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Research paper

Density profile of nitrogen in cylindrical pores of MCM-41

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ABSTRACT

A straightforward approach using radiation scattering (X-ray or neutron) combined with atomistic modelling is used to accurately assess the pore dimensions in the porous silica, MCM-41. The method is used to calculate the density profile of nitrogen absorbed in this material at a variety of fractional pressures, p/p_0, where p_0 is the saturated vapour pressure, up to $p/p_0 = 0.36$ at T = 87 K in the present instance. At this pressure two distinct layers of liquid nitrogen occur on the silica surface, with a relatively sharp gas-liquid interface. It is suggested surface tension effects at this interface strongly influence the growth of further layers.

1. Introduction

The question of how to characterise the surface and pore dimensions of a porous material has been the subject of a debate which extends over many decades, and which even now is not fully resolved [1–7]. The so-called 'BET' method [1] involves measuring the absorbed volume of gas, v, as a function of applied relative pressure, p/p_0, where p_0 is the saturated vapour pressure at the temperature of the experiment, then plotting the value of $\frac{p}{v(p-p_0)}$ versus $\frac{p}{p_0}$, for moderate values of $\frac{p}{p_0} \leqslant 0.3$. Then, by making some simplifying assumptions about how gas is adsorbed on the surface, the slope and intercept of this graph give the values of v_m, the volume of a complete single molecule layer, and a parameter c which is related to the difference in heat energy released when laying down the first molecular layer, compared to that for subsequent layers. In principle, the value of v_m, is a measure of the surface area available for adsorption if an assumption about the thickness of the first layer is available.

Subsequently, Shull [2] discusses the limitations of this approach as the pressure approaches the saturation vapour pressure in narrow capillaries, and discusses a modification to the Kelvin equation for capillary condensation originally proposed by Cohan [8]. The latter author also gives a cogent explanation of the hysteresis that occurs when absorbing and desorbing fluids from cylindrical pores. At this stage it becomes clear that BET theory will underestimate the pressure, and therefore overestimate the layer thickness, at which capillary condensation would occur. Shull further goes on to show how experimental gas adsorption data on 'large' crystals can be used to make up for the deficiencies in the BET theory. Later, Barrett, Joyner and Halenda (BJH) [3] showed how, for cylindrical pores, the adsorption/desorption isotherms might be used to estimate the radius of the pores.

Implicit in all of these approaches is the idea that gas adsorbs on the surface of the pore in a two-stage process, namely 'physical adsorption' in which one or more molecular layers of adsorbate are built up, presumably at liquid-like density, on the substrate surface, followed by capillary condensation at high enough pressure, in which the pore becomes completely filled with liquid. The volume of gas emitted when this capillary condensate desorbs, combined with the volume of liquid remaining as physically absorbed, is then used to estimate the volume of the pore, and hence its dimensions. Both Shull and BJH use this information further to estimate the pore size distribution approximately. Given that the theories being used here take no account of the likely fluid-fluid and fluid-wall interactions (other than via the surface tension of the liquid-gas interface), and that real pore walls are unlikely to be smooth, it is surprising that these methods persist to the present day as standard procedures for characterising porous materials.

Much more recently, approaches to characterising the properties of a fluid on contact with a wall which take some account of the forces of interaction in a mean field sense have been developed using density functional theory [4–7,9]. These methods appear to give a much more realistic and quantitative account of

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experimental absorption data, and point to the limitations of the Kelvin equation at small pore radii. In particular, Ravikovitch [5] observes that the BJH method can underestimate pore diameters by as much as 10 Å or more for smaller pore sizes (see Fig. 9 of that paper), a conclusion which is born out by the present work. Unfortunately these more sophisticated methods do not lend themselves readily to non-expert execution and interpretation and so it is likely the simpler BET/BJH methods will remain in vogue for the purposes of elementary laboratory analysis. As a result confusion has continued right up to the present time on the true nature of the pores in MCM-41. For example a series of experiments that were aimed at exploring the structural and dynamical properties of water confined in MCM-41 repeatedly states the pore diameter to be of order 15 Å [10–13]. Yet the evidence obtained by analysing neutron diffraction data from the Bragg peaks that arise from the hexagonal arrangement of pores in these materials [14,15], and see below, suggests that the pores must be larger than the stated BJH values in reality.

Equally uncertain is the degree of micro-porosity in these materials. This relates to the extent to which fluid molecules can move into the underlying silica matrix, perhaps even exchange with molecules in neighbouring pores. One study [16] used *n*-nonane to block the possible micropores in MCM-41 and found essentially no change to the adsorption/desorption isotherms as a result. The conclusion was that MCM-41 is likely to have negligible microporosity. Yet in attempts to build atomistic models of the amorphous silica in MCM-41, it proves almost impossible to exclude some degree of fluid penetration into the substrate [17] if the latter is assumed amorphous. In this context, the *n*-nonane test might be relevant for demonstrating that larger molecules do not penetrate the amorphous silica substrate, but might not be relevant for smaller molecules like H_2O and N_2.

