Toward the Synthesis of Extra-Large-Pore MCM-41 Analogues

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Received December 8, 2000. Revised Manuscript Received February 15, 2001

A new approach is proposed for the synthesis of extra-large-pore (diameter > 7 nm) MCM-41 analogues, potentially useful as hosts for the synthesis of nanowires and as model porous solids for fundamental research. The approach is based on the recently demonstrated opportunity for elimination of the connecting pores in the walls of SBA-15 silica during high-temperature (about 1243 K) calcination, which afforded MCM-41 analogues, but the latter had a limited pore size (<7 nm) and small pore volume. Herein, we propose an approach to overcome these limitations by judiciously selecting SBA-15 silicas that exhibit a relatively small content of connecting pores (to reduce the shrinkage upon their elimination) and sufficiently large initial pore size. This approach allowed us to obtain materials with uniform pores of diameter up to 8.8 nm, which is much larger than that attainable for good-quality MCM-41, and with adsorption properties expected for MCM-41 analogues and appreciably different from those of SBA-15 prepared using standard procedure. It is expected that MCM-41 analogues with yet larger pore sizes can be obtained, when the proposed methodology will be applied for some of SBA-15 silicas reported to date.

1. Introduction

After the discovery of ordered mesoporous materials, including MCM-41 silica with hexagonally ordered arrays of uniform disconnected pore channels,[1] there has been considerable interest in the application of materials with channel-like mesopores of uniform size as hosts or templates for the synthesis of nanowires[2−11] and as model porous solids for studies of the behavior of matter in confined space.[12−18] In particular, conducting polyaniline filaments,[2] carbon wires,[3] germanium filaments,[4] polymer mesofibers,[5] and platinum nanowires[6] were synthesized in the pores of MCM-41. The resultant one-dimensional nanostructures embedded in the silica host lattice are promising for application in nanoelectronics.[2,3] The synthesis of noble metal,[7−9] polymer composite,[10] and silicon[11] nanowires in the porous structure of SBA-15 silica was also explored. The dissolution of the silica host allowed one to isolate the thus-formed nanostructures.[5,6,8,10] In addition to their usefulness as hosts or templates for nanowires, materials with uniform channel-like pores are fascinating model solids for studies of capillary condensation/evaporation[12−17] and freezing[14,18] in confined geometries, allowing one to investigate these phenomena in well-defined nanospaces without pore network effects. The understanding of the capillary condensation/evaporation and freezing phenomena not only is important from a fundamental point of view but also has far-reaching practical implications in characterization of porous solids using gas adsorption[13,16,17] and NMR.[19]

As discussed above, the availability of materials with uniform mesoporous channels without interconnections and with pore sizes tunable in as wide range as possible, is important in many areas of nanotechnology. The first material that met these expectations was MCM-41, whose pore sizes can be tailored from about 2 to at least 10 nm.[1] The successful synthesis of MCM-41 with pores up to about 10 nm was confirmed on a local level using

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transmission electron microscopy (TEM),[1] but samples with diameters close to this upper limit were composed of MCM-41 phases with appreciable variation of unit-cell parameters.[20] The results of further work on the MCM-41[21−24] and FSM-16[25] (structurally similar to MCM-41[26]) syntheses in the presence of micelle expanders confirmed that the samples with large pore sizes (especially above 7 nm) exhibit a low degree of the global structural ordering. The best currently known methods for the synthesis of well-ordered large-pore MCM-41 are based on postsynthesis hydrothermal treatments[13,27,28] or high-temperature (about 423 K) direct syntheses,[29,30] but the resulting pore sizes were below about 7 nm, since the largest unit-cell size (distance between the centers of adjacent pores) reported was 7.7 nm.[28]

