

Relations between Structural Parameters and Adsorption Characterization of Templated Nanoporous Materials with Cubic Symmetry

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A systematic approach is proposed to structural characterization of templated nanoporous materials with cubic symmetry by gas adsorption. We hypothesize that regular structures of these materials can be described in terms of triply periodic minimal surfaces (TPMS), similarly to bicontinuous mesophases observed in oil–water, lipid, block copolymer, and other amphiphilic systems. We relate topological characteristics of TPMS to the pore structure parameters evaluated from adsorption measurements, such as the specific surface area, pore volume, mean pore size, and also pore wall thickness. The relations obtained can be used for discrimination of possible TPMS morphologies. The method developed is used for characterization of newly synthesized MCM-48 mesoporous materials by low-temperature nitrogen adsorption. We show that adsorption data fully support the minimal gyroid model of MCM-48 structure (*Ia3d* space group) established earlier by the X-ray diffraction (XRD) and transmission electron microscopy studies. The mean pore size of MCM-48 can be accurately described by the hydraulic diameter calculated from the capillary condensation region of nitrogen adsorption isotherms by the nonlocal density functional theory method. Moreover, the adsorption method allows one to estimate the pore wall thickness, which cannot be done by XRD. For a series of high-quality MCM-48 materials reported recently in the literature, the calculated mean wall thickness varied from 0.8 to 1.2 nm. The adsorption method developed is recommended as a complement to X-ray diffraction and electron microscopy techniques for characterization of nanoporous materials.

1. Introduction

Since discovery of the M41S family of mesoporous molecular sieves in 1992,¹ highly ordered periodic nanoporous materials prepared using organic mesophases as templates have attracted considerable attention. A number of new inorganic materials with controlled pore channels in the range of 20–300 Å have been synthesized.^{1–9} These materials exhibit a variety of periodic structures (see ref 5 for review): 2D hexagonal (*p6m*) MCM-41,¹ FSM-16,³ SBA-3,^{6,7} and SBA-15;⁵ cubic (*Ia3d*) MCM-48;^{1,2,4} cubic (*Pm3n*) SBA-1;⁶ cubic (*Pm3m*) SBA-11;⁸ cubic (*Im3m*) SBA-16;^{8,9} 3D hexagonal (*P63/mmc*) SBA-2⁷ and other structures, for example, a zeolite-like material with three-dimensional helical pores.¹⁰ The symmetries of the templated nanostructured solid surfaces

mimic those observed in oil–water, lipid, block copolymer, and other amphiphilic systems.^{11–20}

Along with the X-ray diffraction (XRD) and transmission electron microscopy (TEM), the gas adsorption is used as a primary method for characterization of nanoporous materials. The adsorption isotherm serves as a fingerprint of the internal pore structure of the material and allows one to evaluate the specific surface area, pore volume, pore size distribution, and wall thickness. Most adsorption studies performed in recent years were focused primarily on MCM-41 and related materials, which possess a two-dimensional hexagonal array of nearly cylindrical pore channels. Geometrical relations between the pore structure parameters of hexagonal materials were shown to provide reasonable estimates.^{21–22} Recently we have developed a quantitative model of adsorption in cylindrical channels based on the nonlocal density functional theory (NLDFT)^{23,24} and elaborated new methods for calculating the pore size distributions and pore wall thickness from nitrogen and argon adsorption isotherms.^{25,26} These

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(1) 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. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(2) Monnier, A.; Schüth, F.; Huo, Q.; Kumar, D.; Margolese, D.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.

(3) Inagaki, S.; Fukushima, Y.; Kuroda, K. *J. Chem. Soc., Chem. Commun.* **1993**, 680.

(4) Vartuli, J. C.; Schmitt, K. D.; Kresge, C. T.; Roth, W. J.; Leonowicz, M. E.; McCullen, S. B.; Hellring, S. D.; Beck, J. S.; Schlenker, J. L.; Olson, D. H.; Sheppard, E. W. *Chem. Mater.* **1994**, *6*, 2317.

(5) Stucky, G. D.; Zhao, D.; Yang, P.; Lukens, W.; Melosh, N.; Chmelka, B. F. *Stud. Surf. Sci. Catal.* **1998**, *117*, 1.

