

Physisorption of Nitrogen and Oxygen by MCM-41, a Model Mesoporous Adsorbent

Peter J. Branton, Peter G. Hall and Kenneth S. W. Sing

Department of Chemistry, Exeter University, Exeter, UK EX4 4QD

Physisorption measurements of nitrogen and oxygen reveal that MCM-41 has a well defined mesoporous structure and is a highly promising model adsorbent.

It is well known that mesoporous adsorbents (*e.g.* silica gels and activated aluminas) generally possess broad ranges of irregular pores. The recent disclosures by Mobil scientists^{1,2} of the synthesis of a new family of highly uniform mesoporous materials is therefore of great potential significance. One member of this family, MCM-41, which has been shown to exhibit an hexagonal array of uniform mesopores, has been prepared by the hydrothermal conversion of an aluminosilicate gel in the presence of a quaternary ammonium surfactant. It is claimed¹ that MCM-41 can be synthesised with uniform channels in the approximate range 1.5–10 nm, a typical product having a pore diameter of about 4 nm. However, the few adsorption isotherms reported so far do not appear to have been determined in sufficient detail to confirm the proposed very narrow range of mesopore size.

The work reported here is part of a systematic investigation of the adsorption of various gases and vapours by samples of MCM-41 taken from a batch of material prepared at Mainz University by Keung and Unger.³ Other related adsorption measurements have been undertaken by Reichert and Unger⁴ and the results of our combined studies will be reported in detail elsewhere.

The adsorption isotherms of nitrogen and oxygen reported here were determined at 77 K by using a conventional volumetric technique. Preliminary work involved the investigation of the reproducibility of the nitrogen isotherm after outgassing at temperatures of 150, 200 and 300 °C. Excellent agreement was obtained as indicated in Fig. 1 and the stability of the adsorbent was also demonstrated. The most striking features of the nitrogen isotherm are the sharp step commencing at $P/P_0 = 0.41$ and the reversibility (*i.e.* the absence of adsorption hysteresis). To achieve reversibility in the region of the step it was found necessary to allow at least 1 hour for each desorption point to reach equilibrium.

The long plateau of nitrogen adsorption at $P/P_0 > 0.46$ is a clear indication that pore filling was restricted to the narrow range of $P/P_0 = 0.41$ – 0.46 . Taking the inflection point at $P/P_0 = 0.43$, assuming the application of the Kelvin equation and correcting for multilayer thickness, we obtain 3.32 nm as the effective mean pore diameter.

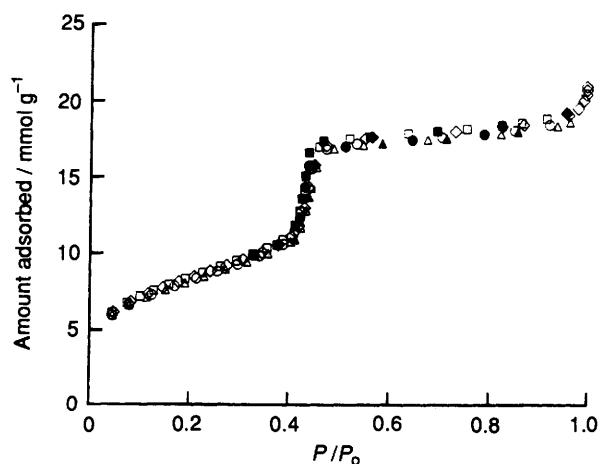


Fig. 1 Adsorption of N₂ on MCM-41 at 77 K. Filled symbols denote desorption; \square \diamond Sample outgassed at 200 °C for 4 h; \circ \triangle sample outgassed at 300 °C for 4 h.

Nitrogen adsorption data on non-porous hydroxylated silica⁵ have been used to construct the comparison plot in Fig. 2. Three well defined stages can be identified: A, monolayer-multilayer adsorption on the pore walls; B, reversible capillary condensation; C, multilayer adsorption on the external surface. The fact that the linear region A can be back-extrapolated to the origin confirms that there was no detectable amount of micropore filling.⁵ This result indicates that the Brunauer–Emmett–Teller (BET) area (655 m² g⁻¹) can be regarded as the extent of 'real' surface available to nitrogen.

