Physisorption of oxygen in narrow mesopores

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Received (in Cambridge, UK) 29th January 1999, Accepted 16th February 1999

Pore filling by oxygen takes place reversibly at 77 K in pores of effective width of *ca.* 2.6 nm, whereas hysteresis is involved in the filling (by capillary condensation) of wider pores; it appears that the oxygen meniscus becomes unstable at cylindrical pore widths $<$ *ca.* 2.9 nm.

The development of MCM-41 and other highly ordered mesoporous materials over the past decade has attracted much attention. Nitrogen adsorption measurements[1–3] at 77 K on a number of these materials have shown that the pore filling of narrow cylindrical mesopores (of effective pore width *ca.* 2–4 nm) can occur reversibly. Nitrogen isotherms given by typical 4 nm samples of MCM-41 exhibit steep and reversible pore filling risers at P/P_0 *ca.* 0.40–0.44, whereas the reversible filling of 2.5 nm pores occurs less sharply (at P/P_0 *ca.* 0.2–0.34). Samples containing wider pores always appear to give type H1 or H2 hysteresis loops.[4] These observations are consistent with the fact[5] that the lower closure points of many nitrogen hysteresis loops are located at P/P_0 *ca.* 0.42 and indicate that the mechanism of mesopore filling is dependent on the pore size.

Although nitrogen continues to be the preferred adsorptive for the characterization of porous solids, it is of interest to investigate the low-temperature adsorptive behaviour of other gases. We have studied oxygen adsorption at 77 K on a number of ordered materials comprising narrow distributions of uniform mesopores with mean pore diameters ranging from *ca.* 2 to 7 nm. Recently determined oxygen isotherms on two of these adsorbents (a narrow-pore version of MCM-41[6] and FSM-12, a modified kanemite[3]) are shown in Fig. 1 and 2, together with the corresponding α_s plots (with non-porous hydroxylated silica taken as the reference adsorbent). It can be seen that the isotherm on FSM-12 in Fig. 1 is completely reversible whereas that on the MCM-41 in Fig. 2 has a narrow type H1 hysteresis loop.

The surface areas of FSM-12 and the MCM-41 (930 and 1170 m^2 g^{-1}, respectively) have been obtained by the BET-nitrogen method and analysis of the nitrogen α_s plots. By assuming these areas to be confined to the walls of non-intersecting cylindrical pores and taking the mesopore volumes as the equivalent volumes of liquid nitrogen adsorbed at $P/P_0 = 0.95$, we arrive at values of the mean pore diameter of 2.6 nm for FSM-12 and 2.9 nm for the MCM-41. If we now make the usual assumption that the same areas are available for oxygen adsorption, we obtain the apparent molecular area, $\sigma(O_2)$, values of 0.142 and 0.149 nm^2 for FSM-12 and the narrow-pore MCM-41.

With the exception of the 2.9 nm sample of MCM-41, all the ordered mesoporous adsorbents studied so far have given $\sigma(O_2) = 0.143 \pm 0.002$ nm^2 (in agreement with the value originally adopted by Brunauer and coworkers[7]). It must be kept in mind that the narrow-pore MCM-41 has a very large specific surface and an appreciable pore volume (0.87 cm^3 g^{-1}) and therefore the pore walls must be extremely thin. It appears likely that this has resulted in some distortion of the surface structure, which could account for the slightly higher value of $\sigma(O_2)$.

The absence of narrow micropores is evident from the form of the α_s plots in Fig. 1 and 2. The upward deviations from linearity begin at similar relative pressures (*i.e.* P/P_0 *ca.* 0.1), but the upswing is clearly more pronounced in Fig. 2. Thus, pore filling by the 2.9 nm MCM-41 has occurred mainly over the range P/P_0 *ca.* 0.13–0.28, which would correspond to a corrected Kelvin diameter range of 2.2–3.5 nm. The apparent consistency of this range with the estimated value of 2.9 nm for the mean pore width may be misleading since the reliability of the Kelvin equation is questionable when applied to such narrow pores.[4]

