

Estimation of pore size distribution in MCM-41-type silica using a simple desorption technique

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Abstract A recently developed dynamic desorption technique is used for obtaining vapor isotherms on porous materials. This gravimetric technique does not require any preliminary calibration and is based on analyzing the kinetics of liquid evaporation from a porous sample under quasi-steady state conditions. The crucial feature of the technique is concerned with the fact that no vapor pressure measurements are necessary. The technique is illustrated by desorption of benzene vapors from mesoporous silica MCM-41. To calculate the pore size distribution, the Derjaguin–Broekhoff–de Boer theory in its combination with the Wheeler model

for capillary condensation is used. In the calculations, the reference data on benzene adsorption on a nonporous silica gel from two different sources (published by different authors) are applied. The mean mesopore sizes estimated from desorption isotherms are shown to be in a fair agreement with the calculations through the geometrical method based on the X-ray diffraction data. The dynamic desorption technique can serve as an additional tool for the characterization of a porous media.

Keywords Desorption · Benzene · MCM-41-type silica · Isotherm · Pore size distribution

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1 Introduction

Sorption and transport properties in porous solids are known to be controlled by pore morphology such as pore shape, curvature radius, size, and interconnectivity. One of the most important characteristics of porous solids is concerned with their pore size distribution (PSD). Methods for the estimation of PSDs are traditionally based on sorption studies, namely, on the measurements of adsorption isotherms (Gregg and Sing 1982).

Adsorption isotherms can be obtained by both static and dynamic methods. Classical static methods include manometric (or volumetric) and gravimetric methods. In the former case, vapor pressure is measured at a fixed weight of an adsorbent and, in the latter case, changes in the weight of the sample are measured at a fixed vapor pressure. Usually, the above traditional techniques are known to be time-consuming and expensive. Recently, several alternative techniques for the characterization of porous media have been developed, which couple vapor adsorption with a physical method such as X-ray reflectometry or ellipsometry at the

ambient temperature (Rouessac et al. 2008). In the X-ray reflectometry, the amount of adsorbed vapors is estimated as a function of vapor pressure, by measuring both thickness and electron density of mesostructured films. In ellipsometry, both thickness and refractive index of the adsorbing film are measured during vapor adsorption.

Dynamic methods such as the programmed thermodesorption of liquids from solid surfaces under quasi-isothermic conditions can also be used (Staszczuk et al. 2000). This simple and rapid method makes it possible to estimate the adsorption capacity as well as to define the mechanism of probe evaporation from the porous solids. An interesting approach was proposed by Beverley et al. (1999a, 1999b). First, gravimetric method for the determination of evaporation rates of liquids was developed (Beverley et al. 1999a). This approach was further extended to measure the rate of evaporation of water contained within the pores of powdered silica particles (Beverley et al. 1999b). The experimental conditions were such that the rate was directly proportional to the water vapor pressure.

In our work we used the recently developed dynamic desorption technique for obtaining vapor isotherms Shkol'nikov and Volkov (1999, 2001). This approach does not require any sophisticated equipment and preliminary calibration. The proposed technique shows excellent agreement with the results obtained by the standard McBain balance technique for the mesoporous silica gel S3/benzene system (Shkol'nikov and Volkov 2001).

The technique is illustrated by desorption of benzene vapors from mesoporous silica MCM-41. This material is known to be a well-studied sorbent containing hexagonally packed cylindrical pores separated by silica walls. The areas of practical application of MCM-41 are broad: from adsorption, separation and catalysis to chemosensors (Selvam et al. 2001; Asefa et al. 2009). The choice of this material is associated with two following reasons. Its well-ordered porous

structure makes it possible to invoke theoretical data (both thermodynamic and statistical mechanics) for the translation of the adsorption data into the PSDs. Moreover, pore sizes of MCM-41 can be estimated by so-called geometrical method based on the X-ray diffraction data. The PSD curves for MCM-41 are constructed on the basis of the Derjaguin–Broekhoff–de Boer (DBdB) theory (Derjaguin 1957; Broekhoff and de Boer 1967, 1968) in its combination with the Wheeler capillary condensation/evaporation model (Wheeler 1955). The average mesopore sizes are compared with results of the geometrical method.

2 Experimental

2.1 Synthesis

The series of MCM-41-type samples was prepared by sol-gel method: silicon alkoxide was used as a silica precursor and alkyltrimethyl ammonium bromides—as surfactants in order to produce the template liquid crystalline mesophase: $C_nH_{2n+1}(CH_3)_3N^+Br^-$, with $n = 12, 14, \text{ or } 16$. The procedure for the preparation of the samples (denoted as Cn) has been described in detail in Klotz et al. (2000, 2001). Prior to measurements, all samples were carefully dried at 250°C for 2 h in air at atmospheric pressure.

