Adsorption of nitrogen, neopentane, *n*-hexane, benzene and methanol for the evaluation of pore sizes in silica grades of MCM-41

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Abstract

Nitrogen, neopentane, *n*-hexane, benzene and methanol adsorption isotherms were determined on five samples of silica grade MCM-41 with different pore sizes and a comparison of different methods for evaluating the pore size was carried out. With nitrogen we found a remarkably good agreement between the results obtained from the non-local density functional theory and geometric methods, with corresponding values obtained by the two methods differing by less than 0.05 nm. On the other hand, the results confirm findings seen before by other workers that, in order to obtain reliable values of pore radii by the hydraulic method, it is necessary to use a cross-sectional area of nitrogen in the monolayer smaller than the normally assumed value of 0.162 nm^2. In addition, it was found that the effective pore volume obtained with the four organic adsorptives was almost constant while the value obtained from nitrogen adsorption data was always higher. The results indicate that, for the nitrogen data, an average density of 0.84 g cm^{-3} can be used to calculate the pore volume and that in this case the surface area should be calculated by considering a value of 0.131 nm^2 for the cross-sectional area. In order to calculate hydraulic pore radii, either this pair of values can be used or if, on the other hand, the usual value of 0.808 g cm^{-3} is considered for the nitrogen density, the value of 0.137 nm^2 must be used for the cross-sectional area. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The well defined pore structure presented by MCM-41 materials [1,2] has made them unique candidates for fundamental studies aimed at testing standard adsorption isotherm analysis methods (e.g. Brunauer–Emmett–Teller (BET), α_s and Barrett–Joyner–Halenda (BJH) for pore size distributions) for the characterization of porous solids [3–10] as well as for the verification of recent theoretical models, such as the non-local density functional theory (NLDFT) and molecular simulations, for predicting phase equilibria in confined

geometries, adsorption in pores and pore size distributions [3,4,11–19].

Several studies have been published [3–10, 12,20–22] in which different methods for obtaining, in particular, the pore size of these materials, have been compared. These include, on the one hand, methods based only on the results of low-temperature nitrogen adsorption isotherms. For instance, methods for calculating pore size distributions based on the Kelvin equation (such as BJH or Broekhoff-de Boer) [3,5,6,8–10,21,22], methods that make use of the concept of hydraulic pore radius ($2V/A$, obtained by applying BET or α_s) [5,6,9,21–24] and the more recent methods based on NLDFT [3,4,17–19,25,26], have all been used. On the other hand, by assuming an ideal structure consisting of a hexagonal array of tubular uniform-sized channels separated by thin amorphous walls, it has been possible to estimate a value of pore size based on geometrical considerations [5,6,8,9,21,27] and using the pore volume obtained from nitrogen adsorption, the unit cell parameter obtained by X-ray diffraction (XRD) and assuming a constant and normal value for the density of the amorphous silica walls.

The studies so far published show that the four types of calculations referred to above give different values for the pore size. It is now well established that the traditional methods based on the Kelvin equation [28,29] using a standard *t*-curve [30] considerably underestimate the pore size [31]. For example, the BJH method is in error even in pores as large as 20 nm [25,26]. Even refined versions that take into account the influence of adsorption forces on the curvature of the meniscus [8–10,32–35] or make calibrations and empirical adjustments for the statistical thickness of the film adsorbed [6] have limited application in the nanopore region due to the breakdown of the Kelvin equation [30]. With regard to the hydraulic pore width approach, it appears that this also gives lower values than the NLDFT and geometric methods, and it has been suggested [6,9,10,36] that this is due to overestimation of the surface area of the pores, whether estimated by the BET or by a comparison method (*t* or α_s). NLDFT, on the other hand, appears to give values slightly higher than those predicted by geometrical considerations based

on the model of the ideal pore structure [5]. However, it should be noted that the geometric method involves a number of assumptions and can only give a rigorous estimate for the mean pore radius if the structure is highly regular (absence of amorphous material) and if the experimental parameters used, namely, unit cell parameters and, especially, pore volume and silica density, are correct. In many cases, there are doubts about the validity of the assumptions involved and the reliability of the experimental parameters. With this in mind, it appears that NLDFT calculations, which are the most independent and theoretically soundest, should be taken as the reference for purposes of comparison.

Most, by far, of the published characterization work has been based on nitrogen adsorption data. However, it has been found by us and others that adsorptives such as neopentane [24], argon [3,4,26, 37–39], carbon dioxide [38,40], sulphur dioxide [38, 40], alcohols [38,41], water [24,38,41–43] and benzene [43] can give lower pore volumes than nitrogen, when expressed using the normal liquid densities for the adsorptives. With the particular exception of water, which alters the pore structure [24,42,44–46], the results obtained with the other adsorptives suggest that the mean density of adsorbate in the pores may be different to that of the normal bulk liquid. However, relatively few studies and using only a limited number of samples have so far been published and there is still a need for more detailed work. With this in mind, we present in this paper a systematic study of the adsorption of several adsorptives in a series of samples with different pore sizes. Analysis of the results indicates that the apparent density of the nitrogen in the pores is higher than that of the normal liquid. In addition, the results show that in order to calculate the surface area of the pore walls, which is needed in order to calculate the hydraulic pore width, a value for the cross-sectional area of the nitrogen molecule lower than the normal value of 0.162 nm^2 must also be used.