The position of the lower closure point of the narrow hysteresis loop in Fig. 2 cannot be specified precisely, but it appears to be in the region of P/P_0 *ca.* 0.2. It is too early to claim that a mean pore diameter of 2.9 nm is close to the limit of stability of the oxygen meniscus at 77 K. However, it is already clear that the smaller pores in FSM-12 are not filled by the classical mechanism of capillary condensation. Furthermore, all

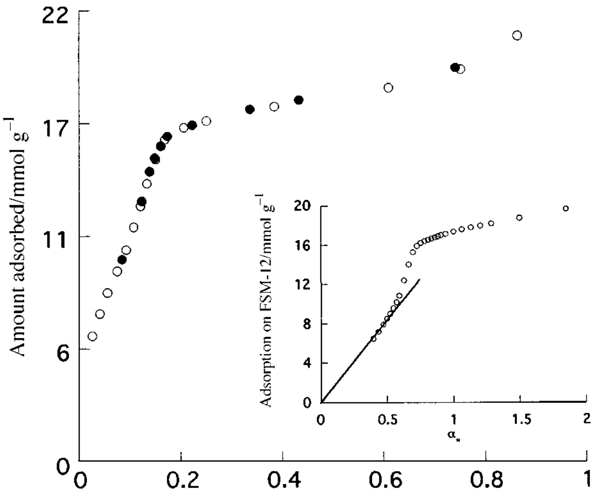

Fig. 1 Adsorption of oxygen at 77 K on FSM-12. Different symbols denote different runs. Open symbols denote adsorption, closed symbols denote desorption.

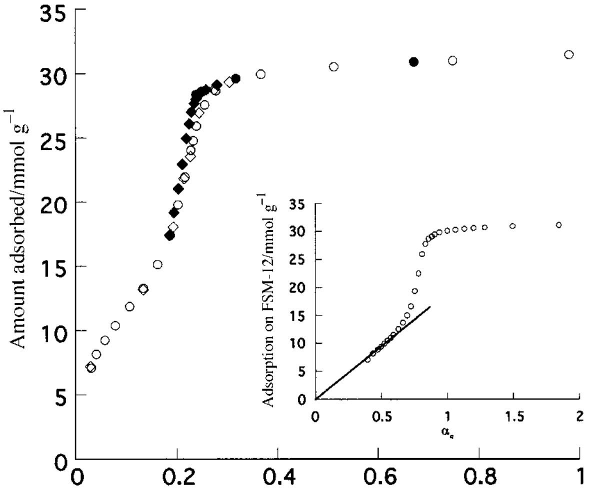

Fig. 2 Adsorption of oxygen at 77 K on MCM-41. Different symbols denote different runs. Open symbols denote adsorption, closed symbols denote desorption.

the ordered materials of wider pore-width studied so far have given hysteresis loops at relative pressures higher than 0.2. The results reported here indicate the distinctive nature of oxygen adsorption at 77 K, but more work will be required to establish its usefulness for the characterization of porous materials.

We should like to thank U. Ciesla and S. Schacht for providing the 2.9 nm sample of MCM-41.

Notes and references

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1 P. J. Branton, P. G. Hall, K. S. W. Sing, H. Reichert, F. Schuth and K. K. Unger, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2965.
2 P. L. Llewellyn, Y. Grillet, F. Schuth, H. Reichert and K. K. Unger, *Microporous Mater.*, 1994, **3**, 345.
3 P. J. Branton, K. Kaneko, N. Setoyama, K. S. W. Sing, S. Inagaki and Y. Fukushima, *Langmuir*, 1996, **12**, 599.
4 F. Rouquerol, J. Rouquerol and K. S. W. Sing, *Adsorption by Powders and Porous Solids*, Academic Press, London, 1999, p. 417.
5 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, New York, 2nd edn., 1982, p. 154.
6 U. Ciesla, S. Schacht, G. D. Stucky, K. K. Unger and F. Schuth, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 541.
7 K. M. Hanna, I. Odler, S. Brunauer, J. Hagymassy and E. E. Bodor, *J. Colloid Interface Sci.*, 1973, **45**, 27.

Communication 9/00795D