2.2 Benzene desorption experiments

The key feature of dynamic desorption technique is concerned with the fact that no vapor pressure measurements are necessary. To reach this goal, a special experimental setup was designed (Fig. 1a). The measuring cell with the sample was placed onto a thermostated analytical balance pan. For on-line measurements, the Sartorius balance (sensitivity of 0.1 mg) was attached to a computer through the balance

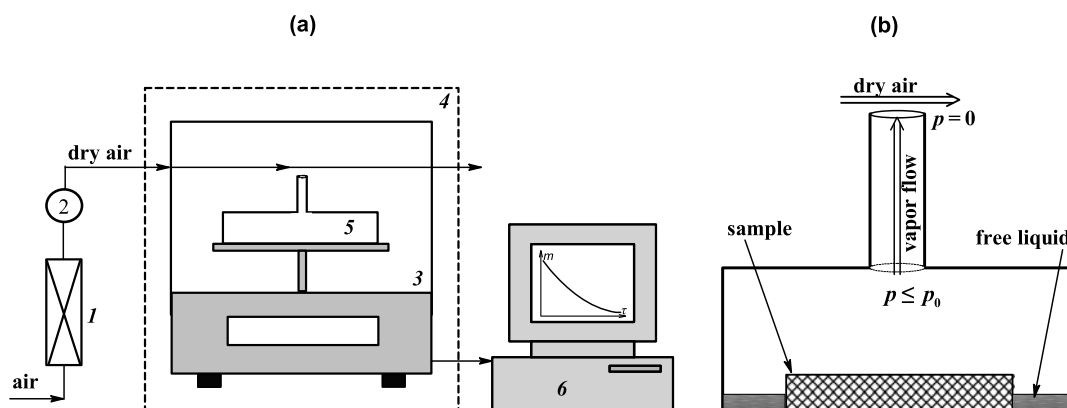


Fig. 1 (a) Schematic representation of a dynamic desorption technique: (1) air drier; (2) flow meter; (3) balance; (4) thermostat; (5) measuring cell; (6) control system (PC) and (b) Schematic of mea-

suring cell with a sample. Vapor pressure of an adsorbate $p = 0$ at the cell outlet. The liquid evaporation rate varies proportionally with the vapor pressure p over the sample

interface RS232. Dry gas (air) is passed over the top end of the cell in order to ensure the complete removal of adsorbate vapors from the cell outlet (Fig. 1b). Changes in the weight loss of the sample with time were recorded.

This method is based on the analysis of the kinetics of liquid evaporation in the quasi-steady state regime. This regime is provided by optimization of the rate of evaporation from the cell containing the sample. With decreasing the measurable rate of vapor removal from the cell, the vapor pressure over the sample tends to reach its equilibrium value (Fig. 1b). Therefore, the rate of liquid evaporation is proportional to the vapor pressure p over the sample. Using geometrical parameters of the offtake tube of the measuring cell, one can estimate the pressure p from the evaporation rate. To avoid calculations of pressure and to reduce possible errors from uncontrolled changes in the experimental conditions, the principle of self-calibration is used. To this end, excessive amounts of the adsorbate (wetting liquid) are supplied into the cell containing the sample saturated with the liquid (Fig. 1b).

Then, it is evident that until all free liquid fully evaporates from the cell, vapor pressure in the cell is equal to the equilibrium pressure p_0 over its surface. This pressure is associated with the maximum rate of evaporation W_0 from the cell. In this case, the time dependence of evaporation rate is characterized by the plateau region. This region is the necessary validation criterion for all experiments, and the W_0 parameter is the reference value for the calculation of the relative pressure in each experimental run. The end of the initial plateau region corresponds to complete evaporation of a free liquid as well as to evaporation of the liquid from the interparticle spaces. As the content of the liquid in the sample decreases further, evaporation of the probe from the porous particles takes place; in this case, vapor pressure is $p < p_0$ and the corresponding evaporation rate is $W < W_0$.

Current relative vapor pressure p/p_0 (with decreasing weight of the adsorbate in the sample) is controlled by the relative rate of liquid evaporation W/W_0 . One can expect that $p/p_0 \approx W/W_0$. More strict analysis requires the account for a stagnant gas layer (dry air) over the sample in the cell. Using the well-known model of steady-state evaporation of a volatile liquid into a stagnant gas layer (so called Stefan diffusion) (Bird et al. 1960), we arrive at the following equation (Shkol'nikov and Volkov 2001):

$$p/p_0 = [1 - (1 - x_0)^{W/W_0}]/x_0, \tag{1}$$

where $x_0 = p_0/P_{\text{atm}}$ is the mole fraction of saturated vapor in the measuring cell, P_{atm} is the overall (atmospheric) pressure of the gas phase. Equation (1) is valid when vapor pressure outside the cell is equal to zero.

Continuous weighing of the sample allows reproducible measurements within a moderately short time period. The

experiment provides nearly infinite number of experimental points together with a detectable random noise of the weighing readings. Therefore, the data should be carefully smoothed by averaging and cubic spline. For the ratio of the adsorbate weight to the dry adsorbent weight (m/m_s), the relative experimental error does not exceed 6%. The measurements were performed at a temperature of $30 \pm 0.1^\circ\text{C}$.

