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Benzene Adsorption Isotherms on MCM-41 and their Use for Pore Size Analysis

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Abstract. This work is focused on the elaboration of methodology for adsorption characterization of porous silicas by using benzene adsorption isotherms measured on good quality MCM-41 materials. Three MCM-41 samples were synthesized by using tetraethyl orthosilicate (TEOS) as silica source and surfactants, octyltrimethylammonium (C8), decyltrimethylammonium (C10) and cetyltrimethylammonium (C16) bromides as templates. A characteristic feature of this synthesis was relatively long hydrothermal treatment (5 days) at 373 K, which gave well ordered samples as evidenced by powder XRD analysis. Benzene adsorption isotherms measured on these MCM-41 samples were used to evaluate such standard quantities as the BET specific surface area, total pore volume, external surface area and the volume of ordered mesopores, and to obtain the statistical film thickness (t-curve) as well as the Kelvin-type relation, which describes the dependence between pore width and condensation pressure for benzene on silica at 298 K. The latter relations were incorporated into the Barrett-Joyner-Halenda algorithm to extend its applicability to calculate the pore size distributions from benzene adsorption data.

Keywords: adsorption, argon, benzene, MCM-41, pore size analysis

Introduction

Gas adsorption is a popular and commonly used method for characterization of surface and structural properties of porous materials allowing the determination of their surface area, pore volume, pore size distribution and adsorption energy distribution (see monographs by Jaroniec and Madey, 1988; Rudzinski and Everett, 1992; Jankowska et al., 1991). Discovered in early nineties ordered mesoporous silicas (OMS) are novel and attractive materials of great importance for adsorption, catalysis, separations and nanotechnology (see reviews by Corma, 1997; Jaroniec et al., 1998 and references therein). Since OMS possess well-defined porous structure, they are often used as model adsorbents to verify and improve the existing methods as well as to elaborate new methods for characterization of adsorption systems. Nitrogen adsorption is most often used for characterization of adsorbents and catalysts, especially for determination of

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their specific surface area. Adsorption data for other adsorbates such as argon and benzene provide also valuable information about porous structure of materials (Kruk and Jaroniec, 2000; Bambrough et al., 1998).

Benzene adsorption at 298 K was used to study a series of OMS materials of hexagonal arrangement of cylindrical pores, known as MCM-41, of different pore widths (Ribeiro, Carrott et al., 2001). It was reported that the pore volumes evaluated from benzene, neopentane, *n*-hexane and methanol adsorption data for the OMS studied were comparable but smaller than the corresponding pore volumes obtained from nitrogen adsorption. Nguyen and Do (2000) used benzene adsorption at 298 and 303 K to determine the pore width of various MCM-41 materials. Hu et al. (2001) measured a series of benzene adsorption isotherms at 298, 310, 320 and 330 K on unmodified and modified MCM-41 materials and employed them for pore size analysis. Their work shows that a specific modification of MCM-41 (possessing cylindrical pores about 3 nm) with tetraethyl orthosilicate led to a microporous material having pores about 1.3 nm. Benzene adsorption isotherms at 294 K were also used to estimate the mechanical strength and stability of MCM-48, which represents OMS with cubic structure (Hartmann and Bischof, 1999). Their study shows that the MCM-48 structure is more stable than the two-dimensional MCM-41 structure but less stable than the crystalline zeolite. Benzene, similarly as nitrogen, toluene, *p*-xylene, mesitylene and water, was used to study the mechanism of adsorption on MCM-41 with incorporated heteroatoms such as Al and Ti (Choudhary and Mantri, 2000a; Rozwadowski et al., 2001; Jeong et al., 2001). This adsorbate was also employed to investigate the temperature programmed desorption from MCM-41 materials (Zhao et al., 2001; Choudhary and Mantri, 2000b).

