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Adsorption of Carbon Tetrachloride by 3.4 nm Pore Diameter Siliceous MCM-41: Isotherms and Neutron Diffraction

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Abstract. Adsorption isotherms of carbon tetrachloride at temperatures between 273 and 323 K have been determined on the pure silica form of MCM-41 of pore diameter ca. 3.4 nm. All isotherms were of Type V, the isotherms at 273, 288 and 303 K showing hysteresis loops, whereas the isotherm at 323 K was completely reversible. Despite the questionable validity of the Kelvin equation when applied to narrow mesopores, changes in the relative pressure positions of capillary condensation and evaporation as a function of the temperature appear to be well described. Neutron diffraction measurements at 200 and 273 K show significant changes in the physical properties of the adsorbed CCl_4 in the MCM-41 from those of bulk adsorbate. The results also suggest a highly heterogeneous surface and appear to show some flexibility in the pore walls upon pore filling. The conditions required for first order reversible capillary condensation are discussed.

Keywords: mesoporous silica, adsorption isotherm measurements, capillary condensation, neutron diffraction

Introduction

A new family of ordered mesoporous materials (designated MCM-41 or M41S) was developed by Mobil scientists in 1992 (Kresge et al., 1992; Beck et al., 1992). Their claim that the new adsorbents contained regular hexagonal arrays of controlled tubular channels immediately attracted considerable interest. Detailed gas adsorption studies have since been undertaken concentrating on MCM-41 materials of pore diameter ca. 2–4 nm (Rathousky et al., 1995; Kruk et al., 1997; Naono et al., 1997; Morishige et al., 1997; Ravikovitch et al., 1997).

Previous work (Branton et al., 1993, 1994, 1995a, 1995b) on a batch of 4 nm aluminosilicate MCM-41 revealed that the adsorption isotherms of nitrogen, argon, oxygen, carbon dioxide, sulphur dioxide and lower alcohols were all of well-defined Type IV in the IUPAC classification (Sing et al., 1985). In each case, mesopore filling and emptying occurred over a narrow range of relative pressures, but the complete reversibility of the nitrogen isotherm at 77 K appeared to be unique (Branton et al., 1993, 1994).

We report here the adsorption isotherms of carbon tetrachloride (at 273, 288, 303 and 323 K) on a pure silica form of MCM-41 with a mean pore diameter of ca. 3.4 nm (Branton et al., 1997). Capillary condensation of the liquid adsorbate is unlikely to occur in its classical form in pores of this size. On the other hand, the pores are too wide to allow any significant overlap of the adsorbent-adsorbate interactions, which would give rise to primary micropore filling (Gregg and Sing, 1982).

The nitrogen isotherm at 77 K on this material has previously been reported (Branton et al., 1997). Carbon tetrachloride was chosen as an adsorptive

complementary to nitrogen because of its molecular size and associated high polarizability. It should be possible to gain a better understanding of the intermediate stages of physisorption between cooperative filling of larger micropores (i.e., Dubinin's (1997) supermicropores) and capillary condensation in small mesopores. Furthermore, the effect of temperature on the isotherm character (particularly on the shape and size of any hysteresis loop) can be readily studied by the measurement of a number of isotherms of carbon tetrachloride at different temperatures.

In addition to the isotherms, neutron diffraction has been used to study the adsorbed CCl_4 and the pore structure. Previous diffraction studies include an investigation of adsorbed hydrogen (Edler et al., 1997a) and methane (Edler et al., 1996) in MCM-41.

Experimental

Following the work of Ryoo and Kim (1995), it is possible to produce higher ordered MCM-41 by adjustment of the pH during the synthesis. The MCM-41 used in the current work was prepared using a slight modification of the synthesis of Edler et al. (1997b) which showed seven reflections in the XRD pattern. A sodium silicate solution (Aldrich, ∼14% NaOH, ∼27% SiO_2) was used as silica source and cetyltrimethylammonium bromide (CTAB, Fluka, 98%) was used as template. The molar composition of the initial start gel was 1.00 CTAB/1.95 SiO_2/0.41 H_2SO_4/140 H_2O. The gel was heated in an autoclave at 100°C for 24 h after which it was titrated with sulphuric acid (1 M) in order to maintain a pH of 10. This procedure was repeated a further three times. The gel was then water washed, filtered, dried and calcined at 500°C for 18 h.

