

Electronic Supplementary Information: Diffusive and Rotational Dynamics of Condensed n -H₂ Confined in MCM-41

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Abstract

The MCM-41 sample used in the neutron scattering study was characterized using a combination of X-ray diffraction and N₂ adsorption isotherm measurements. This document presents and analyzes the characterization data for this sample. In particular, the geometrical properties of the pore space are determined.

1 Sample Characterization

The sample porous material used in the neutron scattering experiment was characterized using a combination of X-ray powder diffraction and N₂ gas sorption isotherm measurements. The X-ray scattering data establishes the phase purity of the sample and the crystallinity of its pore array. The N₂ gas sorption measurements at 77 K verify the open, tubular geometry of the pores. They also permit reliable estimates of the pore size distribution, specific surface area, and total pore volume.

X-ray scattering measurements were performed with a Rigaku RU-200 diffractometer set up in a transmission geometry. The rotating copper anode source was operated at 20 kV and 10 mA. The emerging X-ray beam passed through a 2° Soller slit package. The MCM-41 sample was tightly packed into a 1 mm kapton tube located at the center of the diffractometer, and the sample was measured under ambient conditions. Cu K α radiation ($\lambda = 1.54 \text{ \AA}$; $E = 8.04 \text{ keV}$) was selected using the (002) Bragg reflection of a graphite monochromator located after the sample position. The measured diffraction intensities do not include geometrical, absorption, or polarization corrections because an analysis of peak intensities is not presented here.

The mesopores of MCM-41 are highly organized within a regular, hexagonal lattice structure belonging to plane space symmetry group $p6mm$. As shown in Figure 1, the X-ray scattering data shows a series of clearly discernible small-angle powder diffraction peaks. If the center-to-center spacing of the pores is a then the (hk) Bragg reflection is located at wavevector transfer $Q_{(hk)} = (4\pi/a\sqrt{3}) \sqrt{h^2 + k^2 + hk}$.

The diffraction peaks are located at: $Q_{(10)} = 0.15 \text{ \AA}^{-1}$; $Q_{(11)} = 0.27 \text{ \AA}^{-1}$; $Q_{(20)} = 0.31 \text{ \AA}^{-1}$; $Q_{(21)} = 0.41 \text{ \AA}^{-1}$. The centre-to-centre spacing of the pores a , or lattice constant, is 47 \AA . In the low incident energy ($E_i = 1.6 \text{ meV}$) neutron scattering measurements performed with the Cold Neutron Chopper Spectrometer, four Bragg reflections were observed on the low angle detectors in positions consistent with the X-ray diffraction measurements.

N_2 adsorption isotherm measurements were performed using a Micromeritics ASAP 2020 Physisorption Analyzer. A mass of 0.22 g of the MCM-41 sample used in the neutron scattering experiment was used. The liquid nitrogen bath had an average temperature of 77.2 K . The sample was degassed by an oil free vacuum pump to a hard vacuum while being heated at $120 \text{ }^\circ\text{C}$ for 12 hours . Figure 2 plots the specific molar amount of adsorbed N_2 against the relative vapour pressure P/P_0 , where P_0 is the saturated vapour pressure of the bulk liquid.

The N_2 adsorption isotherm is Type IV according to the 1985 International Union of Pure and Applied Chemistry classification [K. S. W. Sing *et al Pure Appl. Chem.* **57**, 603 (1985)]. The adsorption isotherm can be separated into three sections according to the pore filling mechanism. First, up to a relative pressure $P/P_0 \approx 0.3$, the adsorption proceeds by continuous film growth on the pore walls of MCM-41. Second, within the pressure range $0.30 \leq P/P_0 \leq 0.40$, capillary condensation takes place within the core volume of the primary mesopores. Finally, there is a rapid approach to saturated vapour pressure as the larger, secondary mesopores are filled with liquid N_2 . There is no adsorption-desorption hysteresis loop associated with the capillary condensation branch.