The aforementioned studies indicate that benzene is useful for characterization of adsorption properties of nanoporous materials including OMS. Especially, the discovery of OMS in early nineties (Kresge et al., 1992; Beck et al., 1992) opened new possibilities for characterization of adsorbents and catalysts on the basis of gas adsorption data. The OMS materials possess well-defined porous structures, which make them attractive model adsorbents for the verification and improvement of the existing characterization methods as well as for the development of novel methods. An excellent illustration of the usefulness of OMS as model adsorbents is the elaboration of the Kruk, Jaroniec and Sayari (KJS) method for calculation of the pore size distribution (PSD) of mesoporous siliceous materials (Kruk et al., 1997). The idea of this method was to employ gas adsorption isotherms measured for the MCM-41 samples of the known pore geometry and pore width, determined by independent techniques such as powder X-ray diffraction (XRD) and transmission electron microscopy (TEM), for elaboration of the method for pore size analysis. A set of adsorption isotherms on the MCM-41 samples of known pore widths was used to find the experimental relation between pore width and condensation pressure (Kelvin-type relationship) as well as the statistical film thickness as a function of the relative pressure. Both relations established on the basis of adsorption data for a series MCM-41 samples were introduced into the well-known Barrett-Joyner-Halenda (BJH) algorithm (Barrett et al., 1951) instead of classical relations, which are quite inaccurate. Extensive experimental studies (see review by Kruk and Jaroniec, 2001, and references therein) showed that the incorporation of aforementioned relations to the classical algorithms for the PSD calculation (such as the BJH algorithm) improves substantially the accuracy of pore size analysis.

The aim of the current work is to explore the possibility of using benzene as a probe molecule for adsorption characterization of OMS. Benzene vapor adsorption data for three MCM-41 samples of different pore sizes are used to verify and if necessary, to modify the existing methods for determination of the surface and structural parameters of OMS such as the BET surface area, external surface area, pore volume and pore width. The main focus is given on the adaptation of the BJH method for analysis of benzene adsorption isotherms. The structural parameters obtained for the samples studied on the basis of benzene adsorption isotherms will be compared with the corresponding parameters evaluated from argon adsorption data at 77 K. The latter data were selected for this comparison because argon at 77 K is seldom used to characterize OMS although Ar at 77 K is an attractive adsorbate for studying materials with mesopores below 15 nm (Kruk and Jaroniec, 2002). Of course, this comparison could be done for argon adsorption at 87 K or nitrogen adsorption at 77 K because the KJS pore size analysis method gives very similar results for both adsorbates and temperatures (Kruk and Jaroniec, 2001).

Experimental

Materials

MCM-41 samples were synthesized by using tetraethyl orthosilicate (TEOS) as silica source as well as octyltrimethylammonium bromide, $CH_3(CH_2)_7(CH_3)_3N^+Br^-$, decyltrimethylammonium bromide $CH_3(CH_2)_9(CH_3)_3N^+Br^-$ and cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}(CH_3)_3N^+Br^-$ as surfactant templates (Choma et al., 2001b). 0.021 mol of the surfactant (octyl-, decyl- or cetyltrimethylammonium bromide in the amount of 5.306 g, 5.887 g and 7.667 g, respectively) was added into an Erlenmeyer flask containing 36.5 cm^3 of distilled water. Then 1.80 cm^3 of 5 M sodium hydroxide aqueous solution was added under magnetic stirring. The solution was mixed for half-hour. After that 6.7 cm^3 of TEOS (0.03 mol) was added and the solution was mixed again for an hour. The hydrothermal treatment of this mixture was carried out in an oven at 373 K for 5 days. The synthesized material was filtered and placed in a quartz combustion boat in the furnace and calcined in flowing nitrogen (20 dm^3/h). During calcination process each sample was heated from room temperature to 823 K at a heating rate 1.8 deg/min, and after that at 823 K for 1 hour. After cooling, next day calcination was carried out in flowing air (20 dm^3/h) and again the sample was heated from room temperature to 823 K at a heating rate 1.8 deg/min, and after that at 823 K for 5 hours. For each surfactant used about 1.5 g of the finely powdered material was obtained (Choma et al., 2001b). The resulting materials are denoted as MCM-41 C8, MCM-41 C10 and MCM-41 C14, where Cx stands for the number of carbon atoms in the long chain of the surfactant.

