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Physisorption of Alcohols and Water Vapour by MCM-41, a Model Mesoporous Adsorbent

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Abstract. Adsorption isotherms of methanol, ethanol, propan-1-ol, butan-1-ol and water vapour have been determined on MCM-41, a model mesoporous adsorbent. The isotherms of the alcohols are all of Type IV, whereas the water isotherm is of Type V in the IUPAC classification. Each adsorption isotherm exhibits a sharp step, indicative of capillary condensation within a narrow distribution of mesopores. The isotherms are reversible in the monolayer-multilayer region, but distinctive hysteresis loops are associated with the condensation-evaporation cycle. The area within the loop is dependent on the adsorptive, increasing in scale from methanol to butan-1-ol and water. It is evident that the large internal surface of MCM-41 is somewhat hydrophobic and that its mesopore structure is remarkably uniform and stable.

Introduction

MCM-41 is a member of a new family of highly uniform mesoporous adsorbents, [1, 2] which are prepared by the hydrothermal conversion of aluminosilicate gels in the presence of quaternary ammonium surfactants. It has been established [2] that the mesopores are formed as an hexagonal array of uniform channels, a typical product having a pore diameter of about 4 nm.

The results reported here were obtained on a sample of MCM-41 prepared at Mainz University in the laboratories of Professor K. Unger. Previous work [3] indicated that the adsorbent had a mean pore diameter of about 3.3 nm. The adsorption isotherm of nitrogen, determined on this sample at 77 K, was of an unusual character: [3] it exhibited a sharp *reversible* step in the range $P/P_0 = 0.41$–0.46. Recent work by Franke et al. [4] has similarly revealed reversible mesopore filling of MCM-41 by cyclopentane. The corresponding oxygen isotherm at 77 K had a more normal appearance: [3] in this case the step was associated with the familiar type of hysteresis loop. [5]

In view of this difference between the low-temperature isotherms of nitrogen and oxygen, it was of interest to study the adsorptive properties of MCM-41 in more detail. The work described here was part of a systematic investigation of the adsorption of a wide range of gases and vapours at different temperatures. By using short-chain alcohols and water vapour, we were able to study dependence of the isotherm character on the adsorption of a number of related polar molecules.

Experimental

The sample of MCM-41 was taken from a batch of the material prepared by M. Keung [6] and based on example 4 of the Mobil Oil patent. [7] The molar ratios used were water/silica 35, silica/alumina 29.7, hydroxide/silica 0.13, tetramethyl ammonium ions (TMA^+)/silica 0.11 and hexadecyltrimethyl ammonium ions ($HDTMA^+$)/silica 0.24. The material was slowly taken to a temperature of 540°C (heating rate of 1°C/minute) and held at this temperature for 8 hours. The hydrogen form of the alumino-silicate was obtained by ion exchange with 1 M ammonium nitrate solution, vacuum filtration followed by air drying at room temperature and a second calcination at 550°C for 3 hours.

A manual gravimetric technique was used to determine the adsorption isotherms at the recorded temperatures. The adsorptives were 'Absolute Grade' alcohols and triply distilled water vapour. A spring balance, consisting of two helical quartz springs, gave a resolution of 0.15 mg and the adsorbent (ca. 0.2 g) was contained in a thin-walled silica bucket. A silicone oil manometer was used to measure pressures in the range 0–45 torr. Higher pressures were recorded with a pressure transducer (supplied by Digitron Instrumentation).

The outgassing temperature was slowly increased to 200°C (over a period of about an hour) and held at this temperature for 3–4 hours to give a residual pressure $<10^{-4}$ torr.