(6) Huo, Q.; Margolese, D. I.; Ciesla, U.; Feng, P.; Gier, T. E.; Sieger, P.; Leon, R.; Petroff, P. M.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.

(7) Huo, Q.; Leon, R.; Petroff, P. M.; Stucky, G. D. *Science* **1995**, *268*, 1324.

(8) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.

(9) Zhao, D.; Yang, P.; Melosh, N.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1998**, *10*, 1380.

(10) Gier, T. E.; Bu, X.; Feng, P.; Stucky, G. D. *Nature* **1998**, *395*, 154.

(11) Scriven L. E. *Nature* **1976**, *263*, 123.

(12) Charvolin, J.; Sadoc, J.-F. *J. Phys. (Paris)* **1987**, *48*, 1559.

(13) Mariani, P.; Luzzati, V.; Delacroix, H. *J. Mol. Biol.* **1988**, *204*, 161.

(14) Hyde S. T. *J. Phys. Chem.* **1989**, *93*, 1458.

(15) Fontel, K. *Colloid Polym. Sci.* **1990**, *268*, 264.

(16) Ström, P.; Anderson, D. M. *Langmuir* **1992**, *8*, 691.

(17) Seddon, J. M.; Templar, R. H. *Philos. Trans. R. Soc. London, Ser. A* **1993**, *344*, 377.

(18) Landh, T. *J. Phys. Chem.* **1994**, *98*, 8453.

(19) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1994**, *27*, 4063.

(20) Luzzati, V.; Delacroix, H.; Gulik, A. *J. Phys. II* **1996**, *6*, 405.

(21) Coustel, N.; Di Renzo, F.; Fajula, F. *J. Chem. Soc., Chem. Commun.* **1994**, 967.

(22) Kruk, M.; Jaroniec, M.; Sayari, A. *Chem. Mater.* **1999**, *11*, 492.

(23) Ravikovitch, P. I.; Ó Domhnaill, S. C.; Neimark, A. V.; Schüth, F.; Unger, K. K. *Langmuir* **1995**, *11*, 4765.

(24) Neimark, A. V.; Ravikovitch, P. I.; Grün, M.; Schüth, F.; Unger, K. K. *J. Colloid Interface Sci.* **1998**, *207*, 159.

(25) Ravikovitch, P. I.; Wei, D.; Chueh, W. T.; Haller, G. L.; Neimark, A. V. *J. Phys. Chem. B* **1997**, *101*, 3671.

methods provide a solid basis for consistent characterization of MCM-41-like materials from gas adsorption isotherms.

It is surprising that despite a variety of prospective applications, the cubic mesostructures, such as MCM-48^{1,2,4} and others, have so far received considerably less attention. On the basis of XRD and TEM studies the structure of MCM-48 material is described as the bicontinuous two-phase system centered on the gyroid minimal surface that divides the available pore space into two nonintersecting subvolumes.^{2,27} However, only few detailed adsorption studies have been published in the literature.^{28–31} They confirmed the accessibility of the pore structures in MCM-48 to nitrogen molecules and allowed the authors to make some qualitative conclusions regarding adsorption properties of MCM-48 as compared to other mesoporous molecular sieves.³¹

In this work, we propose a systematic approach to structural characterization of templated nanoporous materials with cubic symmetry by gas adsorption isotherms based on established models of triply periodic minimal surfaces (TPMS).^{32–45} We suggest a series of relations between the topological characteristics of the bicontinuous structures centered on TPMS and the pore structure parameters obtained from the adsorption measurements. We show that the gas adsorption can be used for reasonable estimates of the surface area, pore volume, mean pore diameter, and mean pore wall thickness. Moreover, the relations between the structural parameters obtained from adsorption data in combination with XRD data can be used for discrimination of possible structural morphologies.

