

Synthesis of mesoporous carbons with various pore diameters via control of pore wall thickness of mesoporous silicas

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A synthesis strategy for the systematic control of the pore wall thickness has been developed for the mesoporous silicas with 2-D hexagonal order using ionic and nonionic surfactant mixtures. The mesoporous silicas have been used as templates for the synthesis of 2-D hexagonally ordered mesoporous carbons with controlled pore diameters. The synthesis strategy and results are useful not only for tailoring the properties of the mesoporous materials but also for extending our insights into the synthesis mechanism.

1. INTRODUCTION

Mesoporous carbons are important in many areas of modern science and technology.¹ Recently, ordered mesoporous carbons have been synthesized by casting carbon frameworks with mesoporous silica templates.²⁻⁶ The mesoporous carbons, which are constructed with a regular array of uniform nanopores, exhibit high specific surface areas (typically 1300 ~ 2500 m²g⁻¹), uniform pore diameters (2 ~ 6 nm), large adsorption capacities (1 ~ 2.5 cm³g⁻¹), and high thermal, acid-base, and mechanical stabilities. They have received great technological attention for the development of advanced separation systems, catalysts, hydrogen-storage systems, fuel-cell electrodes⁵, and double-layer capacitors.⁶ The mesoporous 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 to control the pore diameters of mesoporous carbons for various applications. 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. Although there were several ways of tailoring the pore wall thickness of 2-D hexagonal silica, most of the reported methods were insufficient to provide a continuum of the pore wall thicknesses, or they suffered from poor reproducibility.⁷⁻⁹

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.¹⁰

2. EXPERIMENTAL

The synthesis of the hexagonal mesoporous silicas was performed under acidic condition, using sodium silicate as a silica source. The mixture of the hexadecyltrimethylammonium bromide (HTAB) and two polyoxyethylene hexadecyl ethers, $C_{16}H_{33}(C_2H_5O)_2OH$ ($C_{16}EO_2$) and $C_{16}H_{33}(C_2H_5O)_{10}OH$ ($C_{16}EO_{10}$), was used as surfactant. The nonionic surfactants were mixed in HCl solution to give nominally $C_{16}EO_8$. After the silicate and surfactant solutions were mixed 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. The obtained silicas are designated as SiO_2 -3:0, SiO_2 -2:1, SiO_2 -1:2, and SiO_2 -0:3, according to the HTAB: $C_{16}EO_8$ ratios.

The synthesis of carbon was carried out using mesoporous silicas as the templates and sucrose as a carbon source. The silica-to-sucrose ratios were optimized depending on the pore volume of the silica templates. The details of the procedures were performed in the same way as for the synthesis of CMK-3 carbon using SBA-15 silica.³ The CMK-3-type carbons thus obtained are denoted as CMK-3(*x*:*y*), where *x*:*y* refers to the same HTAB: $C_{16}EO_8$ ratio as for the silica templates. X-ray powder diffraction (XRD) patterns were taken with a Rigaku Miniflex instrument. Pore size distribution was analyzed with N_2 adsorption, following the Barrett-Joyner-Halenda algorithm and the KJS calibration.¹¹

3. RESULTS AND DISCUSSION

The XRD patterns in Figure 1 show that all the carbon products have hexagonal structures corresponding to the faithful replication of the silica templates. The hexagonal structures suggest that the $C_{16}EO_8$ surfactant-assembled mesoporous silica (SiO_2 -0:3) should contain a sufficient number of complementary pores that are enough to afford freestanding, 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. The pore size distribution curves of ordered carbons 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: $C_{16}EO_8$ ratio used for the synthesis of templates. The pore size variation of the carbons indicates that the pore-wall thickness of the silica templates increased with the HTAB: $C_{16}EO_8$ ratio, which is reasonable since the silica species interacting with the head group corona¹² through hydrogen bonding¹³ would increase in number with increasing the EO segments per surfactant, while the cationic HTAB surfactant would have the electrostatic interaction with silica species in an almost one-to-one ratio, independent of the various ratios used in the starting mixtures.