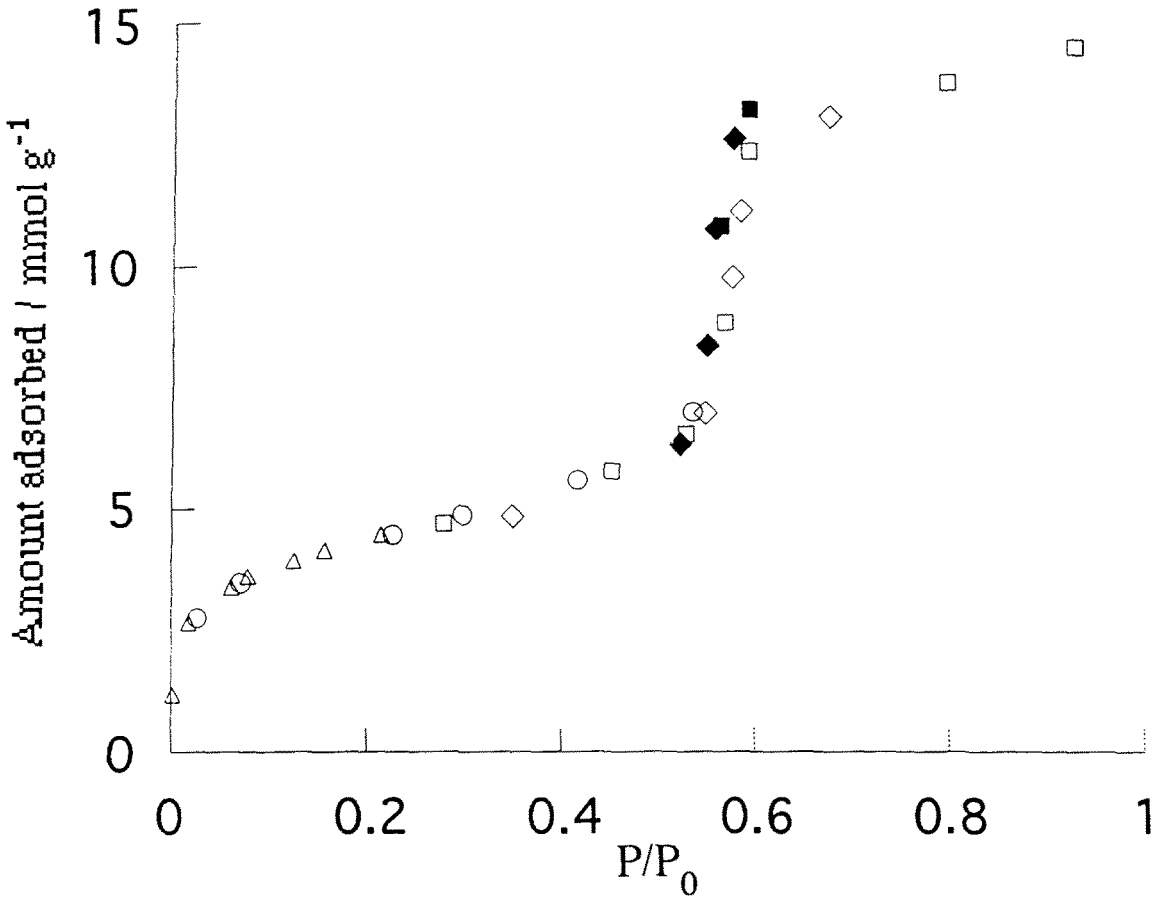

Fig. 1. The adsorption isotherm of methanol on MCM-41 at 290 K.

Results and Discussion

The adsorption isotherm of methanol at 290 K is displayed in Fig. 1. It is apparent that all the runs are in excellent agreement and that there is a very narrow hysteresis loop. The size and position of this loop did not appear to change over the temperature range 273–303 K. The propan-1-ol isotherm (at 298 K) in Fig. 2 is of a similar shape—as are the corresponding isotherms of ethanol (at 292 K) and butan-1-ol (at 314 K). However, the size of the hysteresis loop appears to increase in the order: methanol, ethanol, propanol, butanol. The alcohol isotherms are all of Type IV in the IUPAC classification [5] and thus have the characteristic shape associated with physisorption by mesoporous solids [8] (i.e. monolayer-multilayer adsorption followed by capillary condensation). The adsorption of butanol at 298 K was studied, but the reproducibility of the adsorption branch of the loop was poor. This may be due to the low saturation vapour pressure at this temperature and diffusion effects caused by the bulky nature of the butanol.