Measurements

The powder X-ray diffraction patterns were acquired on a HZG-4 standard diffractometer (VEB Freiberg Präzisionmechanik, Germany) with a modified computer system to control measurements and to acquire data. Cu K_α radiation was used from a FF lamp with the focus dimension 0.04 mm. The measurements were recorded over a range from 0.9° to 8° 2θ with 0.05° steps and 5 sec. counting time.

Adsorption isotherms of benzene vapor were measured on the MCM-41 samples at 298 K by a volumetric method of adsorption manostats (Jankowska et al., 1991). Argon adsorption measurements were performed at 77 K using a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before adsorption measurements all samples were outgassed under vacuum in the degas port of the adsorption analyzer for at least 2 h at 473 K. The relative pressure of argon was calculated as a ratio of the equilibrium pressure to the saturation vapor pressure for the gas-solid equilibrium (measured periodically during the adsorption run) (Kruk and Jaroniec, 2002).

Adsorption Analysis Methods

Argon and benzene adsorption isotherms were used to evaluate the BET specific surface area, external surface area, volume of primary (ordered) mesopores, pore volume, pore width and pore size distributions similarly as described in (Jaroniec and Kruk, 2001). The single-point pore volume was estimated from the amount adsorbed at a relative pressure of 0.99. The BET surface area was calculated from adsorption data in the relative pressure range from 0.01 to 0.1. The molecular cross-sectional areas of 0.138 nm^2 for argon and 0.41 nm^2 for benzene were used in this calculation.

The external surface area and the volume of primary mesopores were evaluated by the α_s method, which is widely used for characterization of porous adsorbents (Gregg and Sing, 1982). According to this method the amount adsorbed on the nonporous reference adsorbent is expressed as the reduced standard adsorption α_s, which is defined as the ratio of the amount adsorbed, a_s at a given relative pressure p/p_o to the amount adsorbed $a_{s,0.4}$ at the relative pressure $p/p_o = 0.4$:

$$\alpha_s = \frac{a_s}{a_{s,0.4}} = \frac{t_s}{t_{s,0.4}} \tag{1}$$

The symbols t_s and $t_{s,0.4}$ denote, respectively, the film thickness of the surface layer at an arbitrary relative pressure and the film thickness at the relative pressure $p/p_o = 0.4$ for a reference nonporous solid. The linear segment of the α_s plot following the completion of the capillary condensation step was used to evaluate the external surface area and the volume of primary mesopores (e.g., see review by Kruk and Jaroniec, 2001).

The pore size distribution (PSD) was calculated from argon adsorption isotherms at 77 K by employing the Barrett, Joyner and Halenda (BJH) method (Barrett et al., 1951) modified by Kruk and Jaroniec

(KJ) (2002). In this modified method an accurate relationship between the pore size and capillary condensation pressure established for cylindrical pores of MCM-41 materials is used instead of Kelvin equation and the statistical film thickness for very low surface area silica calibrated on the basis of adsorption data for MCM-41 samples is used instead of the classical film thickness curves. This approach was found to be very useful for determination of the pore size distribution of mesoporous silicas. Analogous method can be used to evaluate PSD from benzene adsorption isotherms for porous silicas if the statistical film thickness (t-curve) for this adsorbate on a reference nonporous silica is available and if the Kelvin-type dependence is verified. The t-curve for benzene on the silica surface can be established in an analogous way as it was done for argon and nitrogen (Kruk and Jaroniec, 2000; Jaroniec et al., 1999). This approach will require measuring an accurate benzene adsorption isotherm on nonporous silica and a series of benzene adsorption isotherms on the large-pore MCM-41 samples. The latter data could be used to find an empirical factor, by which the reference isotherm needs to be multiply to obtain the statistical film thickness. While this approach was successful for obtaining the t-curve for nitrogen and argon on the silica surface (Jaroniec et al., 1999; Kruk and Jaroniec, 2000) it is less attractive for the determination of this curve for benzene because of some instrumental limitations to collect the low pressure adsorption data for this adsorbate on a nonporous silica and because of the necessity to consider the curvature effects in the filling cylindrical mesopores of MCM-41 by larger adsorbate molecules such as benzene. Although this approach will be explored in future, here the Broekhoff and de Boer method (Broekhoff and de Boer, 1967, 1968) will be used to calculate the t-curve for benzene on the silica surface because it provides a simple way for such calculation and agrees relatively well with density functional theory calculations (Ravikovitch and Neimark, 2002) and other approaches (Choma et al., 2002a; Bhatia and Sonwane, 2001). Also, this t-curve will be used to obtain the reduced standard adsorption α_s for benzene on the silica surface (see Eq. (1)), which is required for the α_s-plot analysis.

