Morphological control of ordered mesoporous silica: formation of fine and rod-like mesoporous powders from completely dissolved aqueous solutions of sodium metasilicate and cationic surfactants

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Fine and rod-like silica-based mesoporous powders with very short diameter and length have been obtained through (1) the complete dissolution of both sodium metasilicate and cationic surfactants and (2) subsequent rapid pH-adjustment for the formation of silica-surfactant mesophase products.

There has been much interest on ordered mesoporous silica molecular sieves because of their large pore sizes with narrow pore size distributions, thermal stability, *etc.*[1–4] It is now apparent that the morphological control as well as handling and texture of mesoporous silica is extremely important in industrial applications. Silica-based mesoporous molecular sieves can be applied to the adsorption and release of moisture and/or lipid components and can be utilized as an adsorbent of perfume, if they are available as minutely sized powders, which is important in the cosmetic industry.

There have been several reports[5–15] which describe methods to control the shape of powders. Rod-like powders were prepared by controlling the surfactant-water content, the concentration of aluminium species, and the condensation rate of silica in the reaction system[7–9] or by bacterial templating.[10] Schacht *et al.* controlled the shape of powders by changing the condensation rate of silica in the phase boundary of O/W emulsion particles and furthermore they obtained individual hexagonal mesoporous silica fibers.[11,12] Precise morphological control of ordered mesoporous powders, in particular, controlling the length of mesopores has not yet been achieved by the procedures described above. The present method is a simple combination of (1) the use of a completely clear solution of both sodium metasilicate and surfactants at low concentrations and (2) rapid pH adjustment (from 13 to 8.5) for the formation of silicate–surfactant mesophase products. Lin *et al.* reported the formation of rod-like mesoporous powders by using a clear surfactant solution and by adjusting the pH value of the final mixture to *ca.* 10 followed by heat treatment at 100 °C for 48 h.[7–9] However, the uniqueness of the present method is the utilization of a clear solution containing both silica species and surfactants and subsequent pH adjustment to 8.5, resulting in instant gel formation, without further heat treatment.

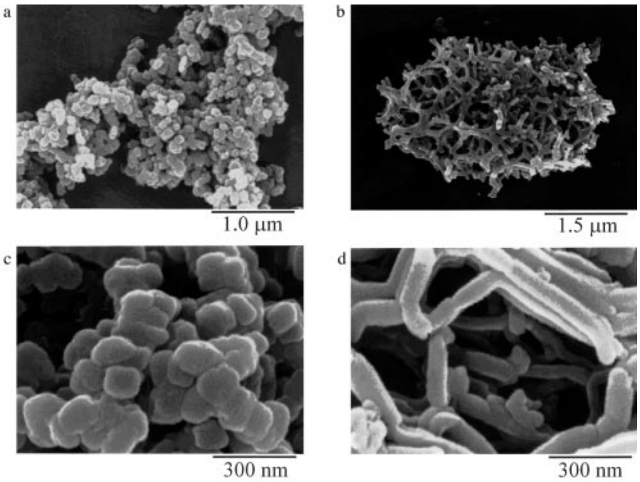

Fig. 1 Field emission scanning electron microscopic (FE-SEM) images of calcined mesoporous powders (Hitachi S-4500, acceleration voltage 15 kV). (a) Fine mesoporous powder (C_{18}-product) (magnification; ×20 000), (b) fine mesoporous powder (C_{18}-product) (magnification; ×100 000), (c) rod-like mesoporous powder (C_{22}-product) (magnification; ×30 000), (d) rod-like mesoporous powder (magnification; ×100 000).

Fine ordered mesoporous powders (C_{18}-product), which have a pore length of *ca.* 100 nm and a particle diameter of *ca.* 100 nm, were synthesized by using stearyltrimethylammonium chloride. Rod-shape ordered mesoporous powders (C_{22}-product), which have a pore length of *ca.* 300 nm and a diameter of *ca.* 50 nm, were also synthesized using behenyltrimethylammonium chloride.

Stearyltrimethylammonium chloride [$C_{18}H_{37}NMe_3Cl$] (STC) (Wako Chemical) and behenyltrimethylammonium chloride [$C_{22}H_{45}NMe_3Cl$] (BTC) (Toho Kagaku) were used in this study. Sodium metasilicate (0.5 mol, Nakarai Tesuku) and STC or BTC (0.1 mol) were dissolved in 1.0 dm^3 deionized water at 70 °C. White precipitates appeared when the pH value of the clear aqueous solution was adjusted to 8.5 by 2 M HCl within 3–5 min at 70 °C. The precipitates after the pH-adjustment were filtered at once, washed five times with water and once with acetone, and dried at room temperature for 12 h. To remove organic materials, the complexes were calcined at 700 °C in air for 5 h.

Powder XRD (JDX 3500 diffractometer) peaks of the C_{18} and the C_{22}-product show four peaks corresponding to (100), (110), (200) and (210) of a hexagonal array, being much broader than those reported for MCM-41 and FSM-16. The *d*-spacings (d_{100}) in the powder XRD patterns of the C_{18}-product before and after calcination were 4.1 and 3.8 nm, respectively. The d_{100} values of the C_{22}-product before and after calcination were 4.8 and 4.3 nm, respectively.

Typical morphologies of the calcined products are shown in Fig. 1. The FE-SEM image at high magnification of the calcined C_{18}-product [Fig. 1(b)] shows fine particles with rounded corners and *ca.* 100 nm diameter.