The specific surface area of the MCM-41 sample can be determined from an analysis of the multilayer film growth part of the adsorption isotherm while the pore size distribution can be extracted from the capillary condensation branch. The N_2 monolayer capacity of the MCM-41 sample determined by a Brunauer-Emmett-Teller (BET) plot using pressures $0.05 \leq P/P_0 \leq 0.25$ is approximately 10.0 mmol/g . Given the accepted projected area of N_2 molecules is 16.2 \AA^2 , the specific surface area of the sample is estimated to be $979 \text{ m}^2/\text{g}$. The value of the BET constant C is 99 , which falls in the typical range 80 - 150 for mesoporous silica [F. Rouquerol *et al Adsorption by Powders and Porous Solids: Principles, Methodology, and Applications* (Academic Press, San Diego, 1999)]. The pore size distribution was calculated from the capillary condensation branch using the Kruk-Jaroniec-Sayari method [M. Kruk *et al Langmuir* **13**, 6267-6273 (1997)]. The pore size distribution, shown as an inset to Figure 2, was fitted to a Gaussian having a centre at 34.5 \AA and a full-width at half-maximum of 2.8 \AA . This corresponds to a polydispersity index of 0.034 . The pore walls have a thickness of 12 \AA . The total pore volume, determined by the volume of liquid nitrogen adsorbed at $P/P_0 = 0.99$, is 0.92 cc/g .

To perform a more thorough analysis of the N_2 adsorption isotherm data, we have also constructed its α_S -plot using standard reference measurements [M. Jaroniec *et al Langmuir* **15**, 5410-5413 (1999)]. When constructing an α_S -plot, one plots the amount of gas adsorbed on the porous solid under study

as a function of the amount adsorbed s on the standard reference material. In this case, the reference material is a macroporous silica which shares a common surface chemistry with MCM-41. In regions where the α_S -plot is linear with a positive slope, the adsorption of gas to the sample under study proceeds by the same mechanism as adsorption on the standard reference material. This means either multilayer film growth or the filling of large mesopores or macropores.

The α_S -plot for the MCM-41 sample used in the neutron scattering experiments is shown in Figure 3. As can be seen by the initial linear portion of the α_S -plot, shown in blue, the initial adsorption of N_2 proceeds by continuous, multilayer film growth. The fact that this portion of the plot has a zero intercept implies that there are no micropores present within our MCM-41 sample. The slope of the blue line is proportional to the total surface area of the sample $S_t = 920 \text{ m}^2/\text{g}$, a value somewhat less than the BET estimate. The filling of the secondary mesopores also produces a linear region, shown in red, within the α_S -plot. Its slope is proportional to the surface area external to the primary mesopores $S_{\text{ext}} = 87 \text{ m}^2/\text{g}$ and its intercept yields the primary mesopores volume $V_p = 0.69 \text{ cc/g}$. The surface area of the primary mesopores is given by: $S_p = S_t - S_{\text{ext}} = 833 \text{ m}^2/\text{g}$. The diameter D_p of the primary mesopores, estimated from their surface-to-volume ratio $D_p = 4V_p/S_p$, is 3.5 nm in good agreement with the calculated pore size distribution.

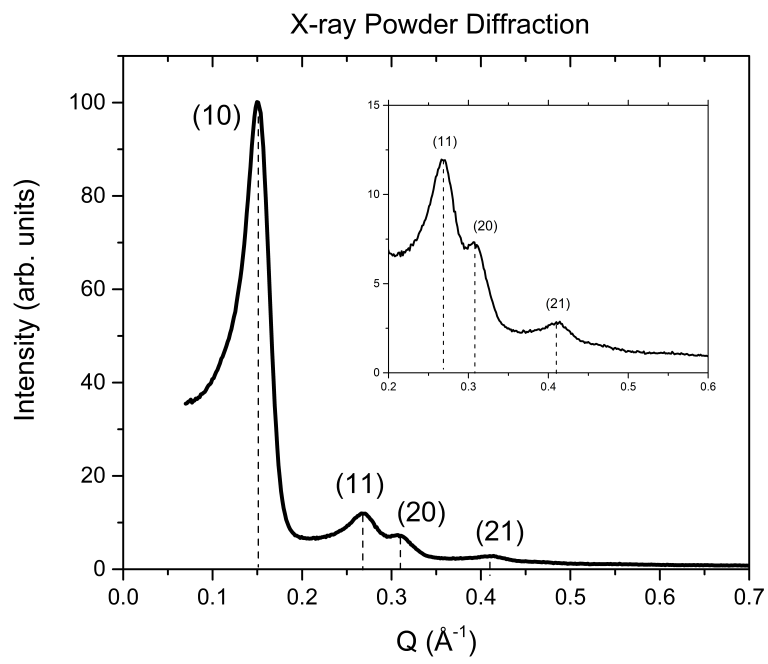


Figure 1: The mesopores are arranged in a two-dimensional hexagonal lattice structure. As a result, the small-angle X-ray diffraction pattern consists of a series of peaks determined by the centre-to-centre spacing of 4.7 nm.