2. Method

We assume that the solid skeleton of the porous material retains the symmetry and topology of the mesophase system used as a template during the synthesis. When the parental mesophases form a bicontinuous periodic structure, the solid phase in templated porous matrixes can be represented as a “swollen” triply periodic minimal surface. The solid phase is seen to be bounded by the so-

Table 1. Properties of Triply Periodic Surfaces (TPS) (from Refs 37–40)

name	symmetry group	volume fraction	area, $\xi_0 = A_0/a^2$	genus, g	energy
G	<i>Ia3d</i> (230)	0.5	3.0919	5	-0.190
S	<i>Ia3d</i> (230)	0.5	5.4145	21	-0.190
GP	<i>Ia3d</i> (230)	0.5	5.4840	21	-0.183
GX1	<i>Ia3d</i> (230)	0.5	7.907	53	-0.186
P	<i>Im3m</i> (229)	0.5	2.34511	3	-0.181
I-WP	<i>Im3m</i> (229)	0.527	3.46460	7	-0.180
C(P)	<i>Im3m</i> (229)	0.5	3.8094	9	-0.162
CPD	<i>Im3m</i> (229)	0.515	4.3588	14	-0.174
BFY	<i>Im3m</i> (229)	0.5	4.9641	19	-0.180
SCN1	<i>Im3m</i> (229)	0.5	7.4288	45	-0.178
F-RD	<i>Fm3m</i> (225)	0.5	4.75564	21	-0.163
D	<i>Pn3m</i> (224)	0.5	3.83779	9	-0.188
DDU	<i>Pn3m</i> (224)	0.529	3.2972	3	-0.181
C(D)	<i>Pn3m</i> (224)	0.5	8.2558	73	-0.174
CD	<i>Pn3m</i> (224)	0.5	8.2257	73	-0.167

called equidistant surfaces located at equal distance from the central triply periodic minimal surface. The structural properties of such porous medium are determined by the topological parameters of the parental surface.

Triply Periodic Minimal Surfaces (TPMS). By definition, a minimal surface has a zero mean curvature, $H = (1/2)(1/R_1 + 1/R_2) = 0$, and negative Gaussian curvature, $K = 1/(R_1R_2)$; here R_1 and R_2 are the local principal radii of curvature. Thus, on a minimal surface $R_1 = -R_2$ in each point, and the surface is saddle shaped everywhere. For a comprehensive review of mathematical aspects of minimal surfaces and their applications, we refer readers to refs 14 and 32–45. Here we give only a brief description.

The Gauss–Bonnet theorem

$$\int_A K \, dA = \langle K \rangle A_{UC} = 2\pi\chi = 4\pi(1 - g) \quad (1)$$

relates the mean Gaussian curvature, $\langle K \rangle$, averaged over the surface, surface area per unit cell, A_{UC} , Euler–Poincaré parameter, $\chi = \langle K \rangle A_{UC}/2\pi$, and genus, g . The latter is an integer number characterizing the surface topology, namely, its ramification. The surfaces with larger genus are more ramified and contain more holes per unit cell. Respectively, the network of pores confined by the surface of larger genus has a larger coordination number.

When dealing with cubic symmetries, it is convenient to use the dimensionless quantities reduced per length of the unit cell $a = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$, which can be obtained from X-ray diffraction. Thus, the dimensionless area per unit cell of TPMS is defined as $\xi_0 = A_{UC}/a^2$. In Table 1 we summarize properties of selected triply periodic surfaces, the structural parameters of which have been reported in the literature.^{37–40} The surfaces listed include well-known minimal surfaces, such as Schwarz' P and D surfaces, Schoen's gyroid G, I-WP, and F-RD surfaces.³² We have also included several recently discovered surfaces GP, GX1, CPD, BFY, SCN1, which have been generated by minimization of the Ginzburg–Landau functional for microemulsions^{37–40} (see Figure 1). Note, that not all of these new surfaces are truly minimal, but their mean curvature $\langle H \rangle$ is close to zero.³⁹ TPMS listed in Table 1 divide the space into two equal or nearly equal subvolumes (so-called balanced surfaces). Several TPMS, i.e., G, P, D, I-WP, and C(P) have been discussed in the literature as models of bicontinuous phases in amphiphilic systems (see, e.g., refs 14–20). All surfaces listed in Table 1 can be considered as possible candidates for model structures of templated nanoporous materials.

(26) Ravikovitch, P. I.; Haller, G. L.; Neimark, A. V. *Adv. Colloid Interface Sci.* **1998**, 76–77, 203.

(27) Alfredsson, V.; Anderson, M. W. *Chem. Mater.* **1996**, 8, 1141.

(28) Van Der Voort, P.; Morey, M.; Stucky, G. D.; Mathieu, M.; Vansant, E. F. *J. Phys. Chem. B* **1998**, 102, 585.

