyond our scan range. The tails of these peaks extend toward smaller Q , giving rise to the extra scattering we perceive as “background”. The strong incoherent scattering of H causes a further increase of the background seen in the H_2O -saturated sample.

Diffraction Peaks. The change in contrast between the host material and the pores causes the peak intensities to change. For thermal neutrons, the contrast is provided by spatial variation of scattering-length density (SLD), a quantity analogous to electron density for X-rays. The host material of MCM-41 is mostly SiO_2 . As an estimate, we will adopt the SLD of low-density SiO_2 (cristobalite), $3.62 \times 10^{-6} \text{ \AA}^{-2}$, for the host material. The SLD of empty pores is zero. For water-filled pores, provided there are no remaining voids, the SLD is $-0.560 \times 10^{-6} \text{ \AA}^{-2}$ for H_2O and $6.40 \times 10^{-6} \text{ \AA}^{-2}$ for D_2O . Thus, contrast matching between the water and the host material can be achieved using a 40:60 $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture for which the SLD is equal to $3.62 \times 10^{-6} \text{ \AA}^{-2}$.

Figure 2b shows the diffraction of a sample soaked with 40:60 $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixture. Clearly, all diffraction peaks have

Figure 3. Diffraction pattern of the dry MCM-41 powder sample (filled circles) and the same sample whose pores are partially filled with 40:60 H₂O/D₂O mixture (open circles). The inset shows the region of the (1,1) and (2,0) peaks on an expanded scale.

disappeared. Exactly the same result has been reported by Glinka et al.⁴ We draw the following conclusions:

1. When MCM-41 powder is mixed with excess water, the water seeps into the entire length of the pores.
2. There are neither voids nor a central hollow space remaining within each pore. The latter would be the case if the water only wets the inside walls of the pores.
3. The SLD of the host material is indeed very close to that of cristobalite, and it is relatively uniform. Without this uniformity, we would not be able to completely wipe out the diffraction peaks regardless of what ratio we mixed H₂O and D₂O.

Figure 3 shows a comparison of two diffraction patterns from the same powder, but at different stages of the adsorption/desorption cycle. Since the measurements were carried out with a cuvette that ensures that a constant amount of powder contributes to diffraction (see above), the intensities of the two scans are directly comparable. The filled circles correspond to the as-prepared dry sample. When the sample was exposed to an excess amount of 40:60 H₂O/D₂O mixture, all the diffraction peaks disappeared (same as in Figure 2b). The sample was then air-dried in stages, and scans were performed with a fixed amount of residual water sealed in the cuvette. As expected, diffraction peaks reappeared when there was no longer sufficient water to fill the pores. The first peak to reappear was the (1,0) peak; however, that is *not*, as may initially be assumed, because it is stronger than the higher order peaks and hence is easier to detect. This fact is best demonstrated by the open circles in Figure 3: although the (1,0) peak had grown to ~80% of its original strength at this relatively late stage of drying, the higher order peaks were still absent within counting statistics (see the inset). The weight ratio between the dry powder and the adsorbed water (H₂O/D₂O mixture) as determined by the on-line weighing was 1:0.13, corresponding to ~6.3% of the pore volume filled by the residual water.

We now consider how the residual water is distributed in the pores. In Figure 3 and all the scans we have taken (not shown), there is no discernible change of the width of the (1,0) peak. We conclude that partial filling of the pores does not introduce additional disorder to the overall SLD distribution, indicating that all the pores are filled, on average, to the same volume fraction and the distribution of water within the pores is well represented by a single function. Further, the absence of higher order Bragg peaks in the diffraction pattern of the partially dried

Figure 4. The schematic variation of SLD for a dry MCM-41 (solid line) where the wall thickness is $\sim 1/10$ of the pore size. The dotted curve is a sine function whose amplitude and period are adjusted to be commensurate with the host lattice. This curve is a close approximation of the SLD variation of contrast-matched water partially filling the pores.

sample indicates that the SLD distribution of the entire sample (SiO₂ + contrast-matched water) resembles very much a sine wave with no discontinuities. Such a distribution is consistent with the picture that the residual water within each pore clings to the inside wall and forms a continuous film whose thickness fluctuates over the coherence length of neutrons ($\lambda^2/\Delta\lambda$ or ~ 400 Å). Since the film is continuous, the SLD of the water near the wall remains contrast-matched to SiO₂. Because of the thickness fluctuation, the SLD decreases away from the walls and tends to a minimum at the center. At early stages of drying, it is a shallow minimum leading to a weak (1,0) peak. The minimum deepens progressively as more water leaves the pores, but the overall SLD distribution remains remarkably close to a sine wave (i.e., without pronounced discontinuities at the pore walls) even when only 6.3% of pore space is filled with water.

A sketch of the proposed model is depicted in Figure 4. For a homogeneous mixture of H₂O and D₂O, the SLD variation is simply the population density of water molecules (i.e., the number of molecules per unit volume) in an arbitrary unit. Hence, we have essentially determined the statistical distribution of water within the partially filled pores.

Further air-drying of the sample did lead to the reappearance of the higher order Bragg peaks. At the end of the air-drying (signified by stability in the measured weight of cuvette), the diffraction pattern looked identical to the original pattern of the dry sample except that the background at the high-*Q* end was ~19% higher and the above-background intensity of the higher order peaks was slightly weaker. This result indicates that most, but not all, water was removed from the pores by the air-drying process.

4. Conclusion

In the presence of excess water, the pores of MCM-41 are fully hydrated for their entire length. When the excess water is allowed to evaporate, even at room temperature, most of the incorporated water leaves the pores. However, before this final stage is reached, the water in each pore redistributes itself to form a layer clinging to the wall of the pore. With a sufficient amount of water remaining in the pores, the coverage of the layer is continuous but the thickness fluctuations develop along the pore length. The resulting population density of water molecules is a simple radial function with a minimum at the center and a maximum near the pore wall. This simple distribution function holds for a wide range of water content, from saturation down to ~6.3% of available pore space filled with water.