

Characterization of High-Quality MCM-48 and SBA-1 Mesoporous Silicas

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MCM-48 and SBA-1 samples were characterized using powder X-ray diffraction and nitrogen adsorption in a wide range of relative pressures. X-ray diffraction provided direct evidence for the high degree of pore structure ordering for the materials under study. Nitrogen adsorption showed that highly ordered MCM-48 materials exhibited sharp steps of capillary condensation and narrow pore size distributions, whereas capillary condensation steps for highly ordered SBA-1 samples were broad, which may be related to a cage-like pore structure of these materials. Surface properties of MCM-48 and SBA-1 with respect to nitrogen molecules were found to be similar to those of macroporous silica gels and thus close to those of MCM-41. High values of the surface area and mesopore volume for MCM-48 silicas indicate that both of the enantiomeric channel systems separated by the silica wall in the structure are fully accessible for nitrogen molecules. Moreover, the absence of detectable microporosity indicates that there are no holes on the nanometer length scale in the pore walls of MCM-48. It was demonstrated that MCM-48, MCM-41, and SBA-1 samples, which exhibited capillary condensation at approximately the same relative pressure, have markedly different ratios for the amount adsorbed on the pore surface to the total adsorption capacity (or alternatively, different pore volume/surface area ratios). As this behavior was attributed to differences in porous structures of these materials, such ratios may provide information which would allow one to differentiate between pore geometries of ordered mesoporous materials.

Introduction

The discovery of ordered mesoporous materials (OMMs)^{1,2} opened a new and rapidly growing field of modern science and technology, expanding the range of periodic porous materials into the mesopore region. Initially, two distinct types of OMM structures were identified: hexagonal (*p6m*) and cubic (*Ia3d*). The hexagonal materials with honeycomb arrays of nonintersecting channels, i.e., MCM-41¹ and FSM-16,² were shown to be the easiest to synthesize. The cubic MCM-48 materials were also obtained under more specified synthesis conditions.¹ Their structure was later identified as consisting of an enantiomeric pair of 3-D channel systems, which were separated by the silica wall corresponding to the periodic G-surface. Further studies led to discovery of several other types of mesoporous silicas with narrow pore-size distributions and well-defined structures. A cubic phase

SBA-1, which was synthesized in acidic media, was suggested to have an ordered 3-D structure with two types of globular cages,³ forming a continuous porous network.⁴ SBA-2 was shown to exhibit a three-dimensional periodic hexagonal array of mesoporous cages.⁴ HMS silicas synthesized via a neutral templating route were claimed to exhibit honeycomb structures similar to that of MCM-41, but with lower degree of structural ordering.⁵ Disordered materials,^{6–9} for instance KIT-1,⁷ were also reported to have uniform channels. Moreover, hexagonal mesoporous silicas SBA-15 with pore sizes from 5 to as large as 30 nm, and a variety of cubic structures were synthesized using oligomers and tri-block copolymers as templates.^{10,11}

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Cubic ordered mesoporous materials are currently attracting a lot of attention.¹² Thus, there is a rapidly growing number of studies devoted to MCM-48,^{1,4,8,12-61}

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which were focused on (i) improvement of the synthesis procedure,^{4,8,14,17-30} (ii) determination of the structure the three-dimensional porous network,^{14-16,31-35} (iii) characterization of the surface and porous properties,³⁶⁻⁴⁰ (iv) assessment^{41,42} and improvement^{26,43} of the hydrothermal and mechanical stability, (v) synthesis and catalytic application of MCM-48 with framework-substituted,^{17,21,30,44-56} grafted,⁵⁷⁻⁵⁹ or immobilized metal heteroatoms or their complexes,⁶⁰ (vi) surface modification via bonding of organosilanes,^{43,53} and (vii) preparation of polymer-silica composites.⁶¹ It is also interesting to note here that the structure of MCM-48 has recently been resolved using single-crystal electron diffraction.³⁵

SBA-1 has been studied less often than MCM-48, which can be attributed in part to the fact that its synthesis requires specific conditions involving acidic media, surfactants with large headgroups (e.g., alkyl-triethylammonium surfactants) and low temperatures.^{3,4,12,13,22,62,63} Only recently has preparation of SBA-1 been accomplished using common alkyltrimethylammonium surfactants.⁶³ Some preliminary work was reported on heteroatom incorporation in the structure of SBA-1.^{12,50}

The aim of the current work is to study highly ordered MCM-48 and SBA-1 silicas using nitrogen adsorption in a wide range of relative pressures in order to gain a better understanding of porous structures of these materials.