(29) Tatsumi, T.; Koyano, K. A.; Tanaka, Y.; Nakata, S. *Stud. Surf. Sci. Catal.* **1998**, 117, 143.

(30) Chen, F.; Yan, X.; Li, Q. *Stud. Surf. Sci. Catal.* **1998**, 117, 273.

(31) Kruk, M.; Jaroniec, M.; Ryoo, R.; Kim, J. M. *Chem. Mater.* **1999**, 11, 2568.

(32) Schoen, A. H. *Infinite periodic minimal surfaces without intersections*. NASA Technical Note TD-5541, 1970.

(33) Andersson, S.; Hyde, S. T.; Larsson, K.; Lidin, S. *Chem. Rev.* **1988**, 88, 221.

(34) Anderson, D. M.; Davis, H. T.; Scriven, L. E.; Nitsche, J. C. C. *Adv. Chem. Phys.* **1990**, 77, 337.

(35) Fischer, W.; Koch, E. *Philos. Trans. R. Soc. London, Ser. A* **1996**, 354, 2105.

(36) Karcher, H.; Polthier, K. *Philos. Trans. R. Soc. London, Ser. A* **1996**, 354, 2077.

(37) Gózdź, W. T.; Holyst, R. *Macromol. Theory Simul.* **1996**, 5, 321.

(38) Gózdź, W. T.; Holyst, R. *Phys. Rev. E* **1996**, 54, 5012.

(39) Gózdź, W. T. Ph.D. Thesis, Institute of Physical Chemistry Polish Academy of Sciences, Warsaw, 1996.

(40) Schwarz, U. S.; Gompper, G. *Phys. Rev. E* **1999**, 59, 5528.

(41) Grosse-Brauckmann, K. *J. Colloid Interface Sci.* **1997**, 187, 418.

(42) Brakke, K. *Philos. Trans. R. Soc. London, Ser. A* **1996**, 354, 1243.

(43) Brakke, K. The Surface Evolver, <http://www.susqu.edu/facstaff/b/brakke/>

(44) Charvolin, J.; Sadoc, J.-F. *Philos. Trans. R. Soc. London, Ser. A* **1996**, 354, 2173.

(45) Klinowski, J.; Mackay, A. L.; Terrones, H. *Philos. Trans. R. Soc. London, Ser. A* **1996**, 354, 1975.

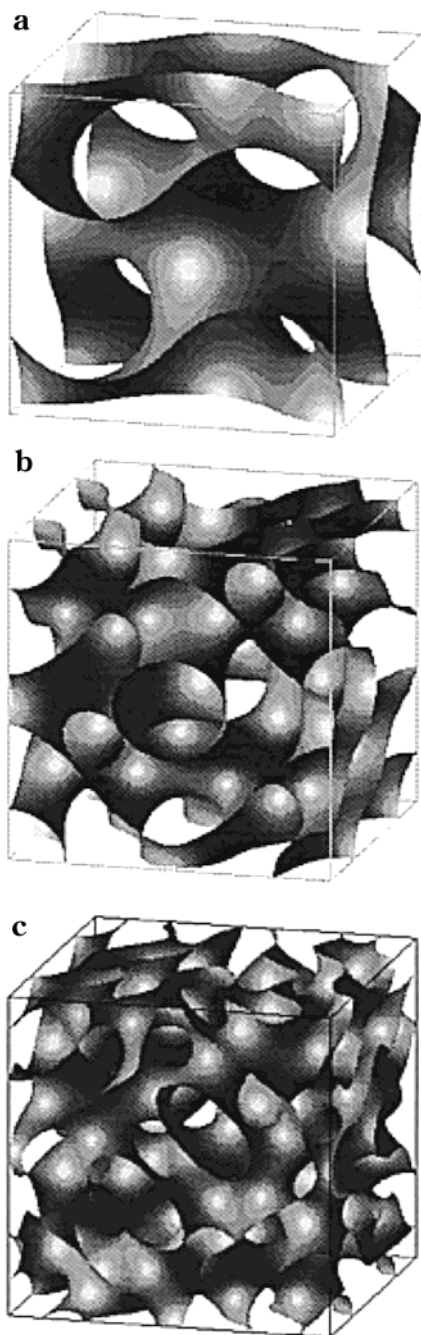


Figure 1. Triply periodic surfaces of $Ia3d$ symmetry: (a) gyroid G ,³² (b) GP and (c) GX1 surfaces.^{37–39}