The Broekhoff and de Boer (BdB) theory for the capillary condensation in open cylindrical pores gives (Broekhoff and de Boer, 1967):

$$\mathrm{RT} \ln \frac{p_o}{p} - F(t) = \frac{\gamma V_l}{r - t_e} \tag{2}$$

Here the BdB Eq. (2) was used for benzene adsorbed in cylindrical pores at 298 K. The symbols used in Eq. (2) are defined as follows: p/p_o denotes the relative pressure, γ is the surface tension at the liquid/vapor interface equal to 28.26 dyn/cm for benzene at 298 K, T is the absolute temperature, R is the universal gas constant, V_l is the molar volume of liquid benzene at 298 K equal to 89.38 cm^3/mol, t_e is the statistical thickness of the layer adsorbed on the wall of cylindrical pore of the radius r, and $F(t)$ is a function of the statistical thickness for the film adsorbed on the flat surface. Note that the film thicknesses for the cylindrically curved surface (adsorption in cylindrical pores) and flat surface are denoted as t_e and t, respectively, and the difference between them increases with decreasing the pore radius. The adsorption equilibrium for open cylindrical pores of a constant radius is described by the following relation:

$$\left[\frac{dF(t)}{dt}\right]_{t=t_e} = \frac{\gamma V_L}{(r - t_e)^2} \tag{3}$$

The function $F(t)$ in Eq. (3) can be replaced by the Harkins-Jura (HJ) equation or another equation for the t-curve. Here the following form of HJ equation for benzene adsorption on the flat surface at 298 K is used:

$$F(t) = 2.3026\,\mathrm{RT}\left(\frac{A}{t^2} + B\right) \tag{4}$$

where $A = 0.0592$ and $B = -0.0156$. Substitution of $F(t)$ in Eqs. (2) and (3) by Eq. (4) gives the following system of equations, the solution of which gives the pore radius r and the statistical film thickness t_e as functions of the relative pressure:

$$\begin{cases} \log \dfrac{p_o}{p} - \dfrac{A}{t_e^2} - B = \dfrac{\gamma V_L}{2.3026\,\mathrm{RT}\,(r - t_e)} \\ \dfrac{2A}{t_e^3} = \dfrac{\gamma V_L}{2.3026\,\mathrm{RT}(r - t_e)^2} \end{cases} \tag{5}$$

As regards capillary evaporation of an adsorbate from cylindrical mesopores the BdB theory (Broekhoff and de Boer, 1967) leads to the following equation:

$$r - t_e = \frac{2\gamma V_L}{\mathrm{RT} \ln \frac{p_o}{p}} + \frac{\int_{t_e}^{r} 2F(t)(r - t)\,dt}{(r - t_e)\mathrm{RT} \ln \frac{p_o}{p}} \tag{6}$$

Substitution of the $F(t)$ function in Eq. (6) by Eq. (4) gives:

$$r - t_e = \frac{2\gamma V_L}{2.3026\ \mathrm{RT}\ \log \frac{p_o}{p}} + \frac{2A\left(\frac{r}{t_e} - 1 - \ln \frac{r}{t_e}\right) + B(r - t_e)^2}{(r - t_e)\log \frac{p_o}{p}} \quad (7)$$