2. Theoretical background

NLDFT model provides an independent method for evaluating the pore size in nanopores. The theory predicts the capillary condensation/desorp-

tion isotherms in cylindrical pores based on the molecular model and given potentials of fluid–fluid and solid–fluid interactions. The pore size distributions are calculated by numerical deconvolution of the generalized adsorption isotherm equation, which represents the experimental isotherm as a weighted sum of the theoretical isotherms in pores of different diameters. To calculate the isotherms in individual pores we used the well established Tarazona's version of the NLDFT, which was described in details elsewhere [3,4,12,14–16]. Parameters of the fluid–fluid potential were chosen to fit the bulk equilibrium properties of N_2, which include the liquid–gas coexistence densities, saturation pressure and the surface tension [12,14–16]. Parameters of the solid–fluid interactions were chosen to obtain the best possible description of the standard adsorption isotherm on non-porous silicas in the multilayer adsorption region [4,15,16,18]. Due to a realistic account for the solid–fluid interactions, the NLDFT predicted adsorption–desorption pressures in pores are substantially lower than those obtained by the Kelvin equation with the standard correction on the multilayer adsorption isotherm. As a result, for 3–4 nm cylindrical pores, the NLDFT based method for pore size analysis predicts ≈1 nm larger pore diameters than the BJH method [3,4]. The results obtained by the two methods become closer only for large pores, >20 nm in diameter [25,26]. It is worth noticing that the relative pressures of the capillary condensation/desorption transitions in pores predicted by the NLDFT model are quite insensitive to the variations in the well depth of the solid–fluid potential [18], which makes the NLDFT a robust method for pore size characterization. This is also supported by the quantitative agreement between the NLDFT and molecular simulation studies of adsorption in MCM-41 materials (see comparison presented in Refs. [4,15,16]). In this work, we use NLDFT as a reference method for obtaining the pore size in MCM-41 materials.

3. Experimental

The five samples, designated C10F, C12F, C14F, C16F and C18F, were prepared by a room-temperature synthesis based on that reported previously [47], using as surfactants, respectively, C_{10}TMABr, C_{12}TMABr, C_{14}TMABr, C_{16}TMABr and C_{18}TMABr (where TMA = trimethylammonium), and the molar ratios of reagents used were 1 (tetraethoxysilane): 0.145 (surfactant):2.96 (NH_3): 155(H_2O). The surfactants and TEOS were supplied by Fluka (purity > 98%, except for C_{18}-TMABr which was >97%) and ammonia by Riedel–de Haën (25%). All chemicals were used as received. In all cases the synthesis products were recovered by filtration and then washed with deionized water, dried at 363 K and finally calcined in air at 823 K (heating rate 5 K/min) for 5 h.

Nitrogen adsorption isotherms at 77 K were determined on a CE Instruments Sorptomatic 1990, using helium and nitrogen of 99.999% purity supplied by Linde and Air Liquide, respectively. The adsorption of neopentane, at 273 K, benzene, *n*-hexane and methanol, at 298 K, were determined gravimetrically using a CI Electronics vacuum microbalance with a DISBAL control unit, with pressure measurement by means of Edwards Barocel 600 capacitance manometers. The temperature was controlled within ±0.1 K using a LTD Grant thermostat. Neopentane of >99% purity was supplied by Linde, while the organic liquids were from Riedel–de Haën (p.a.) and were outgassed by repeated freeze–thaw cycles. In all cases, the MCM-41 samples were outgassed at 423 K prior to the determination of the isotherms. The saturation pressure for each organic adsorptive was calculated using data and equations recommended in the literature [48]. For methanol on C16F, two consecutive adsorption–desorption cycles were carried out to check that this polar adsorptive did not alter the pore structure as had previously been observed with water. The two runs were completely reversible and coincident thereby indicating that this phenomena did not occur.

The XRD experiments were performed using a high-temperature double-crystal diffractometer with a 4-circle goniometer, the Hotbird [49]. It uses a Rigaku rotating anode with 18 kW and a flat Ge(4 4 4) crystal to produce the incident monochromatic radiation (CuKα1 = 0.154056 nm). The beam size used was 100 μm wide and 5 mm high. The position-sensitive detector (MBraun, 80 μm

spatial resolution) was positioned at 600 mm from the sample to conform to an achromatic geometry. In this configuration, the resolution limit is $\sim 30''$. For the determination of the unit cell parameter a_0 the experimental curves were fitted using Voigt functions and a non-linear Levenberg–Marquardt least square fitting procedure.

4. Results and discussion

4.1. Characterization by XRD and nitrogen adsorption

The XRD patterns of the samples are shown in Fig. 1. For the samples C10F and C12F only one peak is clearly visible. However, for samples C14F, C16F and C18F, at least three peaks characteristic of wider pore sized MCM-41 materials can be seen which indicates a highly regular structure of these samples. In the case of sample C16F five Bragg peaks are observed confirming that long-range order is present.

The nitrogen adsorption–desorption isotherms determined on the MCM-41 samples and the corresponding α_s plots constructed using standard data for adsorption of nitrogen on non-porous partially hydroxylated silica [30] are shown in Fig. 2. For the sake of clarity only some of the adsorption points are shown. It can be seen that all isotherms and α_s plots exhibit pore filling steps which occur, in each case, within a fairly narrow range of p/p^0. The steps are less well defined in the case of C10F and C12F due to the smaller pore sizes of these samples, but are quite steep and characteristic of wider pore sized MCM-41 materials with the other samples. Furthermore, with the possible exception of the widest pore sample, C18F, the steps are completely reversible. As previously noted [50] the steepness and reversibility of these steps are consistent with the presence of tubular pores of uniform size in each adsorbent. At higher values of p/p^0, after pore filling was complete, the isotherms were found to be almost horizontal suggesting a reasonably uniform particle morphology and, in particular, the absence of significant inter-particle agglomeration. These features, taken in conjunction with the XRD re-
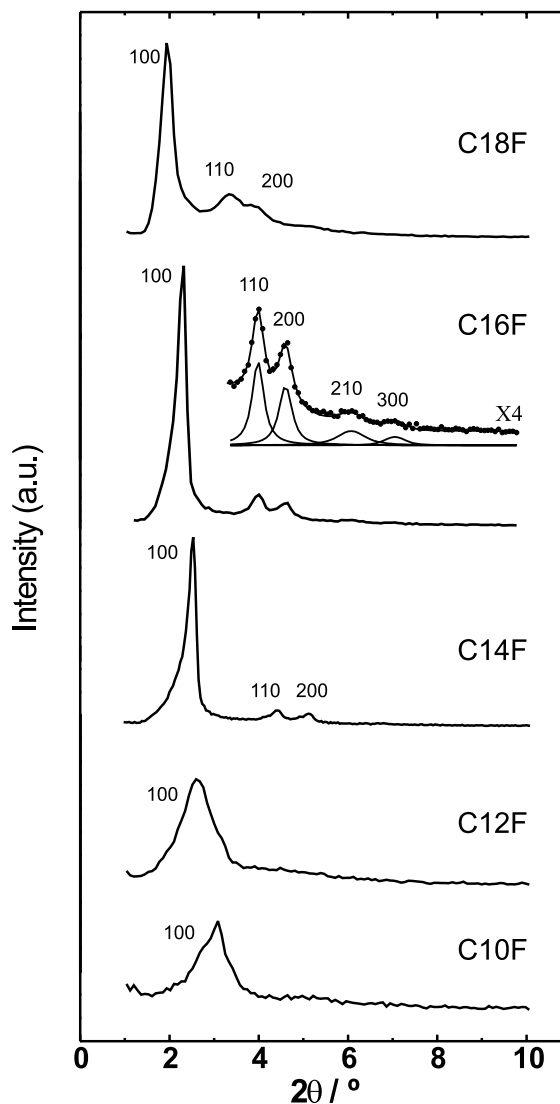

