

Synthesis of Mesoporous Silicas of Controlled Pore Wall Thickness and Their Replication to Ordered Nanoporous Carbons with Various Pore Diameters

Jae-Seung Lee, Sang Hoon Joo, and Ryong Ryoo*

National Creative Research Initiative Center for Functional Nanomaterials and Department of Chemistry,
Korea Advanced Institute of Science and Technology, Daejeon, 305-701, Republic of Korea

Received October 11, 2001

Mesoporous carbons are important in many areas of modern science and technology. Recently, ordered mesoporous carbons with various pore shapes and connectivity have been synthesized by casting carbon frameworks with mesoporous silica templates.^{1–5} The mesoporous carbons, which are constructed with a regular array of uniform nanopores, exhibit high specific surface areas (typically 1300–2000 m² g⁻¹), uniform pore diameters (2–6 nm), large adsorption capacities (1–2 cm³ g⁻¹), and high thermal, acid–base, and mechanical stabilities. The ordered nanoporous carbons are capable of high dispersions of Pt nanoparticles.⁴ The nanopore walls can be functionalized with various organic groups;⁶ thus they have received great technological attention for the development of advanced separation systems, catalysts, hydrogen-storage systems, double-layer capacitors,⁵ and fuel-cell electrodes.⁴

The carbon synthesis procedure consists of infiltration of the silica template with an appropriate carbon precursor, carbonization of the precursor, and subsequent removal of the silica template using HF or NaOH solution. The carbons exhibit wide varieties of pore shapes, connectivity, and pore wall thickness, depending on silica templates that are synthesized with various structures and pore diameters. In addition to these structural variations, it is important for applications of the mesoporous carbons to vary pore diameters. However, until now, this has remained as a challenge since there were no effective methods for the control of pore wall thickness of silica templates. There were several ways of tailoring the pore wall thickness of 2-D hexagonal silicas.⁷ However, most of the reported methods were insufficient to provide a continuum of the pore wall thicknesses, or they suffered from poor reproducibility.

Here we report a synthesis strategy for the systematic control of the pore wall thickness of hexagonal mesoporous silicas, using surfactant mixtures. We demonstrate that the mesoporous silicas are suitable as templates for the synthesis of mesoporous carbons with various pore diameters. We point out that the silica synthesis method would be useful for general applications wherever the variation of the silica wall thickness could offer modulation of interactions between nanowires incorporated or hosted inside the silica pores, such as the electronic and magnetic nanowires.

The synthesis of the hexagonal mesoporous silicas was performed with an aqueous solution of sodium silicate under acidic condition, similar to the procedure reported by Kim and Stucky.⁸ An aqueous solution of sodium silicate with Na/Si = 0.5 (5.0 mass% SiO₂, 1.3 mass% Na₂O, 93.7 mass% H₂O) was prepared by dissolving silica in NaOH solution. Hexadecyltrimethylammonium bromide (HTAB, 99%) was received from ACROS and used without purification. Two polyoxyethylene hexadecyl ether-type surfactants, C₁₆H₃₃-(C₂H₅O)₂OH (C₁₆EO₂) and C₁₆H₃₃(C₂H₅O)₁₀OH (C₁₆EO₁₀), were received from Aldrich. These nonionic surfactants were mixed in HCl solution to give nominally C₁₆EO₈. Both the silicate and

surfactant solutions were preheated to 308 K. The solutions were combined rapidly in a polypropylene bottle, and the bottle was shaken immediately and vigorously. After being shaken for about 1 min, the mixture was magnetically stirred for 10 min at 308 K. The mixture was maintained at 308 K for 12 h under static conditions and then heated to 373 K for 12 h. The products were filtered and calcined at 823 K. Four products were obtained from the starting mole ratios of HTAB:C₁₆EO₈:SiO₂:H₂O:HCl = 3:0:12.2:1920:179, 2:1:12.7:2040:151, 1:2:13.2:2150:123, and 0:3:13.7:2270:94.9, respectively. The silicas are designated as SiO₂-3:0, SiO₂-2:1, SiO₂-1:2, and SiO₂-0:3, according to the HTAB:C₁₆EO₈ ratios.

The synthesis of carbon was carried out using the above silica products. Sucrose was used as a carbon source, similar to our previous work on the synthesis of CMK-3 carbon using SBA-15 silica as template.² The silica-to-sucrose ratios were optimized depending on the pore volume of the silica templates. Briefly, an aqueous solution of sucrose and sulfuric acid was impregnated into the silica pores. The amounts of the sucrose were 1.25 g per gram of silica for SiO₂-3:0 and SiO₂-2:1, and 1.38 g for SiO₂-1:2 and SiO₂-0:3. After being dried at 433 K, the sucrose/silica composite samples were impregnated again with an additional amount of sucrose solution, which corresponded to 60% of the first impregnated quantity of sucrose. After being dried at 433 K, the samples were heated to 1173 K under vacuum. The resultant carbon/silica composites were washed with HF or boiled in 1 M NaOH solution (an EtOH–H₂O mixture) twice with magnetic stirring to remove the silica template completely. The CMK-3-type carbons thus obtained are denoted as CMK-3(x:y), where x:y refers to the same HTAB:C₁₆EO₈ ratio as for silica templates. X-ray powder diffraction (XRD) patterns were taken with a Rigaku Miniflex instrument. Pore size distribution was analyzed with N₂ adsorption, following the Barrett–Joyner–Halenda algorithm and the calibration method suggested by Kruk et al.⁹

