Chem. Mater. **2001,** *13,* 2237−2239

Control of Crystal Morphology of SBA-1 Mesoporous Silica

Shunai Che,[†] Yasuhiro Sakamoto,[‡]
Osamu Terasaki,[‡] and Takashi Tatsumi*,[†]

Division of Materials Science & Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Yokohama 240-8501, Japan, and Department of Physics, Graduate School of Science and CREST, JST, Tohoku University, Sendai, 980-8578, Japan

Received April 13, 2001

Because the control of the particle morphology and size of mesoporous molecular sieves could open up new possibilities for their application, massive efforts have been devoted to the synthesis of mesoporous molecular sieves having morphologies of defined size. For example, mesoporous silica ranging from millimeter- to nanometer-sized spheres,[1] films,[2] hollow tubulars,[3] fibers,[4] spiral, and gyroid shapes[5] have been synthesized under basic or acidic conditions. However, it is uncommon for the mesoporous materials to show the well-ordered crystal morphology in contrast to the microporous zeolite materials. The periodic mesoporous materials showing crystal-like regularity over very large areas would offer new functions and perceived utility in a wide range of applications, for example, to separations, electronics, and photonics elements. Kim et al.[6] have synthesized silica mesoporous material MCM-48 (cubic $Ia3d$ structure) with a decaoctahedron shape described as a cube truncated by hexagons. Guan et al.[7] and Sayari et al.[8] have reported the synthesis of ethane−silica hybrid cubic mesoporous material with well-defined crystal-like external morphologies of decaoctahedron commensurate with the point group $Pm\bar{3}n$ symmetry.

Huo et al.[9] reported that the silica mesophases of the SBA-1 were formed from a combination of cationic surfactant (S^+), halogen anion (X^-), and cationic silicic acid species (I^+) under an acidic medium. Large head-group surfactants such as alkyltriethylammonium $C_nH_{2n+1}(C_2H_5)_3N^+$ ($n = 12, 14, 16, 18$) favored the SBA-1 phase. Very recently, Sakamoto et al.[10] revealed that SBA-1 and SBA-6, SBA-6 being isostructural to SBA-1 but synthesized under basic conditions, possessed a 3D-cubic ($Pm\bar{3}n$) of uniformly sized pore structure, cage type, with open windows. Kim and Ryoo[11] have found that low temperatures were favorable in the formation of the high-quality cubic mesophase. Up to now, surprisingly little research has been reported on SBA-1, compared with other mesoporous materials such as MCM-41 or SBA-3, while the 3D channel network of SBA-1 is much more desirable for catalytic applications than 1D channel materials. It has been found that SBA-1 synthesized by an improved procedure shows a decaoctahedral crystal-like shape.[10] We have investigated the control of the crystal shape of SBA-1 reflecting the crystal symmetry by means of elaborately adjusting synthesis conditions. Here, we report the synthesis of SBA-1 samples with well-defined crystal morphologies of a large number of facets, which are supposed to be obtained as a result of highly isotropic crystal growth under the conditions near thermodynamic equilibrium.

Synthesis of SBA-1 samples was performed as follows: The surfactant cetyltriethylammonium bromide (CTEABr), distilled water, and hydrochloric acid were mixed to obtain a homogeneous solution, which was allowed to react at desired temperatures prior to the addition of the silica source, tetraethyl orthosilicate (TEOS). After the addition of TEOS, the mixture was stirred for 3 min and then the reaction was continued at various temperatures under static conditions for desired times. The reaction temperature was changed from −5 to 40 °C. The resultant white precipitates were filtered (without washing) and dried at 100 °C overnight. The as-synthesized SBA-1 samples were calcined in air under static conditions at 630 °C for 4 h. The molar composition of the reaction mixture was 0.13:1:2.5:125 CTEABr:TEOS:HCl:H_2O.