Relations between Structural Parameters of Porous Solids Templated on TPMS. The unit cell area of TPMS is the most important parameter, which is directly related to the specific surface area obtained from adsorption isotherms on templated mesoporous materials. For minimal surfaces with $\langle H \rangle = 0$, and negative mean Gaussian curvature $\langle K \rangle = \text{constant} < 0$, the area of an equidistant surface located at a distance l is given by the following equation:¹⁴

$$\xi_1 = \xi_0 + 2\pi\chi(l/a)^2 \quad (2)$$

Since the Euler–Poincaré parameter χ is negative, the area of the equidistant surface ξ_1 is always smaller than the area of the central surface ξ_0 . Integration of (2) gives the volume bounded by the central surface and the equidistant surface located at distance l , which is equal

Table 2. Pore Structure Parameters of MCM-48 Materials

a , ^a Å	sample name	ref	D_p^{DFT} , ^b Å	V_p , ^c cm ³ /g	S_p^{CMP} , ^d m ² /g
77.9	C14-MCM-48	31	~33	0.90	1060
86.2	C16-MCM-48 LP	31	~36	0.88	940
86.2	Si-MCM-48 (nonsil)	29	~36	0.76	860
89	18-12-18-MCM-48	28	~40	0.88	900
92.8	C16 MCM-48	31	~39	0.88	880
94.1	MCM-48	30	~37	0.69	820

^a $a = d_{hkl}(h^2 + k^2 + l^2)^{1/2}$ is a cubic lattice parameter calculated from X-ray data. ^b D_p^{DFT} is the mean pore diameter calculated by the NLDFT method.^{24–26} ^c V_p is the primary mesopore volume. ^d S_p^{CMP} is the mesopore surface area calculated from the comparison method.

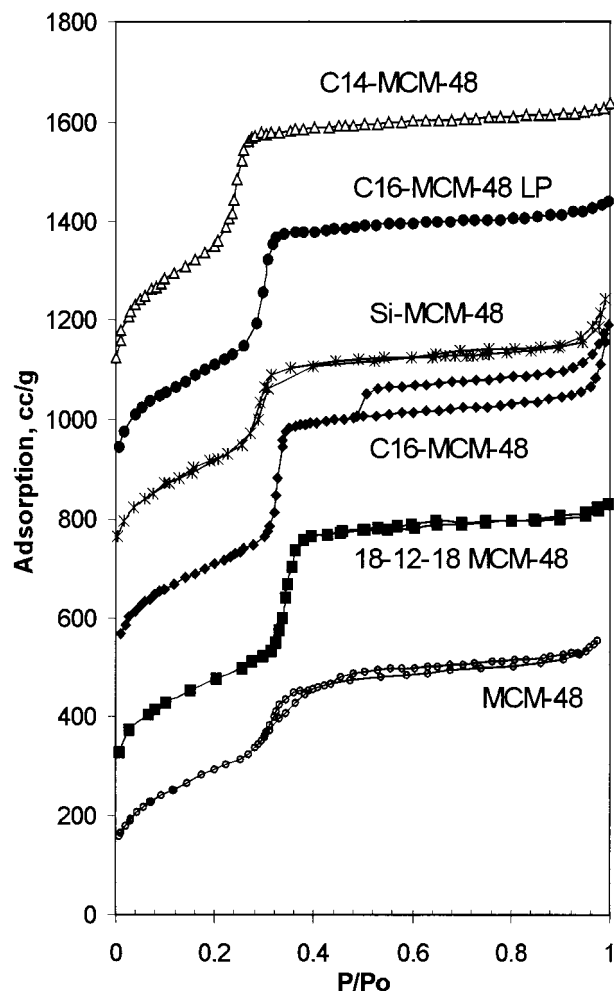


Figure 2. Nitrogen adsorption isotherms on MCM-48 materials.^{28–31} The scale is shifted by 200 cm³/g.

