One-pot Synthesis of Bimodal Dispersed Mesoporous Silica Spheres

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The addition of polyethylene glycol during the reaction led to the synthesis of bimodal dispersed mesoporous silica spheres in a one pot system.

Mesoporous silica has received much attention in the past decade, and has been used for the catalyst, adsorbent and electronic devices because of its uniform mesopores and high specific surface area. The morphology of particles is usually dependent on the synthesis conditions, and the particles with a variety of shapes, for example, fibers,[1–3] sponge-like membranes,[4,5] rod-like powders,[6] films,[7] polyhedral particles,[8,9] and spheres[10–12] have already been synthesized. Non-porous mono-dispersed silica spheres in the micron-sized range were first synthesized by Stöber in 1968[13] using the water–alcohol–ammonia–tetra-alkoxysilane system. Later, this method was modified by the addition of a cationic surfactant and/or other organic solvents instead of alcohol, and the mesophases of silica spheres were synthesized.[14–17]

In our laboratory, we have developed a method for the synthesis of hexagonally ordered and well-defined mono-dispersed mesoporous silica spheres from tetramethoxysilane (TMOS) and *n*-alkyltrimethylammonium bromide.[18–20] Mesoporous mono-dispersed silica spheres in the submicron-sized range were obtained under very controlled and specific conditions.

During the reaction, the clear solution turned opaque suddenly, a white precipitate appearing. Usually, it is reasonable to consider that simultaneous generation, followed by propagation and subsequent termination of each and every particle leads to the formation of mono-dispersed particles. In order to elucidate the formation mechanism, *in situ* particle size development was measured.[20] Just before three minutes after the experiment had started, the particles grew immediately, reaching the final size within 15 s. On the other hand, the scattering intensity, which corresponds to the number of particles, increased gradually, becoming maximum 6 min. later. The results concerning the scattering intensity well matched those of visual examination. This suggested that the particles were generated successively (not at once), growing immediately to the same maximum size one after another for ca. 3 min.

Here, we describe the synthesis of bimodal dispersed mesoporous silica spheres in a one pot system by utilizing the above mentioned formation mechanism for mono-dispersed mesoporous silica spheres.

In a typical synthesis procedure,[20] 3.52 g of hexadecyltrimethylammonium chloride (C_{16}TMACl) and 2.28 g of a 1 M sodium hydroxide solution were dissolved in 800 g of a methanol/water (50/50 = w/w) solution. Then 1.32 g of TMOS was added to the solution with vigorous stirring at 298 K. After addition of TMOS, the clear solution turned opaque suddenly, due to a white precipitate. Just 4 min. after the experiment had started, 2 g of polyethylene glycol (Mw: 20,000) in 50 g of water was added. After 8 h of continuous stirring the mixture was aged overnight. The white powder was then filtered and washed with distilled water at least three times, and dried at 318 K for 72 h. The powder obtained was calcined in air at 823 K for 6 h to remove organic species.

The particle size of the mono-dispersed porous silica spheres was influenced by the synthesis temperature, methanol/water ratio, and silica source.[19] It was also affected by the addition of a polymer.[21] It is assumed that the addition of a polymer during the reaction brings to the formation of mono-dispersed spheres with different particle sizes if particles are generated successively. In order to confirm this assumption, polyethylene glycol (PEG) was added 4 min. after the experiment had started, at which time the particle size had become maximum but the scattering intensity was still increasing.[20] Since the scattering intensity at 4 min. was around half the maximum value, it is expected that half of the particles generated are of different sizes. Scanning electron micrographs of mono-dispersed mesoporous silica spheres with or without the addition of PEG are shown in Figure 1. The average particle size of the mono-dispersed mesoporous silica spheres without the addition of PEG (Figure 1a) was 0.65 μm (standard deviation: 0.023 μm). When