Fig. 1. X-ray powder diffraction patterns of the siliceous MCM-41 samples. To illustrate the data analysis performed, the individual Voigt functions used to adjust the higher order Bragg peaks of sample C16F are shown in the inset.

sults, indicate that samples C14F, C16F and C18F have highly regular and uniform tubular pore structures. In the case of samples C10F and C12F, on the other hand, the smallness of the pore sizes makes assessment of the uniformity and regularity of the pore structures more uncertain. An interesting observation is that all MCM-41 samples
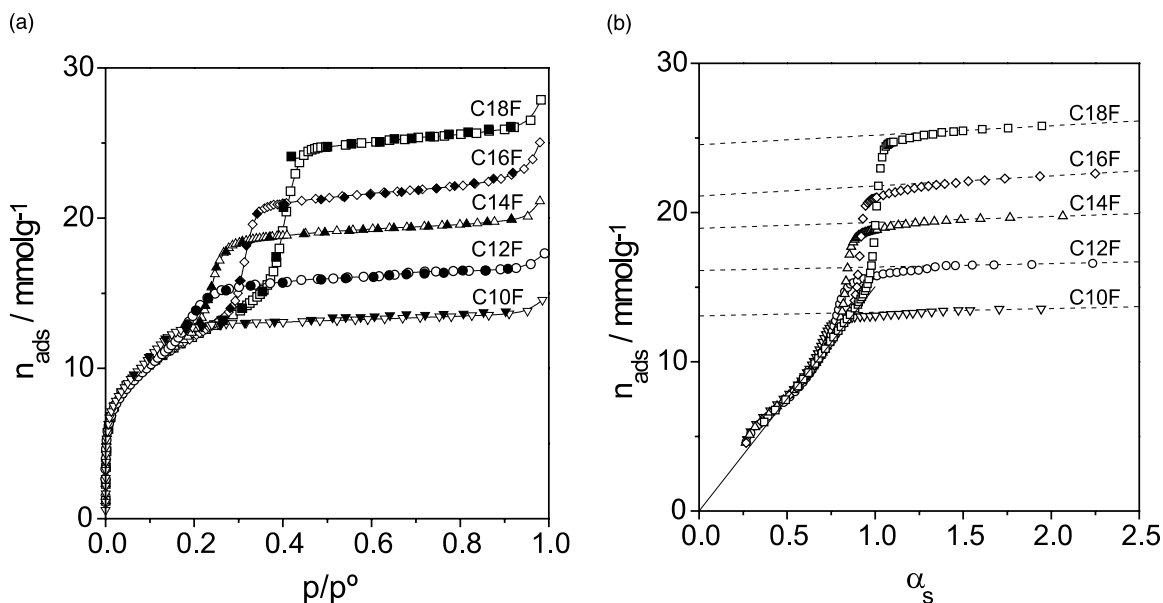
(a)

(b)

Fig. 2. (a) Nitrogen adsorption isotherms determined at 77 K on a series of samples of siliceous MCM-41. Open symbols: adsorption, filled symbols: desorption. (b) α_s plots corresponding to the isotherms of nitrogen adsorption at 77 K.

from this series have approximately the same surface area, as indicated by the similarity of the isotherms in the monolayer adsorption region.

It can be seen from Fig. 2(b) that, after an initial very low pressure deviation but prior to the pore filling step, each α_s plot exhibits a linear region which can be back-extrapolated through the origin, indicating the absence of primary microporosity. The deviations from linearity which can be seen on the α_s plots at very low surface coverage therefore suggest an enhancement of adsorption in relation to the reference. This could be due to several factors, such as curvature effects of the surface, roughness of the surface, differences between the exact degree of surface hydroxylation of the MCM-41 samples and of the reference or to a higher degree of localization of the nitrogen molecules on the surface of MCM-41. However, it appears that at relative pressures above about 0.03 these effects are screened by the adsorbed phase, and a linear region of the α_s plot is obtained. From the corresponding slopes, the values of total surface area, A_s, of each sample were calculated. An independent estimate of the total surface area was also calculated by applying the BET equation to

the data. In most cases it was found that the range of pressure from approximately $0.03p^0$ to no more than $0.1p^0$ was the most appropriate and, as can be seen from the results in Table 1, it was possible to obtain excellent agreement between the two estimates, A_s and A_{BET}, of the total surface area. The external surface areas, A_{ext}, and pore volumes, V_p, of the samples were determined from the α_s plots in the usual manner from the slope and intercept of the linear high p/p^0 region. For the calculation of pore volumes, expressed as equivalent liquid volumes, a value of 0.808 g cm^{-3} was used for the density of liquid nitrogen at 77 K. The results, given in Table 1, confirm that all samples had quite low external areas, being less than 5% of the total surface area in all cases, and that the pore volumes of most of the samples were quite high.