Because of the difficulties in the synthesis of MCM-41 with pore sizes above 7 nm, the recently reported synthesis of SBA-15 with hexagonally ordered uniform pores similar to those of MCM-41 was widely believed to provide MCM-41 analogues with pores well beyond 7 nm.[31,32] SBA-15 unit-cell size can be tailored up to at least 19 nm using different block-copolymeric templates, cosolvents, and/or micelle expanders.[33−35] SBA-15 has already attracted much attention as a host or template for the synthesis of nanowires[7−11] and as a model material to study the capillary condensation and freezing in uniform disconnected pores.[15] However, it has been demonstrated that ordered large pores of SBA-15 are connected via micropores and narrow mesopores in the pore walls.[36−40] These connecting pores will be referred to as connecting micropores, keeping in mind that some of these pores may be of diameter beyond the micropore range and may be located in the pore walls in such as way that they actually do not connect the adjacent pores. The most appealing evidence for the pore connectivity in the SBA-15 structure came from the fact that this silica can be used as a template for the synthesis of platinum and carbon nanostructures with 2-D hexagonal arrangement of rods, as verified using X-ray diffraction (XRD) and TEM.[37−40] Connecting micropores of SBA-15 can be essentially completely closed by calcining the material at temperatures above 1173 K, as inferred from nitrogen adsorption data[37,40] and from the unsuccessful attempts to prepare ordered carbon replicas.[40] However, the elimination of these pores was accompanied by a prominent loss of the pore volume (almost 3-fold) and marked pore size decrease (down to below 7 nm).[37,40] The presence of connecting micropores in SBA-15 is a logical consequence of the properties of the triblock copolymer template,[36,37] whose poly(ethylene oxide) blocks are known to penetrate silicate[41,42] and organoaluminosilicate[43] templated structures. This idea was additionally confirmed by recent work on other silicas templated using polymers with poly(ethylene oxide) blocks, wherein the microporosity was clearly detected.[44] It should be noted that the presence of microporosity in SBA-15 had been suggested[45,46] before the pore connectivity was revealed.[36−40]

There is currently significant interest in the synthesis of SBA-15 without connecting micropores. In particular, some SBA-15 samples synthesized at about 373 K were claimed to be essentially nonmicroporous.[47,48] However, these samples were prepared under conditions highly similar to those used in the case of SBA-15 silicas successfully used to template ordered carbon and platinum nanostructures,[37−40] thus suggesting superficial nature of these claims. Other studies suggested the possibility of elimination of microporosity during the treatment of calcined SBA-15 in water,[46] or as-synthesized SBA-15 in alcohol solution of block copolymer template.[49] The first of these results is questionable, since SBA-15 pore wall undergoes degradation in basic aqueous solutions,[49] but the other one appears highly promising,[49] although in both cases the ultimate test of the disconnected pore nature would involve platinum or carbon replication procedures.[37−40] It is demonstrated here that the calcination of SBA-15 at temperatures of 1173 K or higher is a promising way to obtain extra-large-pore MCM-41 analogues. In this case, a major challenge lies in the mitigation of the pore volume loss and pore size reduction upon the removal of connecting micropores. Herein, we propose to achieve this goal by judiciously choosing SBA-15 materials with low content of connecting micropores and sufficiently large initial pore size.

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Table 1. Structural Properties of the SBA-15 Samples[a]

sample	S_{BET} (m^2 g^{-1})	V_t (cm^3 g^{-1})	V_p (cm^3 g^{-1})	S_{ex} (m^2 g^{-1})	w (nm)	$w(S_{BET}\text{-}S_{ex})/V_p$	$w(S_{BET} - S_{ex})/V_p \cdot w/(w - \sigma)$
CA813	630	1.09	0.97	80	10.6	6.0	6.2
CA1073	500	0.90	0.79	70	9.7	5.3	5.5
CA1173	410	0.73	0.63	60	8.8	4.9	5.1
CA1223	380	0.66	0.57	60	8.4	4.8	5.0
CA1273	280	0.42	0.36	40	6.7	4.6	4.9

[a] S_{BET}, BET specific surface area; V_t, total pore volume; V_p, primary pore volume; S_{ex}, external surface area; w, primary pore diameter; σ, diameter of nitrogen molecule ($\sigma = 0.354$ nm is used here). Surface areas, pore volumes, and pore sizes were rounded to the nearest 10 m^2 g^{-1}, 0.01 cm^3 g^{-1}, and 0.1 nm, respectively.

