J. Am. Chem. Soc. **2001,** *123,* 7723−7724

Polystyrene Bead-Assisted Self-Assembly of Microstructured Silica Hollow Spheres in Highly Alkaline Media

Guangshan Zhu,[†,‡] Shilun Qiu,*[,†] Osamu Terasaki,*[,‡] and
Yen Wei[†,§]

Department of Chemistry and State Key Laboratory of
Inorganic Synthesis & Preparative Chemistry
Jilin University, Changchun 130023, China
CREST & Physics Department
Tohoku University, Sendai 980-8578, Japan
Chemistry Department, Drexel University
Philadelphia, Pennsylvania 19104

Received March 25, 2001
Revised Manuscript Received June 22, 2001

The impetus to the active research on the preparation of silica with regular pores of the diameter in the range of 1−2 nm, particularly 1−1.5 nm, emanates from their potential application to shape-selective catalysis.[1,2] Zeolites UTD-1[3] and PCH[4] are two crystalline aluminosilicates with the largest pores of 0.9−1.0 nm. Many efforts to decrease the pore size of mesoporous silica below 2 nm have been made to prepare MCM-41 films,[5] small pore MCM-41,[6,7] SBA-8,[8] and SBA-1[9] with various surfactants as structure-directing agents. Recently, hexagonally ordered silica with X-ray diffraction (XRD) interplanar spacing as small as 2.69 nm has been synthesized using mixtures of short double-chain alkylammonium templates.[10] Despite limited success, the preparation of microstructured silica with pore diameters of 1−2 nm, especially 1−1.5 nm, is still difficult to achieve.

The mesoporous silicates can be synthesized in basic, acidic, and neutral media with various templates. As examples, M41S were synthesized with cationic surfactants under alkaline conditions at pH of 10−12.[11] The syntheses of SBA[12] silica mesostructures with di- or tri-block copolymers as templates were performed at pH $\leq$ 3. MSU mesoporous materials were prepared with nonionic surfactants under neutral condition.[13] Mesoporous silica could also be synthesized from sodium silicate and nonionic surfactants in the pH range of 3−10.5.[14] To our knowledge, there has been no report on the synthesis of mesostructured silica with surfactants at pH > 12. Under such a highly alkaline condition, the reaction mixtures remained a clear solution throughout the synthesis process.[1]

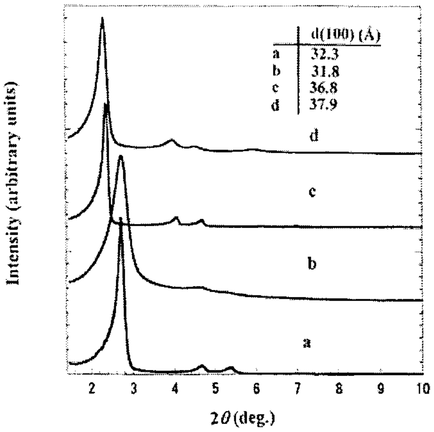

Figure 1. XRD patterns of (a) calcined C_{12}-MCM-41, (b) TEOS−C_{16}-MHS, (c) calcined C_{16}-MCM-41 and (d) TEOS−C_{16}MS.