4.2. Comparison of nitrogen adsorption with the organic adsorptives

For each sample the adsorption isotherms of neopentane, benzene, n-hexane and methanol, together with the corresponding nitrogen isotherm, are shown in Fig. 3(a)–(e). All data are expressed

Table 1
Results of the analysis by the BET and α_s methods of the adsorption isotherms of nitrogen at 77 K and neopentane at 273 K on MCM-41 samples

Sample	Nitrogen adsorption[a]				Neopentane adsorption		
	A_{BET} (m^2 g^{-1})	A_s (m^2 g^{-1})	A_{ext} (m^2 g^{-1})	V_p (cm^3 g^{-1})	A_{ext} (m^2 g^{-1})	V_p (cm^3 g^{-1})	$\rho_{ads}(N_2)$ (g cm^{-3})[b]
C10F	963	964	16	0.45	15	0.43	0.85
C12F	937	937	15	0.56	15	0.53	0.85
C14F	953	956	25	0.66	25	0.63	0.85
C16F	954	955	43	0.73	41	0.70	0.84
C18F	961	958	41	0.85	41	0.82	0.84

[a] Assuming $\sigma_{N_2} = 0.162$ nm^2 and $\rho_l = 0.808$ g cm^{-3}.
[b] $\rho_{ads}(N_2) = 0.808 V_p(N_2)/V_p(neop)$.

as equivalent liquid volumes by assuming the adsorbates to have the normal bulk liquid density, that is, using 0.808 g cm^{-3} for the density of adsorbed nitrogen and, for the other adsorptives, the values of density (0.613, 0.871, 0.654 and 0.785 g cm^{-3} for neopentane, benzene, *n*-hexane and methanol, respectively) calculated from data and equations recommended in the literature [48].

With the exception of the isotherms of the hydrocarbons on C10F, all isotherms present a step indicating pore filling occurring in a narrow p/p^0 range which is dependent on the adsorptive, pore size and probably also on the temperature. For each adsorptive this p/p^0 range shifts to higher values as the pore size increases. For the adsorption of *n*-hexane, benzene and neopentane on C10F there is no step and the isotherms are type I, indicating that in these cases there is a different mechanism of adsorption, with no multilayer formation prior to pore filling. This difference clearly illustrates the effect of the ratio pore size/molecular dimension on the mechanism of adsorption. The pores of sample C10F behave as secondary micropores towards the smaller nitrogen molecule and are therefore filled by a condensation mechanism preceded by monolayer–multilayer formation. With the larger organic molecules, on the other hand, the ratio pore size/molecular dimension is much lower and the pores behave as primary micropores being filled by a volume filling mechanism. In the case of C12F the step is just visible in the hydrocarbon isotherms indicating that with this sample the ratio pore size/molecular dimension is, for the hydrocarbon adsorptives, just

past the limit between primary micropores and secondary micropores.

The same effect can also be seen from Fig. 4 in which the neopentane isotherms and the corresponding α_s plots are presented. These plots were constructed using standard data for adsorption of neopentane on non-porous silicas [51]. In contrast to the corresponding nitrogen α_s plots, none of the neopentane α_s plots show a linear region at low surface coverages. Furthermore, the degree of distortion of the plots increases as the pore size decreases indicating a corresponding increase in the enhancement of the adsorption provoked by the increasing proximity of the pore walls in relation to the dimension of the adsorbing molecules. It follows that, in the case of neopentane, there is little sense in attempting to calculate a value for the total surface area. Tentative estimates to calculate the "apparent" total surface area gave, as might be expected, values considerably higher than those obtained from nitrogen. On the other hand, estimates of the external surface area can be calculated from the upper linear region of the α_s plots and the values obtained, included in Table 1, are very similar to those obtained with nitrogen.