The morphology of the C_{22}-product is rod-like (*ca.* 50 nm in diameter and 300–500 nm in length) [Fig. 1(d)]. The powders have much shorter diameters and lengths than those of rod-like mesoporous powders reported previously,[7,12] and the rod-like powders formed a 3D-network structure. These results clearly show that the shape of powders can be controlled by a change in alkyl chain lengths of the surfactants.

TEM images (Fig. 2) of the calcined C_{18} and C_{22}-product also clarify the uniqueness of the powders. All the images of the C_{18}-product show ordered mesophases of *ca.* 100 nm in length [Fig. 2(a) and 2(b)]. Because such very short channels reduce the flow time of guest molecules in the mesoporous channels, the C_{18}-product should be an excellent reaction medium for organic substances. The TEM image of the C_{22}-product shows a rod-like shape which has a limited number of channels [Fig. 2(c)].

The N_2-adsorption isotherms (Micromeritics ASAP 2400) of the C_{18} and C_{22}-product showed typical behavior of ordered mesoporous silica. The C_{18} and C_{22}-product have BET specific surface areas of 1050 and 900 $m^2 g^{-1}$, and pore diameters of 3.0 and 3.5 nm (BJH method), respectively. In addition to the mesopores, the calcined C_{22}-product had a broader range of pore size distribution of 30–100 nm, arising from the 3D network structure of the rods. This finding affords us an additional larger range of pores indicating a short-range hierarchical mesoporous structure. The total pore volumes including mesopores and macropores of the calcined C_{18} and C_{22}-product were 1.3 and 2.8 ml g^{-1}, respectively. Although the specific surface area of the C_{22}-product was a little lower than that of the C_{18}-product, the total pore volume of the C_{22}-product was approximately twice that of the C_{18}-product, which is due to the network formation of rod-like mesoporous powders.

The a_0 values of hexagonal structure [$a_0 = 2d_{100}/\surd 3$] of the calcined C_{18}- and C_{22}-product were 4.4 and 5.0 nm, respectively. The wall thicknesses of these mesoporous materials are estimated from the a_0 values and the pore diameters. Although the calcined C_{22}-product has a different shape from the calcined C_{18}-product, the wall thicknesses for each showed very similar values (*ca.* 1.5 nm). This result suggests that the C_{18} and C_{22}-product were obtained *via* the same formation mechanism.

Because both sodium metasilicate and the surfactants are dissolved completely in water at 70 °C, the surfactants form micelles and silicate ions adhere on them. The shape of surfactant micelles is controlled by several complex factors including (1) the concentration of surfactants, (2) the alkyl chain lengths of surfactants, (3) the concentration of formed salts by adding HCl, and (4) the concentration of silicate species for which the ionic charge varies with pH. Since an increase of the aggregation number of micelles in salt–surfactant solution has been reported,[16] the possible increase of aggregation number (which induces the formation of rod-like micelles) is speculated to be due to silicate ions which can play the role of a salts and the shape of micelles will change from spherical to rod-like. Silicate ions show two condensation steps which depend on the pH of the solution. The first step is the condensation of silicate ions on micelles and the second is the condensation between polymerized silicate species adsorbed on each micelle.[17] The second step gives self-assembled materials with hexagonal structure. Rapid pH adjustment ($<$3–5 min) prevents further aggregation of the mesophase, since condensation of silicate ions occurs instantly and uniformly in the solution.

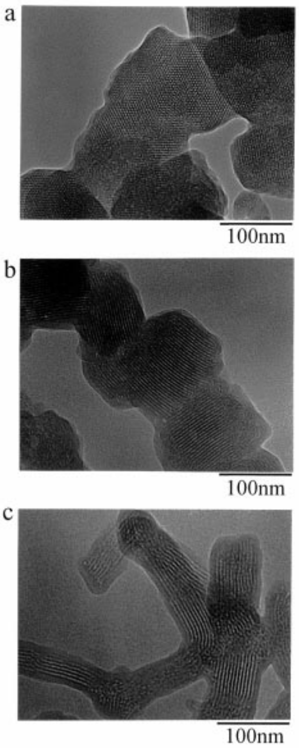

Fig. 2 Transmission electron microscopic (TEM) images of calcined mesoporous powders (Hitachi S-800, 200 kV). (a) Fine mesoporous powder (C_{18}-product) (magnification; ×200 000), (b) fine mesoporous powder (C_{18}-product) (magnification; ×200 000), (c) rod-like mesoporous powder (C_{22}-product) (magnification; ×200 000).

The shape of mesoporous powders is thought to be controlled by the competition between the rate of change in the shape of the surfactant assemblage (from rod-like to spherical by pH adjustment) and the condensation rate of silicate ions during the pH adjustment. If the condensation rate of silicate ions is faster than that of the change in the shape of the surfactant assemblage, the shape of the surfactant does not change markedly, therefore, the shape of the product should conform to the long rod-like shape of the micelles.

Because BTC, with longer alkyl chains, can lead to a longer assembled state relative to STC, the formation of a rod shape of the C_{22}-product is speculated to be due to the faster condensation rate of silicate ions than that of the structural change of the micelles. The same reaction pathways are expected for the system with STC, and the appearance of the C_{18}-product strongly suggests shorter assembled states of STC in aqueous solution.

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