ChemComm

Synthesis of highly ordered mesoporous silica materials using sodium silicate and amphiphilic block copolymers

Ji Man Kim and Galen D. Stucky*

Department of Chemistry, University of California at Santa Barbara, Santa Barbara, CA 93106, USA.
E-mail: stucky@chem.ucsb.edu

Received (in Columbia, MO, USA) 22nd March 2000, Accepted 17th May 2000

A commercially important synthetic approach to highly ordered mesoporous silica materials (SBA-family) with 2-D hexagonal (*P6mm*), 3-D hexagonal (*P*6$_3$/*mmc*) and cubic (*Im*3*m* and *Pm*3*m*) structures, using sodium silicate as the silica source and amphiphilic block copolymers as the structure-directing agents is demonstrated.

It is well known that mesoporous silica materials are synthesised by synergistic self-assembly between surfactant and silica species to form mesoscopically ordered composites.[1,2] Generally, two types of surfactants are used for the formation of mesoporous silica materials: ionic surfactants such as alkyltrimethylammonium bromide[1,3] and nonionic surfactants such as alkylamine[4] and poly(ethylene oxide)-type copolymers.[5–7] The ionic surfactants interact electrostatically with inorganic species, whereas the nonionic surfactants result in the formation of mesocomposites through hydrogen bond or van der Waals interaction. The nonionic surfactants give commercially important advantages compared with the ionic surfactants. They are easily removable, nontoxic, biodegradable and relatively inexpensive. Pinnavaia and coworkers[6] have reported the synthesis of MSU-*X* mesoporous materials with several nonionic surfactants. These materials are composed of worm-like channels, which are disorderedly arrayed. Stucky and coworkers[7] have reported the synthesis of SBA mesoporous silica materials, which have well-ordered channel and cage structures, using amphiphilic di- and triblock copolymers as the structure directing agents at or below the isoelectric point (pH $\leqslant$ 3). However, these synthetic procedures using nonionic surfactants are not as commercially viable as they might be due to the use of tetraethyl orthosilicate (TEOS) as a silica source. Recently, Guth and coworkers[8] have pointed this out and reported the synthesis of mesoporous silica material using nonionic surfactant and sodium silicate in the pH range 3–10.5. However, the mesoporous materials thus obtained exhibit irregular or disordered channel connectivity and broad pore size distributions.

Here, we report the synthesis of highly ordered mesoporous silica materials that include 2-dimensional (2-D) hexagonal SBA-15 (*P*6*mm*), 3-dimensional (3-D) hexagonal SBA-12 (*P*6$_3$/*mmc*) and cubic SBA-16 and SBA-11 (*Im*3*m* and *Pm*3*m*) using sodium metasilicate as the silica source and nonionic amphiphilic block copolymers as the structure-directing agents.

Triblock copolymers such as Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800) and Pluronic P85 ($EO_{26}PO_{39}EO_{26}$, M_{av} = 4600) and diblock copolymer, $C_nH_{2n+1}(OCH_2CH_2)_xOH$ (C_nEO_x, n = 12–18, x = 9–23), were used as received from BASF, Aldrich and Sigma. Sodium metasilicate ($Na_2SiO_3{\cdot}9H_2O$) and concentrated hydrochloric acid (c-HCl, 37.6%) were obtained from Fisher Scientific. In a typical synthesis batch, 3.0 g of $C_{18}EO_{10}$ was dissolved in 57.4 g of distilled water and then 8.8 g of sodium metasilicate was added at room temperature with magnetic stirring, giving a clear solution. To this reaction mixture, 17.7 g of c-HCl was quickly added with vigorous magnetic stirring. The resulting gel mixture was stirred for 1 day at room temperature and subsequently heated for 1 day at 373 K in an oven to increase the degree of silanol group condensation. In the case of Pluronic triblock polymers, the reaction temperature was 313 K before heating to 373 K. The solid product was filtered off and dried at 373 K. The product was then slurried in ethanol–HCl mixture, filtered off, washed with ethanol, dried in an oven, and calcined in air under static conditions at 823 K. The product yield in a typical synthesis batch was above 90% on the basis of the silica recovery.