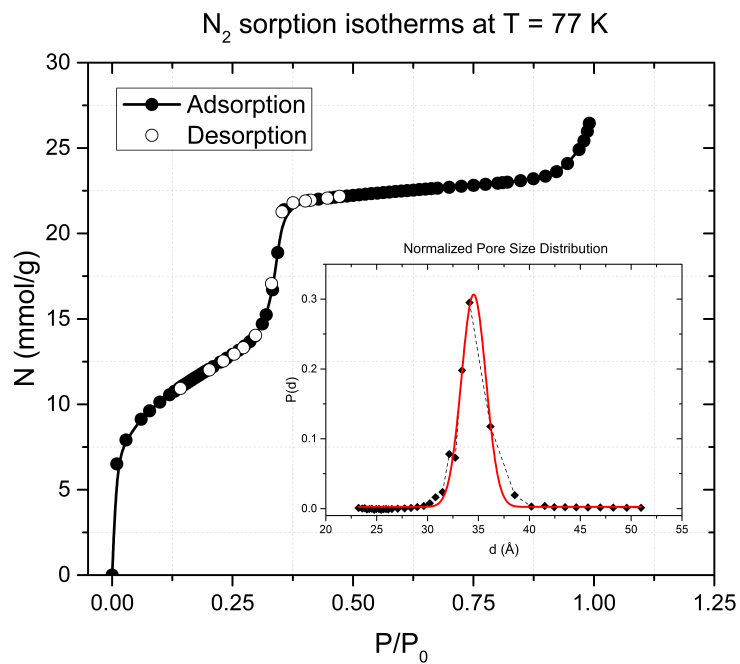


Figure 2: The N₂ adsorption isotherm of the MCM-41 sample at 77 K. The inset plots the normalized pore size distribution which is centered at 3.5 nm and has a full-width at half-maximum which is somewhat less than 0.3 nm. The BET specific surface area of the sample is 979 m²/g.

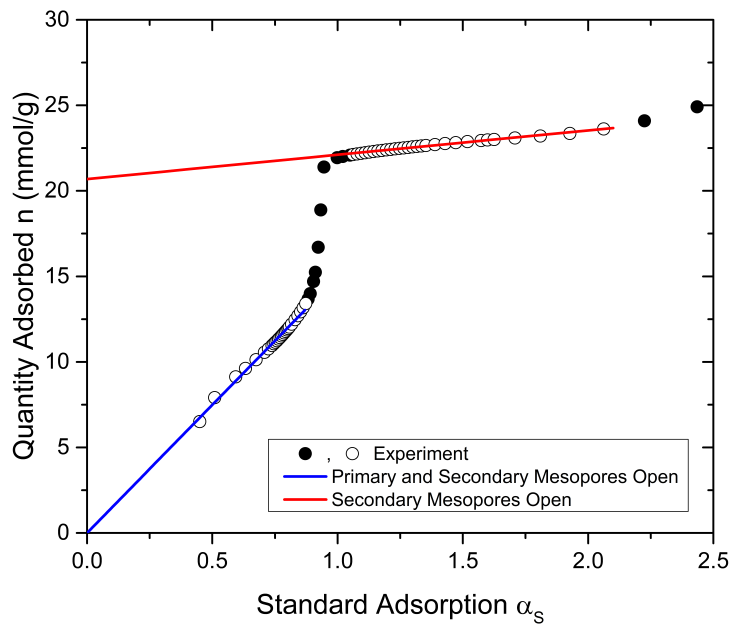


Figure 3: This α_S -plot demonstrates that the N_2 adsorption to the MCM-41 sample can be separated into three distinct regions according to the pore filling mechanism, as described in the text of this Electronic Supplementary Information. The closed and open circles designate experimental data, while the open circles denote points within linear regions. The blue line demarcates the initial region where multilayer film growth takes place as N_2 gas is adsorbed. The zero intercept implies that there are no micropores in the sample since there is no prior volume to fill before multilayer film growth can take place.