2. Materials and Methods

2.1. Materials. Pluronic P123 poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$) was donated by BASF, tetraethyl orthosilicate (TEOS) was acquired from Fluka, and hydrochloric acid was purchased from Fisher Scientific. All reagents were used as received. The synthesis of SBA-15 silica was similar to that reported in refs 31 and 32, with slight modifications. In our typical synthesis, 4 g of Pluronic P123 was dispersed in 28 g of water and 122 g of 1.97 M HCl solution with magnetic stirring at 313 K. Then, 8.6 g of TEOS was added dropwise to that homogeneous solution under mechanical and magnetic stirring at 313 K. The following overall composition was used: 1.0 TEOS/0.0167 P123/5.82 HCl/190 H_2O. About 15 min after the TEOS introduction, the precipitation was observed. The synthesis gel was kept under stirring at 313 K for 24 h and then was transferred into a Teflon-lined autoclave and heated therein at 373 K for 2 days. Then the solid product was filtered, washed exhaustively with deionized water, and dried in air at room temperature. Finally, the as-synthesized sample was calcined under dry nitrogen flow (100 mL min^{-1}) at 813 K using a heating rate of 1 K min^{-1}. After heating for 5 h at 813 K, the gas flow was switched from nitrogen to dry air and the calcination was continued for additional 3 h. The calcination of as-synthesized samples at temperatures of 1073, 1173, 1223, and 1273 K was carried out as described above, but in these cases the final temperature was maintained for 3 h (instead of 5 h) before the flowing gas was switched from nitrogen to air, and thus, the overall time of calcination at the final temperature was 6 h. The samples are denoted as CA*x* where *x* provides the calcination temperature in kelvins. For comparative purposes, data for two SBA-15 silica samples calcined at 823 K are included. These materials reported in refs 38 and 40 are referred to as SBA-15-A and SBA-15-B, respectively.

2.2. Measurements. Nitrogen adsorption measurements were performed at 77 K using a Micromeritics ASAP 2010 volumetric adsorption analyzer. Before the measurements, the samples were outgassed under vacuum at 473 K.

2.3. Methods. The specific surface area was evaluated using the BET method in the relative pressure range from 0.04 to 0.2.[50] The total pore volume was calculated from the amount adsorbed at a relative pressure of about 0.99.[50] The primary pore volume (defined here as a sum of volumes of ordered pores and connecting micropores) and external surface area were assessed using the α_s plot method.[50] These calculations were performed using the reference adsorption isotherm for macroporous silica[51] in the standard reduced adsorption, α_s, interval from 2 to 2.5 for CA813 sample and from 1.8 to 2.5 for the other samples. It should be noted that α_s is defined as the amount adsorbed at a given relative pressure divided by the amount adsorbed at a relative pressure of 0.4. The primary pore area was evaluated as a difference between the BET specific surface area and the external surface area. The pore size distribution (PSD) was calculated using the procedure proposed by Barrett, Joyner, and Halenda (BJH)[52] but without the simplifying assumptions employed by these authors, and the relation between the pore size and capillary condensation pressure calibrated using MCM-41 silicas with pore sizes from 2 to 6.5 nm.[13] The statistical film thickness curve suitable for the PSD calculations was reported elsewhere.[51] The primary mesopore size (that is the size of ordered pores) is defined as the maximum on PSD.

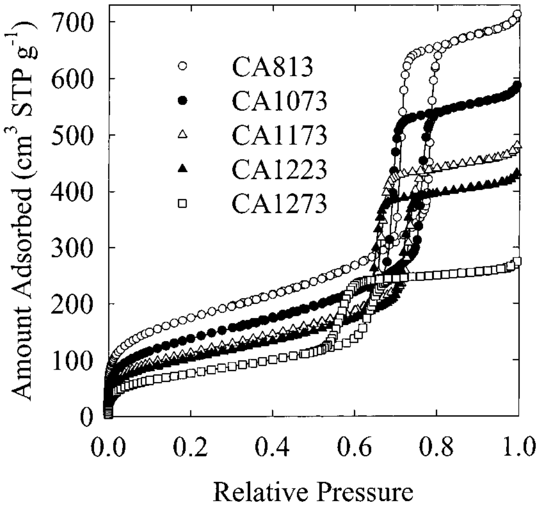

Figure 1. Nitrogen adsorption isotherms for the SBA-15 samples calcined at different temperatures.