The water isotherm (at 303 K) in Fig. 3 is a typical

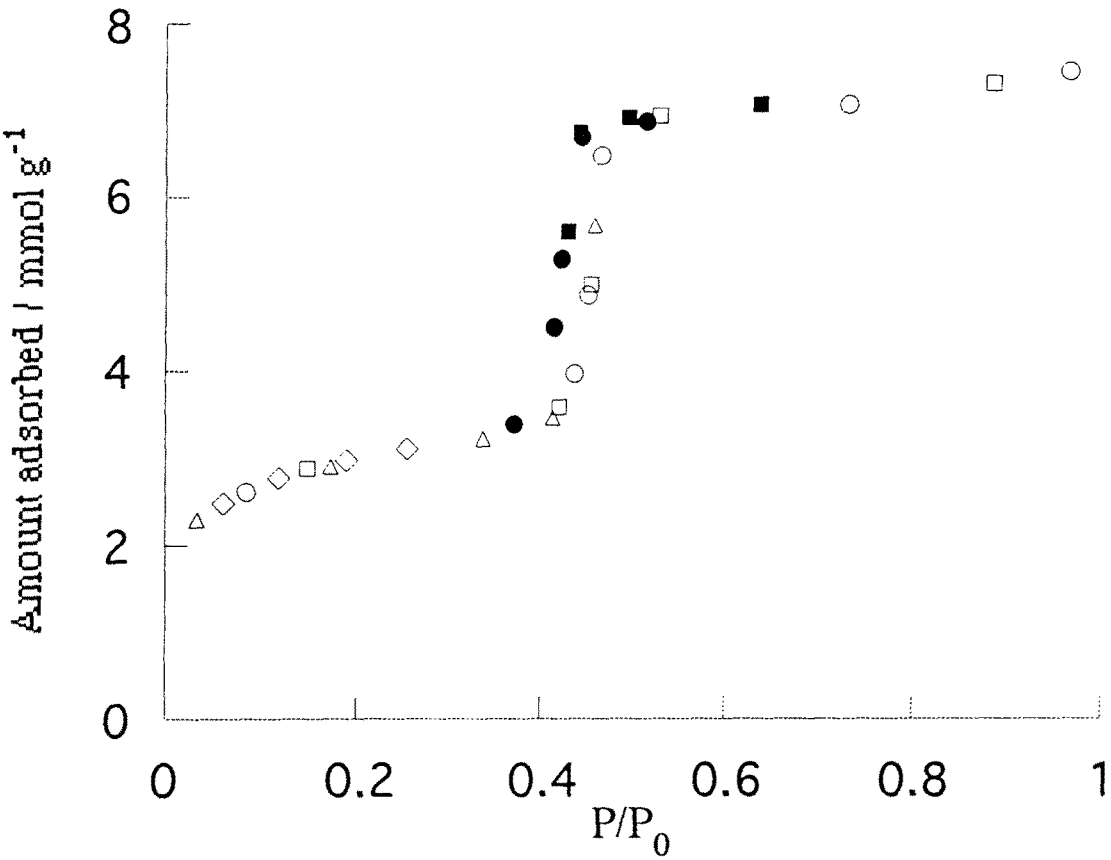

Fig. 2. The adsorption isotherm of propan-1-ol on MCM-41 at 298 K.

Type V isotherm: in this case, the low adsorption affinity can be attributed to the weak adsorbent-adsorbate interactions associated with a 'hydrophobic' surface. [5] The initial monolayer adsorption was evidently confined to a very small part of the total internal surface, but capillary condensation has occurred in the mesopores in an apparently normal manner around $P/P_0 = 0.6$.