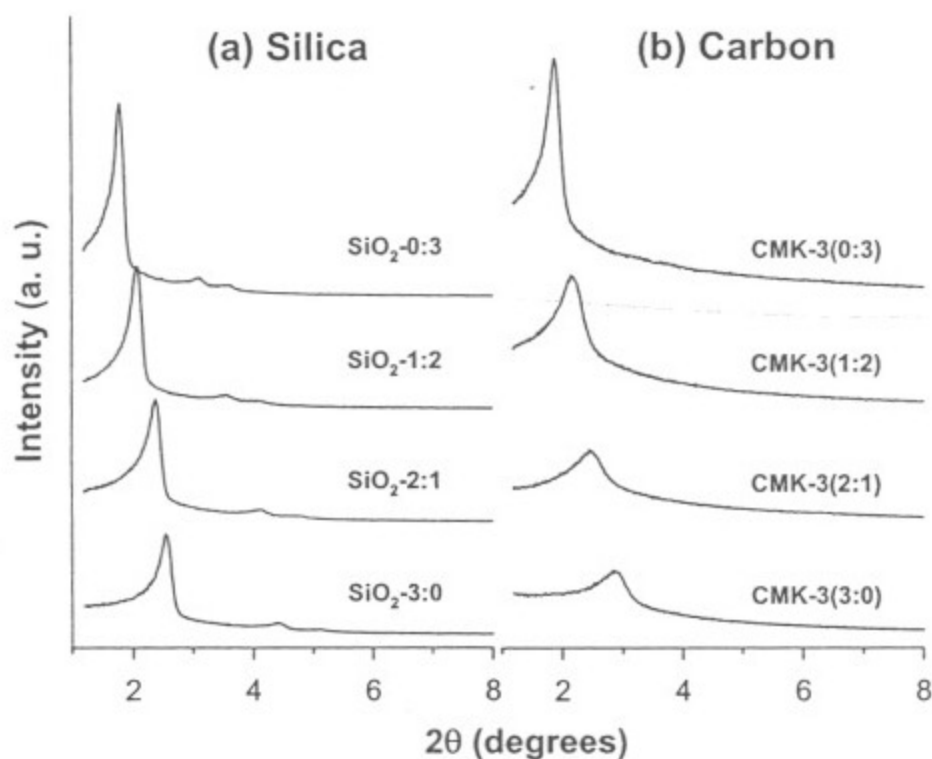


Fig. 1. XRD patterns for calcined mesoporous silicas and templated carbon samples

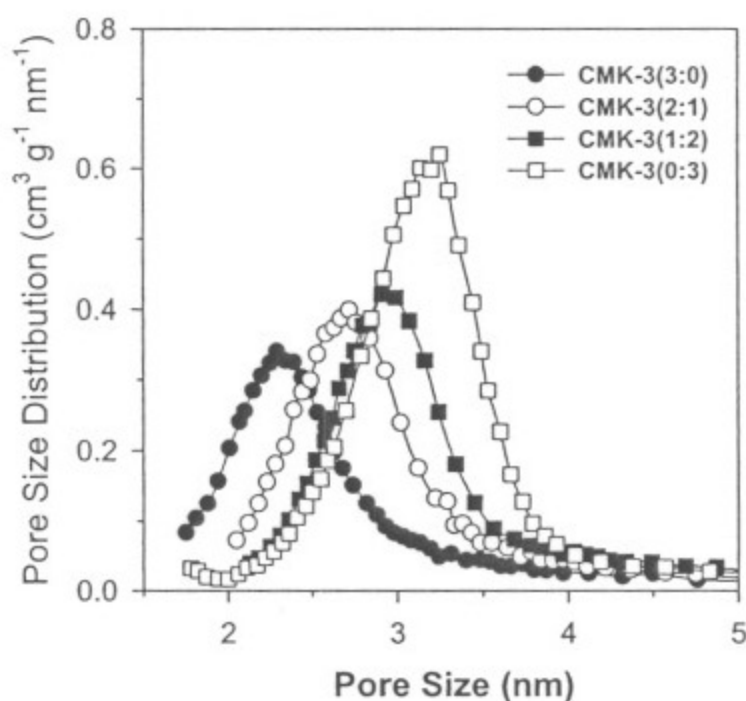


Fig. 2. Pore size distribution of the carbon samples from nitrogen adsorption

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.¹⁴ Both MCM-41 and the SiO₂-3:0 sample are synthesized with HTAB and sodium silicate, but their difference in synthesis conditions (acidic condition for SiO₂-3:0 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 Stucky¹³) has the mesoporous channels somewhat interconnected by complementary pores in the silica pore wall.

4. CONCLUSIONS

In this work, 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. 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.

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REFERENCES

1. C. R. Bansal, J.-B. Donnet and F. Stoeckli, *Active Carbon*, Marcel Dekker, New York, 1988.
2. R. Ryoo, S. H. Joo and S. Jun, *J. Phys. Chem. B*, 103 (1999) 7743.
3. S. Jun et al., *J. Am. Chem. Soc.*, 122 (2000) 10712.
4. R. Ryoo, S. H. Joo, M. Kruk and M. Jaroniec, *Adv. Mater.*, 13 (2001) 677.
5. S. H. Joo et al., *Nature*, 412 (2001) 169.
6. J. Lee et al., *Chem. Commun.*, (1999) 2177.
7. F. Di Renzo et al., *Stud. Surf. Sci. Catal.*, 105 (1997) 69.
8. A. Sayari, P. Liu, M. Kruk and M. Jaroniec, *Chem. Mater.*, 9 (1997) 2499.
9. M. Kruk, M. Jaroniec, C. H. Ko and R. Ryoo, *Chem. Mater.*, 12 (2000) 1961.
10. J.-S. Lee, S. H. Joo and R. Ryoo, *J. Am. Chem. Soc.*, 124 (2002) 1156.
11. M. Kruk, M. Jaroniec and A. Sayari, *Langmuir*, 13 (1997) 6267.
12. M. Imp  rator-Clerc, P. Davidson and A. Davidson, *J. Am. Chem. Soc.*, 122 (2000) 11925.
13. Q. Huo et al., *Nature*, 368 (1994) 317.
14. R. Ryoo, unpublished result.