A manual gravimetric technique based on the quartz spring balance of McBain and Bakr was used for the determination of the CCl_4 adsorption isotherms. Outgassing was undertaken at 110°C until a residual pressure $<4 \times 10^{-4}$ Torr was attained. A water bath was used for the temperature control during the measurement of the isotherms and was accurate to ±0.05°C. Pressures were recorded using a baratron gauge accurate to ±0.1 Torr. A sample mass of ca. 50 mg was used and increases in mass of 0.02 mg could be determined by using a cathetometer to measure the extension of the quartz spring.

For the diffraction experiments, 1.5 g samples of MCM-41 were placed in aluminium cans of 50 mm in height, 16 mm internal diameter and 1 mm wall thickness. The samples were outgassed at 110°C and doped with the desired amounts of CCl_4 vapour at a temperature of 0°C, before being sealed. Experiments were performed using the multidetector Medium Resolution Powder Diffractometer (MRPD) at the Australian Nuclear Science & Technology Organisation's nuclear reactor HIFAR. A wavelength of 1.980 Å (calibrated with rutile standard) was used, and the scattering angle range was 2–140°. The MCM-41 was doped with 7.5 m mol g^{-1} (corresponding to completely filled mesopores) and 2.5 m mol g^{-1} CCl_4 (just prior to pore filling commencing in the mesopores) and patterns recorded at 200(1) and 273(1) K. The diffraction pattern was also recorded for an outgassed sample containing no CCl_4, and for comparison purposes with pure CCl_4 at 273 and 200 K (wavelength 1.668, annular can of smaller path length).

Results and Discussion

Adsorption Isotherms

The adsorption isotherms of carbon tetrachloride (at the temperatures of 273, 288, 303 and 323 K) are shown in Fig. 1. It is evident that all the isotherms are essentially Type V in the IUPAC classification (Sing et al., 1985). The isotherms at 273, 288 and 303 K exhibit narrow,

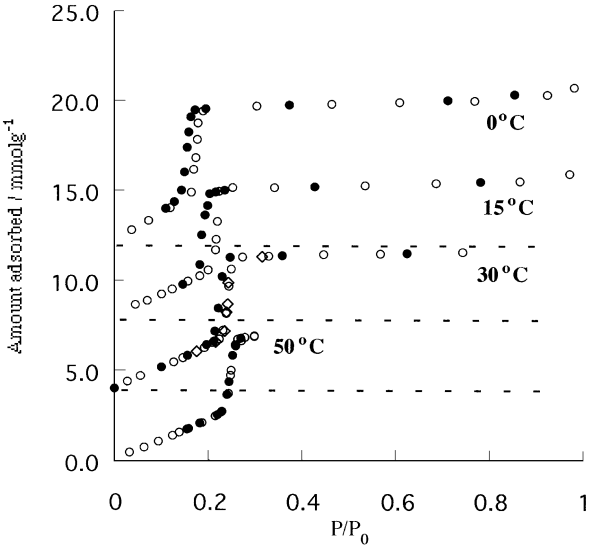

Figure 1. Adsorption of carbon tetrachloride by MCM-41. Different symbols denote different runs; open symbols denote adsorption, filled symbols denote desorption. Isotherm at 30°C offset by 4 m mol g^{-1}. Isotherm at 15°C offset by 8 m mol g^{-1}. Isotherm at 0°C offset by 12 m mol g^{-1}.

almost vertical hysteresis loops of Type H1, whereas the isotherm at 323 K is completely reversible. From ca. $P/P_0 = 0$–0.2, each isotherm is almost linear with no indication of any well-defined stage of monolayer completion, i.e., no detectable Point B (Emmett and Brunauer, 1937). However, the onset of pore filling can be seen as an upward swing. This upward departure from the equivalent isotherm on a non-porous silica surface is even more striking when the isotherm is plotted in the α_s form (Branton et al., 1997).

The fact that the pore filling approach to the isotherm plateau is so steep is a clear indication that the distribution of pore size is extremely narrow. A range of effective pore width of 2.8–3.5 nm was obtained by the application of the corrected Kelvin equation to a nitrogen isotherm determined on the same adsorbent at 77 K (Branton et al., 1997) From the pore volume/area ratio, the corresponding value of mean pore width appeared to be 3.4 nm. By assuming the mesopores to be filled with liquid adsorbate, a total pore volume at 273 K (taken at $P/P_0 = 0.95$) of 0.81 $cm^3\ g^{-1}$ is obtained which is only slightly lower than the value of 0.84 $cm^3\ g^{-1}$ calculated from the nitrogen isotherm. This is an indication that complete filling of the 3.4 nm diameter pores by the bulky CCl_4 molecules can occur.