Equation (2) with $F(t)$ substituted by Eq. (4), and Eq. (7) form the system of two equations:

$$\begin{cases} \log \frac{p_o}{p} - \frac{A}{t_e^2} - B = \frac{\gamma V_L}{2.3026\ \mathrm{RT}(r - t_e)} \\ r - t_e = \frac{2\gamma V_L}{2.3026\ \mathrm{RT} \log \frac{p_o}{p}} \\ \quad + \frac{2A\left(\frac{r}{t_e} - 1 - \ln \frac{r}{t_e}\right) + B\,(r - t_e)^2}{(r - t_e)\log \frac{p_o}{p}} \end{cases} \quad (8)$$

Solution of this system of equations gives the dependence between the pore radius r and the relative pressure for capillary evaporation process as well as the statistical film thickness t_e as a function of the relative pressure.

As was mentioned above the statistical film thickness evaluated on the basis of the BdB theory was used to calculate the reduced standard adsorption α_s for benzene on the silica surface according to Eq. (1) and to correct Kelvin equation for the formation of benzene film on the silica surface. This corrected Kelvin equation (see below) was employed in the BJH method (Barrett et al., 1951) to calculate PSD from the adsorption branch of the isotherm.

$$w = \frac{4\gamma V_L}{\mathrm{RT}\ \ln(p_o/p)} + 2t_e(p/p_o) + \xi \quad (9)$$

where w is the pore diameter, t_e is the statistical film thickness of benzene adsorbed on the silica surface calculated on the basis of the BdB theory (as shown above) and ξ is the empirical correction, which was introduced to extend the applicability of the Kelvin equation to the range of small mesopores. The need for this correction was explained in Refs. (Kruk and Jaroniec, 2000; Kruk et al., 1997) which report the improvement of the pore size analysis based on the argon and nitrogen adsorption isotherms.

Results and Discussion

Figure 1 presents the diffraction spectra for the calcined MCM-41 samples under study, i.e., C8, C10 and C16 samples synthesized by using octyltrimethylammonium, decyltrimethylammonium and cetyltrimethylammonium bromides, respectively. According to the previous work (Choma et al., 2002b), the main (100) diffraction peak is shifted in the direction of small angles with increasing the length of surfactant chain used as template in the synthesis of MCM-41. The relatively narrow (100) peak and the presence of (110) and (200) peaks indicate a good quality of the samples studied. Unfortunately, low sensitivity of the XRD instrument used did not allow for accurate determination of the (110) and (200) peaks.

Experimental benzene adsorption isotherms measured at 298 K are shown in Fig. 2. Each of these isotherms exhibits a steep step, which is characteristic for materials with uniform mesopores and in this case reflects the capillary condensation of benzene in cylindrical mesopores of MCM-41. This step determines the condensation relative pressure for benzene in the MCM-41 mesopores, which is similar for the C8 and C10 samples (about 0.05) and much lower than that for the C16 sample (about 0.16), suggesting similar pore widths for the C8 and C10 samples but smaller than the pore width for C16 MCM-41. The observed condensation steps are not perfectly perpendicular to the relative pressure axis indicating small dispersion of pore widths in the samples studied. For all samples studied

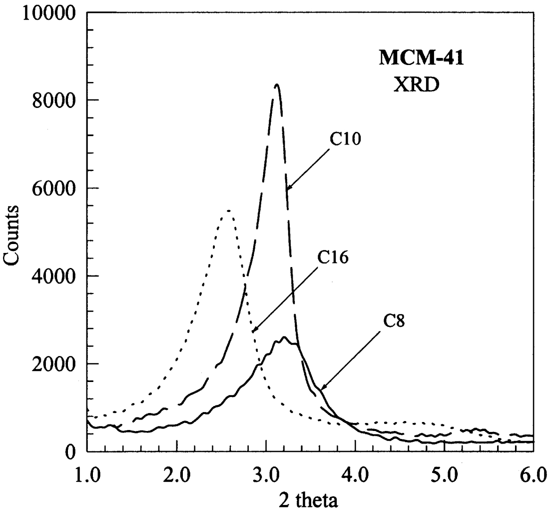

Figure 1. XRD patterns for the calcined MCM-41 samples studied.