Values of the BET monolayer capacity, n_m (BET), in Table 1 have been calculated from the isotherm data for the adsorption of the four alcohols. However, the interpretation of n_m (BET) is questionable since each BET plot was non-linear above $P/P_0 = 0.2$ and the corresponding Point B somewhat indistinct. The apparent molecular area, $\mathbf{a}_m$, is derived from n_m (BET) by taking the BET-nitrogen area (of 655 $m^2\ g^{-1}$) [3] as the true surface area available for the adsorption of each vapour. [3] It is evident that the values of $\mathbf{a}_m$ are much larger than the molecular areas for the corresponding close-packed monolayers [9] (e.g. 0.24 nm^2 for butanol on water). [10]

In the light of previous studies of the adsorption of the n-alcohols on various oxides, [11–16] it is not surprising to find that the BET-monolayers are not close-packed. Indeed, the work of A.V. Kiselev [11] revealed

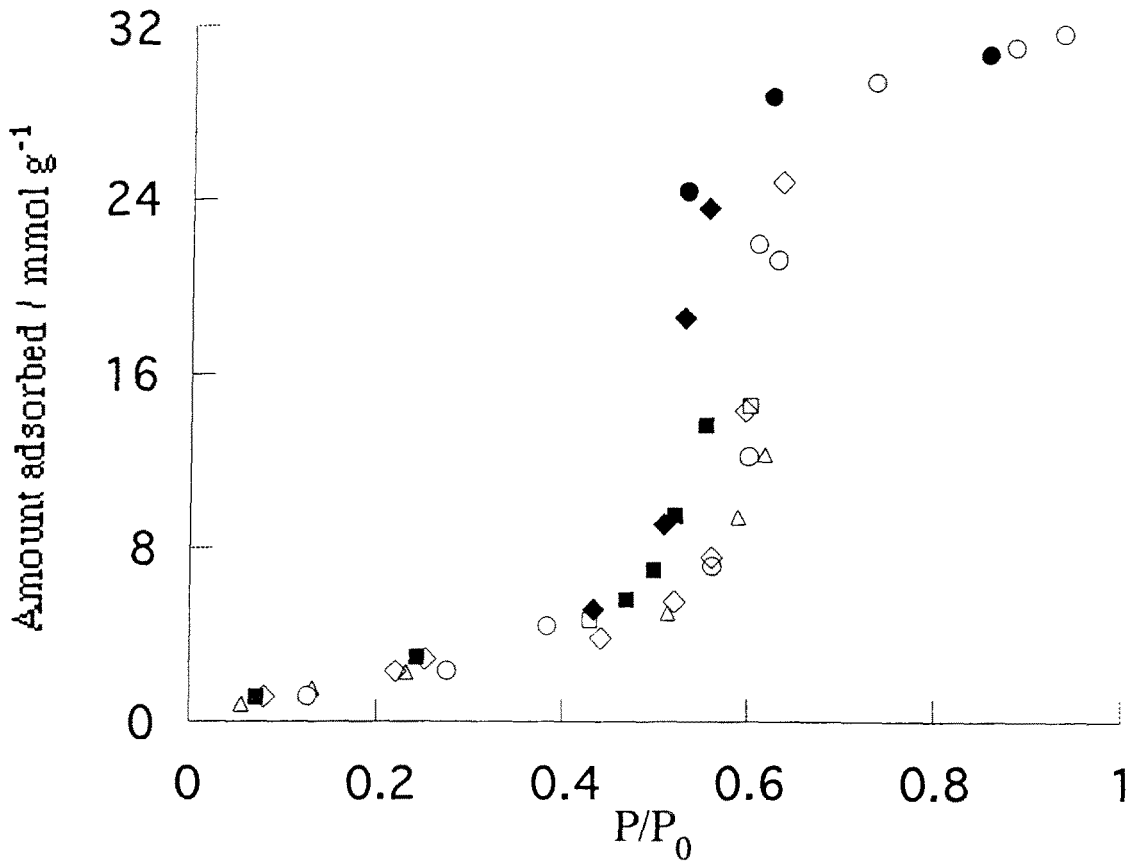

Fig. 3. The adsorption isotherm of water vapour on MCM-41 at 303 K.