The SBA-1 samples were synthesized at various temperatures for 4 days. All the samples showed one broad peak in the powder X-ray diffraction (XRD) pattern around $2\theta = 20°$ for Cu Kα radiation, indicating that the wall of SBA-1 is amorphous silica. The as-synthesized powders obtained in the temperature range from −5 to 5 °C showed three well-resolved sharp XRD diffraction peaks in the region of $2\theta = 1.5°−3.0°$, which are indexed to the 200, 210, and 211 diffractions, based on the cubic system.[9−11] The XRD patterns of the SBA-1 sample synthesized at 0 °C are exhibited in Figure 1. With increasing synthesis temperature to 40 °C, the XRD intensities were decreased and the lines were merged to a single broad peak. These results indicate that low temperatures were favorable for the formation of the highly ordered SBA-1 cubic mesophase for the longer reaction time (4 days).

---

* To whom correspondence should be addressed. Telephone: (81)-45-339-3943. Fax: (81)45-339-3943. E-mail: ttatsumi@cms.ynu.ac.jp.

[†] Yokohama National University.

[‡] Tohoku University.

(1) (a) Huo, Q.; Feng, J.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1997**, *9*, 14. (b) Grun, M.; Lauer, I.; Unger, K. K. *Adv. Mater.* **1997,** *9*, 254. (c) Schacht, S.; Huo, G.; Voiget-Martin, I. G.; Stucky, G. D.; Schüth, F. *Science* **1996**, *273*, 768. (d) Qi, L.; Ma, J.; Cheng H.; Zhao, Z. *Chem. Mater.* **1998**, *10*, 1623. (e) Cheng, Y. R.; Lin, H. P.; Mou, C. Y.; *Phys. Chem. Chem. Phys.* **1999**, *1*, 5051.

(2) Ogawa, M. *J. Am. Chem. Soc.* **1994**, *116*, 7941.

(3) Lin, H. P.; Cheng, Y. R.; Mou, C. Y. *Chem. Mater.* **1998**, *10*, 3772.

(4) Bruinsma, P. J.; Kim, A. Y.; Liu, J.; Baskaran, S. *Chem. Mater.* **1997**, *9*, 2507.

(5) (a) Yang, H.; Coombs, N.; Ozin, G. A. *Nature* **1997**, *386*, 692. (b) Ozin, G. A.; Yang, H.; Sokolov, I.; Coombs, N. *Adv. Mater.* **1997**, *9*, 662.

(6) Kim, J. M.; Kim, S. K.; Ryoo, R. *Chem. Commum.* **1998**, 259.

(7) Guan, S.; Y. Inagaki, S.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 5660.

(8) Sayari, A.; Hamoudi, S.; Yang. Y.; Moudrakovski, I. L.; Ripmeester, J. R. *Chem. Mater.* **2000**, *12*, 3857.

(9) (a) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chemelka, B. F.; Schüth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176. (b) Huo, Q.; Margolese, D. I.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 1147.

(10) Sakamoto, Y.; Kaneda, M.; Terasaki, O.; Zhao, D.; Kim, J. M.; Stucky, G.; Shin, H. J.; Ryoo, R. *Nature* **2000**, *408*, 449.

(11) Kim, M. J.; Ryoo, R. *Chem. Mater.* **1999**, *11*, 487.

10.1021/cm010297f CCC: $20.00

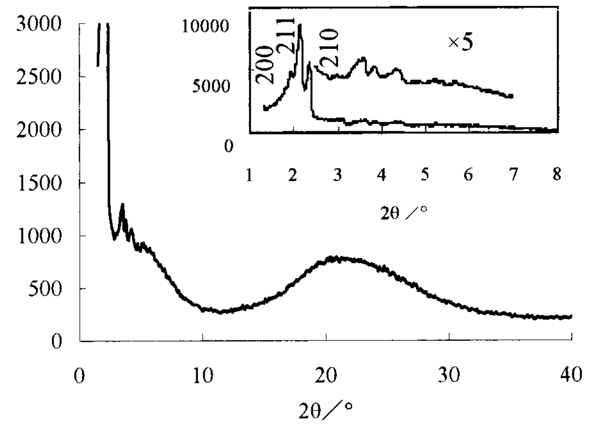

Figure 1. XRD patterns of as-synthesized SBA-1 at 0 °C for 4 days.