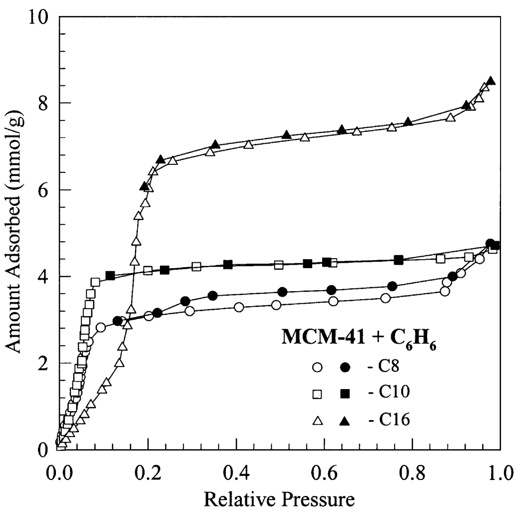

Figure 2. Benzene adsorption isotherms for the MCM-41 samples studied at 298 K.

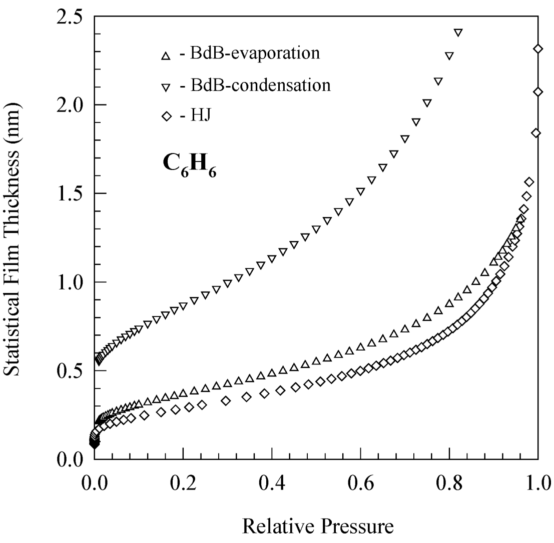

Figure 3. The statistical film thickness curves for benzene on the silica surface calculated by using the BdB Eqs. (8) and (11) derived for capillary condensation and evaporation, respectively, in comparison to the Harkins-Jura t-curve.

the benzene condensation/evaporation in primary (ordered) mesopores is reversible as evidenced by the lack of hysteresis. Also, there is no significant hysteresis associated with benzene adsorption in secondary (textural) mesopores except the C8 sample, which shows hysteresis in the relative pressure range between 0.2 and 0.9.

The α_S-plot analysis of benzene adsorption isotherms was performed to evaluate the volume of primary mesopores and the external surface area of the MCM-41 samples studied. The BdB theory was used to calculate the statistical film thickness (t-curves) for benzene on the silica surface, which was converted to the reduced standard adsorption α_S according to Eq. (1). This theory generates two t-curves, one of them obtained by solving the system of Eq. (5) derived for capillary condensation, and another one generated by solving the system of Eq. (9) derived for capillary evaporation. Both t-curves are shown in Fig. 3 in comparison to the Harkins-Jura (HJ) t-curve calculated according to Eq. (4). As can be seen from this figure the t-curve calculated by solving the system of Eq. (5) for capillary condensation differs significantly from the HJ t-curve as well as the t-curve obtained from Eq. (9) for capillary evaporation. The latter curve lies much close to the HJ t-curve than that generated by the BdB equations for capillary condensation. Also the mutual position of the HJ t-curve and that generated by Eq. (9) for capillary evaporation of benzene is analogous to that observed for the HJ and KJS t-curves for nitrogen, where the KJS t-curve was calibrated for a series of high quality MCM-41 samples (Jaroniec et al., 2002). It should be mentioned that the relation between the pore width and evaporation pressure generated by the BdB theory lies very close to that established experimentally for capillary condensation (Jaroniec et al, 2002) as well as that generated by density functional theory (Ravikovitch and Neimark, 2000). Therefore, the t-curve generated by the BdB Eq. (9) will be used to calculate the reduced standard adsorption α_S for benzene on the silica surface according to Eq. (1) as well as to represent the statistical film thickness for this adsorbate in the Kelvin-type Eq. (9), which is the basis of the BJH method for the PSD determination.