3. Results and Discussion

Nitrogen adsorption isotherms for the SBA-15 silica calcined at different temperatures are shown in Figure 1, whereas selected structural parameters for the resulting samples are listed in Table 1. The SBA-15 sample calcined under typical conditions (813 K) exhibited a high degree of structural ordering, as inferred from the steepness of the capillary condensation step on the adsorption isotherm. The sample exhibited relatively low BET specific surface area (630 m^2 g^{-1}), although its adsorption capacity and the position of capillary condensation step (and thus the primary mesopore size) were similar to those commonly observed for SBA-15. This combination of structural features attracted our attention, since it was indicative of low content of connecting pores in the pore walls. To compare the SBA-15 CA813 sample with other pertinent materials, including SBA-15 and MCM-41 silicas, the value of the expression: primary mesopore diameter· primary pore area/primary pore volume (denoted as *wS*/*V* hereafter) was evaluated. The *wS*/*V* ratio was found to be a useful quantity for an empirical description of silica structures with uniform cylindrical pores. In the case of SBA-15 samples with ratios above about

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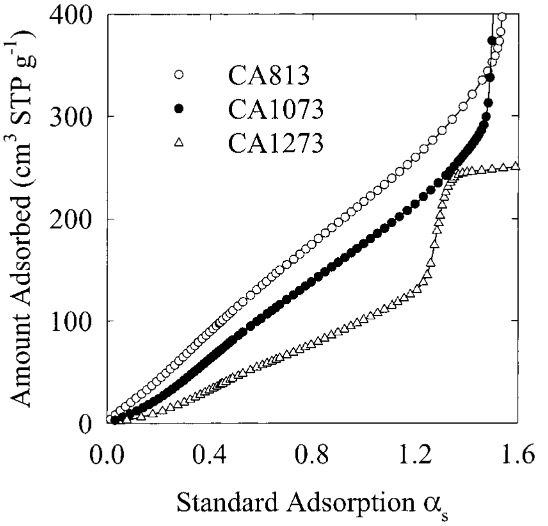

Figure 2. α_s plots for selected SBA-15 samples.

5, it was shown to be possible to synthesize their hexagonally ordered carbon replicas.[40] In particular, good-quality replicas were obtained where *wS*/*V* was equal to 6.8[38] and 7.6,[40] whereas a replica with only slightly inferior properties, as seen from XRD and nitrogen adsorption was obtained for *wS*/*V* = 5.3.[40] Some residual ordering or no ordering was observed for carbons prepared SBA-15 templates with *wS*/*V* = 4.9.[40] So, *wS*/*V* below 5 appears to correspond to SBA-15 structures with essentially disconnected primary mesopores, whereas values above 5 appear to correspond to the structures with primary mesopores connected by complementary pores. It should be noted that the aforementioned values of wS/V of 5.3 and 4.9 were observed for SBA-15 samples calcined at temperatures of 1153 K or higher, which resulted in such a prominent structural shrinkage that the resulting primary mesopore size was below 7 nm, that is in the range attainable for MCM-41. In addition, it is also important to realize that MCM-41 prepared under typical conditions was not found suitable for templating of ordered porous carbons.[53,54] Two independent groups verified that MCM-41-templated carbon is completely disordered. The data reported in one of these studies[54] allow one to determine that wS/V for MCM-41 template was 4.6, consistent with the discussion presented above.