Figure 2 shows evaporation curves of benzene from the three MCM-41-type silica samples. Evaporation rate $W = -dm/d\tau$ is calculated by differentiation of the smoothed weight-time curve. The curve $W(\tau)$ shows the plateau region at the early desorption stage. Within the initial period of time, evaporation rate should be approximately equal to the evaporation rate of the a pure liquid, W_0 . The W_0 value was estimated in the preliminary experiments: pure benzene was placed into the cell and evaporated under nearly the same conditions as those used for the desorption measurements; it was found that $W_0 \approx 4$ mg/h. Profiles of the curves $m(\tau)$ and $W(\tau)$ are related to the sample porous structure. The desorption isotherm (the dependence of m/m_s on p/p_0) is obtained by combining these curves using (1).

3 Mesopore size evaluation

3.1 Characterization of samples by the XRD

The powder XRD patterns were collected on an X-ray diffractometer using the Ni-filtered $\text{CuK}\alpha$ -radiation. The interplanar spacing, d_{100} (nm), was estimated from the XRD patterns as $d_{100} = 0.154/2 \sin \theta$ where the diffraction angle θ corresponds to the diffraction peak. For the C12, C14, and C16 samples, the following values were calculated: $d_{100} = 3.27$ nm, 4.21 nm, and 4.42 nm, respectively. These d -spacing values were used to calculate the diameters of ideal hexagonally packed nonintersecting capillaries through the well-known equation (see e.g. Kruk et al. 1999):

$$D_{\text{XRD}} = cd_{100} \left(\frac{\rho V_{\text{mes}}}{1 + \rho V_{\text{mes}}} \right)^{1/2}, \tag{2}$$

where ρ is the density of pore walls; $c = 1.213$ for circular pores; V_{mes} is the volume of primary mesopores. Density of pore walls in MCM-41 is assumed to be equal to that of amorphous silica (2.2 g/cm^3). Pore wall thickness can be expressed as

$$e = 2 \cdot 3^{-1/2} d_{100} - D_{\text{XRD}} \tag{3}$$

It should be noted that the above equations are valid for a fully ordered mesostructured sample without micropores in the silica walls.

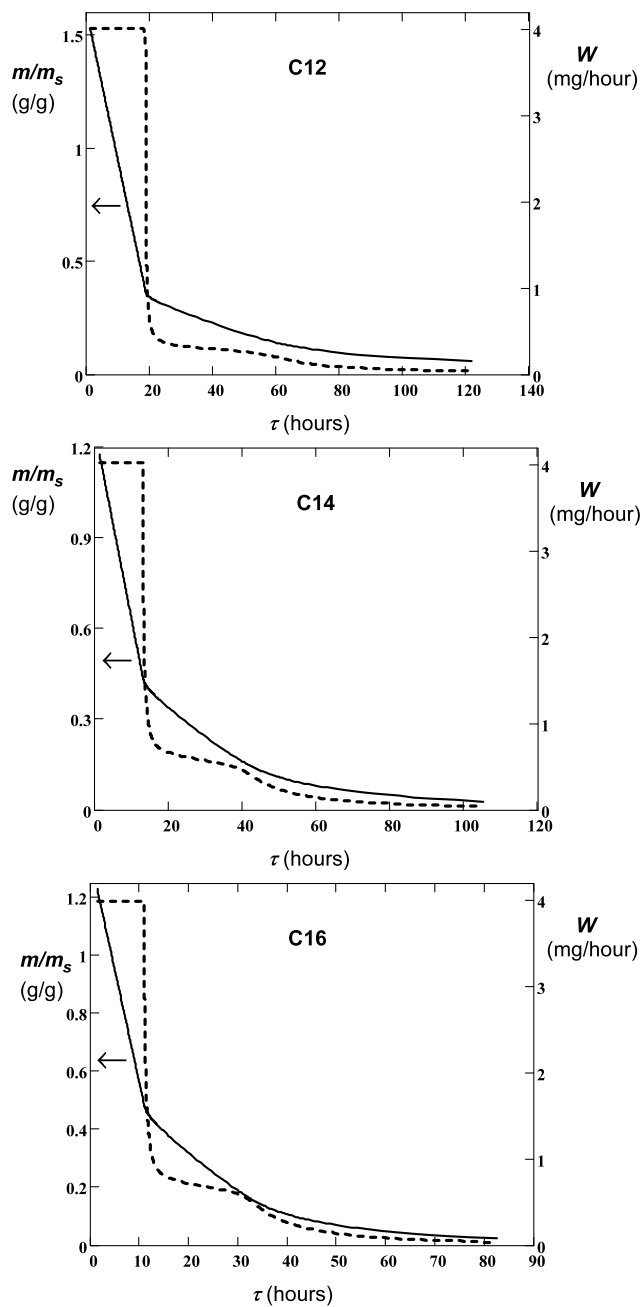


Fig. 2 Experimental evaporation curves for C12, C14, and C16 samples after smoothing procedure: the weight of the adsorbate per gram of adsorbent versus time (solid lines) and corresponding evaporation rate (dashed lines)

3.2 PSD calculation

To translate desorption isotherms into PSDs, it is necessary to derive the relationship between evaporation pressure and pore radius. For this purpose, we used the well-known the DBdB theory. It should be mentioned that the DBdB theory is often used for studying adsorption/desorption processes in the ordered mesoporous materials (Lukens et al. 1999; Qiao et al. 2004; Kowalczyk et al. 2005). Furthermore, the DBdB

theory fairly agrees with the experimental data (Morishige and Tateishi 2006) and appears to be competitive with the density functional theory (Ustinov et al. 2005).