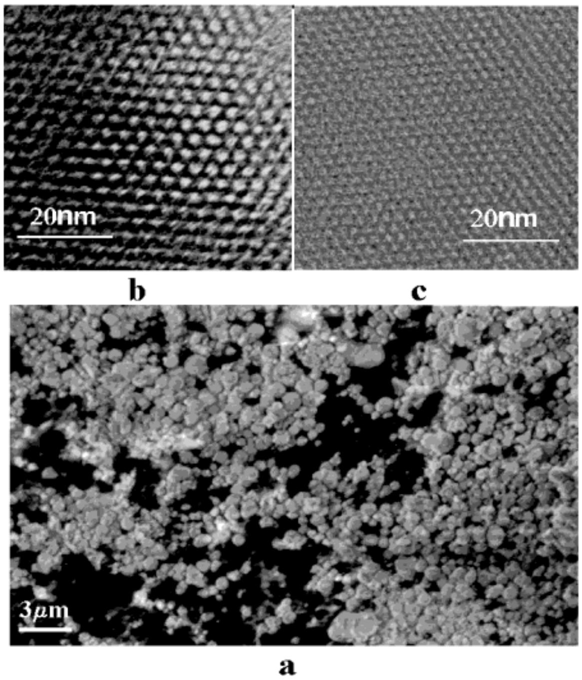

Figure 2. (a) SEM image of TEOS−C_{16}-MHS prepared using 2.2 μm colloidal PS beads as template and TEM images of (b) TEOS−C_{16}-MS and (c) TEOS−C_{16}-MHS.

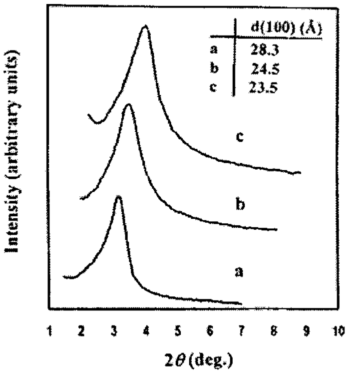

Figure 3. XRD patterns of (a) TMOS−C_{16}-MHS, (b) TEOS−C_{12}-MHS, and (c) TMOS−C_{12}-MHS.

This paper presents a novel approach, based on a colloidal-assisted self-assembly process,[15,16] to synthesize microstructured silica hollow spheres (MHS) with pore size in microporous region.

[†] Jilin University.
[‡] CREST, JST & Tohoku University.
[§] Drexel University.
(1) Corma, A. *Chem. Rev.* **1997**, *97*, 2373.
(2) Ying, J. Y.; Mehnert, C. P.; Wong, M. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 56.
(3) Braun, P. V.; Osenar, P.; Stupp, S. I. *Nature* **1996**, *380*, 325.
(4) Galarneau, A.; Barodawalla, A.; Pinnavaia, T. J. *Nature* **1995**, *374*, 529.
(5) Ogawa, M.; Kikuchi, T. *Adv. Mater.* **1998**, *10*, 1077.
(6) (a) Eswaramoorthy, M.; Neeraj, S.; Rao, C. N. R. *Microporous Mesoporous Mater.* **1999**, *28*, 205. (b) Park, M.; Komarneni, S.; Lim, W. T.; Heo, N. H.; Choi, J. *J. Mater. Res.* **2000**, *15*, 1437.
(7) Bagshaw, S. A.; Hayman, A. R. *Chem. Commun.* **2000**, 533.
(8) Zhao, D.; Huo, Q.; Feng, J.; Kim, J.; Han, Y.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 2668.
(9) Kim, J.; Ryoo, R. *Chem. Mater.* **1999**, *11*, 487.
(10) Ryoo, R.; Park, I.-S.; Jun, S.; Lee, C. W.; Kruk, M.; Jaroniec, M. *J. Am. Chem. Soc.* **2001**, *123*, 1650.
(11) (a) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Bech, J. S. *Nature* **1992**, *359*, 710. (b) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. T.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.
(12) (a) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548. (b) Zhao, D.; Feng, J.; Huo, Q.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024.
(13) Bagshaw, S. A.; Pronzet, E.; Pinnavaia, T. J. *Science* **1995**, *269*, 1242.
(14) Sierra, L.; Lopez, B.; Gil, H.; Guth, J. L. *Adv. Mater.* **1999**, *11*, 307.