The carbon products have hexagonal structures, which correspond to the negative replication of silica templates. The XRD patterns of the carbon products, characteristic of the hexagonal structures, are similar to those of the silica templates as shown in Figure 1. The pore size distribution curves are shown in Figure 2. The pore diameters are very narrow in distribution, and the pore size at the maximum of the distribution is systematically shifted from 2.2 to 3.3 nm against the HTAB:C₁₆EO₈ ratio used for the synthesis of templates. As shown in Table 1, the thickness of the silica pore walls increased with the HTAB:C₁₆EO₈ ratio. The pore wall thickening was reasonable, so we used the HTAB–C₁₆EO₈ mixtures, expecting that the silica species interacting with the headgroup corona¹⁰ through hydrogen bonding¹¹ would increase in number with increasing EO segments per surfactant. In addition to the pore wall change, there was also an increase in the silica pore diameter due to the EO content of the surfactants. These

* To whom correspondence should be addressed: rryoo@mail.kaist.ac.kr.

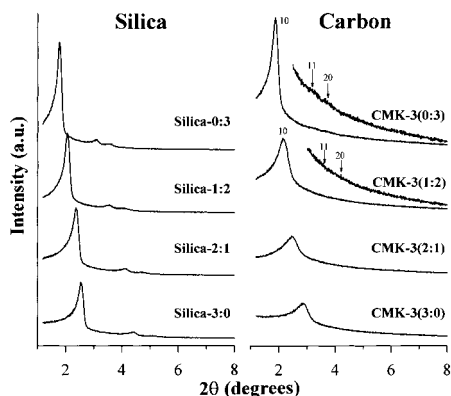


Figure 1. XRD patterns for calcined mesoporous silicas and templated carbons.

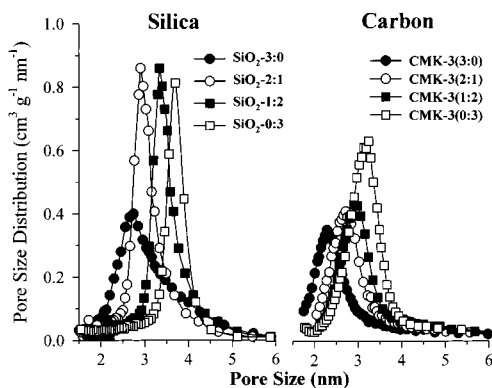


Figure 2. Pore size distributions of calcined mesoporous silicas and templated carbons from the N_2 adsorption branch.

Table 1. Structural Properties of Calcined Mesoporous Silicas and Templated Carbon Samples Depending on the HTAB: $C_{16}EO_8$ Ratio

| HTAB: $C_{16}EO_8$ | SiO_2 lattice constant (nm) ^a | SiO_2 pore diameter (nm) | SiO_2 wall thickness (nm) ^b | pore diameter of CMK-3 carbons (nm) |
|-----------------------|---|-------------------------------|---|--|
| 3:0 | 4.0 | 2.8 | 1.4 | 2.2 |
| 2:1 | 4.3 | 2.9 | 1.5 | 2.7 |
| 1:2 | 5.0 | 3.3 | 1.8 | 2.9 |
| 0:3 | 5.7 | 3.7 | 2.2 | 3.3 |

^a $2(3^{-1/2})d_{100}$, where d_{100} is d spacing of XRD (100) reflection. ^b Lattice constant – pore diameter/1.05 (calculated as in ref 12)

simultaneous changes indicate that the EO groups contribute in part to the formation of the silica pore walls and to the silica mesopores. Compared with the multiple interaction sites in the C_nEO_m surfactant, the cationic alkyl-TAB surfactants are singly charged. Their electrostatic interactions with silica species may occur in an almost 1:1 ratio, independent of the various ratios used in the starting mixtures. The nearly stoichiometric interactions seem to be the reason the thickness of the silica pore walls in MCM-41 and MCM-48 was reported to remain almost constant despite the variation of the surfactant tails from C_{12} to C_{22} alkyl chains.¹²

It is reasonable that the $C_{16}EO_8$ surfactant-driven mesoporous silica should contain a sufficient number of complementary pores that are enough to afford free-standing, highly ordered carbon structure, as in the case of SBA-15-templated CMK-3 synthesis. The amount of the complementary pores contained in the silica pore walls seems to decrease with the increase of cationic surfactant, as revealed by less resolved XRD peaks in carbons as the HTAB: $C_{16}EO_8$ ratio in surfactants increases. It is interesting to note that, even in the case of the mesoporous silica template synthesized using only the cationic HTAB surfactant—the same surfactant as for the synthesis of MCM-41—the templated carbon, CMK-3(3:0), still retains the ordered structure as shown in Figure 1. This result is

comparable to the carbon synthesis using MCM-41, where entangled nanofiberlike carbons are obtained.¹³ Both MCM-41 and the SiO_2 -3:0 sample are synthesized with HTAB and sodium silicate, but their difference in synthesis conditions (acidic condition for SiO_2 -3:0 as compared with basic condition for MCM-41) seems to cause a remarkable difference in the pore connectivity. The formation of the fiberlike carbon is evidence for the one-dimensional channel structure of MCM-41 without connectivity. On the other hand, the synthesis of the hexagonally structured carbon from SiO_2 -3:0 indicates that the mesoporous silica from acidic synthesis conditions (designated as SBA-3 following Stucky¹¹) has the mesoporous channels somewhat interconnected by complementary pores in the silica pore wall.