The examination of data for the sample selected for the current study leads to the conclusion that SBA-15 CA813 had *wS*/*V* = 6.0. This value is low as for SBA-15 silicas, but is still indicative of the presence of a significant amount of connecting micropores in the walls of primary mesopores. It is important here to note that comparative plot methods used by some researchers to distinguish between SBA-15 samples with or without micropores would suggest that the connecting microporosity for the CA813 sample is negligible. This is because the initial part of the comparative plot exhibited good linerity (see Figure 2) and the calculated micropore volume (α_s range from 0.9 to 1.2 was used) was 0.01 cm^3 g^{-1}, which is well within experimental error (from our experience, micropore volumes of ±(0.01−0.02) cm^3 g^{-1} are commonly obtained for MCM-41, MCM-48 and other ordered mesoporous silicas). In fact, the α_s plot of similar shape and only slightly larger micropore volume determined by α_s plot analysis (0.03 cm^3 g^{-1}) were obtained using the comparative plot method for the SBA-15 sample (denoted herein as SBA-15-A), which was successfully used to template 2-D hexagonal carbon with high degree of structural ordering, as seen from XRD, TEM, and nitrogen adsorption.[38] This demonstrates that comparative analysis of adsorption data may be grossly misleading in characterization of micropores of SBA-15, providing indications of their absence where these pores are present in significant amounts. Consequently, the claims of the possibility to synthesize SBA-15 without microporosity, which were based solely[47] or largely[48] on the comparative plot analysis need to be treated with caution and should be reexamined using other techniques, preferably those involving replication, or more conveniently but less conclusively those based on the examination of the *wS*/*V* ratio. In the latter case, it is of paramount importance to determine the *w*, *S*, and *V* quantities using the methods equivalent to those used in the current study; otherwise, it would be necessary to additionally determine the threshold wS/V value.

Calcination at 1073 K resulted in a marked drop of *wS*/*V* ratio to 5.3. However, this value is still in the range for SBA-15 with connecting microporosity. It is noted that in this case the comparative plot method indicated the lack of micropores (a negative micropore volume, which is not physical, but serves as indication of the absence of micropores). As will be discussed below, this result is related to the change of properties of the silica surface upon high temperature treatment. Only after calcination at 1173 K or higher was the *wS*/*V* ratio below 5, and therefore, there is a good reason to expect that the content of connecting microporosity was negligibly small and thus the obtained materials can be regarded as those with essentially disconnected pores. It should be noted that *wS*/*V* below 5 was attained in the current study after pore size reduction by only 17%, whereas in the case of SBA-15 samples with higher initial (that is after calcination at 813 K or so) *wS*/*V* ratio, the decrease of *wS*/*V* to 5 or lower resulted in 25% pore size decrease.[37,40] Moreover, the primary pore volume reduction was only 34% in case of the CA1173 sample, whereas the analogous degree of elimination of connecting microporosity resulted in the pore volume decrease by at least 65% for the SBA-15 samples previously studied.[37,40] As seen in Figure 3 and Table 1, the samples with the *wS*/*V* value indicative of negligible connecting microporosity exhibited pore sizes up to 8.8 nm, which is a marked improvement when compared with the values below 7 nm obtained for previous SBA-15 with connecting micropores eliminated by high-temperature calcination.[37,40] To highlight the differences between the SBA-15 samples with negligible micropore content and typical SBA-15 samples, the comparison of the corresponding reduced nitrogen adsorption isotherms is provided in Figure 4. It is clear that typical SBA-15 samples (data taken from refs 38 and 40) exhibit much larger reduced adsorption before the onset of capillary condensation and smaller increase

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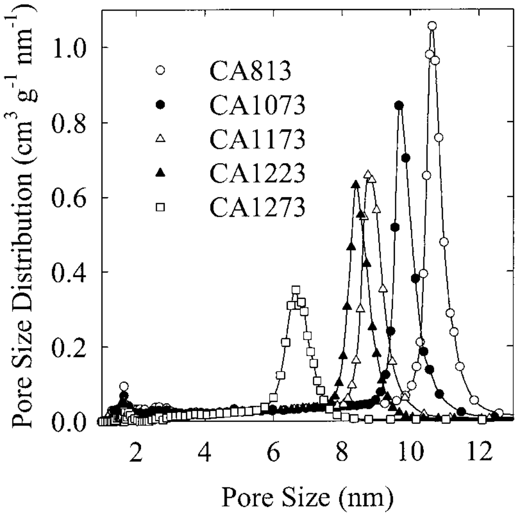

Figure 3. Pore size distributions for the SBA-15 samples calcined at different temperatures.