Before values of pore size can be derived from the carbon tetrachloride isotherms in Fig. 1, it is necessary to consider how we can best deal with the correction for the multilayer thickness. By assuming that the same surface area is available for the adsorption of carbon tetrachloride and nitrogen, we are able to evaluate the extent of the carbon tetrachloride surface coverage—provided that we know, or assume, a value for the molecular area. If we take 0.34 nm^2/molecule, we arrive at the value $n_m = 4.8$ m mol g^{-1} as a 'notional' monolayer capacity. It is therefore apparent that pore filling has begun at an apparent surface coverage of ~40%. It should be emphasized that the Kelvin equation is of questionable validity when applied to such narrow mesopores (say, of $d_p < 5$ nm). Nevertheless, it is of interest to calculate the values of the Kelvin hemispherical meniscus diameter (i.e., the equivalent core diameter, d_k) which would be required to bring about the capillary condensation of carbon tetrachloride at the relative pressures indicated by isotherm steps in Fig. 1. If we now assume the t correction to be of molecular thickness and take 0.6 nm as the diameter of the carbon tetrachloride molecule (Breck, 1974), we can calculate the pore diameter, d_p. Values of the range of pore filling, the core diameter and the pore diameter for each temperature are given in Table 1. It can be seen that there is excellent agreement between values of d_p calculated at each temperature. These values are only slightly larger than the mean pore diameter of 3.4 nm calculated from the nitrogen isotherm.

Table 1. Application of Kelvin equation to CCl_4 adsorption isotherms. d_k is the core diameter, d_p is the pore diameter by allowing for thickness of adsorbed molecules on the pore walls.

Temperature (°C)	Range of pore filling (P/P_0)	d_k (nm)	d_p (nm)
0	0.13–0.19	2.4–2.9	3.6–4.1
15	0.18–0.23	2.6–3.0	3.8–4.2
30	0.22–0.25	2.6–2.9	3.8–4.1
50	0.24–0.26	2.5–2.6	3.7–3.8

As already mentioned, the carbon tetrachloride isotherms display a long range of initial linearity. This unusually long range of apparent conformity to Henry's law is difficult to explain. A preliminary assessment of the variation of the isosteric enthalpy, q^{st}, with coverage indicates a fairly high degree of energetic heterogeneity. (Two recent studies have shown strong heterogeneity of the MCM-41 surface using low pressure nitrogen adsorption (Kruk et al., 1997; Maddox et al., 1997).) Thus, over the adsorption range of 1–2 m mol g^{-1}, q^{st} appears to decrease by ca. 2 kJ mol^{-1} before remaining approximately constant at 38.8 kJ mol^{-1}. Since the isotherm linearity cannot be attriubuted to uniformity in the adsorbent-adsorbate interactions, it seems likely that there is a compensatory entropic contribution brought about by the clustering of molecules around the most favourable sites.

It may seem surprising that the hysteresis loops in Fig. 1 are located in the region of $P/P_0 \sim 0.2$. However, it has been noted earlier (Gregg and Sing, 1982) that there is evidence in the literature that carbon tetrachloride at 298 K gives a limiting lower closure point of its hysteresis loop at $P/P_0 \sim 0.2$–0.25. The work of Everett (Burgess et al., 1989) and Findenegg (Findenegg et al., 1994) has revealed that for a given system, the size and location of a Type H1 hysteresis loop is dependent on pore size, temperature and the limits of stability and metastability of the adsorbed multilayer. Furthermore, Evans et al. (1986) have predicted that the condensation step should decrease in size with increase in temperature and that the associated hysteresis should also vanish at a capillary critical temperature. We may tentatively conclude that in the pores of our MCM-41, the carbon tetrachloride capillary condensate is at, or very close to, its stability limit.

