Synthesis of Large-Pore $Ia\bar{3}d$ Mesoporous Silica and Its Tubelike Carbon Replica**

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Following the designed synthesis of mesoporous silica materials, such as MCM-41 and MCM-48 with small pore sizes (2–4 nm),[1] which are templated by quaternary ammonium cationic surfactants with different chain lengths, numerous ordered large-pore (8–30 nm) mesoporous silicas, such as SBA-15 and SBA-16,[2] have been synthesized by using block-copolymer nonionic surfactants as templates. Recently, a series of ordered rodlike mesoporous carbon materials have been synthesized by using mesoporous silica materials with a large range of pore diameters, such as MCM-48 and SBA-15, as hard templates.[3] Furthermore, it has been reported that new two-dimensional hexagonal mesoporous carbon materials with connected tubelike pores can be synthesized with large-pore mesoporous silica SBA-15.[4]

The mesoporous material, with a bicontinuous cubic structure of $Ia\bar{3}d$ symmetry, is one of the most interesting materials among the varied mesoporous silica materials reported to date. The independent and intricately interwoven three-dimensional networks of mesoporous channels are much more attractive for use as adsorbents and catalyst supports than the two-dimensional channels of hexagonal mesoporous silica MCM-41 and SBA-15. In spite of the recent discovery of large-pore cubic $Ia\bar{3}d$ mesoporous silica,[5a–c] the hydrothermal method for synthesizing a highly ordered material has not been fully developed. Therefore, the devel-

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[**] The authors are grateful to Makoto Watanabe (Hitachi Science System) and Yasushi Nakaizumi (Hitachi High-Technologies Corporation) for scanning electron micrography. S.C. thanks Prof. S. Iijima and Dr. M. Yudasaka (ICORP-JST) for their advice and comments. S.C. thanks the Japan Society for the Promotion of Science for a postdoctoral fellowship. X.Y.L. and D.Y.Z. thank NSFC support (No. 29925309 and 20173012). T.T. thanks Grant-in-aid for Priority Areas Research (No. 13134101) from the Ministry of Education, Culture, Sports, Science and Technology.

DOI: 10.1002/ange.200351752

opment of a controlled method for thermally and hydrothermally synthesizing stable, large-pore mesoporous silica materials with cubic $Ia\bar{3}d$ symmetry would seem to be important. The synthesis of rodlike mesoporous carbon monoliths with bicontinuous cubic $Ia\bar{3}d$ symmetry[5d] has been reported. However, to date, the synthesis of a tubelike mesoporous carbon with a bicontinuous cubic $Ia\bar{3}d$ structure has not been reported. Such novel architectures are of great technological interest for the development of advanced catalysts, adsorbents, and electrochemical systems.

In this paper, we present a hydrothermal synthetic route towards high-quality large-pore mesoprous silica with a cubic $Ia\bar{3}d$ structure by co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTS) using a block-copolymer surfactant as a template. We have developed a novel synthesis route to highly ordered mesoporous carbon using propylsulfonic acid groups anchored onto the silica wall,[6] which act as an acid catalyst for carbon-source polymerization; this synthesis route was found to be an excellent and simple method for carbonizing the carbon source. The acid catalyst can be obtained by a direct synthetic method, and the acidity can be controlled over a wide range, as compared with aluminosilicates. More importantly, tubelike mesoporous carbon materials with a bicontinuous cubic structure of $Ia\bar{3}d$ symmetry were synthesized by using the highly ordered large-pore silica as a hard template. This is the first report on the synthesis of a tubelike mesoporous carbon replica of a cubic mesoporous material. Selected structural properties of the silica templates and its tubelike carbon replicas are listed in Table 1.