Materials and Methods

Materials. Three MCM-48 samples designated as C16-MCM-48, C16-MCM-48 LP, and C14-MCM-48 were obtained in the pure silica form, following a hydrothermal synthesis procedure using sodium silicate as the silica source, *n*-alkyltrimethylammonium bromides as the surfactant, and ethanol as an additive for the mesophase control.²⁶ Briefly, the C16-MCM-48 sample was synthesized by hydrothermal crystallization for 4 days at 373 K, with a starting mixture consisting of 1 mol of SiO₂:0.25 Na₂O:0.65 hexadecyltrimethylammonium bromide (C16TMABr):5 ethanol:100 H₂O. The crystallized product was treated in the following sequence: filtered, washed with doubly distilled water, dried at 413 K in oven, washed with a mixture of ethanol-HCl-H₂O, and finally calcined at 823 K under a static air condition. This sample consisted of irregular particles less than 1 μm in diameter as shown previously by scanning electron microscopy.²⁶ The C16-MCM-48 LP sample was synthesized under the same conditions, except that hydrothermal crystallization was carried out for 20 h at 413 K. The sample consisted of particles with crystal morphologies 1-3 μm in diameter.²⁶ The C14-MCM-48 sample

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was synthesized by the same hydrothermal procedure used for C16-MCM-48, except for use of tetradecyltrimethylammonium bromide (99%, Acros) instead of C16TMABr.

A high-quality SBA-1 sample was prepared in the pure silica form by a synthesis procedure using tetraethyl orthosilicate (98% TEOS, Aldrich) as the silica source and C16TEABr as the surfactant.⁶³ The molar composition of the starting mixture was 1 TEOS:0.2 surfactant:56 HCl:700 H₂O. Briefly, C16TEABr, HCl, and distilled water were mixed homogeneously. The surfactant solution was cooled in an ice bath. Precooled TEOS was added to the surfactant solution while being vigorously stirred. Precipitation of the silica-surfactant assembly was completed within 4 h of stirring. Precipitate formed at 273 K was aged in the reaction mixture for 1 h at 373 K, to improve cross-linking of the silica framework. The framework was still so weak that the structural order was lost during washing with distilled water or organic solvents. Hence, the precipitate was filtered without washing. The framework was cured further through vacuum-drying at room temperature and subsequent drying in air at 433 K. This material was washed with an ethanol-HCl-H₂O mixture and calcined at 823 K in the same way used for MCM-48.

Measurements. Powder X-ray diffraction (XRD) spectra were acquired on a Rigaku D/MAX-III instrument using Cu K α radiation. Nitrogen adsorption isotherms were measured at 77 K using an ASAP 2010 volumetric adsorption analyzer (Micromeritics, Norcross, GA). Before the measurements, samples were outgassed for 2 h at 473 K in the degas port of the adsorption analyzer.

Calculations. The BET specific surface area, S_{BET} ,⁶⁴ was calculated using adsorption data in the relative pressure range from 0.04 to 0.1. The total pore volume, V_t ,⁶⁴ was estimated on the basis of the amount adsorbed at the relative pressure of about 0.99. The primary mesopore volume, V_p , external surface area, S_{ex} , and micropore volume, V_{mi} , were evaluated using the α_s -plot method.^{64,65} V_p and S_{ex} were assessed on the basis of data in the standard reduced adsorption, α_s , range from 1.3 to 2.0. A chromatographic silica gel LiChrospher Si-1000 (EM Separations, Gibbstown, NJ) was used as a reference adsorbent in the α_s -plot analysis.⁶⁵ The BJH mesopore size distributions were calculated from adsorption branches of isotherms employing the corrected Kelvin equation for cylindrical pores⁶⁶ and the statistical film thickness curve for silicas,⁶⁶ both calibrated using a series of MCM-41 silicas with pore sizes covering a wide range of values. The BJH pore size is defined as the maximum of the BJH pore size distribution.

Results and Discussion

Powder XRD spectra for the cubic mesoporous materials under study are shown in Figure 1. The XRD patterns are well-resolved and characteristic of high-quality MCM-48 and SBA-1 silicas.