The α_S plots for the MCM-41 samples studied plotted by using the reduced standard adsorption α_S obtained from the aforementioned t-curve for benzene according to Eq. (1) are shown in Fig. 4. The linear segment of these plots in the α_S range from 1.0 to 2.0 was used to evaluate the volume of primary mesopores and the external surface area. The numerical values for both quantities are summarized in Table 1 together with the corresponding values obtained from argon adsorption isotherms at 77 K (Choma et al., 2002b). As can been seen from this comparison both sets of parameters are analogous. The external surface area for C10 MCM-41 is small in comparison to that for C16

Table 1. Comparison of the parameters obtained from analysis of adsorption isotherms for benzene at 298 K and argon at 77 K measured on the MCM-41 samples studied.

MCM-41 sample	Adsorbate	S_{BET}[a] (m^2/g)	S_{ex}[b] (m^2/g)	V_{me}[b] (cm^3/g)	V_p[c] (cm^3/g)	w[d] (nm)
C8	Benzene	500	77	0.27	0.43	2.40
	Argon[e]	568	61	0.34	0.40	2.39
C10	Benzene	720	24	0.37	0.42	2.49
	Argon[e]	733	38	0.48	0.51	2.48
C16	Benzene	465	90	0.58	0.76	3.46
	Argon[e]	600	103	0.68	0.78	3.41

[a] The BET surface area S_{BET} was calculated in the relative pressure range from 0.01 to 0.1 for benzene and from 0.01 to 0.08 for argon to avoid points close to the condensation step.

[b] The external surface area S_{ex} and the volume of primary mesopores V_{me} were evaluated by the α_s plot analysis.

[c] The single-point pore volume was obtained from the amount adsorbed at the relative pressure about 0.98.

[d] The pore width w corresponds to the maximum of PSD evaluated by the BJH method, which employs the modified Kelvin equation.

[e] Parameters evaluated from argon adsorption isotherms taken from Ref. (Choma et al., 2002b).

MCM-41 indicating that a significant textural (secondary) porosity in the latter case. In addition, Table 1 contains the BET surface area and the single-point pore volume calculated from benzene adsorption isotherms shown in Fig. 2. For the purpose of comparison the corresponding values obtained from argon adsorption data at 77 K are summarized too (Choma et al., 2002b). The single-point pore volume obtained from benzene adsorption isotherm was obtained by converting the amount of adsorbed benzene at the relative pressure about 0.98 and using the molar volume of benzene at 298 K equal to 89.38 cm^3/mol. As can be seen from Table 1 the single-point pore volumes are not much greater than the volumes of primary mesopores indicating that the textural porosity in the samples studied is small.

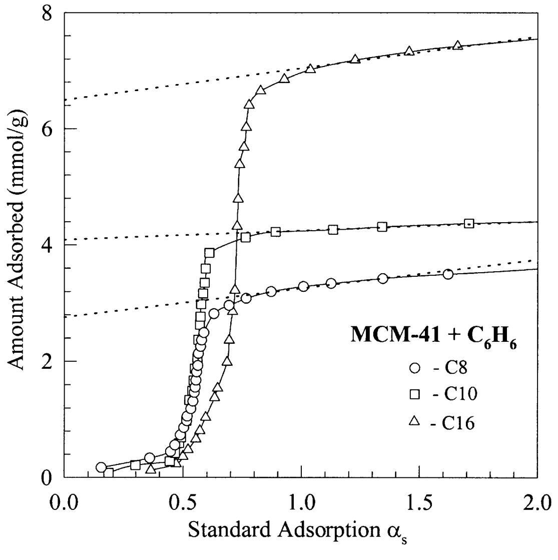

Figure 4. The α_s plots obtained from benzene adsorption isotherms measured on the MCM-41 samples studied.