This approach offers a set of two equations for desorption from the cylindrical open-ended pores:

$$\ln(p_0/p) = F(t_e) + \frac{\gamma V_m}{R_g T (R - t_e)}, \quad (4)$$

$$\ln(p_0/p) = \frac{2}{(R - t)^2} \int_{t_e}^R (R - t) F(t) dt + \frac{2\gamma V_m}{R_g T (R - t_e)}, \quad (5)$$

where t_e is the equilibrium thickness of an adsorbed layer in a pore of radius R at the relative pressure p/p_0 ; γ and V_m are the surface tension and the molar volume of a liquid adsorbate, respectively; R_g is the gas constant. The $F(t)$ function describes adsorbate/adsorbent interactions and represents the difference between the chemical potentials of a bulk liquid and a multimolecular adsorption layer with thickness t (in $R_g T$ units). By eliminating $\ln(p_0/p)$ from (4) and (5), we arrive at the equation relating pore radius and equilibrium adsorption layer thickness:

$$\frac{2}{(R - t_e)^2} \int_{t_e}^R (R - t) F(t) dt - F(t_e) + \frac{\gamma V_m}{R_g T (R - t_e)} = 0 \quad (6)$$

According to the Broekhoff and de Boer approximation, the $F(t)$ function can be estimated from the adsorption isotherm on a flat surface (i.e. the t -curve) of a reference solid. We used two data sets for the reference t -curve: benzene adsorption/desorption on a quartz powder with a specific surface of $6 \text{ m}^2/\text{g}$ at 293 K (Isirikyan 1957; Isirikyan and Kiselev 1958) (data set I) and adsorption of benzene vapor on pulverized quartz particles ($S_{\text{BET}} = 1.57 \text{ m}^2/\text{g}$) at 298 K (Naono et al. 1994) (data set II). Figure 3 shows the reference experimental data for the $F(t)$ function. This function can be closely approximated by the Frenkel–Halsey–Hill equation:

$$F(t) = K/t^m \quad (7)$$

Parameters K and m were obtained by regression (with t in nm): $K = 0.1885$ and $m = 1.7005$ for the data set I and $K = 0.1772$, $m = 1.8825$ for the data set II. Note that long time ago this function has been applied by Dubinin (1980) but it was recently used (with $m = 3$) for the analysis of adsorption in MCM-41 (Lukens et al. 1999). Substitution of this function in (6) gives:

$$\frac{2F(t_e)}{2 - m} \frac{x}{1 - x} \left(\frac{1 - x^{m-1}}{(m-1)(1-x)} - 1 \right) - F(t_e) + \frac{\lambda}{t} \frac{x}{1-x} = 0, \quad (8)$$

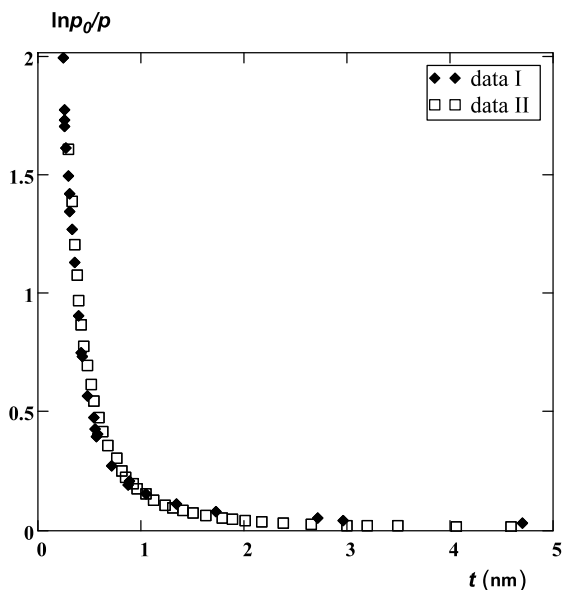


Fig. 3 Isotherms (t -curves) for the reference silica adsorbent for data sets I (Isirikyan 1957) and II (Naono et al. 1994)

where $F(t_e) = K/t_e^m$, $x \equiv t_e/R$ and $\lambda \equiv \gamma V_m/R_g T$. The “length parameter” is $\lambda \cong 1.02$ nm with $\gamma = 28.88 \times 10^{-3}$ J/m², $V_m = 88.76 \times 10^{-6}$ m³/mol at $T = 303$ K. Numerical solution of (8) gives the function $t_e(R)$. Then, from (4), one can find the dependences of the equilibrium thickness of the adsorbed layer and the pore radius on the relative evaporation pressure.