A notable feature of Fig. 3(a)–(e) is that, for each sample, the uptakes of the different hydrocarbon adsorptives at the isotherm plateaux are almost identical and always lower than the corresponding nitrogen uptake. For methanol, the top of the pore filling step reaches the plateau of the isotherms of the other organic adsorptives, but at higher relative pressures goes slightly above, although still below nitrogen. This is confirmed by
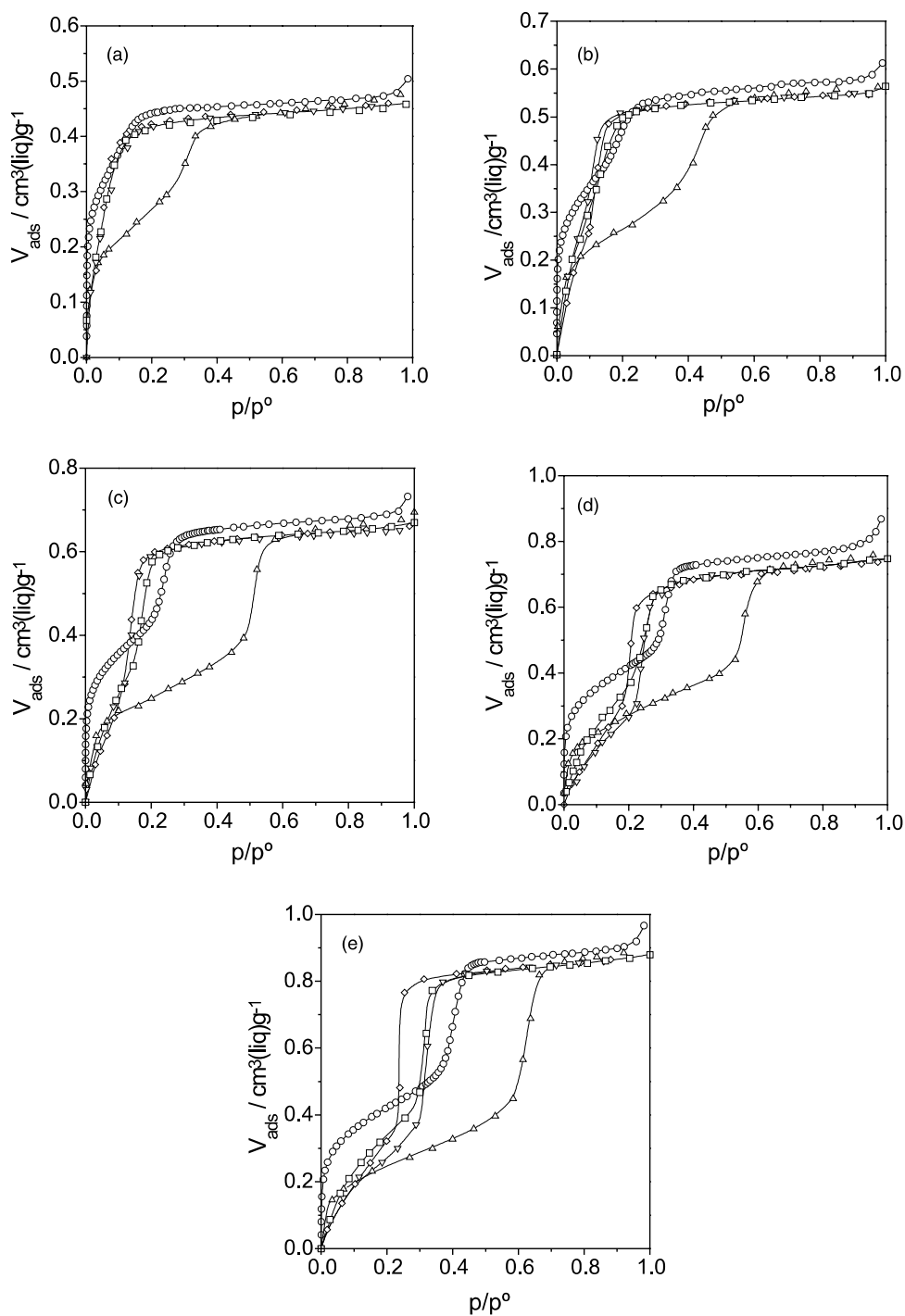
Fig. 3. Nitrogen at 77 K (○), neopentane at 273 K (□), hexane at 298 K (◇), benzene at 298 K (▽) and methanol at 298 K (△) adsorption isotherms obtained on samples: (a) C10F; (b) C12F; (c) C14F; (d) C16F and (e) C18F. In all cases the amounts adsorbed are expressed as equivalent liquid volume using the normal liquid density for each adsorptive.
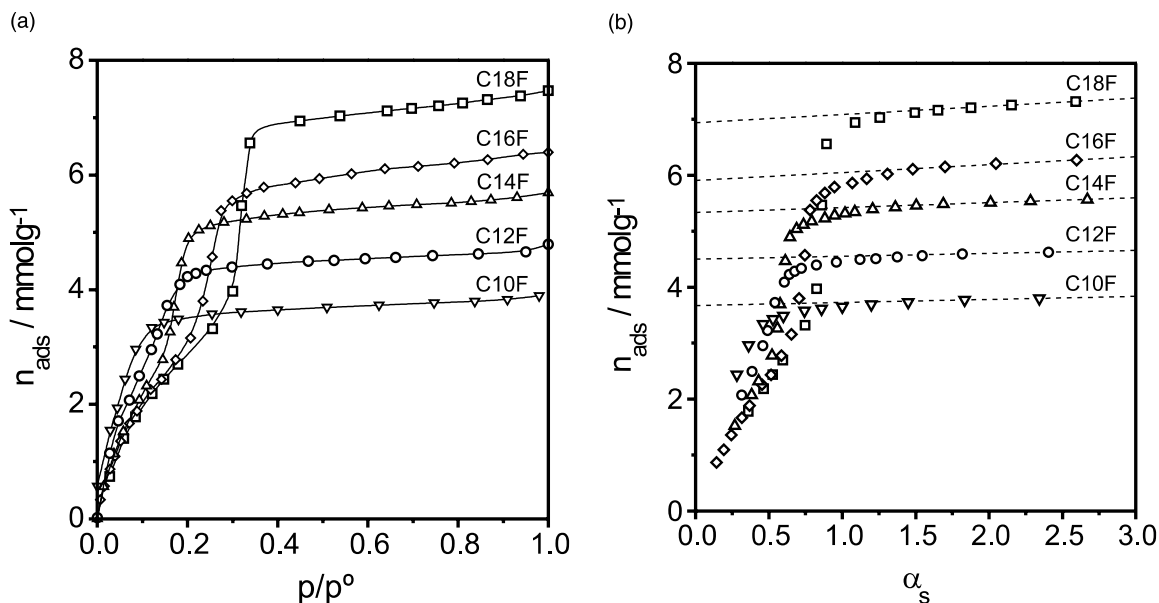
(a)

(b)

Fig. 4. (a) Neopentane adsorption isotherms determined at 273 K on a series of samples of siliceous MCM-41. (b) α_s plots corresponding to the isotherms of neopentane adsorption at 273 K.

the values of the total adsorbed volume at $0.9p^0$ given in Table 2. It can be seen that in almost all cases a constant value is given by the organic adsorptives and a higher value is given by nitrogen. Strictly speaking, a more correct comparison would require considering the effective pore volume obtained after correcting for multilayer adsorption on the external surface. We can only make this correction to the nitrogen and neopentane data as it is only for these adsorptives that standard adsorption data is available. The corrected neopentane pore volumes, obtained from the neopentane α_s plots previously referred to, are included in Table 1 and it can be seen that they are

on average 4–5% lower than those obtained with nitrogen.

Several tentative explanations can be put forward to explain the higher pore volume obtained with nitrogen. One is that it could be due to molecular sieving effects, that is, that the samples could contain a small amount of micropores accessible to nitrogen but not to the other molecules. However, although a small molecular sieving effect could be possible for the bulkier hydrocarbons, it is very unlikely that it occurs with methanol as, although its kinetic diameter is only slightly larger than that of nitrogen (0.38 and 0.36 nm, respectively [52]), it is known that methanol at around

Table 2
Values of total adsorbed volumes at $0.9p^0$ for each adsorptive on the MCM-41 samples calculated using the corresponding normal liquid density

Sample	V_{ads} at $p = 0.9p^0$ (cm³ g⁻¹)				
	Benzene	*n*-hexane	Neopentane	Methanol	Nitrogen
C10F	0.46	0.46	0.45	0.47	0.48
C12F	0.55	0.55	0.55	0.56	0.58
C14F	0.65	0.66	0.66	0.67	0.69
C16F	0.73	0.73	0.74	0.75	0.79
C18F	0.86	0.86	0.86	0.88	0.90

ambient temperature can readily adsorb in micropores which completely exclude nitrogen at 77 K [53]. The possibility that the polar methanol molecule might have altered the pore structure can also be excluded, as it was found that the methanol isotherm was reproducible on consecutive runs as already mentioned in the experimental section. Another possible explanation could be that the difference is associated with a more rigid structure of the solid material at the much lower temperature used for nitrogen adsorption. A significantly lower vibration frequency of the wall atoms at 77 K could lead to an effective free volume for nitrogen higher than for the other molecules adsorbed at around 270–300 K. However, to our knowledge there is so far no convincing experimental evidence that these structural effects are significant.