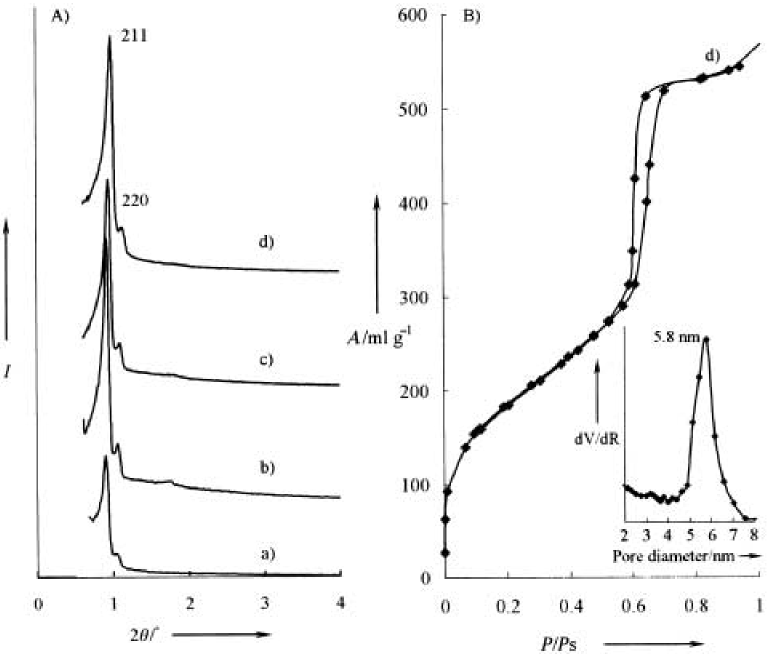

Figure 1. A) XRD patterns of the large-pore mesoporous silica with cubic $Ia\bar{3}d$ structure: a) as-synthesized, b) after extraction, c) after oxidation, and d) after neutralization with NH_4OH; B) nitrogen adsorption–desorption isotherm and pore-size distribution for material after neutralization (I = relative intensity).

Figure 1 A shows XRD patterns of the as-synthesized, extracted, oxidized, and neutralized materials obtained from the starting mixture of Pluronic P123 (4.0 g), TEOS (0.0394 mol), MPTS (0.0035 mol), HCl (0.08 mol), and H_2O (5.8 mol). To obtain the stable mesophase, the starting mixture was heated to 373 K for 48 h. All the samples showed two well-resolved sharp XRD diffraction peaks in the region of $2\theta = 0.5$–1.5°, which correspond to 211 and 220 reflections, based on the cubic system.[3a,7] The bicontinuous cubic $Ia\bar{3}d$ symmetry was confirmed by combining the XRD pattern with SEM and HRTEM images, as shown below. After extracting, oxidizing, and neutralizing treatments, the high regularity of the pore arrangement was maintained, which indicates that this mesophase is very stable. In addition, the hydrothermal synthesis provided a large-pore cubic $Ia\bar{3}d$ silica with much improved structural integrity and thermal and hydrothermal stability. Figure 1 A shows that the three treatments were essentially unaccompanied by structural shrinkage. After the as-synthesized sample was calcined in air at 550 °C, the XRD patterns remained well-resolved despite a slight shrinkage. Very recently, Flodström synthesized the cubic $Ia\bar{3}d$ mesophase in the presence of NaI.[5c] In the course of our synthesis, which uses P123 as a template surfactant, it was found that the cubic $Ia\bar{3}d$ mesostructure could not be formed without MPTS, even when the synthesis conditions were varied over a wide range. Thus, such a mesostructure seems difficult to prepare without additives.

Table 1: Properties of large-pore mesoporous silica with cubic $Ia\bar{3}d$ symmetry and its tube- and rodlike mesoporous carbon replicas.

Sample	Synthesis conditions		Unit cell a [nm]	S_{BET}[b] [m^2 g^{-1}]	V_p[c] [mm^3 g^{-1}]	d_{BJH}[d] [nm]	b[d,e] [nm]
	FA/SiO$_2$	t [min][a]					
Figure 1 (d)	–	–	22.5	740	791	5.8[f]	2.5[g]
Figure 2 (a$_1$)[h]	1.0	60	18.5	175	183	4.0[i]	–
Figure 2 (a$_2$)[j]	1.0	60	18.6	1421	1154	4.0	2.4
Figure 2 (b$_1$)[h]	2.4	–[j]	17.7	8.97	5.9	–	–
Figure 2 (b$_2$)[j]	2.4	–[j]	17.8	1324	734	–	2.4