The PSDs have been constructed according to the model proposed by Wheeler (1955). The principal result of this approach for the adsorption/desorption in cylindrical pores reads as:

$$\begin{aligned}
 V_0 - V &= \pi \int_R^\infty (r - t_e)^2 L(r) dr \\
 &= \int_R^\infty \left(\frac{r - t_e}{r}\right)^2 f(r) dr,
 \end{aligned}
 \tag{9}$$

where V is the volume of sorbed vapors at pressure p ; V_0 is the volume of sorbed vapors at the saturation pressure p_0 . The PSD can be characterized by the number $L(r)$ or volume distribution function $f(r)$. By differentiating (9) with respect to R , we arrive at the following equation:

$$\begin{aligned}
 f(R) &= \left(\frac{R}{R - t_e}\right)^2 \frac{dV}{dR} - 2\left(\frac{R}{R - t_e}\right)^2 \\
 &\quad \times \frac{dt_e}{dR} \int_R^\infty \frac{r - t_e}{r^2} f(r) dr
 \end{aligned}
 \tag{10}$$

The PSD function $f(R)$ was calculated through the iteration procedure:

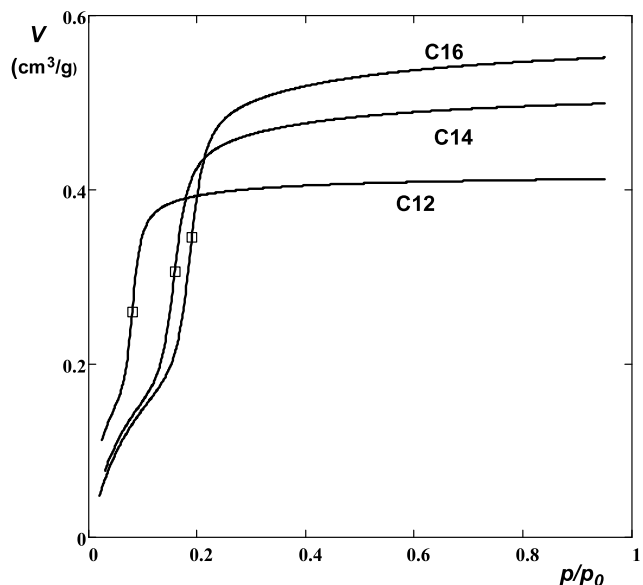


Fig. 4 Benzene desorption isotherms for the C12, C14 and C16 MCM-41 samples ($T = 303$ K); the inflection points are shown by squares

$$\begin{aligned}
 f_n(R) &= f_0(R) - 2\left(\frac{R}{R - t_e}\right)^2 \frac{dt_e}{dR} \int_R^\infty \frac{r - t_e}{r^2} f_{n-1}(r) dr, \\
 n &\geq 1
 \end{aligned}
 \tag{11}$$

where zero-order approximation $f_0(R)$ is given by the first term in (10). This procedure proves to be fast converging because zero-order approximation yields a fair estimation of PSD. Second-order approximation is sufficient for the calculation of PSD. The calculated PSD function should obey the following equation:

$$V(R) = \int_{R_{\min}}^R f(r) dr + \int_R^{R_{\max}} f(r) \left[1 - \left(\frac{r - t_e}{r}\right)^2\right] dr
 \tag{12}$$

This equation is an alternative form of (9) and states that the experimental volume adsorbed at a given relative pressure $p/p_0 = p/p_0(R)$ is the sum of two terms. The first term is the capillary condensed volume at $r < R$; the second term is the volume of the adsorbed film on pores larger than R . The lower integration limit in (12) was defined by the condition of non-negativity of the cumulative pore volume; the upper limit is confined by $R_{\max} = 25$ nm (the nominal upper limit of mesopores). The cumulative pore volume and surface area are defined as follows:

$$V_c(R) = \int_{R_{\min}}^R f(r) dr, \quad S_c(R) = \int_{R_{\min}}^R \frac{2f(r)}{r} dr
 \tag{13}$$

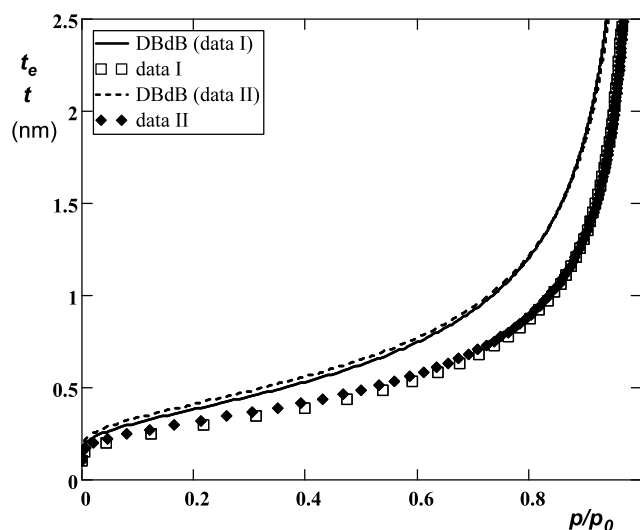


Fig. 5 Evolution of adsorbed benzene film thickness versus relative evaporation pressure—DBdB results: t_e (solid lines); reference t -curves (points)

4 Results and discussion

Figure 4 shows the desorption isotherms (in cm^3 of liquid benzene per g of the solid vs. relative pressure). These type IV isotherms are similar to those obtained for nitrogen, argon, and benzene adsorption, which have been earlier reported in literature (Beck et al. 1992; Selvam et al. 2001; Nguyen and Do 2000; Choma et al. 2004). The desorption isotherms exhibit a characteristic step at a relative pressure 0.08–0.19, depending on the pore size of the sample. The step (inflection) in the isotherm reflects the emptying of the primary mesopores. Position of this step shifts to higher pressures as the chain length of the surfactants used for the synthesis is increased. This fact is in line with the increase in the interplanar spacing from C12 to C16 samples.