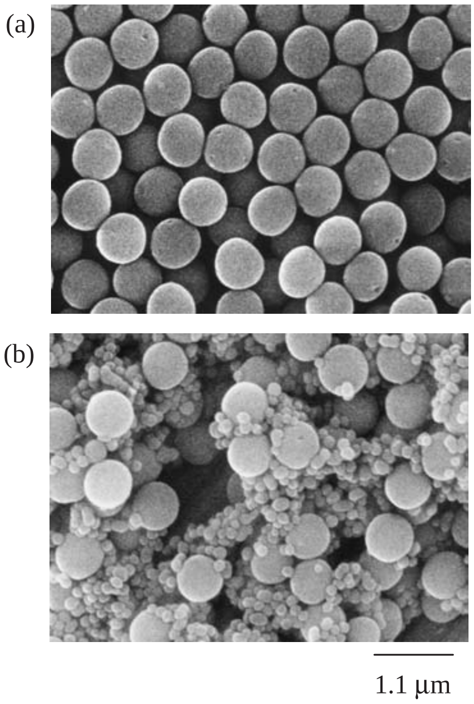

Figure 1. Scanning electron micrographs (SEMs) of samples synthesized without (a) and with (b) the addition of polyethylene glycol (PEG) (M.W. 20,000) after 4 min. The SEM pictures were obtained with a SIGMA-V (Akashi Seisakusho). The surface of the samples was coated with gold before the measurements.

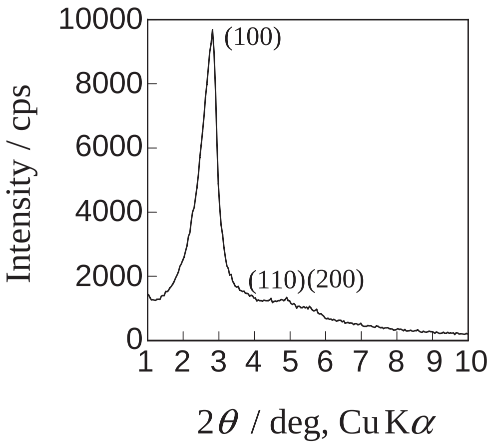

Figure 2. X-ray diffraction pattern of the sample obtained with the addition of PEG. X-ray measurement was performed with a Rigaku Rint-2200 X-ray diffractometer using Cu Kα radiation.

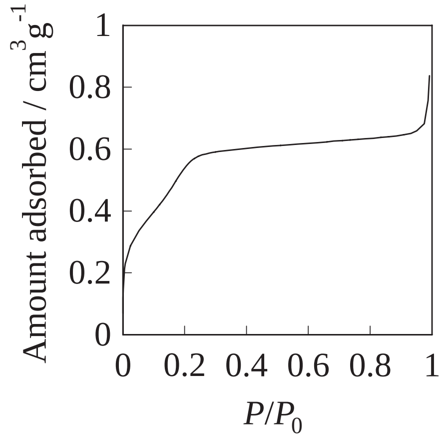

Figure 3. Nitrogen adsorption isotherm of the sample obtained with the addition of PEG. Desorption branch was identical to the adsorption's. A nitrogen adsorption isotherm was measured using a Quantachrome Autosorb-1 at 77 K. The sample was evacuated at 353 K under 10^{-3} mmHg before measurement.

PEG was added during the reaction, not only large particles (average particle size = 0.65 µm) but also small particles, of which the average size was 0.15 µm (standard deviation: 0.02 µm), were obtained (Figure 1b). Further, when PEG was added before the experiment had started (before TMOS addition), mono-dispersed mesoporous silica spheres with average particle size of 0.61 µm (standard deviation: 0.02 µm) were obtained. These results support the above mentioned assumption that particles are generated successively, growing immediately to the same maximum size one after another during the reaction. Particle size distribution was measured through the experiment by laser scattering measurement. After the addition of PEG, particles with smaller size appeared suddenly and the average size unchanged during the reaction. It is deduced that TMOS oligomers present in the reaction solution are forced to precipitate by the addition of PEG. The XRD pattern of the mono-dispersed mesoporous silica spheres with the addition of PEG is shown in Figure 2. The first low angle diffraction peak assigned to the (100) plane as well as the other peaks assigned to the diffraction of the (110) and (200) planes were observed, indicating that this material had a highly hexagonal symmetry. A nitrogen adsorption isotherm is shown in Figure 3. Although a steep increase on the high pressure side ($P/P_0 \geq 0.95$) was observed because of the co-aggregation of the small particles, this material had a high specific surface area (1200 m^2 g^{-1}) and a large pore volume (0.6 mL g^{-1}). This indicated that both large and small particles possessed mesopores inside.