Fig. 1a–c show powder X-ray diffraction (XRD) patterns for SBA-15 materials, obtained from $C_{12}EO_9$, $EO_{26}PO_{39}EO_{26}$ and $EO_{20}PO_{70}EO_{20}$, after calcination. All exhibit XRD patterns with a very intense diffraction peak and two or more weak peaks, which are characteristic of a 2-D hexagonal (*P*6*mm*) structure.[1,5,7] The SBA-15 obtained from $EO_{20}PO_{70}EO_{20}$ shows (210) and (300) peaks, which indicates excellent textural uniformity of the material. There were no significant changes upon calcination, except for the expected increase in XRD peak intensity and lattice contraction (7–12%). Fig. 2a is a transmission electron microscopic (TEM) image for SBA-15 (Fig. 1c). The TEM image also indicates that the material has a highly ordered 2-D hexagonal structure, similar to that of SBA-15 obtained from TEOS.[7] Other 2-D hexagonal silica materials in Fig. 1a and b give similar TEM images except for their different channel sizes. The N_2 adsorption–desorption isotherms and pore size distribution curves for the present SBA-15 materials are essentially the same as those of SBA-3 and SBA-15.[3,7] Lattice parameters and pore sizes are listed in Table 1.

Fig. 1d and e show XRD patterns for the mesoporous silica materials obtained from $C_{12}EO_{23}$ and $C_{16}EO_{20}$, respectively. The XRD patterns can be indexed as cubic *Im*3*m* for Fig. 1d and cubic *Pm*3*m* for Fig. 1e.[7] It is interesting and important that cubic *Im*3*m* mesoporous silica (SBA-16) can be obtained using

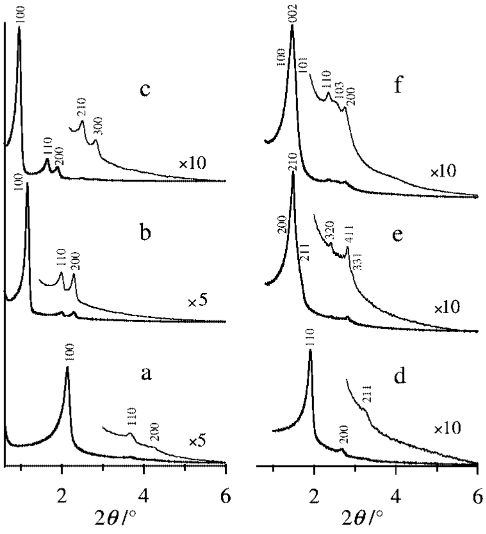

Fig. 1 XRD patterns for the mesoporous silicas obtained from (a) $C_{12}EO_9$, (b) $EO_{26}PO_{39}EO_{26}$, (c) $EO_{20}PO_{70}EO_{20}$, (d) $C_{12}EO_{23}$, (e) $C_{16}EO_{20}$ and (f) $C_{18}EO_{10}$. XRD patterns were collected with a Cu-Kα X-ray source using a Sintag X_2 instrument.

DOI: 10.1039/b002362k

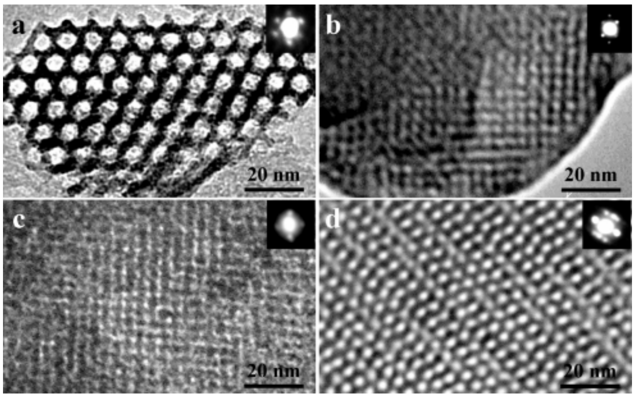

Fig. 2 TEM images and ED patterns for the calcined mesoporous silicas obtained from (a) $EO_{20}PO_{70}EO_{20}$, (b) $C_{12}EO_{23}$, (c) $C_{16}EO_{20}$ and (d) $C_{18}EO_{10}$. The TEM image was taken with a 2000 FX JEOL instrument operating at 200 kV.

Table 1 Lattice parameter, pore diameter and BET surface area of mesoporous silicas

Polymer	Mesophase	Cell parameter/nm[a]	Pore size nm[b]	Surface area/m^2 g^{-1}
$C_{12}EO_9$	2-D hexagonal	4.79	3.8	1055
$C_{12}EO_{23}$	cubic *Im*3*m*	6.70	3.5, 4.3[c]	701
$C_{16}EO_{20}$	cubic *Pm*3*m*	13.25	4.2, 5.0[c]	637
$C_{18}EO_{10}$	3-D hexagonal	7.43, 12.02[d]	4.5, 5.4[c]	572
$EO_{26}PO_{39}EO_{26}$	2-D hexagonal	8.83	5.6	849
$EO_{20}PO_{70}EO_{20}$	2-D hexagonal	10.68	7.6	600