The pore size distributions were evaluated from adsorption branches of the isotherms shown in Fig. 2 by the BJH method (Barrett et al., 1951), in which the modified Kelvin-type Eq. (9) was used with the t-curve obtained by the BdB theory for capillary evaporation. The constant ξ in Eq. (9) was assumed to be equal to 0.25. This value was obtained to assure the best fit of the resulting pore size distributions with the corresponding ones obtained from argon adsorption isotherms, which were reported elsewhere (Choma et al., 2002b). The PSD curves calculated from benzene adsorption isotherms for the samples studied are shown in Fig. 5 in comparison to the corresponding distributions obtained from argon data. Figure 6 shows a comparison of the PSD curves obtained from benzene adsorption data with those evaluated from nitrogen adsorption isotherms, which were reported by Choma et al. (2002a). As can be seen from both figures there is a good agreement between the PSD curves for the adsorbates studied. The PSD peaks are relatively narrow, which allowed us to use the pore width at the maximum of PSD as the characteristic parameter (see Table 1). A larger PSD dispersion is observed for C16 MCM-41, which also has larger external surface area in comparison to the remaining samples.

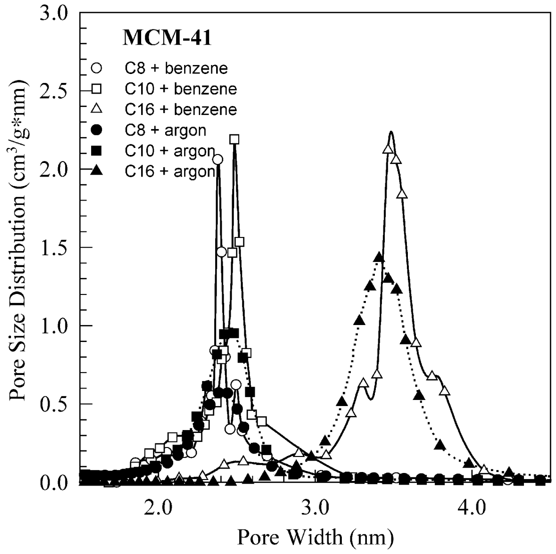

Figure 5. Comparison of the pore size distributions obtained from benzene at 298 K and argon at 77 K adsorption isotherms.

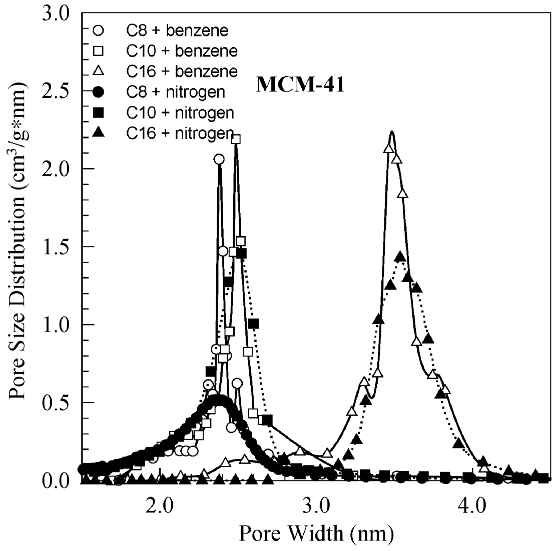

Figure 6. Comparison of the pore size distributions obtained from benzene at 298 K and nitrogen at 77 K adsorption isotherms.

Conclusions

Three MCM-41 samples obtained by using different surfactants were employed to measure benzene adsorption isotherms at 298 K and examine their utility for characterization of ordered mesoporous silicas. The statistical film thickness for benzene on the silica surface was calculated by using the Broekhoff and de Boer theory and employed to obtain the reduced standard adsorption for the α_s plot analysis and to introduce the film correction term in the Kelvin equation. It is shown that an additional constant correction needs to be introduced to the Kelvin equation to extend its applicability to the range of small mesopores. This correction $\xi = 0.25$ was found by comparing the pore size distributions from benzene adsorption isotherms with those from argon adsorption isotherms. This work shows that the incorporation of the modified Kelvin equation into the BJH method makes this method useful for the PSD determination from benzene adsorption data.

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