Thickness of the adsorption layer in the pores estimated according to the DBdB approach appears to be higher than that of the layer on a flat surface at the same p/p_0 value (as compared with t , relative increase in t_e exceeds 30%) (Fig. 5). The $t_e(p/p_0)$ curves for the two reference data sets are seen to be virtually identical; somewhat higher values are obtained for the Naono data.

Figure 6 shows the calculated differential and cumulative distribution functions. All PSDs are seen to be narrow, and pore diameters can be estimated by the maximum of these functions. Their values and some other calculated parameters are summarized in Table 1. Noteworthy is that the most probable pore diameters for the three MCM-41 samples fit the results obtained from the X-ray diffraction data. The calculated parameters of the porous structure appear to be sensitive to the reference data corresponding to sorption on the nonporous silica adsorbent. For example, the use of

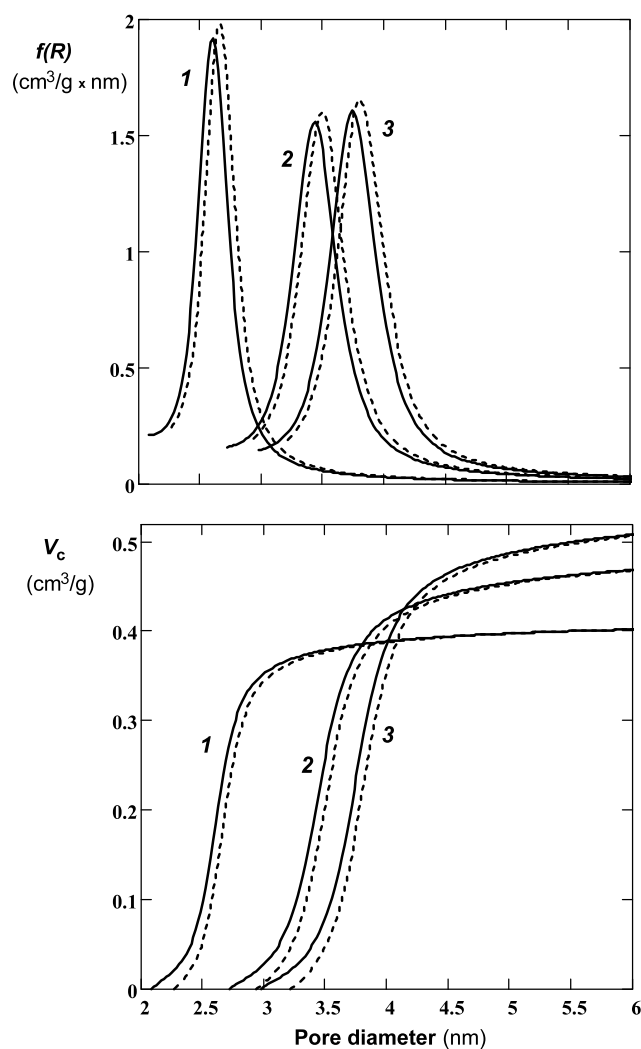


Fig. 6 Differential (top) and cumulative (bottom) pore volume distributions of C12 (1), C14 (2) and C16 (3) samples calculated using the data set I (solid line) and the reference data set II (dotted line)

the t -curve according to Naono et al. (1994) gives somewhat higher values of pore sizes as compared with the data collected by Isirikyan (1957).

Figure 7 shows the pore radius plotted against the pressure at which capillary evaporation occurs. The dependence of the pore radius on the relative evaporation pressure can be fitted by the following relationships: $\ln(p_0/p) = 3.394/R^{1.121}$ (for data set I) and $\ln(p_0/p) = 3.493/R^{1.137}$ (for data set II). The results of the DBdB theory are comparable with the Kelvin equation for evaporation via a hemispherical meniscus:

$$R = \frac{2\gamma V_m}{R_g T \ln(p_0/p)} + t \quad (14)$$

This equation is the special case of (5); t in (14) corresponds to the thickness of the adsorbed layer on the flat solid surface. The Kelvin equation is known to provide somewhat

Table 1 Calculated characteristics of the three mesoporous silica samples

Sample	p/p_0^a	D_{XRD}^b (nm)	e^c (nm)	V_{mes}^d (cm ³ /g)	S_{mes}^d (m ² /g)	D^e (nm)
C12	0.08	2.71	1.06	0.40 (0.40)	601 (584)	2.61 (2.66)
C14	0.16	3.64	1.22	0.47 (0.47)	534 (520)	3.44 (3.50)
C16	0.19	3.89	1.21	0.51 (0.51)	533 (520)	3.75 (3.81)

^aThe p/p_0 position of the inflection point of the isotherm

^bPore diameter D_{XRD} is calculated through (2)

^cThe pore wall thickness is calculated through (3)

^dPrimary mesopore volume V_{mes} and surface area S_{mes} are computed by (13) at $R = 3$ nm ($p/p_0 \approx 0.37$)