Therefore, the most likely explanation for the differences in pore volumes is that they are related with the proper values of liquid density which should be used to calculate the pore volumes. Either a higher value for the density of nitrogen at 77 K in the pores should be used, or a lower than normal density for the other adsorptives should be used. For the bulkier molecules a change in density could be associated with effects of molecular dimension (neopentane) or pore shape (benzene and n-hexane) on the packing of the adsorbed molecules in the pores. It has in fact been suggested that this does occur with certain other porous materials containing very narrow pores [54]. However, it would be much less likely in the case of most of the present samples, which have pore sizes in the range of secondary micropores or small mesopores. Furthermore, if it was the density of the hydrocarbon adsorptives which was in error it would seem rather unlikely that all three would be affected in exactly the same way. Therefore, it seems more likely that it is the density of the adsorbed nitrogen which should be corrected to a higher value. By assuming that the same volume of pores is accessible to all adsorbates, estimates of the correct nitrogen adsorbate density can be calculated by comparing the pore volumes obtained from the α_s plots of nitrogen and neopentane. The values obtained are included in the last column of Table 1, and it can be seen that they are between 0.84–0.85 g cm^{-3}. For comparison, the same calculations were carried out for all of the adsorptives using total adsorbed volumes at $0.9p^0$ and values ranging from 0.83–0.88 g cm^{-3} were obtained, although in this case the estimates are subject to a higher degree of uncertainty. The reason for the higher density and the implications will be considered below.

4.3. Estimates of pore size

We have calculated the pore size distributions from the nitrogen isotherms using the NLDFT method [3,4,14]. The average pore radii are given in column 3 of Table 3 and were estimated from the maxima on the pore size distribution curves shown in Fig. 5.

Table 3
Pore sizes of the MCM-41 samples estimated by different methods and cross-sectional area of adsorbed nitrogen at 77 K

Sample	a_0 (nm)	r_p(DFT) (nm)	Using V_p (nitrogen)				Using V_p (neopentane)			
			r_p(H) (nm)	r_p(g) (nm)	σ_{N_2} (nm^2)[a]	σ_{N_2} (nm^2)[b]	r_p(H) (nm)	r_p(g) (nm)	σ_{N_2} (nm^2)[a]	σ_{N_2} (nm^2)[b]
C10F	3.27	1.25	0.95	1.21	(0.128)	(0.124)	0.91	1.20	(0.123)	(0.118)
C12F	3.89	1.53	1.21	1.52	(0.129)	(0.128)	1.15	1.50	(0.124)	(0.122)
C14F	3.97	1.65	1.42	1.60	0.143	0.138	1.35	1.59	0.137	0.133
C16F	4.47	1.89	1.60	1.84	0.141	0.137	1.54	1.83	0.135	0.131
C18F	5.23	2.21	1.85	2.22	0.136	0.136	1.79	2.20	0.131	0.130
					0.140[c]	0.137[c]			0.134[c]	0.131[c]

[a] $\sigma_{N_2} = 0.162 r_p(H)/r_p(g)$.
[b] $\sigma_{N_2} = 0.162 r_p(H)/r_p(DFT)$.
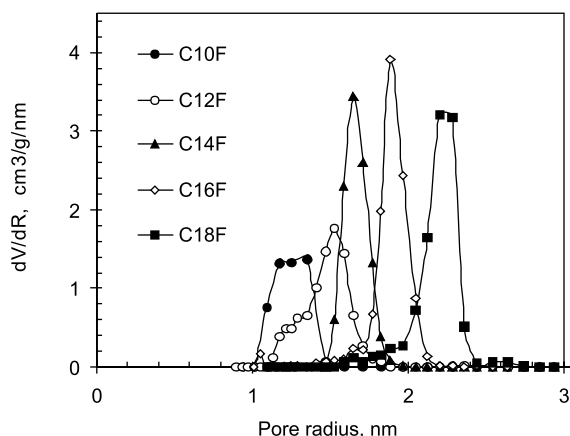[c] Average value.

Fig. 5. Pore size distributions calculated from nitrogen isotherms by the NLDFT method.

For each sample, estimates of the mean pore radius can also be obtained from the results of the analyses of the corresponding nitrogen and neopentane α_s plots by assuming a non-intersecting cylindrical pore structure and making use of the concept of hydraulic pore radius [55]. In this case, what we will refer to as the hydraulic pore radius, can be calculated from the relationship:

$$r_p(H) = \frac{2V_p}{A_s - A_{ext}} \tag{1}$$

where V_p is the pore volume, A_s is the total surface area and A_{ext} the external surface area. It follows that $(A_s - A_{ext})$ gives the area just of the walls of the pores, that is, the internal surface area of the samples. The estimates of $r_p(H)$ are given in columns 4 and 8 of Table 3 where it is implicitly assumed that the adsorbed nitrogen maintains its normal density (column 4) or that the adsorbed neopentane maintains its normal density and that the true density of the adsorbed nitrogen is therefore, as already mentioned above, between 0.84–0.85 g cm^{-3} (column 8). In all cases the total area obtained from the nitrogen isotherm was used.

A third estimate of the pore size can be obtained by assuming the ideal model of a hexagonal array of non-intersecting cylindrical pores. From geometrical considerations this model leads to the following expression:

$$r_p(g) = a_0 \sqrt{\frac{\sqrt{3}}{2\pi} \left(\frac{\rho_{sil} V_p}{1 + \rho_{sil} V_p} \right)} \tag{2}$$

where a_0 is the unit cell parameter obtained from XRD, ρ_{sil} is the density of the silica wall material and V_p is the pore volume. In this case two sets of values are also presented, the first calculated by considering the pore volume obtained from nitrogen (column 5) and the other by considering the pore volume obtained from neopentane (column 9). In all cases a density of 2.2 g cm^{-3} was assumed for the silica material constituting the walls.