Table 1. Characteristic adsorptive properties of MCM-41.

Adsorptive	Nitrogen	Methanol	Ethanol	Propan-1-ol	Butan-1-ol	Water
T/K	77	290	292	298	314	303
n_m(BET)/ mmol g^{-1}	6.71	3.59	2.94	2.47	2.21	1.7*
a_m/nm^2	(0.162)	0.30	0.37	0.44	0.49	0.64
V_p/cm^3 g^{-1}	0.64	0.59	0.56	0.55	0.54	0.57
Range of Pore Filling, P/P_0	0.41–0.46	0.53–0.58	0.47–0.53	0.42–0.48	0.35–0.42	0.46–0.63
d_p/nm	3.3–4.3	4.2–6.5	4.6–6.9	5.1–7.4	4.9–7.2	5.1–11.1

*Uptake at $P/P_0 = 0.1$

Table 2. Adsorption on non-porous and mesoporous oxides. Amount adsorbed at $P/P_0 = 0.1/\mu$mol m^{-2}.

Adsorptive	Methanol	Ethanol	Propan-1-ol	Butan-1-ol	Water
MCM-41 (this work)	5.7	4.7	4.1	3.8	1.7
Hydroxylated Silicas [11, 12, 15]	7.0	5.0–5.4	–	–	4.7
Dehydroxylated Silicas [11, 16]	3.0	–	–	–	1.0
Aluminas [13, 15]	10.7	8.2	6.4	6.3	8.8
Hydrated Rutile [14]	–	4.7	–	–	4.7

that the physisorption of such polar molecules is highly specific and dependent on the surface chemistry. To explore these effects it is expedient to express the amount adsorbed at $P/P_0 = 0.1$ as $n(0.1)$ μ mol m^{-2}, i.e. per unit surface area—by assuming the validity of the BET-nitrogen area.

In Table 2 the values of $n(0.1)$ derived from isotherms reported here are compared with corresponding data in the literature for the adsorption of methanol, ethanol, propanol, butanol and water on certain well-defined oxide surfaces. It is apparent that the number of molecules adsorbed per unit area is inversely related to chain length although the difference between propanol and butanol is quite small. With respect to the adsorption of methanol and ethanol, the behavior of MCM-41 is more like that of hydroxylated silica and hydrated rutile than alumina.

The total mesopore volume, V_p, is usually taken as the volume adsorbed at the plateau of a Type IV isotherm—assuming that the pores are filled with condensed adsorptive in the normal liquid state. [8] Thus, in the present work the values of V_p in Table 1 were obtained from the uptake of each vapour at $P/P_0 = 0.95$ by taking the normal liquid density at the operational temperature. The agreement appears to be fairly good (average $V_p = 0.56$ cm^3 g^{-1}), but the values of V_p previously obtained from low-temperature nitrogen and oxygen isotherms (both giving 0.64 cm^3 g^{-1}) were significantly higher. The reasons for these differences are not clear, but it must be kept in mind that the density of the adsorbed phase is unlikely to be exactly the same as that of the liquid adsorptive and curvature of some isotherms at high P/P_0 leads to uncertainty in the location of the upper limit for pore filling.

The sharp step in the middle region of each alcohol isotherm and the associated narrow hysteresis loop provide clear evidence of capillary condensation taking place within a narrow range of uniform mesopores.

Table 3. Experimental data for the adsorption of alcohols by MCM-41.