Several points can be addressed in conclusion from the present results. In general, the thickness of mesoporous silica pore walls can be controlled systematically by the number of the functional groups that can attract silica species such as the ethylene oxide portion of the surfactant. A particular route is to use the $C_{16}EO_8$ –HTAB surfactant mixture. The silica products with various pore wall thicknesses are suitable as templates for mesoporous carbons with controlled pore diameters, which would be of great interest for applications requiring fine-tuning of pore diameters. The merit of the silica products with various pore wall thicknesses would not be limited to the present carbon synthesis. The mesoporous silicas would also be of general use as hosts for nanowire systems for which the variation of the silica wall thickness can offer modulation of interactions between the incorporated nanowires such as the electronic and magnetic materials. Further, the present synthesis strategy may be extended to silica–organic composite mesoporous materials.¹⁴

Acknowledgment. This work was supported in part by the Creative Research Initiative Program of the Korean Ministry of Science and Technology, and by the School of Molecular Science through the Brain Korea 21 project.

Supporting Information Available: N_2 adsorption isotherms of mesoporous silicas and templated carbons (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Ryoo, R.; Joo, S. H.; Jun, S. J. *Phys. Chem. B* **1999**, *103*, 7743. (b) Kruk, M.; Jaroniec, M.; Ryoo, R.; Joo, S. H. *J. Phys. Chem. B* **2000**, *104*, 7960. (c) Joo, S. H.; Jun, S.; Ryoo, R. *Microporous Mesoporous Mater.* **2001**, *44–45*, 153.
- (2) (a) Jun, S.; Joo, S. H.; Ryoo, R.; Kruk, M.; Jaroniec, M.; Liu, Z.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **2000**, *122*, 10712. (b) Shin, H. J.; Ryoo, R.; Kruk, M.; Jaroniec, M. *Chem. Commun.* **2001**, 349.
- (3) Ryoo, R.; Joo, S. H.; Kruk, M.; Jaroniec, M. *Adv. Mater.* **2001**, *13*, 677 and references therein.
- (4) Joo, S. H.; Choi, S. J.; Oh, I.; Kwak, J.; Liu, Z.; Terasaki, O.; Ryoo, R. *Nature* **2001**, *412*, 169.
- (5) Lee, J.; Yoon, S.; Hyeon, T.; Oh, S. M.; Kim, K. B. *Chem. Commun.* **1999**, 2177.
- (6) Jun, S.; Ryu, S.; Lee, H.-Y.; Ryoo, R. *Angew. Chem., Int. Ed.*, submitted.
- (7) (a) Di Renzo, F.; Coustel, N.; Mendiboune, M.; Cambon, H.; Fajula, F. *Stud. Surf. Sci. Catal.* **1997**, *105*, 69. (b) Cheng, C.-F.; Zhou, W.; Park, D. H.; Klinowski, J.; Hargreaves, M.; Gladden, L. F. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 359. (c) Sayari, A.; Liu, P.; Kruk, M.; Jaroniec, M. *Chem. Mater.* **1997**, *9*, 2499. (d) Mokaya, R. *J. Phys. Chem. B* **1999**, *103*, 10204. (e) Kruk, M.; Jaroniec, M.; Ko, C. H.; Ryoo, R. *Chem. Mater.* **2000**, *12*, 1961. (f) Feng, P.; Bu, X.; Pine, D. J. *Langmuir* **2000**, *16*, 5304.
- (8) Kim, J. M.; Stucky, G. D. *Chem. Commun.* **2000**, 1159.
- (9) Kruk, M.; Jaroniec, M.; Sayari, A. *Langmuir* **1997**, *13*, 6267.
- (10) Impéror-Clerc, M.; Davidson, P.; Davidson, A. J. *Am. Chem. Soc.* **2000**, *122*, 11925.
- (11) Huo, Q.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P.; Gier, T. E.; Sieger, P.; Chmelka, B. F.; Schüth, F.; Stucky, G. D. *Nature* **1994**, *368*, 317.
- (12) Kruk, M.; Jaroniec, M.; Sakamoto, Y.; Terasaki, O.; Ko, C. H.; Ryoo, R. *J. Phys. Chem. B* **2000**, *104*, 292.
- (13) Ryoo, R., unpublished result.
- (14) Sayari, A.; Hamoudi, S. *Chem. Mater.* **2001**, *13*, 3151 and references therein.

JA012333H