[a] t = polymerization time. [b] Surface area calculated by the BET method. [c] Primary pore volume determined by using the high-resolution t-plot method. [d] Internal tube diameter calculated using the BJH method from the adsorption branch of the N_2 isotherm of the carbon replicas with silica walls. [e] Intertubular pore size; the pore was formed by removing the silica wall. [f] Pore diameter of mesoporous silica with cubic $Ia\bar{3}d$ symmetry. [g] Pore-wall thickness calculated by using an equation based on the pore volume.[8a] [h] Silica/carbon composite. [i] Pore diameter of silica/carbon composite. [j] Carbon material obtained after removing the silica wall. [k] Synthesized by a two-step FA polymerization and without evacuation.

As can be seen in Figure 1 B, nitrogen adsorption–desorption isotherms for the silica template featured narrow capillary condensation steps, which indicate the high degree of pore-size uniformity. The mesoporous silica exhibited a unit cell size (a) of 22.5 nm, primary mesopore size (d_p) of 5.8 nm, and a wall thickness (b) of

2.5 nm; the value of a is about twice that of MCM-48 synthesized using the longer quaternary ammonium cationic surfactant eicosyltrimethylammonium bromide ($(CH_3(CH_2)_{19}(CH_3)_3NBr)$).[9]

Figure 2 shows scanning electron microscopy (SEM) images of the surfactant-extracted mesoporous silica. The samples were composed of particles that were uniform in shape (not shown); a typical morphology is shown in Figure 2a. The mesoporous silica particles in the SEM image suggest the growth of irregular shaped particles that display domains. The high-resolution SEM images of the apex reveal the regular pore distribution. The mesostructure was confirmed by EM observations to be bicontinuous with cubic $Ia\bar{3}d$ symmetry.

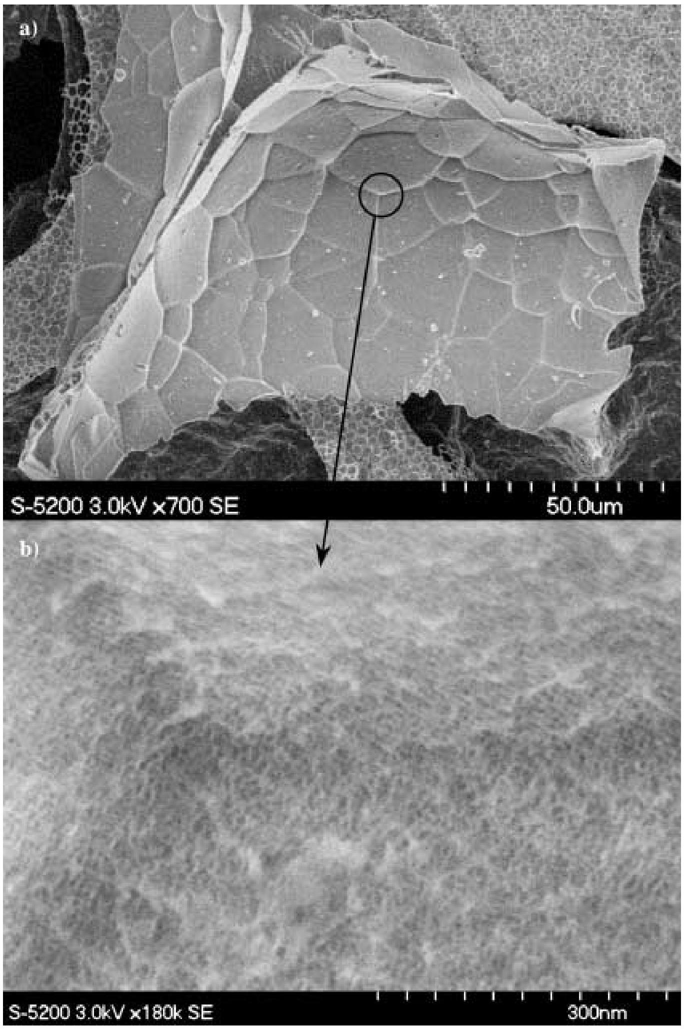

Figure 2. SEM images of mesoporous silica with a cubic $Ia\bar{3}d$ structure. Image b) shows the enlargement of the circled area in a).