Nitrogen adsorption isotherms for the samples are shown in Figure 2. Selected pore structure parameters are listed in Table 1. Adsorption isotherms for the MCM-48 samples featured narrow steps of capillary condensation, which provides clear evidence for narrowly defined diameter range for mesoporous channels of these materials. In contrast, the adsorption isotherm for SBA-1 exhibited a broad capillary condensation step, despite high periodicity of the structure of this material, as inferred from the XRD data. Other highly ordered SBA-1 samples studied had very similar nitrogen adsorption isotherms, sometimes with even broader capil-

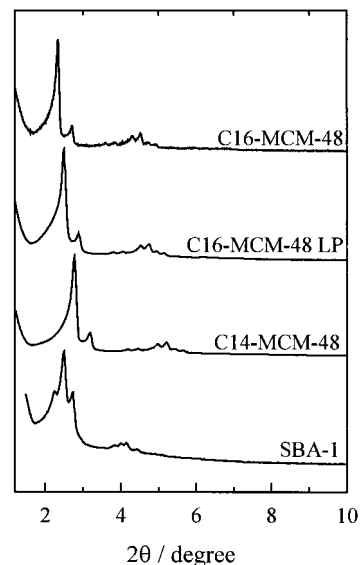


Figure 1. Powder XRD spectra for the MCM-48 and SBA-1 silicas. The lattice parameters obtained from XRD for C16-MCM-48, C16-MCM-48 LP, C14-MCM-48, and SBA-1 are 9.28, 8.62, 7.80, and 7.87 nm, respectively.

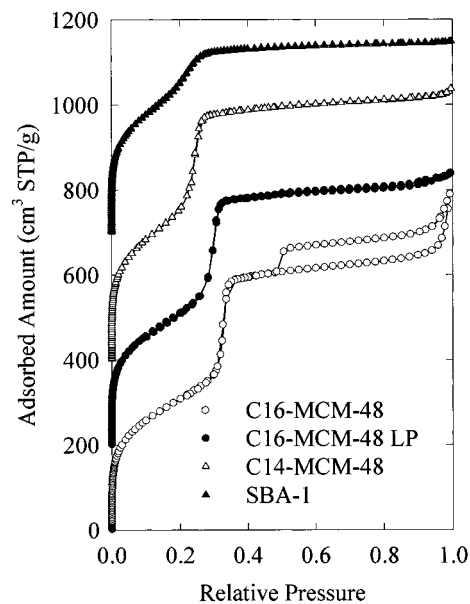


Figure 2. Nitrogen adsorption isotherms for the MCM-48 and SBA-1 silicas.

Table 1. Structural Parameters of the MCM-48 and SBA-1 Materials under Study

sample	d (nm)	S_{BET} (m ² /g)	V_p (cm ³ /g)	V_t (cm ³ /g)	S_{ex} (m ² /g)	w_{BJH} (nm)
C16-MCM-48	3.79 ^b	1100	0.88	1.17	120	3.7
C16-MCM-48 LP	3.52 ^b	1110	0.88	0.98	70	3.5
C14-MCM-48	3.18 ^b	1220	0.90	0.98	60	3.2
SBA-1	3.52 ^c	1180	0.67	0.69	20	3.0

^a Abbreviations: d , XRD interplanar spacing; S_{BET} , BET specific surface area; V_p , primary mesopore volume; V_t , total pore volume; S_{ex} , external surface area; w_{BJH} , BJH pore size. ^b d_{211} . ^c d_{210} .

lary condensation steps. As can be seen in Figure 3, the BJH mesopore size distribution (PSD) for SBA-1 was broad and featured a noticeable shoulder at about 2.6 nm. This shoulder may arise from the presence of smaller mesoporous cages in addition to larger ones, as already suggested,³ but since the BJH calculations are

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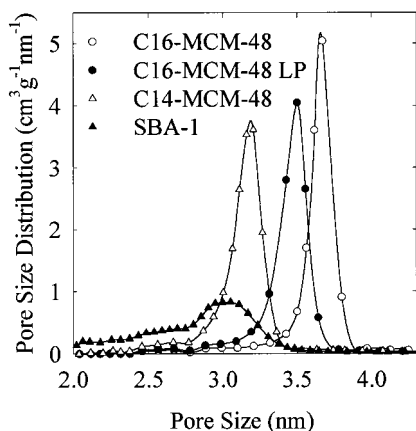


Figure 3. BJH mesopore size distributions for the MCM-48 and SBA-1 silicas.