to the half volume occupied by the solid phase in the unit cell. Thus, the porosity of the templated porous solid defined as the fraction of pores in the unit cell equals

$$\epsilon = 1 - 2\xi_0(l/a) - (4/3)\pi\chi(l/a)^3 \quad (3)$$

Introducing the hydraulic pore diameter $D_h = 2a(\epsilon/\xi_1)$ and mean wall thickness $\langle h \rangle = a(1 - \epsilon)/\xi_1$, the following equation relates the parameters of TPMS with a mean pore size in bicontinuous structure

$$a/\xi_1 = \langle h \rangle + D_h/2 \quad (4)$$

Note, that in the above consideration the mean pore wall thickness $\langle h \rangle$ does not necessarily equal $2l$. However,

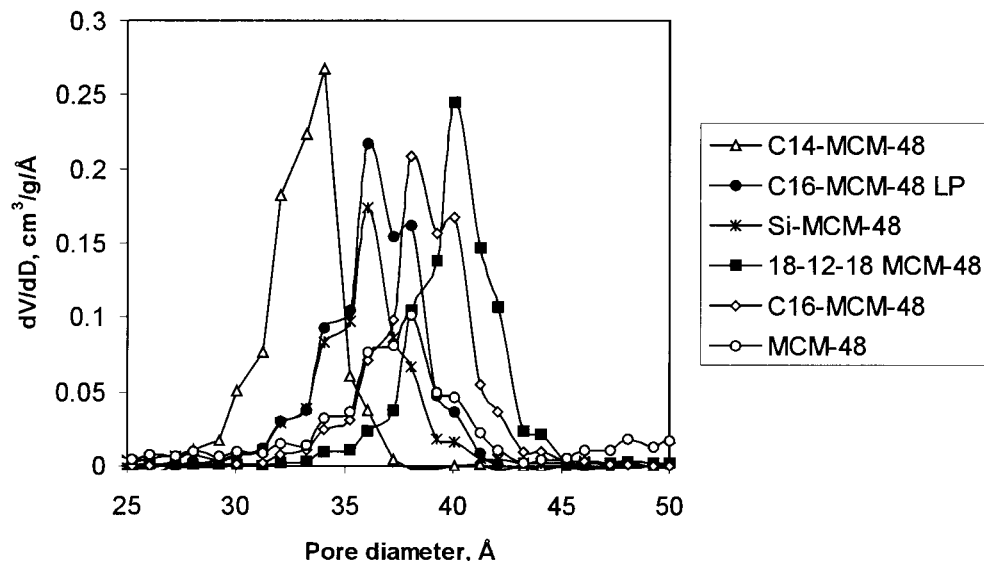


Figure 3. Pore volume distributions of MCM-48 materials^{28–31} calculated by the nonlocal density functional theory (NLDFT) method.^{24–26}

when the Euler–Poincaré parameter χ is small (low genus structures) and/or the ratio (l/a) is small, $\xi_1 \approx \xi_0$, which is equivalent to a slab model of the wall. In this case, setting $\langle h \rangle = 2l$, one arrives at the following simplified equations:

$$\epsilon = 1 - \xi_0 \langle h \rangle / a \quad (3a)$$

and

$$a/\xi_0 = \langle h \rangle + D_h/2 \quad (4a)$$

Adsorption Measurements and Parameters of TPMS. From adsorption measurements, one obtains the parameters per unit mass, i.e., the specific pore volume V_p (cm^3/g) and the specific surface area, S (m^2/g). By use of a true density of solid, ρ_s (g/cm^3), which can be obtained from helium pycnometry (in case of siliceous materials $\rho_s = 2.2 \text{ g}/\text{cm}^3$, the density of amorphous silica), then the porosity is

$$\epsilon = \rho_s V_p / (1 + \rho_s V_p) \quad (5)$$

and the reduced area of the unit cell surface

$$\xi_1 = (1 - \epsilon) \rho_s a / (S/2) \quad (6)$$

3. Examples. Characterization of MCM-48 Materials

We apply the method to characterization of MCM-48 materials, for which the minimal G (gyroid) model satisfactory fits XRD and TEM data which reveal $Ia3d$ symmetry.^{2,27} Among other periodic surfaces with $Ia3d$ symmetry, G and S surfaces have the lowest energy⁴⁰ (Table 1). We have chosen several high-quality MCM-48 materials, for which nitrogen adsorption isotherms, XRD patterns, and TEM pictures have been published.^{28–31} The materials are listed in Table 2, and the adsorption isotherms are presented in Figure 2. All the isotherms show formation of mono- and multilayer adsorption films at low relative pressures and then a sharp capillary condensation step indicating narrow pore size distribution. Primary mesopore volumes were estimated from the plateau on the isotherm after the capillary condensation step. The surface areas were determined by the comparison