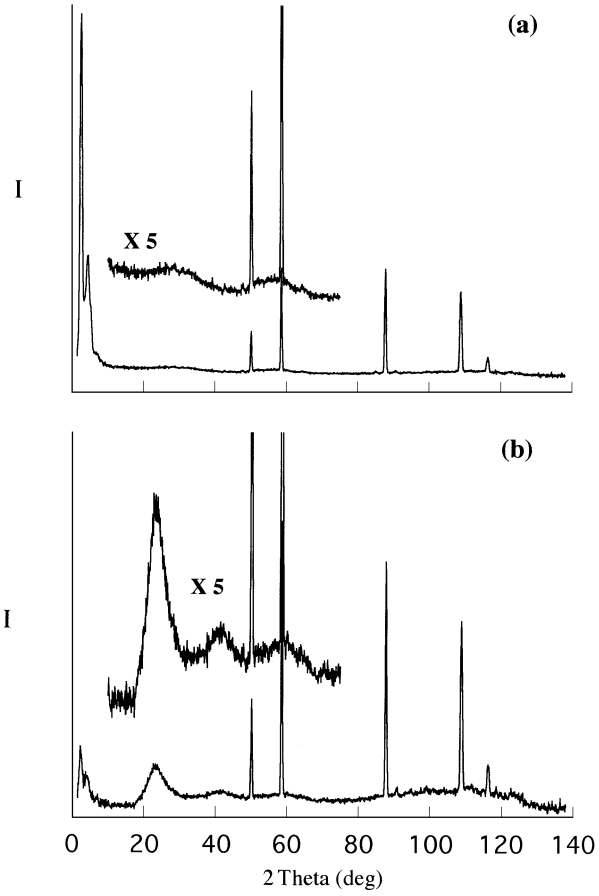

Figure 2. Neutron diffraction pattern for MCM-41 at 273 K. (a) Loaded with 2.5 m mol g^{-1} of CCl_4; (b) Loaded with 7.5 m mol g^{-1} of CCl_4.

Neutron Diffraction

The neutron diffraction patterns at 273 K for CCl_4 loadings of 2.5 and 7.5 m mol g^{-1} are shown in Fig. 2. The diffraction pattern for MCM-41 was nearly the same as the material loaded with 2.5 m mol g^{-1} CCl_4, the only difference being in the peak intensities, i.e., any scattering effects due to the CCl_4 could not be detected at the lower loading.

All peak positions and their assignments are given in Table 2. There are four different sources contributing to the observed neutron diffraction patterns: diffraction from the MCM-41 host hexagonal lattice at $2\theta <$ ca. 15°; diffraction from CCl_4, and amorphous silica (broad peaks between ca. 17° and 67°); and the expected sharp peaks from 50° to 110° from the aluminium can which we will not discuss further.

Three orders of diffraction from the hexagonal net of mesopores could be seen for the MCM-41: the 10, 11 and 21 peaks. As the CCl_4 content is increased, the peak intensities increase for a loading of 2.5 m mol g^{-1} CCl_4 and then diminish in size. This behaviour may indicate some surface roughness (Branton et al., 1995a). The 10 reflection shifts from a d-spacing of 44–48 Å for the fully loaded sample. There is thus an indication of a swelling of the lattice on CCl_4 adsorption which is consistent with thin walls which is a consequence of the very large surface area ($\sim$1000 m^2 g^{-1}) of MCM-41. The decrease in intensities with increased CCl_4 loading is expected since, by filling with CCl_4, we are reducing the contrast in neutron scattering length density between pores and silica walls.

For MCM-41 and MCM-41 + 2.5 m mol g^{-1} CCl_4, we observe two broad peaks at d-spacings of ca. 4 and 2 Å, due to the presence of some amorphous silica. These peaks are not observed for the fully loaded MCM-41, as they are probably obscured by peaks due to CCl_4-CCl_4 interactions in the same region of the diffraction patterns, i.e., at 4.8, 2.8 and 1.9 Å. These correspond in position and relative intensity to the neutron diffraction peaks of liquid CCl_4 (Rao, 1968).