based on the assumption of cylindrical pore geometry, the BJH data are not sufficient to draw a definite conclusion about the presence of two types of cage-like pores. In the case of the MCM-48 samples, pore size distributions were remarkably narrow. The results presented above suggest that variation of the pore diameter is an inherent feature of SBA-1, possibly due to its cage-like pores,^{3,12,13,62} in contrast to MCM-48, which exhibits a three-dimensional system of uniform interconnected channels.^{14,32,35}

All the cubic mesoporous materials under study exhibited high BET specific surface areas (more than 1000 m²/g). Moreover, the MCM-48 samples have relatively large primary mesopore volumes of about 0.9 cm³/g, which are higher than those of many MCM-41 silicas with comparable pore sizes.^{65,67} Recently, it was speculated that only one of the two disconnected channel systems in the structure of the MCM-48 particles may be accessible from the exterior of the particles, whereas the other channel system may be closed.^{33,34} If this is the case, the MCM-48 samples under study would actually have BET surface areas of mesoporous channels larger than 2000 m²/g and primary mesopore volumes as large as 1.8 cm³/g. These values of structural parameters would exceed by a factor of 2 the values reported for MCM-41 silicas (if one excludes incorrect estimates related mostly to the application of the BET method in the capillary condensation region or to the use of grossly inaccurate calculation procedures), which are known to have fully accessible pores.⁶⁸ Thus, these exceptionally large values of the specific surface area and primary mesopore volume would imply the presence of extremely thin pore walls and thus do not seem to be likely. This in turn strongly suggests that both of the channel systems in the MCM-48 particles are accessible from the exterior. In addition, one needs to keep in mind that pores of the MCM-48 materials become accessible after removal of the surfactant during calcination. If one of the channel systems of as-synthesized MCM-48 is closed, it can be expected that the products of surfactant decomposition formed during calcination would have no possibility of leaving the particle of the material without causing coke formation and some damage to the pore

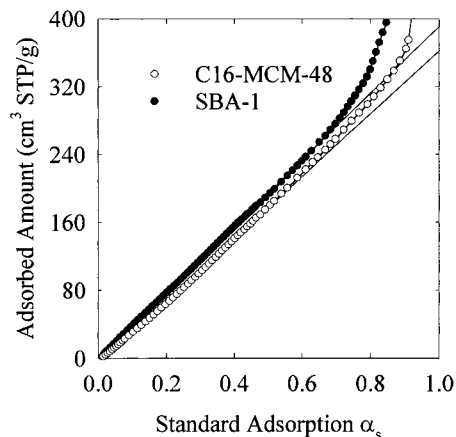


Figure 4. α_s plots for the MCM-48 and SBA-1 silicas.

walls. Yet, the structures of the calcined MCM-48 particles were often found to be highly ordered without dark coloration,^{26,33–35} which makes such a possibility highly unlikely. The closing of one of the channel systems during calcination, after the structure has already been freed of the surfactant, is also rather improbable. The surfactant content of as-synthesized MCM-48 is similar to that of MCM-41. Besides, more than 95% of the surfactant can be easily removed by washing with ethanol–HCl. Thus, it is evident that both of the channel systems in the MCM-48 structure are freely accessible for molecules of at least the size of the surfactant.

Nitrogen adsorption isotherms for most of the cubic mesoporous silicas under study were rather flat at relative pressures above the capillary condensation pressure characteristic of primary mesopores. This indicates small secondary mesoporosity. Only C16-MCM-48 had an appreciable secondary mesopore volume ($V_t - V_p$) of about 0.3 cm³/g, and its nitrogen adsorption isotherm featured a pronounced hysteresis loop at relative pressures above 0.48, resulting from the capillary condensation in secondary mesopores. It is interesting to note that C16-MCM-48 LP prepared under conditions facile for growth of large truncated rhombic dodecahedron particles (several micrometers in diameter) had an external surface area much higher than that expected for uniform particles of such a size. The adsorption isotherm for this material featured a poorly pronounced, yet noticeable hysteresis loop. These findings suggest the existence of a certain amount of structural defects in the micrometer-sized particles and/or the presence of a fraction of smaller particles in this material.