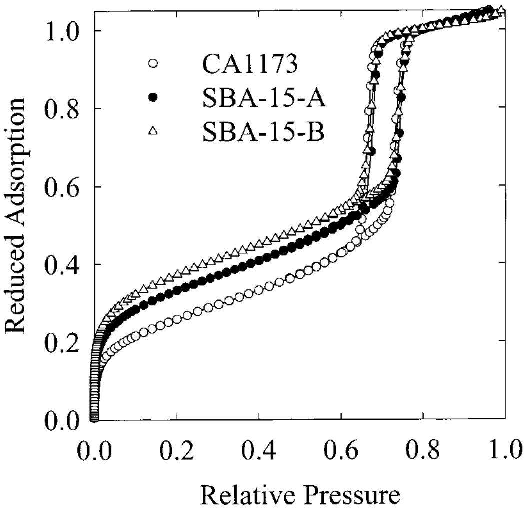

Figure 4. Comparison of reduced adsorption isotherms (the amount adsorbed at given relative pressure divided by the amount adsorbed at a relative pressure of 0.8) for the SBA-15 sample reported herein (calcined at 1173 K) with typical SBA-15 samples calcined at 823 K.

in the reduced adsorption upon the primary mesopore filling. This is attributable largely to the presence of micropores, which are filled well before the onset of capillary condensation and thus contribute primarily to adsorption at lower relative pressures. It is thus clear that the calcination of the judiciously chosen SBA-15 silica at sufficiently high temperature allowed us to obtain materials, whose properties are not only distinctly different from those of typical SBA-15, but also indicative of a negligible amount of micropores. In addition, the pore size of thus obtained samples is above that attainable for good-quality MCM-41. This suggests that the methodology proposed herein is suitable for the synthesis of extra-large-pore MCM-41 analogues with hexagonally ordered systems of disconnected channels, unlike those of SBA-15 calcined at lower temperatures, which exhibit interconnected pore channels.[36−40] The starting SBA-15 materials can be selected so as to minimize initial *wS*/*V* ratio (to reduce the shrinkage upon elimination of connecting micropores) and to appropriately choose the initial pore size. For instance, the high-temperature calcination of some of the SBA-15 materials described in the literature[33,34,55] promises to provide MCM-41 analogues with pore sizes of 10 nm or larger and with primary pore volumes larger than 0.5 cm^3 g^{-1}. These novel opportunities in the materials synthesis can facilitate the production of isolated nanowires and the studies of phase transitions in porous media of well-defined pore geometry. The resultant MCM-41 analogues may be less suited for application in adsorption and catalysis, due to their unremarkable specific surface areas and pore volumes, although they appear to be highly attractive from the point of view of their high thermal stability and expected remarkable hydrothermal stability. Further studies of the transformation of SBA-15 into extra-large-pore MCM-41 analogues will be needed to ascertain the disconnected nature of pores of the materials prepared as proposed herein, but the comparison with the already obtained results[40] indicates that this goal was successfully achieved during the current work.

It should be noted that silicas calcined at temperatures above 1073 K may have largely dehydroxylated surfaces,[56−58] which manifests itself for instance in somewhat smaller low-pressure adsorption of nitrogen.[58] This is expected to be responsible for a slight downward bend of the initial part of the α_s plots[59] (see Figure 2) and negative values of the micropore volume determined using the α_s plot method for some of the SBA-15 samples discussed herein. The modification of surface properties may affect to some extent the accuracy of the BET analysis and therefore may influence the values of the *wS*/*V* ratios. In fact, extreme differences in the surface properties may lead to large alterations of the *wS*/*V* ratios expected for a given pore geometry. Because the surface properties with respect to nitrogen of the silicas calcined at high temperature were still quite close to those for the silica reference adsorbent (as seen from comparative plot analysis data discussed above), the resulting bias introduced in the *wS*/*V* ratios should be below about 5%.