Table 2. Diffraction peak analysis at 273 K.

	d-spacing (Å)					
Reflection	(10)	(11)	(21)	Amorphous silica	Intermolecular CCl_4-CCl_4 interference	Al
MCM-41	44	25	16	4, 2 (broad)	—	2.3, 2.0, 1.4, 1.2
MCM-41 + 2.5 m mol g^{-1} CCl_4	”	”	”	”	—	”
MCM-41 + 7.5 m mol g^{-1} CCl_4	48	28	—	—	4.8, 2.8, 1.9	”
CCl_4	—	—	—	—	4.8, 2.8, 1.9	—
					→	
					Increasing peak broadness	

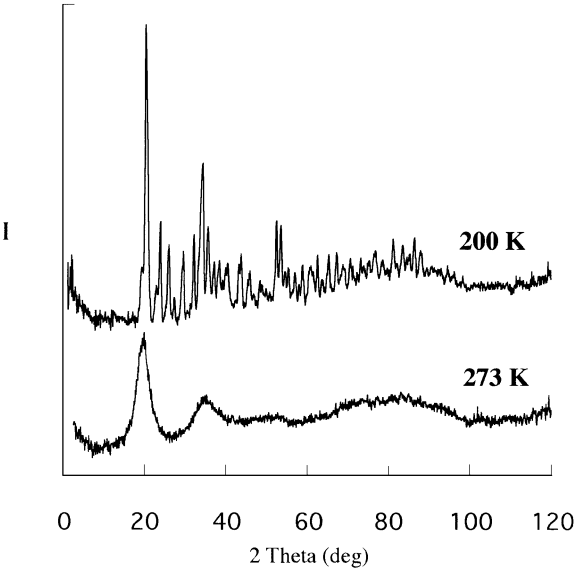

Figure 3. Neutron diffraction pattern for carbon tetrachloride.

The diffraction patterns of CCl_4 at 273 and 200 K are shown in Fig. 3 in which significant changes can be seen. For MCM-41 and MCM-41 + 2.5 m mol g^{-1} CCl_4, no changes were observed on changing the temperature from 273 to 200 K. For the fully loaded MCM-41, there was a slight sharpening of the peaks due to CCl_4-CCl_4 interactions on decreasing the temperature. There was no change in peak intensity. The lack of change in peak position and intensity suggests that no phase transition of the CCl_4 occurs in the mesopores in the temperature range 200 to 273 K. We note that bulk liquid CCl_4 crystallises at 250 K and undergoes a solid state phase transition at 225 K. Thus, the CCl_4 in the mesopores is not crystallising but is present as a supercooled liquid or glass.

At 273 K, the slight increase in peak broadness for the fully loaded sample (f.w.h.m. of 4.8 Å peak = 1.0 Å at 273 K) compared to pure CCl_4 liquid (f.w.h.m. = 0.8 Å) at the same temperature is an indication of less uniformity of the CCl_4 molecules in the pores.

No CCl_4-CCl_4 ordering is detectable for the MCM-41 + 2.5 m mol g^{-1} CCl_4 which suggests that the initially adsorbed CCl_4 molecules have silica nearest neighbours and not other CCl_4 molecules. It seams that localized adsorption has occurred on the highly heterogeneous surface. However, it is possible that there is some clustering which cannot be detected at the level of instrument resolution.

Conclusions

Carbon tetrachloride isotherms have been measured on the pure silica form of MCM-41 of pore diameter ca. 3.4 nm. Isotherms were of Type V in shape, the size and position of the capillary condensation/evaporation isotherm step being highly dependent on the temperature over the range studied of 273–323 K. As in the case of the nitrogen isotherm at 77 K on the same material, all the CCl_4 isotherms show a sharp transition in the physisorption mechanism due to capillary condensation in an extremely narrow distribution of mesopores. In spite of its questionable validity, the Kelvin equation appears to describe the observed changes in position as a function of temperature of capillary condensation/evaporation in the mesopores.

A requirement for *reversible* capillary condensation is that filling occurs below a critical relative pressure governed by both the stability of the condensed adsorptive and the temperature. Reversible capillary condensation has been observed for adsorbents of other pore geometry and with broad pore size distributions (Gregg and Sing, 1982) but in the case of MCM-41 with its narrow distribution of tubular pores, capillary condensation is clearly visible and suitable for a more detailed analysis.

Neutron diffraction studies of carbon tetrachloride adsorption on MCM-41 show a change in physical properties from bulk CCl_4. The adsorbed CCl_4 remains as a supercooled liquid to at least 50 K below its melting point of 250 K and the expansion-contraction and ordering of the adsorbed CCl_4 is different to bulk. Similar to the results obtained from the isotherms, there is evidence of a highly heterogeneous MCM-41 surface and relatively weak vapour-solid interactions. The d-spacing changes by some 8% upon total pore filling indicating flexibility of the walls.

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