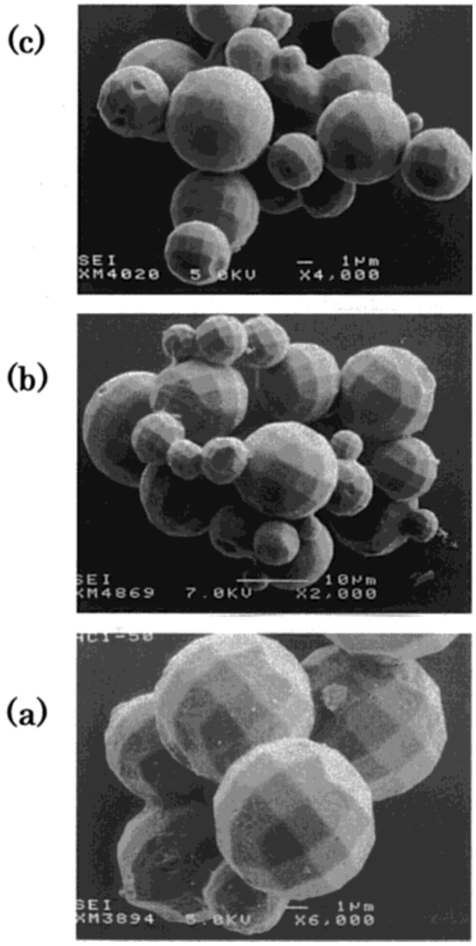

Figure 2. SEM images of SBA-1 samples synthesized at low temperatures for 4 days: (a) 5 °C, (b) 0 °C, and (c) −5 °C.

Scanning electron microscope (SEM) images of SBA-1 samples synthesized at −5, 0, and 5 °C are shown in Figure 2. The samples were composed of particles uniform in shape: the particles have well-defined external morphologies, depending on the synthesis temperature. The sample synthesized at 5 °C (Figure 2a) consisted exclusively of 54 very clear crystal faces, which is composed of 6 {100}, 24 {210}, and 24 {211} planes indexed as shown in Figure 3a. The crystal had four 3-fold axes and exhibited cubic symmetry. The sample synthesized at 0 °C (Figure 2b) consisted of crystals with 74 faces as well as those with 54 faces. The 74 facets are described as the 54-face crystal to which 12 elongated hexagons and 8 triangles are added. The elongated hexagons and triangle are {110} and {111} planes in the cubic structure, respectively, as shown in Figure 3b. The sample synthesized at −5 °C was composed of crystals with 54, 74, or more faces; however, each face was clearly seen on those crystals (Figure 2c). The crystal faces became unclear with increasing synthesis temperature from 5 °C and the morphology was entirely changed to an amorphous shape when the synthesis was conducted at 80 °C.

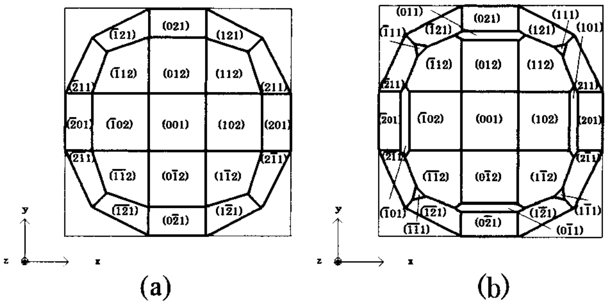

Figure 3. Mutual orientation diagrams of the SBA-1 particles having 54 or 74 crystal faces.