[a] Lattice parameters calculated from *d* spacings in XRD patterns. [b] Pore size distribution obtained from N_2 adsorption–desorption isotherms following the BdB analysis with cylindrical and spherical models.[9,10] [c] Numbers denote pore opening size and largest diameter in spherical cage structure, respectively. [d] Numbers represent lattice parameters *a* and *c*, respectively.

the $C_{12}EO_{23}$ diblock copolymer as well as with the triblock copolymer $EO_{106}PO_{70}EO_{106}$ (Pluronic F127).[7] TEM images for the cubic materials are shown in Fig. 2b and c. The images show well-ordered structures viewed along the [001] direction, suggesting that both mesoporous silica materials have highly ordered cubic structures.

Fig. 1f and Fig. 2d are the XRD pattern and TEM image, respectively, for the mesoporous silica obtained from $C_{18}EO_{10}$. The XRD pattern can be indexed as a 3-D hexagonal ($P6_3/mmc$) structure with cell parameters a = 7.43, 12.03 nm. The cell parameter ratio (c/a) is 1.62, which is very similar to ideal ratio (1.633) for a typical hexagonal close-packed (hcp) phase and those of SBA-12[7] and SBA-2.[3] Fig. 3 shows N_2 adsorption–desorption isotherms and pore size distribution curves for the 3-D hexagonal material. The N_2 isotherm is of type IV with a H2 hysteresis loop, which indicates this material has bottle shaped pores similar to those of SBA-2.[3]

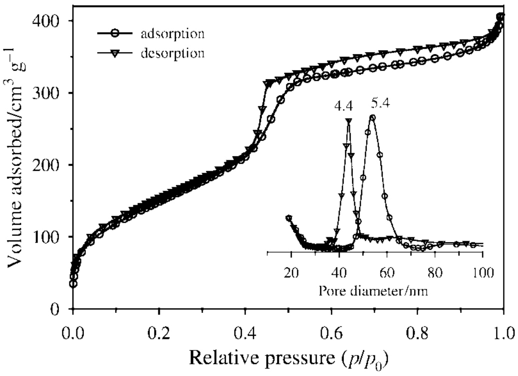

Fig. 3 N_2 adsorption–desorption isotherms for the mesoporous silica material obtained from $C_{18}EO_{10}$ and the corresponding pore size distribution curves. N_2 adsorption isotherms were obtained at liquid N_2 temperature using a Micromeritics ASAP 2000 instrument and pore size distributions were calculated by the BdB (Broekhoff and de Boer) method[9,10] with a spherical model.

In conclusion, we have developed a new synthetic method for highly ordered mesoporous silicas using sodium metasilicate as the silica source and amphiphilic block copolymers as the structure-directing agents. The replacement of TEOS by sodium metasilicate leads to the low cost production of mesoporous silica materials for practical applications. In addition, other substituents such as aluminium, titanium, *etc.* can be incorporated into the silica framework of the present SBA materials for applications such as catalysis and ion exchange.

This work is supported by the National Science Foundation and the Army Research Office.

Notes and references

1 Q. Hou, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth and G. D. Stucky, *Nature*, 1994, **368**, 317.

2 A. Firouzi, D. Kumar, L. M. Bull, T. Besier, P. Sieger, Q. Hou, S. A. Walker, J. A. Zasadzinski, C. Glinka, J. Nicol, D. Margolese, G. D. Stucky and B. F. Chmelka, *Science*, 1995, **267**, 1138.

3 Q. Huo, R. Leon, P. M. Petroff and G. D. Stucky, *Science*, 1995, **268**, 1324.

4 P. T. Tanev, M. Chlbwe and T. J. Pinnavaia, *Nature*, 1994, **368**, 321; P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865.

5 G. Attard, J. C. Glyde and C. G. Göltner, *Nature*, 1995, **378**, 366.

6 S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, 1995, **269**, 1242.

7 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548; D. Zhao, Q. Hou, J. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 6024.

8 L. Sierra, B. Lopez, H. Gil and J.-L. Guth, *Adv. Mater.*, 1999, **11**, 307; L. Sierra and J.-L. Guth, *Microporous Mesoporous Mater.*, 1999, **27**, 243.

9 J. C. P. Broekhoff and J. H. de Boer, *J. Catal.*, 1967, **9**, 8.

10 W. W. Lukens, P. Schmidt-Winkel, D. Zhao and G. D. Stucky, *Langmuir*, 1999, **15**, 5403.