10.1021/ja0158758 CCC: $20.00

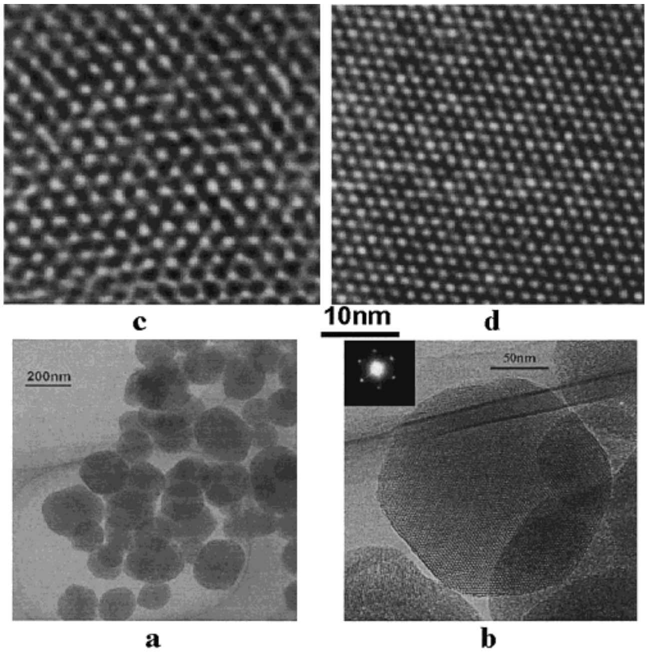

Figure 4. (a) TEM of TMOS−C_{12}-MHS and (b) an image at higher magnification with an electron diffraction pattern (insert). High-resolution electron microscopy (HREM) of (c) TMOS−C_{12}-MHS shown in (b) and of (d) nanocrystal zeolite LTL along the [001] direction.

In this work, negatively charged colloidal polystyrene (PS) beads were used to assist the self-assembly of inorganic silica and the surfactant micelles in the clear reaction solution at pH > 12. Positively charged surfactant micelles were absorbed on the surface of PS beads because of the electrostatic interaction. Silicate species and the surfactant micelles were self-assembled into 2-dimensional (2D) hexagonal arrangement on the surface of PS beads. Upon the calcination at high temperatures, both PS beads and the surfactant molecules were removed, leading to the formation of microstructured silica hollow spheres. The surfactant directed the silica into mesoporous 2-D hexagonal arrangement while the PS beads organized the material into hollow sphere. Upon thermal treatment, the pore of mesoporous silica hollow spheres falls into 1−2 nm region. The as-made mesostructured silica sphere containing the PS core is denoted as MS, whereas MHS is the microstructured hollow sphere after the removal of PS beads as well as the surfactants by calcination.

As a typical synthesis, 4 g of $C_{16}H_{33}N(CH_3)_3Br$ (C_{16}-CTAB), or similar molar amounts of C_{12}-CTAB, was first dissolved in 40 mL of water at 40 °C. The solution was cooled to room temperature, followed by adding 10 mL of 2 M NaOH and 3 g of PS sulfate-modified beads with average diameter of 0.1, 0.2, 0.47, 0.8, 1.1, or 2.2 μm (from Aldrich). Then, 5 g of tetraethyl orthosilicate (TEOS), or similar molar amounts of tetramethyl orthosilicate (TMOS), was added dropwise into the solution under stirring. The reaction mixture was stirred at 42 °C for 3 weeks. During that period, the growth of silica species on the surface of PS beads was observed under an optical microscope if larger PS beads were used as the templates. If no PS beads were added or the amount of NaOH was lowered to make the pH of the reaction mixture below 12, no product was obtained, or MCM-41 as aggregated particles precipitated. The resulting solids were collected repeatedly by centrifugation, followed by dispersing in distilled water, until the pH of the dispersion was near 7. This water washing was to remove extra alkali and surfactant adsorbed on the surface of the product. The product, MS, was obtained after drying at 50 °C for 4 h. MS samples were treated with tetrahydrofuran (THF)/acetone (1:2 v/v) for 24 h to remove extra polystyrene to ensure the accuracy of TG and DTA data. Both PS beads and the surfactant were completely removed by calcination at 600 °C for 7 h. The TG analysis shows that the THF/acetone treated TEOS−C_{16}-MS sample lost about 78% of its weight in the range of 230−650 °C, accompanied by two exothermic processes in DTA corresponding to the decomposition of PS beads in the spherical particles and of the surfactant molecules in the mesopores.