Figure 3 A displays the XRD patterns of the mesoporous carbon replicas before and after removing the silica wall, which were synthesized by using sulfonic acid groups embedded in the silica wall as a catalyst. The tube- and rodlike mesoporous carbon materials were synthesized with different furfuryl alcohol (FA) to silica ratios and FA polymerization times (Table 1). Both samples synthesized with FA/silica ratios of 1.0 and 2.4 exhibited XRD patterns characteristic of the silica support used for their preparation. It has been reported that carbon replicas formed in an MCM-48 silica template of cubic $Ia\bar{3}d$ symmetry tend to undergo a transformation to cubic $I4_1/a$ symmetry as the template is removed. In this case, the structure of the carbon replicas were not altered upon removal the silica template. This result can be explained in terms of the presence of the micropores in the walls of the triblock-copolymer-templated materials, which make the replication of SBA-15 possible, and allow for the retention of the cubic $Ia\bar{3}d$ symmetry. The two carbon frameworks formed in the enantiometric channel systems of the silica with cubic $Ia\bar{3}d$ symmetry are likely to be connected to one another through the bridges formed in the micropores in the silica walls. In a similar manner to SBA-15,[4b] the intensity of the XRD pattern of the silica/carbon composite (before removal of the silica wall) decreased with an increase in the thickness of the carbon tubes formed within the silica channels (Figure 3(a_1) and (b_1)) and vice versa for the carbon obtained by removing the silica wall (Figure 3(a_2) and (b_2)). A more systematic study on the significant change in XRD intensity depending on the carbon thickness is ongoing, and the results will be reported elsewhere.

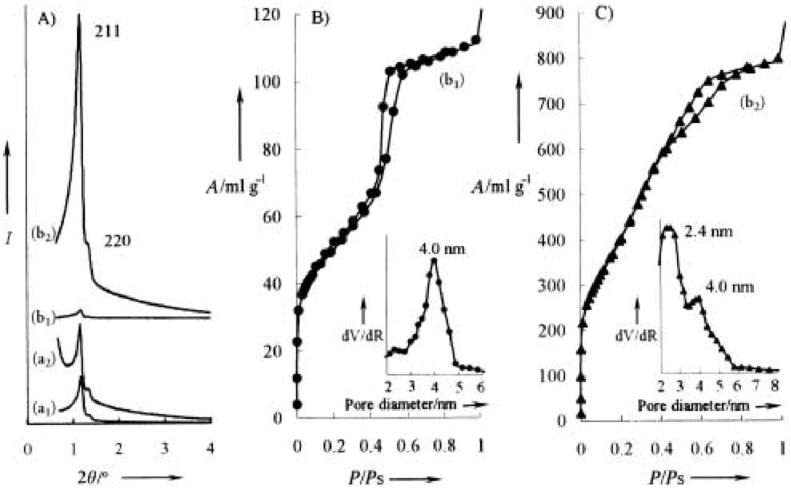

Figure 3. A) XRD patterns of silica/carbon composites (a_1) and (b_1) formed under different conditions (Table 1), and the resulting carbon materials (a_2) and (b_2) formed after removing the silica walls. B) and C) Nitrogen adsorption–desorption isotherms and pore-size distributions for carbon replicas before (B) and after (C) removing the silica wall (I = relative intensity; A = adsorbed amount).