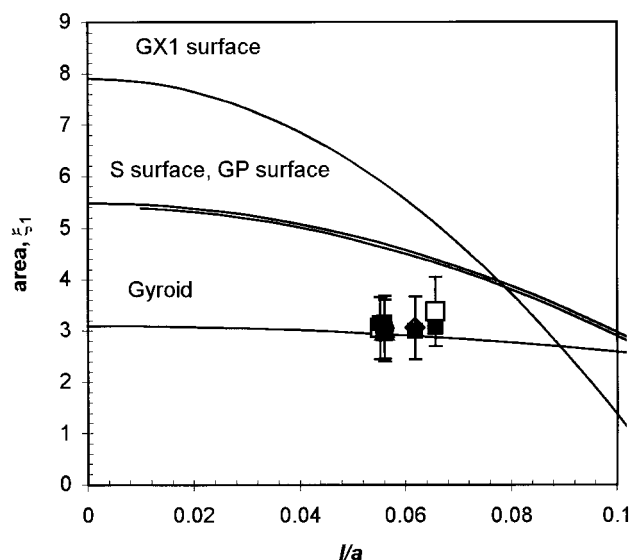


Figure 4. The dimensionless area of equidistant surfaces (eq 2) for several TPMS belonging to the $Ia3d$ symmetry group. Theoretical values calculated by eq 2 using data from Table 1 (lines). Experimental data obtained from nitrogen adsorption isotherms on MCM-48 materials; the semithickness of the wall (l/a) calculated from the pore volume V_p by eqs 5 and 3 using parameters for the gyroid structure; the area ξ_1 calculated from the comparison method surface area S by eq 6 (open symbols), and from the hydraulic diameter (closed symbols). The error bars represent possible 20% percent uncertainty in determination of the surface area by the comparison method.

method using as the reference the adsorption isotherm on a well-characterized MCM-41 material,²³ for which the surface area had been determined from a combination of the NLDFT method^{23–26} and geometrical considerations (Table 2). Note that, as shown recently,^{46,47} the BET method may overestimate the surface areas of silica-based materials by up to 20%.

Calculations Using the Surface Area and Pore Volume. The dimensionless areas of several periodic surfaces calculated by eq 2 using data from Table 1 are shown in Figure 4. To correlate them with the experi-

(46) Gelb, L.; Gubbins, K. E. *Langmuir* **1998**, *14*, 2097.

(47) Galarneau, A.; Desplandier, D.; Dutartre, R.; Di Renzo, F. *Microporous Mesoporous Mater.* **1999**, *27*, 297.