In summary, we have developed the novel synthesis method for bimodal dispersed mesoporous silica spheres in a one-pot system. For densely packing, mixing smaller particles with larger particles is considered. However, it is difficult to disperse smaller particles because of aggregation. This finding would bring close packing of monodispersed mesoporous silica spheres with different average sizes.

References and Notes

1 P. Yang and D. Zhao, *Chem. Mater.*, **10**, 2033 (1998).
2 P. J. Bruinsma, A. Y. Kim, J. Liu, and S. Baskaran, *Chem. Mater.*, **9**, 2507 (1997).
3 H.-P. Lin, L.-Y. Yang, C.-Y. Mou, H.-K. Lee, and S.-B. Liu, *Stud. Surf. Sci. Catal.*, **129**, 7 (2000).
4 D. Zhao, P. Yang, B. F. Chmelka, and G. D. Stucky, *Chem. Mater.*, **11**, 1174 (1999).
5 D. Zhao, J. Sun, Q. Li, and G. D. Stucky, *Chem. Mater.*, **12**, 275 (2000).
6 S. Shio, A. Kimura, M. Yamaguchi, K. Yoshida, and K. Kuroda, *Chem. Commun.*, **1998**, 2461.
7 S. H. Tolbert, T. E. Schaffer, J. Feng, P. K. Hansma, and G. D. Stucky, *Chem. Mater.*, **9**, 1962 (1997).
8 J. M. Kim, S. K. Kim, and R. Ryoo, *Chem. Commun.*, **1998**, 259.
9 S. Guan, S. Inagaki, T. Ohsuna, and O. Terasaki, *J. Am. Chem. Soc.*, **122**, 5660 (2000).
10 L. Qi, J. Ma, H. Cheng, and Z. Zhao, *Chem. Mater.*, **10**, 1623 (1998).
11 H.-P. Lin, Y.-Ru. Cheng, and C.-Y. Mou, *Chem. Mater.*, **10**, 3772 (1998).
12 Q. Huo, J. Feng, F. Schuth, and G. D. Stucky, *Chem. Mater.*, **9**, 14 (1997).
13 W. Stöber and A. Fink, *J. Colloid Interface Sci.*, **26**, 62 (1968).
14 M. Grün, G. Büchel, D. Kumar, K. Schumacher, B. Bidlingmajer, and K. K. Unger, *Stud. Surf. Sci. Catal.*, **128**, 155 (2000).
15 M. Grün, I. Lauer, and K. K. Unger, *Adv. Mater.*, **9**, 254 (1997).
16 K. Schumacher, S. Renker, K. K. Unger, R. Ulrich, A. D. Chesne, H. W. Spiess, and U. Wiesner, *Stud. Surf. Sci. Catal.*, **129**, 1 (2000).
17 Q. Luo, L. Li, Z. Xue, and D. Zhao, *Stud. Surf. Sci. Catal.*, **129**, 37 (2000).
18 K. Yano and Y. Fukushima, *Bull. Chem. Soc. Jpn.*, **75**, 1977 (2002).
19 K. Yano and Y. Fukushima, *J. Mater. Chem.*, **13**, 2577 (2003).
20 K. Yano and Y. Fukushima, *J. Mater. Chem.*, **14**, 1579 (2004).
21 Our laboratories data.

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