^eDiameter corresponding to the PSD maximum. Values of V_{mes} , S_{mes} and D are presented for data set I and for data set II (in brackets)

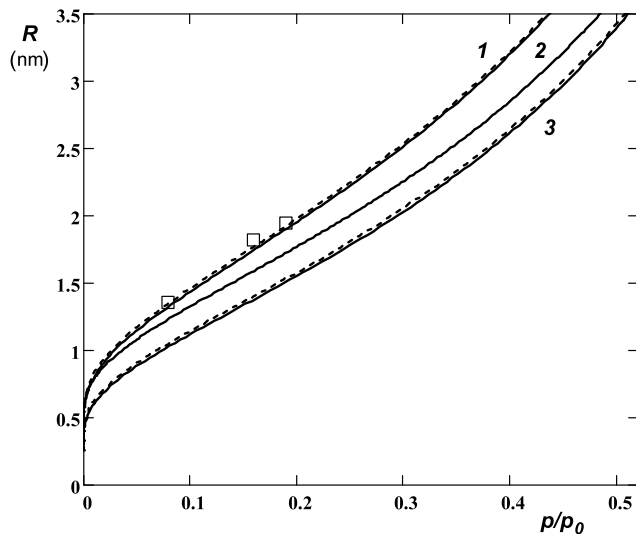


Fig. 7 Pore radii calculated by different methods versus relative pressure: the DBdB theory (1), the Choma et al. (15) (2) and the Kelvin (14) (3). Curves 1 and 3 are constructed using the data set I for the reference t -curve (solid line) and data set II (dotted line). Radii of primary mesopores evaluated by geometrical method (2) for C12, C14, and C16 samples are shown (points): in this case, relative pressures correspond to the inflection points of the desorption isotherms

underestimated pore sizes. When studying benzene adsorption on MCM-41, Choma et al. (2004) used the following Kelvin-type equation:

$$R = \frac{2\gamma V_m}{R_g T \ln(p_0/p)} + t_e + \frac{\xi}{2}, \tag{15}$$

where t_e is the film thickness in terms of the DBdB theory and $\xi = 0.25$ is an empirical parameter. Note that for the function $F(t)$, Choma et al. have used the Harkins–Jura equation, rather than the Frenkel–Halsey–Hill equation. Equation (15) gives somewhat higher pore sizes as compared with (14) but the values are still lower than those estimated through the DBdB theory in our study. According to Fig. 7, the DBdB theory appears to be in a fair agreement

with the pore sizes of the samples estimated by the geometrical ($V_{\text{mes}} + \text{XRD}$) method.

Unfortunately, these results cannot be directly compared with the data obtained in some other works. The morphology of the MCM-41 samples is markedly controlled by the synthesis conditions so that, even at a specified length of surfactant molecules, parameters of the porous structure in the final samples can be slightly differ. Analysis of the literature data reveals a broad (up to ~ 1 nm) dispersion in the values of pore diameter for the samples with the same surfactant.

Therefore, one can conclude that analysis of the experimental evaporation data collected by the proposed dynamic desorption technique in terms of the combined DBdB–Wheeler approach makes it possible to calculate pore dimensions which fairly agree with the X-ray diffraction data even for small-sized mesopores.

5 Conclusions

In this work, the porous structure of the three MCM-41-type silica samples was studied by benzene desorption measurements. This study is based on a simple dynamic desorption technique which makes it possible to construct desorption isotherms without any measurements of relative vapor pressure. The DBdB theory (accounting for the effect of pore surface curvature) offers the relationship between the pore radius and relative vapor pressure. As a starting point for the DBdB theory, the benzene t -curve based on two different experimental data sets for the nonporous silica was used. Calculation of PSDs for the three samples was performed according to the Wheeler model and the results fairly agree with the pore dimensions estimated by the geometrical method. This evidence makes it possible to conclude that the recently developed dynamic desorption method can serve as a reliable simple alternative to the traditional methods for the characterization of the porous media.