The oxygen isotherm in Fig. 3 also exhibits a distinctive step, but in this case it is associated with a hysteresis loop. Pore filling and emptying now occur over the range of $P/P_0 = 0.34$ – 0.44 , which would correspond to an approximate pore diameter range of 3.0–3.7 nm (again based on the application of the Kelvin equation with a multilayer thickness correction).

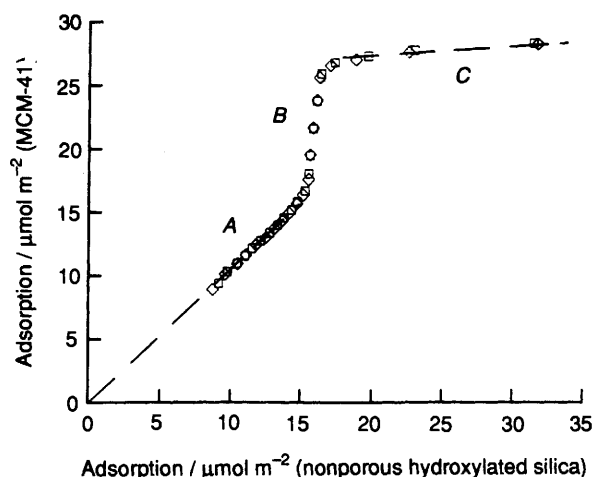


Fig. 2 Comparison of adsorption of N₂ at 77 K on MCM-41 and a nonporous hydroxylated silica: 2 runs; samples were outgassed for 4 h at 200 °C between runs

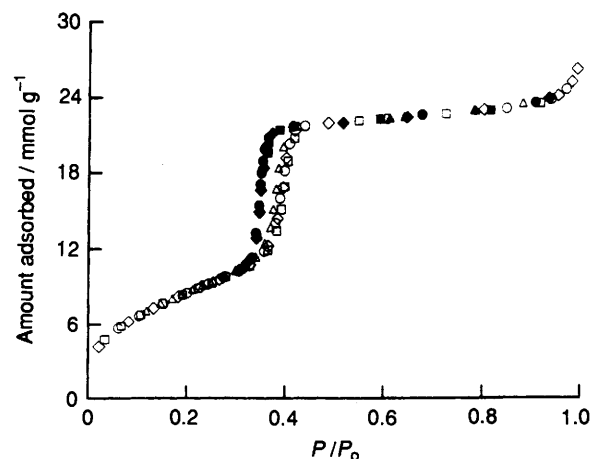


Fig. 3 Adsorption of O₂ on MCM-41 at 77 K. Filled symbols denote desorption; samples were outgassed at 200 °C for 4 h between runs.

If the effective area of the oxygen molecule is taken⁶ as 14.3 \AA^2 , we find that the oxygen isotherm gives a BET area of $648 \text{ m}^2 \text{ g}^{-1}$, in remarkably good agreement with that obtained by nitrogen adsorption.

It is evident that MCM-41 has unique properties and shows considerable promise as a model mesoporous adsorbent. The Mainz sample exhibits an extremely large and stable specific area ($655 \text{ m}^2 \text{ g}^{-1}$) which is apparently located within a narrow range of mesopores (range of effective diameter, 3.2–3.6 nm). The nitrogen isotherm (at 77 K) is of unusual character: it is a reversible Type IV isotherm (in the IUPAC classification⁷). Thermodynamic reversibility of adsorption–desorption would appear to be of considerable advantage, but it must be kept in mind that the position of the step appears to coincide with the region of instability of the liquid nitrogen meniscus.⁸ Therefore, the application of the Kelvin equation may give a false assessment of the true pore size distribution. To explain these effects, further work will include the determination of nitrogen isotherms at different temperatures and the use of other adsorptives.

We thank M. Keung and K. Unger for the MCM-41 and one

of us (P. J. B.) thank the SERC for the award of a research grant.

Received, 6th May 1993; Com. 3/02616G

References

- 1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
- 2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- 3 M. Keung and K. Unger, unpublished work.
- 4 H. Reichert and K. Unger, personal communication.
- 5 M. R. Bhambhani, P. A. Cutting, K. S. W. Sing and D. H. Turk, *J. Colloid Interface Sci.*, 1972, **38**, 109.
- 6 S. J. Gregg and K. S. W. Sing, *Adsorption Surface Area and Porosity*, 2nd edn., Academic Press, New York, 1982, p. 82.
- 7 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603.