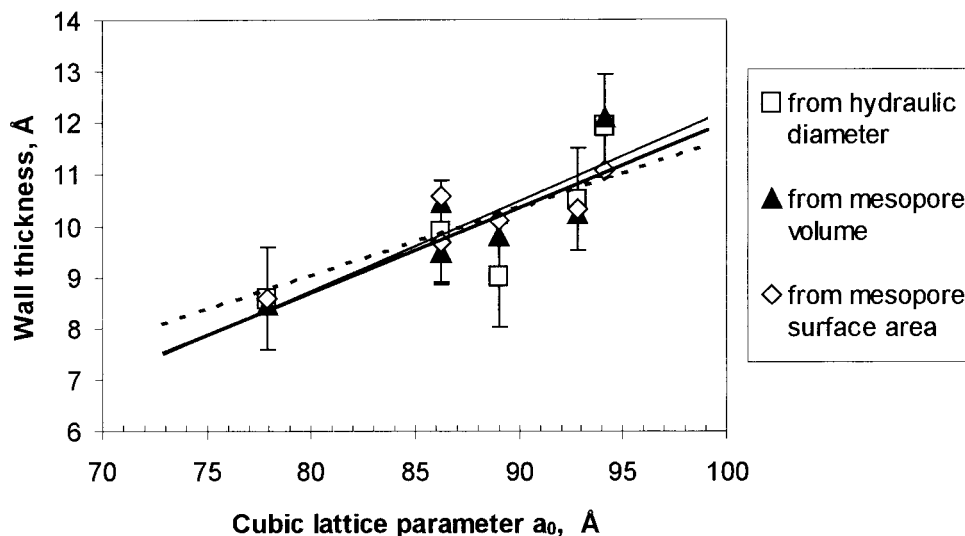


Figure 5. The wall thickness of MCM-48 materials calculated (1) from the comparison method surface area, $h = 2/(\rho_s S)$, (2) from the mesopore volume (porosity), $h = 2l = (1 - \epsilon)a/\xi_0$, and (3) from the mean pore diameter, $h = a/\xi_0 - D_h/2$. The mean pore diameter D_h has been obtained by the NLDFT method from the capillary condensation data (see Table 2). The error in the pore diameter (and in the wall thickness) is estimated as ± 1 Å.

mental data on MCM-48 materials, the semithickness of the wall (l/a) has been calculated from the pore volume V_p using eqs 5 and 3 and parameters $\xi_0 = 3.0919$ and $\chi = -8$ for the G gyroid structure. The area ξ_1 has been calculated from the comparison method surface area, S , by eq 6. The experimental points are shown with an error bar, which represents possible 20% percent uncertainty in determination of the surface area by different methods (Figure 4). Nevertheless, it is evident that the G surface only fits the adsorption data.

Calculations Using Capillary Condensation Data.

The capillary condensation steps on the adsorption isotherms occur at different relative pressures, indicating the difference in the pore sizes in these materials (Figure 2). We have calculated the pore size distributions by the NLDFT method^{24–26} assuming the cylindrical shape of pore channels (Figure 3). The desorption branch was used for the MCM-48 sample for which the hysteretic isotherm was reported.³⁰ Substituting the mean pore sizes taken from the pore size distribution curves (Table 2) into the formula for the hydraulic diameter, we obtain another estimate for the reduced surface area $\xi_1 = 2ae/D_h$. These values agree with the minimal gyroid model indicating the consistency of our approach (Figure 4). This also means that the NLDFT method is suitable for calculating the pore size distributions in MCM-48 materials.

Simplified Approach. Noting that the (l/a) ratio (Figure 4) for all MCM-48 materials is fairly small, we applied the simplified formulas (3a) and (4a) assuming $\xi_1 \approx \xi_0$. This allowed us to calculate the wall thickness by three different routes: (1) from the comparison method surface area $h = 2/(\rho_s S)$, (2) from the pore volume (porosity) $h = 2l = (1 - \epsilon)a/\xi_0$, using ξ_0 for gyroid; and (3) from the hydraulic diameter $h = a/\xi_0 - D_h/2$. The results are fairly consistent with each other (Figure 5). The error in the mean pore diameter (and in the wall thickness) has been estimated to be ± 1 Å. The wall thickness varies from 8 to 12 Å and appears to increase with the increase of the lattice spacing (Figure 5).

The hydraulic pore diameter is unambiguously related to the pressure of the capillary condensation step.

Moreover, the formula (4a) for calculating the mean pore wall thickness does not depend on any absolute quantity (per unit weight), such as the specific surface area or the specific pore volume, which may be inaccurate due to impurities in the sample or inaccuracies in weight measurements. It also does not require the knowledge of the true density of the material. Thus, the formula $h = a/\xi_0 - D_h/2$, with $\xi_0 = 3.0919$ for gyroid, seems to be the preferred way for calculating the wall thickness in MCM-48 materials.

Conclusions

We have presented a systematic approach to characterization of templated mesoporous materials with cubic symmetry by gas adsorption. The approach is based on the assumption that solid skeletons of these materials resemble triply periodic surfaces of parental bicontinuous cubic mesophases, similar to those in amphiphilic systems. It is shown that adsorption data can be used for reliable estimates of the specific surface area, pore volume, mean pore size, and mean wall thickness. Moreover, the relations between the structural parameters obtained from adsorption data can be used for discrimination of possible structural morphologies. The method developed has been applied to structural characterization of newly synthesized MCM-48 materials. Analysis of adsorption data fully supports the minimal gyroid model of MCM-48 structure ($Ia3d$ space group) established earlier by the X-ray and TEM studies. For a series of high-quality samples with the cubic lattice parameters from 77 to 94 Å, it has been shown that the wall thickness in MCM-48 materials varies from 8 to 12 Å. The adsorption method developed is recommended as a complement to XRD and TEM techniques for characterization of newly synthesized templated materials.

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