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References

- Asefa, T., Duncan, C.T., Sharma, K.K.: Recent advances in nanostructured chemosensors and biosensors. *Analyst* **134**, 1980–1990 (2009)
- Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T.-W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higgins, J.B., Schlenker, J.L.: A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.* **114**, 10834–10843 (1992)
- Beverley, K.J., Clint, J.H., Fletcher, P.D.I.: Evaporation rates of pure liquids measured using a gravimetric technique. *Phys. Chem. Chem. Phys.* **1**, 149–153 (1999a)
- Beverley, K.J., Clint, J.H., Fletcher, P.D.I., Thubron, S.: Evaporation rates of water contained within porous silica particles. *Phys. Chem. Chem. Phys.* **1**, 909–911 (1999b)
- Bird, R.B., Stewart, W.E., Lightfoot, E.N.: *Transport Phenomena*. Wiley, New York (1960)
- Broekhoff, J.C.P., de Boer, J.H.: Studies on pore systems in catalysts. IX. Calculation of pore distributions from the adsorption branch of nitrogen sorption isotherms in the case of open cylindrical pores. A. Fundamental equations. *J. Catal.* **9**, 8–14 (1967)
- Broekhoff, J.C.P., de Boer, J.H.: Studies on pore systems in catalysts. XIII. Pore distributions from the desorption branch of a nitrogen sorption isotherms in the case of cylindrical pores. B. Applications. *J. Catal.* **10**, 377–390 (1968)
- Choma, J., Kloske, M., Jaroniec, M., Klinnik, J.: Benzene adsorption isotherms on MCM-41 and their use for pore size analysis. *Adsorption* **10**, 195–203 (2004)
- Derjaguin, B.V.: Correct form of the equation of capillary condensation in porous bodies. In: *Proc. Intern. Congr. Surface Activity*, 2nd edn. London, vol. 2, pp. 153–159 (1957)
- Dubinin, M.M.: Capillary effects and information concerning adsorbent pore structures. 3. Refinement of the theory of capillary vaporization from adsorbent mesopores. *Russ. Chem. Bull.* **29**, 15–18 (1980)
- Gregg, S.J., Sing, K.S.W.: *Adsorption, Surface Area and Porosity*, 2nd edn. Academic Press, New York (1982)
- Isirikyan, A.A.: Dissertation. Moscow State University, Moscow (1957) (in Russian)
- Isirikyan, A.A., Kiselev, A.V.: The heat of adsorption of benzene and hexane vapors on quartz. *Dokl. Akad. Nauk USSR (Phys. Chem.)*, **119**, 731–734 (1958) (in Russian)
- Lukens, W.W. Jr., Schmidt-Winkel, P., Zhao, D., Feng, J., Stucky, G.D.: Evaluating pore sizes in mesoporous materials: a simplified standard adsorption method and a simplified Broekhoff-de Boer method. *Langmuir* **15**, 5403–5409 (1999)
- Klotz, M., Ayrál, A., Guizard, C., Cot, L.: Synthesis conditions for hexagonal mesoporous silica layers. *J. Mater. Chem.* **10**, 663–669 (2000)
- Klotz, M., Ayrál, A., Guizard, C., Cot, L.: Synthesis and characterization of silica membranes exhibiting an ordered mesoporosity. Control of the porous texture and effect on the membrane permeability. *Separation/Purification Technol.* **25**, 71–78 (2001)
- Kowalczyk, P., Jaroniec, M., Terzyk, A.P., Kaneko, K., Do, D.D.: Improvement of the Derjaguin–Broekhoff–de Boer theory for capillary condensation/evaporation of nitrogen in mesoporous systems and its implications for pore size analysis of MCM-41 silicas and related materials. *Langmuir* **21**, 1827–1833 (2005)
- Kruk, M., Jaroniec, M., Sayari, A.: Relations between pore structure parameters and their implications for characterization of MCM-41 using gas adsorption and X-ray diffraction. *Chem. Mater.* **11**, 492–500 (1999)
- Morishige, K., Tateishi, M.: Accurate relations between pore size and the pressure of capillary condensation and the evaporation of nitrogen in cylindrical pores. *Langmuir* **22**, 4165–4169 (2006)
- Naono, H., Hakuman, M., Nakai, K.: Determination of pore size distribution of mesoporous and macroporous silicas by means of benzene-desorption isotherms. *J. Colloid Interface Sci.* **165**, 532–535 (1994)
- Nguyen, C., Do, D.D.: Sizing of cylindrical pores by nitrogen and benzene vapor adsorption. *J. Phys. Chem. B* **104**, 11435–11439 (2000)
- Qiao, S.Z., Bhatia, S.K., Nicholson, D.: Study of hexane adsorption in nanoporous MCM-41 silica. *Langmuir* **20**, 389–395 (2004)
- Rouessac, V., van der Lee, A., Bosc, F., Durand, J., Ayrál, A.: Three characterization techniques coupled with adsorption for studying the nanoporosity of supported films and membranes. *Microporous Mesoporous Mater.* **111**, 417–428 (2008)
- Selvam, P., Bhatia, S.K., Sonwane, C.G.: Recent advances in processing and characterization of periodic mesoporous MCM-41 silicate molecular sieves. *Ind. Eng. Chem. Res.* **40**, 3237–3261 (2001)
- Shkol'nikov, E.I., Volkov, V.V.: Dynamic desorption porometry: a new method for the analysis of membrane porous structure. In: *Proc. Intern. Symp. "Euromembrane 99"*, Leuven, Belgium, September, 19–22, vol. 2, pp. 482 (1999)
- Shkol'nikov, E.I., Volkov, V.V.: Obtaining vapor desorption isotherms without monitoring pressure. *Dokl., Phys. Chem.* **378**, 152–155 (2001)
- Staszczuk, P., Nasuto, R., Rudy, S.: Studies of benzene adsorption layers on silica gels by thermal analysis and McBain balance methods. *J. Therm. Anal. Calorim.* **62**, 461–468 (2000)
- Ustinov, E.A., Do, D.D., Jaroniec, M.: Equilibrium adsorption in cylindrical mesopores: a modified Broekhoff and de Boer theory versus density functional theory. *J. Phys. Chem. B* **109**, 1947–1958 (2005)
- Wheeler, A.: Reaction rates and selectivity in catalyst pores. In: *Emmett, P.H. (eds.) Catalysis*, vol. 2, pp. 105–165. Reinhold, New York (1955)