Another factor in these materials is the likely roughness of the pore surface. The pore template in MCM-41 is laid down by a cylindrical aqueous micelle, and atomistic models of spherical micelles highlight the relatively rough nature of the surfaces that are created by this technique [18]. Atomistic computer simulation of the pores in MCM-41 also confirms they are likely to be relatively rough, and hence BET analysis might give incorrect results [19]. In fact the conclusions of this latter paper closely matches the conclusions of the present work to be presented below.

What therefore emerges in this analysis is that despite the extensive studies that have been done over many years, there remains a great deal of uncertainty about the nature of these porous materials at the molecular level. Most likely each instance of MCM-41 has a slightly different morphology to the next, and this will make obtaining consistent results from gas absorption and similar experiments hard to obtain. Most important of all however is the fact that the pore diameter and surface structure needs to be carefully ascertained before any experiments are performed with these materials. To this end we propose here that a (relatively) simple procedure using X-ray or neutron diffraction to measure the low-wave-vector (Q) and high wave-vector diffraction pattern, followed by atomistic modelling of the measured data, can go a long way towards determining the pore volume, likely structure of the substrate, and degree of pore-size distribution. Typically in a good sample of MCM-41 one observes about 4 main Bragg diffraction peaks [5,20] in the low Q region, while the high Q region is sensitive to the local arrangement of silica. Atomistic fitting to these data already gives a lot of direct information on the structure of these materials and eliminates much of the uncertainty and speculation that comes from more indirect methods. At the very least it should corroborate the indirect evidence from gas adsorption/desorption isotherms.

In the sections that follow, we describe the experimental and atomistic modelling techniques that were employed here, then perform a study of dry MCM-41 to obtain the pore diameter. This is followed by a study of nitrogen absorbed on MCM-41, where a clear layering of the nitrogen is observed. The paper finishes with some concluding remarks.

2. Experimental

Samples of MCM-41 were obtained from Sigma-Aldrich and used without further purification. We understood these had been synthesized with C16TAB surfactant. Nitrogen adsorption and desorption isotherms were interpreted using the BJH method, from which it was concluded the average nominal pore diameter by this method was 2.24 nm, which was within the specification supplied by the manufacturer. A mass of 0.611 g of MCM-41 was placed in a flat plate container made from an alloy of Ti and Zr in the mole ratio 0.676:0.324. This alloy contributes almost zero coherent scattering to the diffraction pattern because of the near cancellation of the Ti and Zr neutron scattering lengths at this composition. The wall thickness was 1 mm, and the space between the walls occupied by the sample was 2 mm. The lateral dimensions of the container, which was placed at right angles to the neutron beam, was 40 mm high by 35 mm wide. A gas handling rig was connected to the cell to control the amount of nitrogen absorbed, and the whole assembly was mounted on a closed cycle helium refrigerator to control the temperature within ±1 K. Total neutron scattering measurements were performed on the NIMROD diffractometer [21] at the ISIS Spallation Neutron Source.

The experimental protocol was as follows. With the sample initially under vacuum, its temperature was lowered to 123 K and held there for around 5½ h while the neutron diffraction pattern of the dry sample was measured. Then nitrogen was introduced at 1 bar, corresponding to a relative pressure $p/p_0 = 0.035$ and the diffraction pattern monitored repeatedly for short periods of around 6 min each. Subsequently, holding the nitrogen pressure stable in the range 0.73–1.0 bar, the temperature was ramped down to 87 K over a period of approximately 4 h, corresponding to a final relative pressure of $p/p_0 = 0.368$. These relative pressures are calculated on the basis of the stated saturated vapour pressure of nitrogen at these temperatures [22]. Finally the sample was held under these conditions for a further 5 h, during which time there was only very slight further absorption of nitrogen. Fig. 1 (top) shows the temperature and the relative nitrogen pressure as a function of elapsed time. Unfortunately no data are available on the actual amount of nitrogen absorbed by the sample in this case.

The neutron scattering data were subject to the standard corrections for background scattering, multiple scattering, container scattering, and self attenuation, and put on an absolute scale of differential scattering cross section (DCS) per atom of material, using the scattering from a standard 3 mm vanadium slab [23]. In the present instance, because the material is a powder, while the pore diameter and the atomic number density are only known approximately, it is necessary to supply a correction factor to the data which is derived from the expected value of the DCS at high Q, that is the single atom scattering. This value is given by the expression for the total DCS of a material:-

$$\frac{d\sigma}{d\Omega}(Q) = \sum_{\alpha} c_\alpha b_\alpha^2 + \sum_{\alpha,\beta \geqslant \alpha} (2 - \delta_{\alpha\beta}) c_\alpha c_\beta b_\alpha b_\beta \left\{ 4\pi\rho \int_0^\infty r^2 (g_{\alpha\beta}(r) - 1) \frac{\sin Qr}{Qr} dr \right\} \quad (1)$$

where c_α and b_α are the atomic fraction and neutron scattering length of atom α, ρ is the total atomic number density of the material respectively, and $g_{\alpha\beta}(r)$ the site-site radial distribution function between sites α and β, with Q the wave vector change in the scattering experiment. The first term on the LHS of (1) is the single atom

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