The nitrogen adsorption isotherms and the pore-size distribution of the silica/carbon composite (before removal of the silica wall) (Figure 3B) show that the inner diameter of the mesoporous carbon tube was 4.0 nm. For the carbon material obtained after removing the silica wall, two capillary condensation steps were observed on the adsorption and desorption branches of the nitrogen isotherms in the pressure range of 0.1–0.3 and 0.4–0.6, which correspond to pore sizes of 2.4 and 4.0 nm (see inset of Figure 3C), respectively. The pore size of the silica/carbon composite is in agreement with the larger one of the carbon material, thus indicating that the mesoporous carbon replica, with pores of 4.0 nm inner diameter, and another pore system of 2.4 nm diameter that is formed between the tubes, was obtained by using cubic $Ia\bar{3}d$ mesostructured mesoprous silica with a pore diameter of 5.8 nm as the template. This result indicates that the thinnest possible tubes were 0.9 nm in wall thickness. In our previous work,[4b] we found that it was difficult to prepare carbon tubes with walls less than 1.6 nm thick by aluminosilicate-catalyzed FA polymerization. The mesostructure was not formed when the FA/silica ratio was smaller than 1.0, or when the polymerization time was shorter than 1 h, for the case where aluminosilicate acid was used as the catalyst of FA polymerization. Thus, much thinner carbon walls can be formed by sulfonic-acid-catalyzed FA polymerization. The silica/carbon composition synthesized with a higher (FA)/silica ratio of 2.4 and a two-step FA polymerization did not show any porosity (Table 1), which indicates that the rodlike mesoporous carbon material had been formed. Both carbon replica samples show the same morphology before and after removing the silica wall (not shown), which is a similar situation to that shown in Figure 2.

Figure 4 shows high-resolution transmission electron microscopy (HRTEM) images of the silica, silica/carbon composite, and tubelike mesoporous carbon materials obtained by removing the silica wall. The images show the structure of these materials parallel to the [111] direction. Insets show the corresponding Fourier diffractograms (FDs). The carbon materials synthesized with FA/silica ratios both higher and lower than 1.0 exhibit cubic $Ia\bar{3}d$ symmetry, identical to the silica template. However, we have not yet confirmed that the structure is tubular by TEM observation. A qualitative analysis of these and other images reveals differences in the contrast patterns before and after removal of the silica walls, with a reversal of contrast observed in the carbon replicas. Quantitative analysis of these contrast patterns is currently being conducted by means of Fourier analysis.[3c]

In conclusion, we have presented for the first time a hydrothermal synthesis route for stable large-pore mesoporous silica and its tubelike mesoporous carbon replica with a bicontinuous cubic structure displaying $Ia\bar{3}d$ symmetry, by using sulfonic acid incorporated into the silica during the synthesis step as a catalyst for carbon-source polymerization.