P/P_0	Methanol adsorbed	Ethanol adsorbed	Propan-1-ol adsorbed	Butan-1-ol adsorbed
0.02	4.1	3.6	3.3	3.2
0.05	4.9	4.2	3.7	3.5
0.10	5.7	4.7	4.1	3.8
0.15	6.3	5.1	4.4	4.0
0.20	6.8	5.3	4.6	4.1
0.25	7.1	5.6	4.7	4.2
0.30	7.3	5.8	4.8	4.3
0.35	7.6	6.0	4.9	4.4
0.40	8.4	6.2	5.1	6.7
0.45	8.9	6.5	7.1	8.3
0.50	9.6	9.0	10.5	8.5
0.55	11.4	13.6	10.6	8.6
0.60	19.4	13.8	10.6	8.6
0.65	19.8	13.9	10.7	8.7
0.70	20.0	14.0	10.7	8.8

Methanol data obtained at 290 K, ethanol data at 292 K, propan-1-ol data at 298 K and butan-1-ol data a 314 K. Adsorption given in units of μ mol m^{-2}, based on the BET-nitrogen surface area.

Values of P/P_0 corresponding to the lower and upper limits of each hysteresis loop are given in Table 1 along with the derived values of pore diameter, d_p, which have been calculated by application of the Kelvin equation with allowance made for multilayer adsorption on the pore walls. [8] The imperfect agreement is not surprising in view of the assumptions involved in the computation of pore size, but even so the total range of ~2 nm represents a remarkably narrow mesopore size distribution.

For future reference, interpolated data for the adsorption of alcohols and water vapour by MCM-41 are given in Tables 3 and 4 respectively. The amounts adsorbed have been reduced to unit surface area, as determined by the BET-nitrogen method.

Table 4. Experimental data for the adsorption of water vapour by MCM-41 at 303 K.

P/P_0	Water adsorbed
0.05	1.0
0.10	1.7
0.15	2.5
0.20	3.0
0.25	3.9
0.30	4.7
0.35	5.5
0.40	6.2
0.45	6.8
0.50	7.7
0.55	9.5
0.60	27
0.65	41
0.70	44

Adsorption given in units of μ mol m^{-2}, based on the BET-nitrogen surface area.

Conclusions

Analysis of the adsorption isotherms of the four alcohols has revealed that the physisorption of these polar molecules proceeds in a similar manner to that of oxygen at 77 K. Thus, monolayer-multilayer adsorption on the internal surface of MCM-41 is followed by capillary condensation, which is associated with a well-defined hysteresis loop. The size of the loop is a feature of the system at a given temperature. In contrast, nitrogen at 77 K gives a completely reversible Type IV isotherm, but whether this is so at other temperatures remains to be investigated. At present, we can only speculate about the reason for this very unusual behavior, but it seems significant that in the case of nitrogen the capillary condensation step occurs at $P/P_0 = 0.42$, which has been identified [17] as the limiting closure point for nitrogen hysteresis loops at 77 K. Under these conditions, it seems that this is the lowest P/P_0 at which nitrogen can undergo the classical form of capillary condensation. Of course, micropore filling occurs reversibly at lower P/P_0, but this does not involve meniscus formation.

The low initial affinity of MCM-41 for water vapour is another important property of this adsorbent. An interesting feature of the water isotherm is its reversiblity in the prehysteresis region. In this respect, MCM-41 behaves more like a mesoporous carbon [18] than a dehydroxylated silica. [15] Thus, there appears to be no indication of any dissociative chemisorption of water on the internal surface.

Nomenclature

d_p = Pore Diameter/nm
P/P_0 = Pressure/Saturation vapour pressure at the temperature of the isotherm run
T = Temperature of isotherm run/K
n_m = BET monolayer capacity/mmol g^{-1}
$n(0.1)$ = Amount adsorbed at relative pressure $P/P_0 = 0.1/\mu$ mol g^{-1}
a_m = Cross sectional area of an adsorbed molecule/nm^2
V_p = Effective pore volume/cm^3 g^{-1}

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