Figure 1 shows the XRD patterns of (a) calcined C_{12}-MCM-41, (b) TEOS−C_{16}-MHS, (c) calcined C_{16}-MCM-41 and (d) TEOS−C_{16}-MS. Compared with MCM-41s, C_{16}-MHS can be indexed on a hexagonal phase, its reflection peaks are broader. The [100] peak shifts to a higher 2θ angle after calcination. A peak shift after thermal treatment has been noted for MCM-41[11] and SBAs[12] before. Such a large shift occurring for MHS has only been observed for the mesoporous silica film.[5]

Figure 2a shows the SEM image of TEOS−C_{16}-MHS, indicating a spherical geometry with a narrow particle-size distribution. TEM images of both TEOS−C_{16}-MS (Figure 2b) and TEOS−C_{16}-MHS (Figure 2c) exhibit ordered hexagonal arrangement. Compared with TEOS−C_{16}-MS, pore diameters of TEOS−C_{16}-MHS at thin regions of the TEM images are reduced significantly, and this corresponds well to the large shift of the [100] peak in the XRD patterns after calcination.

Figure 3 shows that the d(100)-spacings of MHS can be varied from 31.8 to as small as 23.5 Å by changing silica source and chain length of the surfactant. A TEM image of TMOS−C_{12}-MHS at low magnification is given in Figure 4a. Spherical particles of 150−200 nm can be observed. The detailed texture is clearly shown, in the form of discrete bright spots, in Figure 4b. The electron diffraction pattern shown in the insert reveals that TMOS−C_{12}-MHS is also an ordered hexagonal phase. By comparing the pore size of TMOS−C_{12}-MHS (Figure 4c) with that of the 12-membered rings (MR) of crystalline zeolite LTL (Figure 4d), it appears that TMOS−C_{12}-MHS has a larger pore size than 12-MR (diameter: 7.1 Å). From the TEM image analysis with allowing for ca. 10% error, the pore size of TMOS−C_{12}-MHS is estimated to be ca. 11 Å, which indeed belongs to microporous region.

N_2 adsorption−desorption isotherm measurements show that MHS materials have large specific surface areas (690−1830 m^2/g) and pore volumes (0.36−1.1 cm^3/g). TMOS−C_{12}-MHS exhibits typical Langmuir isotherms (type I), characteristic of the micropores,[17] having a narrow BJH pore size distribution with a maximum at 1.1 nm, which is consistent with the TEM estimation. The N_2 sorption isotherms of TEOS−C_{12}-MHS, TMOS−C_{16}-MHS, and TEOS−C_{16}-MHS show distinct condensation steps at relative pressures (P/P_o) of 0.07, 0.12, and 0.17, respectively, similar to those of small pore MCM41.[6,7,18] The MHS materials are stable at 850 °C, but the intensity of XRD [100] peaks diminished on heating in boiling water for 10 h.

In conclusion, microstructured silica hollow spheres have been successfully prepared from the self-assembly of the surfactant and silica species on the surface of colloidal PS beads in highly alkaline media (pH > 12). By changing silica source or hydrocarbon chain length of the surfactants, the pore size of MHS can be obtained in the range of about 1 to 2 nm, which bridges the gap between micropores and mesopores.

Acknowledgment. We are grateful to the helpful discussions of Dr. Jihong Yu and Prof. Ruren Xu, and the financial support from the State Basic Research Project (G2000077507) and CREST, Japan Science and Technology Corporation (JST).

Supporting Information Available: Graphs (1) of N_2 adsorption−desorption isotherms and BJH pore size distribution curves; Table 1 of pore parameters obtained by various methods (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0158758

---

(15) Walsh, D.; Mann, S. *Nature* **1995**, *377*, 320.
(16) Caruso, F.; Caruso, R. A.; Mohwald, H. *Science* **1998**, *282*, 1111.
(17) Sing, K. S. W. *Pure Appl. Chem.* **1985**, *57*, 603.
(18) Sayari, A.; Yang, Y. *J. Phys. Chem. B* **2000**, *104*, 4835.