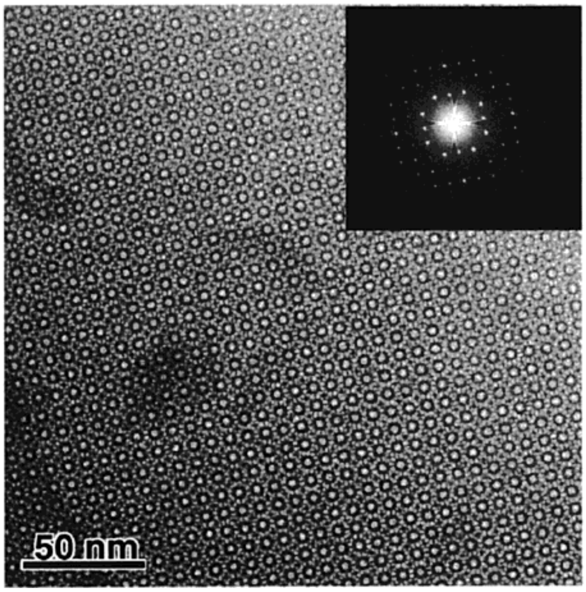

Figure 4. High-resolution transmission electron microscopy images for the calcined SBA-1 sample.

Figure 4 shows a high-resolution transmission electron microscope (HRTEM) image of the calcined SBA-1 sample synthesized at 0 °C, taken in the [001] direction. The corresponding Fourier diffractogram shown in the inset indicates extinction conditions for the reflections. The image revealed regular periodicity over very large areas and this clearly indicates the crystal is a single crystal with a well-ordered mesostructure. The $Pm\bar{3}n$ space group with the same mesostructure as previously reported[10] was confirmed by an analysis of a set of HRTEM images. HRTEM images projected along other incident beam directions [102], [112], [110], and [111] also support the SBA-1 pore configuration. The EM experiments indicated that the particles are remarkably perfect single crystals.

Each sample having high periodicity of the cubic structure showed a type IV N_2 adsorption−desorption isotherm. The samples with well-ordered mesostructures exhibited almost identical pore sizes and had very similar BET specific surface areas and primary mesopore volumes of about 1000 m^2/g and 500 mm^3/g, respectively.

Although use of cetyltrimethylammonium bromide instead of CTEABr usually affords SBA-3, the SBA-1 mesostructure was obtained under highly acidic conditions starting with a clear solution with a molar ratio of 0.20:1:32:150 CTMABr:TEOS:HCl:H_2O. This SBA-1 sample exhibited a decaoctahedral shape similar to the recently reported one.[10] The fewer crystal faces would be due to the kinetically controlled more anisotropic growth because of a very high amount of acid.

It is considered that the crystals having a great number of crystal faces are formed through highly isotropic crystal growth and that those having fewer crystal faces reflect anisotropic crystal growth, which are due to the difference in growth rate depending on the crystal faces. Synthesis under highly acidic or relatively high temperature conditions would make crystallization more kinetically controlled, leading to more anisotropic growth. At lower acidity or lower temperature, the crystallization is slowed and would proceed under more thermodynamically controlled, near equilibrium conditions, leading to more isotropic growth. It is noteworthy that in each SEM image of Figures 2b and 2c smaller particles display less faces and vice versa, suggesting the shift to more isotropic crystallization during the crystal growth.

In conclusion we have developed a method for highly ordered mesoporous silica with well-resolved XRD patterns and particular morphology having 54 or more crystal faces by adjusting temperature, synthesis time, acidity, and surfactant concentration. Details of the control of the morphology of crystals will be reported later.

Acknowledgment. The authors are grateful to Y. Shimada (Instrumental Analysis Center, Yokohama National University,) for taking scanning electron micrographs. For financial support, O.T. thanks CREST, JST and T.T. thanks JCII.

CM010297F