It can be seen that the agreement between the DFT radii and the geometrical pore radii is very good, with the DFT values being always only slightly higher, except for C18F. On the other hand, and in agreement with what was previously noted in the introduction, the hydraulic pore radii are always lower than the others. Furthermore, it can also be seen that corresponding values in columns 5 and 9 are almost the same. That is, the geometric pore radii are only slightly affected by uncertainty over the true density of nitrogen (or neopentane) in the pores. On the other hand, corresponding values in columns 4 and 8 show slightly greater differences indicating that the hydraulic pore radii are more sensitive to the values used for the densities of the adsorbed phases.

It is evident that the low values of $r_p(H)$ cannot be explained by adjusting the density of the adsorbed phase. From Eq. (1), it must therefore be due to an overestimation of the internal surface area which, in practical terms, is most likely to be caused by overestimation of the nitrogen cross-sectional area in the monolayer, and this will be considered below.

4.4. Estimates of the cross-sectional area of nitrogen adsorbed on the surface of the pores

If we assume that $r_p(DFT)$ or $r_p(g)$ is correct, then we can estimate σ_{N_2} from the relationship:

$$\sigma_{N_2} = 0.162 \frac{r_p(H)}{r_p(DFT \text{ or } g)} \tag{3}$$

In columns 6 and 7 and columns 10 and 11 of Table 3 we present the values obtained by com-

paring $r_p(H)$ with $r_p(g)$ and $r_p(DFT)$, assuming the normal (columns 6/7) and the higher (columns 10/11) density of nitrogen. It can be seen that for each set nearly constant values are obtained for samples C14F, C16F and C18F. For C10F and C12F the values are slightly lower. However, as already mentioned, the smallness of the pore size in C10F and C12F makes quantitative assessment of the results more uncertain and the corresponding estimates of σ_{N_2} should therefore be considered with more caution. Considering only the results obtained with the three samples with bigger pore sizes, we can see that the values are in all cases close to 0.14 nm², if the pore volume from nitrogen is considered, and closer to 0.13 nm² if the pore volume from neopentane is correct. Both values are in agreement with previous findings on various oxides [56], including silicas, and on MCM-41 [9,10,36]. From a comparison of the surface areas obtained from nitrogen and argon adsorption data values of ≈0.13 nm² for oxides [56] and ≈0.14 nm² for MCM-41 [36], have been suggested. Other authors have also suggested 0.135 nm² for nitrogen adsorbed on silica [58] which was found to be appropriate for MCM-41 [9,10].

Several possible explanations can be put forward for these low values of the cross-sectional area. On the one hand, they are physically acceptable for a nitrogen molecule which assumes an orientation which is more perpendicular to the surface than that of a molecule in the normal liquid which would not show any preferential orientation. For instance, it appears that the orientation of the nitrogen molecules is dependent on the surface structure and that it changes with the degree of hydroxylation of the silica surface, presumably due to specific interactions involving the nitrogen quadrupole and the dipolar surface hydroxyl groups [56,57].

In addition, we can also consider that there is some inherent roughness of the pore walls. If this is the case, the total surface area of the pore walls and, consequently, the amount adsorbed in the monolayer will be greater than those corresponding to the surface of smooth cylinders with the same effective diameter. Therefore, to obtain the area of the ideal smooth cylinder, which is the one that should be used in the hydraulic pore approach, we need to make a correction to the values of the monolayer capacities or surface areas. This can be achieved by multiplying them by an appropriate factor, which in practical terms is equivalent to the use of a cross-sectional area lower than 0.162 nm².

It is worth noticing that in recent simulation studies of siliceous porous glasses, Gelb and Gubbins [59] estimated the ratio of accessible surface area to ideal surface area in their model systems to be near 1:1.2. This degree of surface roughness is precisely the value of the corrections to the cross-sectional area of nitrogen discussed above. Also, the same modelling studies [59] showed an appreciable increase (≈10%) in the monolayer density of the adsorbed nitrogen (modelled as a spherical molecule) with decrease in pore size due to enhancement of the solid–fluid interactions. This may be another reason for the need to use a smaller value of the nitrogen cross-section, which is needed to obtain an ideal surface area of MCM-41 materials. The extent to which these two factors (roughness and increase in the monolayer density) are significant for MCM-41 and other siliceous adsorbents is not yet fully understood.

At first sight, it might seem strange that the surface area obtained from the α_s method needs to be corrected by the cross-sectional area of the adsorbate molecules as this parameter is apparently not directly involved in the method. However, the surface area is obtained by multiplying the slope of the α_s plot by the ratio $A(\text{ref})/n_{0.4}(\text{ref})$ where the surface area, $A(\text{ref})$, of the reference material is invariably obtained by applying the BET method to the nitrogen adsorption isotherm. Hence a value for the cross-sectional area of the nitrogen molecule has to be assumed. Furthermore, it is implicitly assumed that the cross-sectional area of the nitrogen molecule is the same on the test material and on the reference. If this is not the case then, in order to obtain correct values of the surface area, the slope of the α_s plot of the test sample has to be multiplied by the ratio of the cross-sectional areas as well as by the factor $A(\text{ref})/n_{0.4}(\text{ref})$.

Considering in more detail the 4 sets of values in Table 3 for the nitrogen cross-sectional area we see that they are not very different and therefore it

is somewhat difficult to ascertain which is the most correct. If we consider first the comparison between the values calculated using $r_p(DFT)$ and $r_p(g)$, we see that the differences are small. However, it should be noted that the geometrical pore radius involves the use of two experimental values, a_0 obtained from XRD and the pore volume obtained from nitrogen adsorption, and errors in these values will obviously affect the corresponding estimate of $r_p(g)$. It is also necessary to assume a value for the silica density and, as this is not easy to determine experimentally with sufficient accuracy, the normal amorphous silica bulk density is invariably used. However, it has been suggested that the walls may be defective [60] or even porous [61] and this may result in the density of the silica of the walls being lower than the normally assumed value of 2.2 $g\,cm^{-3}$. Therefore, the value of $r_p(DFT)$ is likely to be more reliable for comparison as it does not depend on any of these parameters, but is obtained only by the position of the step in the isotherm.