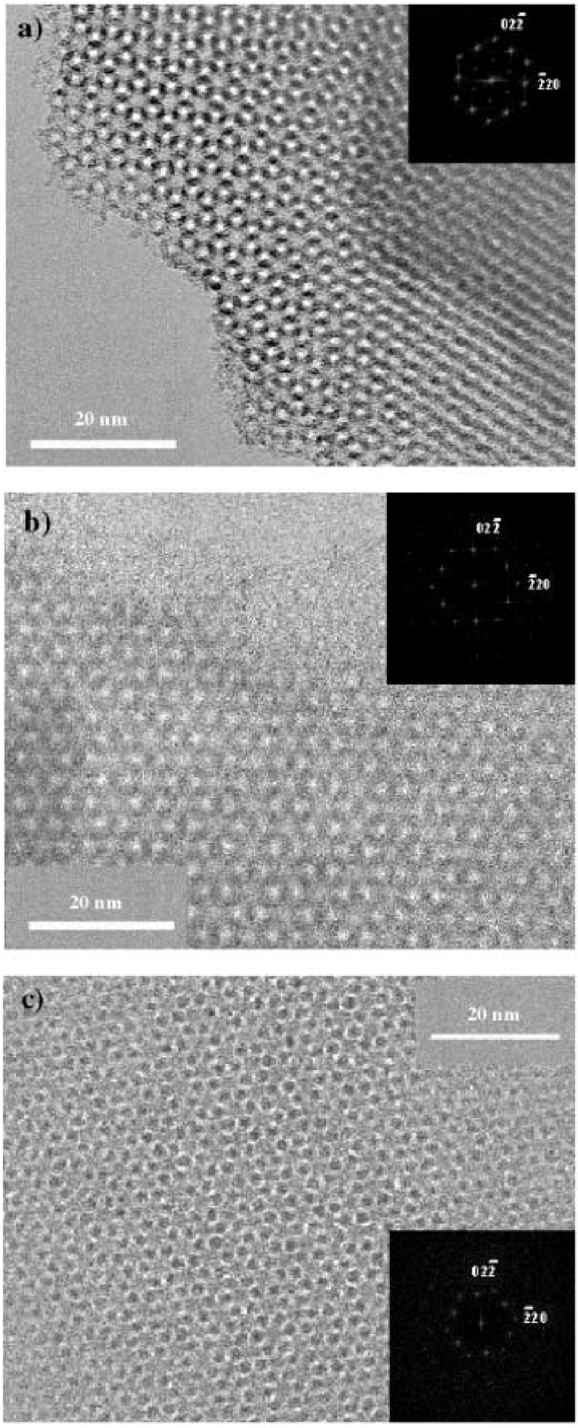

Figure 4. HRTEM images and their Fourier diffractograms of silica (a), a silica/carbon composite (b), and a tubelike mesoporous carbon replicas (c) with cubic $Ia\bar{3}d$ symmetry. The images were recorded along the [111] direction.

Experimental Section

Mesoporous silica with a cubic $Ia\bar{3}d$ mesostructure was synthesized by the co-condensation of TEOS and MPTS using triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$, BASF) as a surfactant template. In a typical synthesis, a mixture of TEOS (8.19 g) and MPTS (0.69 g) was added to a mixture of P123 (4.0 g), HCl (8.0 g, 35 wt%), and deionized water (100 ml) at 40 °C. After the mixture was stirred for 24 h, the mesostructured product formed was cured at 100 °C for an additional 48 h. The products were filtered without washing and dried at 60 °C. The surfactant was removed by exhaustive solid–liquid extraction using 1N HCl/ethanol solution at 70 °C for 24 h.

The carbon replica was synthesized by using large-pore cubic $Ia\bar{3}d$ mesoporous silica as the template and furfuryl alcohol (FA, $C_5H_6O_2$) as a carbon source. First, oxidation of the mercaptopropyl group of the sulfonic acid was achieved by treating the extracted sample with

H_2O_2 (33 vol %), followed by washing, acidification with 1M sulfuric acid, washing again, and drying at 60 °C. Second, the sulfonic acid was partially neutralized by washing with 1N NH_4OH solution (because the acidity of the sulfonic acid was found to be too high to be used for the polymerization of FA). The pore volume of the mesoporous silica was filled with varying amounts of FA by the incipient-wetness technique. The sulfonic-acid-functionalized mesoporous silica containing FA was treated at 60 °C for different polymerization times (Table 1), which resulted in the acid-catalyzed polymerization of FA in the form of a layer coating the pore walls. The unpolymerized FA remaining in the core of the template pores was removed by subsequent evacuation at 60 °C. To obtain the rodlike carbon material, a two-step method was employed to fill the material with FA. Oxalic acid was used as an acid catalyst in the second step, because the sulfonic-acid-functionalized wall was covered with FA polymer in the first step and therefore could not catalyze the polymerization further. The polymerized FA was converted to carbon inside the silica template by pyrolysis at 900 °C for 6 h under vacuum. The porous carbon was obtained after subsequent dissolution of the silica framework in 5 % HF acid at room temperature.

XRD patterns were recorded on an MX Labo powder diffractometer equipped with $Cu_{K\alpha}$ radiation (40 kV, 20 mA) at the rate of 1.0 deg min^{-1} over the range of 1.5–10.0° (2θ). The samples were prepared as thin layers on glass slides.

Microscopic features of all the samples were observed by SEM (Hitachi, S-5200). The samples were observed without any metal coating. Using a low accelerating voltage, we were able to obtain selective information from the surface region.[4b, 10]

HRTEM images were taken on a JEM-3010 microscope operating at an accelerating voltage of 300 kV. All samples were crushed in an agate mortar, dispersed in ethanol, and deposited on a microgrid.