In general, low-pressure nitrogen adsorption properties of MCM-48 and SBA-1 samples were found to be similar to those of macroporous chromatographic silicas. As can be seen in Figure 4, the α_s plots for the samples described in the current study exhibited good linearity in the low-pressure range, which indicates that surface properties of these materials were similar to those of the macroporous reference silica. The comparative plots were linear from the origin, which provides a clear indication of the lack of microporosity. The α_s plots for other MCM-48 materials described in the current study were very similar to that for C16-MCM-48. It was recently noted by Anderson that it is not fully clear whether the MCM-48 walls contain holes.³³ Since no

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microporosity was detected in the MCM-48 samples under study, it is suggested that their walls are free of holes of the size below 1–2 nm. This is also in accord with the recently elucidated single-crystal structure of MCM-48.³⁵ It should be noted that some SBA-1 materials were found to exhibit slightly different low-pressure nitrogen adsorption properties in comparison to those of macroporous silicas and ordered mesoporous materials such as MCM-41, MCM-48, and KIT-1. This behavior might have been due to some structural defects or differences in concentration of silanols on the surface, and the samples carefully prepared as reported recently⁶³ usually exhibited low-pressure nitrogen adsorption properties similar to those of other ordered mesoporous silicas.

One can expect that differences in porous structures of ordered mesoporous materials would be reflected in their different pore volume/surface area ratios for materials with similar pore sizes. For instance, in the case of interconnected system of cylindrical pores (an approximation of the MCM-48 structure), pore volume/surface area ratio is expected to be higher than that for disconnected cylindrical pores (an approximation of MCM-41 structure) of the same diameter. Moreover, both of these ratios should be higher than the ratio for connected cage-like pores (for instance, a hypothetical SBA-1 structure) of the same diameter as the interconnected or disconnected cylindrical pores. To examine this problem in more detail, MCM-48, MCM-41, and SBA-1 samples were selected, which exhibited very similar capillary condensation pressures and thus are expected to have comparable pore sizes. To compare the adsorption data for periodical silicas of different structures, adsorption isotherms for primary mesopores were evaluated by subtracting the amounts adsorbed on the external surface area from the adsorption isotherms.⁶⁶ To calculate the degrees of mesopore filling (as functions of relative pressure), the obtained adsorption isotherms for primary mesopore were normalized by dividing them by the corresponding amounts adsorbed at the relative pressure of 0.8. The MCM-41 sample used here was described in detail elsewhere (the material was denoted there as MCM-41-12).⁶⁷

As can be seen in Figure 5, the heights of capillary condensation steps on the adsorption isotherms for the C14-MCM-48, MCM-41, and SBA-1 samples are markedly different. It should be noted that amounts adsorbed

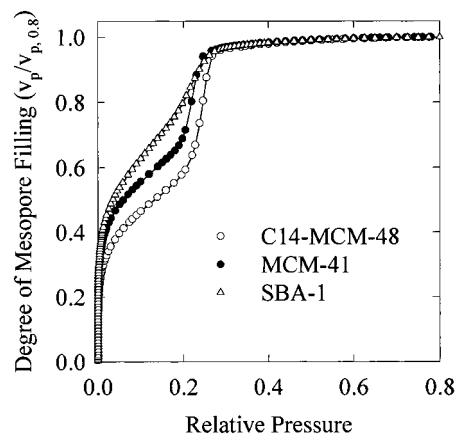


Figure 5. Degrees of mesopore filling for highly ordered MCM-48, MCM-41, and SBA-1 samples with similar pressures of capillary condensation in primary mesopores.

below the capillary condensation (in this case, relative pressure about 0.15–0.2) are related to the specific surface areas of the materials, whereas the heights of the capillary condensation steps are related to the volume of the pore space confined by adsorbate film on the pore walls. It is thus clear that SBA-1 and MCM-48 exhibited the lowest and the highest pore volume/surface area ratios, respectively, among the three samples considered. More specifically, primary mesopore volume/primary mesopore surface area ratios ($V_p/(S_{BET} - S_{ex})$) were 0.78, 0.65, and 0.58 nm for MCM-48, MCM-41, and SBA-1 samples, respectively. Thus, the order of these ratios was consistent with expectations based on the pore geometry of these materials, as discussed above. It can be concluded that the course of adsorption in the capillary condensation region reflects the pore geometry, and the pore volume/surface area ratio in particular. Thus, our study shows that MCM-41 and MCM-48 indeed have markedly different nitrogen adsorption properties and are clearly distinguishable, in contrast to earlier claims⁴⁰ that adsorption isotherms of such materials are indistinguishable.

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