If we now compare the values obtained by considering the pore volumes from nitrogen and from neopentane, it is difficult to establish which is more correct and if in fact the density of nitrogen is higher than in the normal liquid. However, it should be noticed that the same considerations mentioned above to justify a use of a cross-sectional area smaller than in the normal liquid will also justify the use of a higher density for nitrogen adsorbed in the pores in order to calculate the volume used in the hydraulic pore radius approach. Either a more vertical orientation, roughness of the surface or higher monolayer density will lead to an amount of nitrogen adsorbed in the monolayer greater than if these factors were absent. This will make the total amount in the pores higher too, as the amount adsorbed in the monolayer is relatively significant. For instance, by a simple calculation using the monolayer capacity from the BET method and the total amount adsorbed in the pores from the α_s plot we find for C18F that the amount adsorbed in the monolayer is about 40% of the total. Therefore even if the density of nitrogen condensed in the core volume is the same as in the normal liquid, we will have to use an overall mean density of the adsorbate in the pores higher, in

order to obtain the adequate pore volume to calculate the hydraulic radius. Furthermore, it should also be noticed that neopentane is a more spherical molecule and being a bigger molecule may not be sensitive to the surface roughness. Also, we have seen that in the case of neopentane there was no clear monolayer formation. In this sense it is likely that neopentane would give a more correct value for the pore volume to be used in the calculation of the $r_p(H)$.

From what has been discussed, it may seem that nitrogen is not the most suitable adsorptive to obtain the pore volume and also that the hydraulic pore width method is unreliable due to the uncertainty over the values to use for pore volume and surface area. However, it can be seen that from neopentane it is not possible to obtain the surface area. Therefore, the need to carry out measurements of two adsorptives to obtain both surface area and pore volume can be avoided if we continue to use nitrogen but take into account appropriate values for the cross-sectional area and apparent density for the nitrogen adsorbed in the pores, which our work shows to be 0.131 nm^2 and 0.84 $g\,cm^{-3}$. With regard to the hydraulic pore radius, as it is obtained from a ratio of those two quantities, we can obtain estimates of $r_p(H)$ which agree with $r_p(DFT)$, for example, by altering the values of the nitrogen cross-sectional area and, optionally, density. We have a choice of considering a density of 0.84 $g\,cm^{-3}$ and a cross-sectional area of 0.131 nm^2 or of assuming the normal density of nitrogen and a cross-sectional area of 0.137 nm^2. The absolute values of pore volume and surface area will be different in the two cases but the corrected hydraulic pore radius will be the same, as long as the nitrogen cross-sectional area and density are consistent.

It is worthwhile pointing out here that this method also has some other particular advantages due to the fact that it involves a ratio. For instance, it is not affected by the presence of non-porous material, usually designated by "amorphous material" nor by any errors involved in the mass of solid used in the measurements (either in the initial weighing of the sample or loss of sample during outgassing). If any of these situations occurs, the absolute values of V_p, A_T and A_{ext} will all

be altered, as they are expressed per gram of material, but the ratio $V_{\mathrm{p}}/(A_{\mathrm{T}} - A_{\mathrm{ext}})$, from which the hydraulic pore radius is calculated, will not be affected.

5. Conclusions

We performed a comprehensive comparison of different methods for evaluating the pore size in silica grade MCM-41 materials using nitrogen, neopentane, *n*-hexane, benzene and methanol adsorption isotherms. We compared different methods for evaluating the pore size from nitrogen isotherms: the NLDFT method, the hydraulic radius approach and the geometric method based on the ideal model. We found remarkably good agreement between the results obtained from the NLDFT and geometric methods: for five samples of MCM-41 with different pore sizes the pore radii obtained by the two methods differ by less than 0.05 nm. The comparison of values of hydraulic pore radius with those obtained from DFT and with the geometric method, confirms findings seen before by other workers, that in order to obtain reliable values of pore radius by the hydraulic method it is necessary to use a cross-sectional area of nitrogen in the monolayer smaller than the normally assumed value of 0.162 nm^2 calculated from the normal liquid density.

In addition, our work shows that the effective pore volume obtained from nitrogen adsorption data is always higher than that obtained with the four organic adsorptives studied for which a fairly constant volume is obtained. One possible explanation for the difference is that the mean overall density of the nitrogen adsorbed in the pores of MCM-41 may be higher than that in the normal liquid, which is consistent with a lower value for the cross-sectional area. A density value of about 0.84–0.85 g cm^{-3} must be used in order to obtain agreement of nitrogen with the other adsorptives. If an average density of 0.84 g cm^{-3} is used to calculate the liquid volume, the surface area obtained by nitrogen adsorption should be calculated by considering a value of 0.131 nm^2 for the cross-sectional area instead of the normally used value. In this case, agreement between the hydraulic pore radius and the radius estimated by NLDFT, can be achieved. The same values of the hydraulic pore radius are also obtained if, on the other hand, the usual value of 0.808 g cm^{-3} is considered for the nitrogen density and 0.137 nm^2 is used as the cross-sectional area. That is, in order to calculate the pore size using the hydraulic radius approach it is not necessary to know the real density of the nitrogen adsorbed in the pores, as long as the appropriate value of cross-sectional area is used. While NLDFT is not readily available to the majority of workers, the hydraulic pore radius corrected in this way probably provides the most reliable alternative estimate of the pore size of MCM-41. Nevertheless, uncertainty still remains with regard to the absolute values of pore volume and surface area, and more evidence is still needed to confirm the exact value to use for the mean density and consequently for the cross-sectional area of nitrogen adsorbed at 77 K in the pores in order to obtain those two quantities. Therefore, it is important to always clearly state the values of density and cross-sectional area used when presenting values of hydraulic pore radius, pore volume and surface area of MCM-41 materials.

Acknowledgements

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