Finally, it is appropriate to discuss the idea underlying the *wS*/*V* calculations. So far, this quantity was considered herein merely as an empirical factor, but in fact, it is directly related to the pore geometry considered. For ideal cylindrical pores and accurately determined pore size, surface area and pore volume, *wS*/*V* is equal to 4, whereas for ideal hexagonal pores this quantity assumes the value of 4.2 under the same assumptions. However, when one needs to evaluate this quantity from experimental data, errors in the determination of the pore structure parameters come into play. In particular, the BET specific surface area calculated using typically assumed nitrogen cross-sectional area (that is 0.162 nm^2) and commonly used ranges of relative pressures (for instance from 0.05 to 0.3) is known to be significantly overestimated,[13,60,61]

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most likely because of the overestimation of the monolayer capacity.[13,61] Consequently, the value of the specific surface area of primary pores (denoted as S) used to calculate wS/V is markedly overestimated, and consequently wS/V is overestimated. The degree of overestimation will require further studies and we did not attempt to evaluate it here, therefore we use empirical values of the wS/V ratios, whose physical meaning is judged on the basis of studies of the good-quality MCM-41 samples as well as for the SBA-15 samples characterized using independent methods, including carbon replication. The results for the SBA-15 samples have already been discussed. In addition, the wS/V ratios for two series of six highly ordered MCM-41 silicas with pore sizes covering the range from 3 to 5 nm[62,63] were examined and found to be between 4.5 and 4.8. Also, the examination of data for six large-pore (from 4.9 to 6.2 nm) MCM-41 samples[13,64,65] of somewhat lower quality provided wS/V between 4.6 and 5.0. This provides a general confirmation of the conclusion based on carbon replication of the SBA-15 structure that the wS/V ratio below 5 is characteristic of cylindrical pores without interconnections. It also should be noted that in the case of comparison of the samples with a wide range of pore sizes, it is helpful to introduce a correction pertinent to surface area calculations for cylindrical pores. The specific surface area is usually calculated using the monolayer capacity (the number of molecules forming a statistical monolayer on the surface) and the molecular cross-sectional area.[50] In the case of cylindrical pores, the multiplication of these two quantities provides an approximate area of the cylinder of diameter equal to the pore diameter minus one molecular diameter.[61] Thus, to get a much better estimate of the actual specific surface area of cylindrical pores, the area determined from the number of molecules and their cross-sectional area (as is the case for the BET analysis) needs to be multiplied by a factor equal to $w/(w - \sigma)$, where σ is the molecular diameter.[61] In comparative studies of samples with similar pore sizes, this factor affects wS/V to a similar extent for all samples, and thus can be omitted. However, when comparing samples of appreciably different pore diameters, for instance MCM-41 and SBA-15, it is better to correct the wS/V value by multiplying it by $w/(w-\sigma)$ term. The obtained values for the SBA-15 samples under study are listed in Table 1, and the ones for the aforementioned MCM-41 samples were found to be within the range from 5.0 to 5.3, which confirms our suggestions that CA1173, CA1223 and CA1273 samples reported herein are MCM-41 analogues.

4. Conclusions

In the process of the thermal elimination of connecting micropores in the SBA-15 structure, the pore size decrease and pore volume loss is moderate, when the SBA-15 sample is selected in such a way that it exhibits a small content of micropores. The relation between the primary mesopore size, primary pore surface area and primary pore volume can serve as a useful indicator of the micropore content, provided the structural parameters employed are calculated in a consistent and reliable way. The combination of this criterion with selection of SBA-15 with large pore size allows one to synthesize MCM-41 analogues with uniform pores of diameter unattainable so far for good-quality MCM-41. Although further studies will be needed to fully examine and refine the methodology proposed herein, it is expected that this approach will open new opportunities in the synthesis of hosts or templates for nanowires, in the synthesis of nanoreactors of tailored pore size and pore connectivity, and in fundamental studies of behavior of matter in well-defined confined environments.

Acknowledgment. We gratefully acknowledge Professor Ryong Ryoo (KAIST, Korea) for many helpful discussions on various aspects of the synthesis, characterization, and stability of SBA-15. J.R.M. and L.P.M. are thankful for support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), fellowships under grants 99/11170-5 and 99/11171-1. M.J. and M.K. gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank BASF (Mt. Olive, NJ) for providing P123 triblock copolymer.

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