The surface area and the pore size were measured at −196 °C on a Belsorp 28SA sorptometer. Samples were pretreated for 2 h at 200 °C and 1.33×10^{-4} Pa. The BET specific surface area, S_{BET}, was calculated from adsorption branches in the relative pressure range from 0.04 to 0.1. The primary mesopore volume V_p was determined by using the high-resolution t-plot method. The pore-size distribution was calculated from adsorption branches of isotherms by the BJH method.

Received: April 25, 2003 [Z51752]

Keywords: carbon · mesoporous materials · nanotubes · self-assembly · silica

[1] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710; b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.* **1992**, *114*, 10834.

[2] a) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548; b) D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024.

[3] a) R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B* **1999**, *103*, 7743; b) M. Kaneda, T. Tsubakiyama, A. Carlsson, Y. Sakamoto, T. Ohsuna, O. Terasaki, S. H. Joo, R. Ryoo, *J. Phys. Chem. B* **2002**, *106*, 1256; c) J. Lee, S. Yoon, S. M. Oh, C.-H. Shin, T. Hyeon, *Adv. Mater.* **2000**, *12*, 359; d) S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **2000**, *122*, 10712; e) S. S. Kim, T. J. Pinnavaia, *Chem. Commun.* **2001**, 2418.

[4] a) S. H. Joo, S. J. Chol, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* **2001**, *412*, 169; b) S. Che, K. Lund, T. Tatsumi, S. Iijima, S. H. Joo, R. Ryoo, O. Terasaki, *Angew. Chem./Angew. Chem. Int. Ed.* **2003**, in press.

[5] a) X. Liu, B. Tian, C. Yu, F. Gao, S. Xie, B. Tu, R, Che, L. Peng, D. Zhao, *Angew. Chem.* **2002**, *114*, 4032; *Angew. Chem. Int. Ed.* **2002**, *41*, 3876; b) Y. T. Chan, H. P. Lin, C. Y. Mou, S. T. Liu, *Chem. Commun.* **2002**, 2878; c) K. Flodström, V. Alfredsson, N. Källrot, *J. Am. Chem. Soc.* **2003**, *125*, 4402; d) H. Yang, Q. Shi, X. Liu, S. Xie, D. Jiang, F. Zhang, C. Yu, B. Tu, D. Zhao, *Chem. Commun.* **2002**, 2842.

[6] a) I. Díaz, C. Márquez-Alvarez, F. Mohino, J. Pérez-Pariente, E. Sastre, *J. Catal.* **2000**, *193*, 283; b) I. Díaz, C. Márquez-Alvarez, F. Mohino, J. Pérez-Pariente, E. Sastre, *J. Catal.* **2000**, *193*, 295.

[7] A. Carlsson, M. Kaneda, Y. Sakamoto, O. Terasaki, R. Ryoo, H. Joo, *J. Electron Microsc.* **1999**, *48*, 795.

[8] a) The pore thickness (b) for mesoporous silica with cubic $Ia\bar{3}d$ symmetry was calculated by the method proposed by Ravikovitch and Neimark[8b] using an equation based on the pore volume: $b = \left(1 - \frac{V_{\pi\rho}}{1+V_{\pi\rho}}\right)\frac{a}{x_0}$, where ρ is the pore-wall density (assumed to be 2.3 g cm^{-1}), a is the unit-cell parameter, and x_0 is a constant ($x_0 = 3.0910$); b) P. I. Ravikovitch, A. V. Neimark, *Langmuir* **2000**, *16*, 2419.

[9] M. Kruk, M. Jaroniec, R. Ryoo, S. H. Joo, *J. Phys. Chem. B* **2000**, *104*, 7960.

[10] "Structure and Structure Determination": O. Terasaki in *Electron Microscopy Studies in Molecular Sieve Science in Molecular Sieves-Science and Technology, Vol. 2* (Eds.: H. G. Karge, J. Weitkamp), Springer, Heidelberg, **1999**, pp. 71 – 112.