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The Effect of the Counteranion on the Formation of Mesoporous Materials under the Acidic Synthesis Process

Shunai Che,[†] Sunghyun Lim,[†] Mizue Kaneda,[‡] Hideaki Yoshitake,[§] Osamu Terasaki,[‡] and Takashi Tatsumi*,[†]

Division of Materials Science & Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogayaku, Yokohama 240-8501, Japan; Department of Physics, Graduate School of Science, and Center for Interdisciplinary Research, Tohoku University, Sendai, 980-8578, Japan; and Graduate School of Environment and Information Science, Yokohama National University, 79-5 Tokiwadai, Hodogayaku, Yokohama 240-8501, Japan

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In the energetic self-organization process, it is thought that the packing of the organic surfactant and the charge density matching between the surfactant and the inorganic precursor are essential for the formation of the ordered mesostructure.[1] The surfactant packing depends on the molecular geometry of the surfactant species, such as the number of carbon atoms in the hydrophobic chain, the degree of chain saturation, and the size or charge of the polar headgroup.[1,2] In addition, it has been reported that the formation of mesostructures was affected by the solution conditions, including the surfactant concentration, pH, the presence of cosurfactant, and its concentration and temperature.[3−5]

However, although it has been shown that counteranions affect the formation of the mesophase structure[2,6] and the kinetics,[7] the effect has still remained poorly understood and elusive, largely because of the complicated nature of the multicomponent mixtures, which often requires elaborate control of the synthesis conditions and examination of the results.

Here, we have found that four types of well-ordered mesophases, 3D-hexagonal $P6_3/mmc$, cubic $Pm\bar{3}n$, 2D-hexagonal $p6mm$, and cubic $Ia\bar{3}d$, can be synthesized with the same surfactant cetyltriethylammonium bromide (CTEABr), in the presence of various acids. The 3D-hexagonal $P6_3/mmc$ mesophases have been rationally explained by EM observations, scanning electron microscope (SEM), and high-resolution transmission electron microscope (HRTEM). The cubic $Ia\bar{3}d$ phase has been first synthesized under acidic conditions.

Mesoporous materials were synthesized by using CTEABr as the surfactant and tetraethyl orthosilicate (TEOS) as a silica source in the presence of various acids: H_2SO_4, HCl, HBr, and HNO_3. Typically, the molar composition of the reaction mixture was CTEABr:TEOS:acid:H_2O 0.13:1:x:125, where x was 3.6, 7.2, 5.0, and 1.0 for H_2SO_4, HCl, HBr, and HNO_3, respectively. The mixture was allowed to react at 0 °C under static conditions for 1 day after homogenization. The resultant white precipitates were filtered and dried at 100 °C overnight. Surfactants were removed by calcination in air under static conditions at 600 °C for 6 h.

Figure 1a shows the X-ray diffraction (XRD) patterns of the sample synthesized in the presence of H_2SO_4. The three well-resolved peaks in the range of $2\theta = 1.5-3°$ and the additional three weak peaks in the range from 3.5° to 6° are characteristic of the 3D-hexagonal $P6_3/mmc$ mesophase[8] with the unit cell parameters $a = 49.5 \pm 0.4$ Å and $c = 81.0 \pm 0.4$ Å for the as-synthesized sample. This gives a c/a ratio of 1.64, which is close to the ideal c/a ratio of 1.633 for the hexagonal close-packed (hcp) structure of hard spheres. This sample demonstrates 20 distinct crystal faces with one six-fold axis (Figure 2a). The surfaces of the particles are indexed as shown in Figure 2b, which is consistent with $6/mmm$ point group symmetry.

The electron transmission micrograph of the $P6_3/mmc$ crystallite taken with the [100] incidence is presented in Figure 2c. Obviously, cages are stacked along the c-axis solely in the “ABAB...” sequence characteristic of the hcp structure. The corresponding electron diffractogram (inset) supports extinction conditions of the reflections, for the 3D-hexagonal symmetry.

The powder from synthesis gels with HCl shows an XRD pattern (Figure 1b) of the cubic $Pm\bar{3}n$ mesostructure.[9] The morphology, surface indices, and HRTEM images of this material have already been reported.[10] When the HBr acid was used in the synthesis, the material shows the 2D-hexagonal $p6mm$ system (Figure 1c). This sample has spiral or gyroid morphology (not shown), the typical morphologies of the 2D-hexagonal $p6mm$ mesophases synthesized under acidic conditions.[11] From the XRD patterns presented in Figure 1d, it can be seen that highly ordered mesoporous materials consistent with the cubic $Ia\bar{3}d$ symmetry are obtained with HNO_3. We cannot observe a crystal with morphology characteristic of the symmetry.

Figure 3 shows the diagrams of the products for the silica−surfactant mesophases synthesized in the presence of various acids at 0 °C for 1 day. In each of the “triangles”, 69 experiments were performed. The 3D-hexagonal $P6_3/mmc$ mesostructures are obtained with H_2SO_4 or HCl as acid; H_2SO_4 gives this mesophase in the wider composition range than HCl. The cubic $Pm\bar{3}n$ mesostructures are obtained with three acids of H_2SO_4, HCl, and HBr; HCl gives this mesophase in the widest composition range. The 2D-hexagonal $p6mm$ mesostructure is synthesized in a wide range of reactant compositions when HBr or HNO_3 is used. Only HNO_3 produces the cubic $Ia\bar{3}d$ mesophase among the tested acids. It is noteworthy that the diagrams are dependent on the H_2O/TEOS molar ratio and temperature as well as the synthesis time. For example, the 3D-hexagonal $P6_3/mmc$ mesostructures appeared in the wider composition range with a lower H_2O/TEOS molar ratio and at higher temperature in the HCl synthesis system; only the 2D-hexagonal $p6mm$ mesophase appeared in the phase diagram with a longer synthesis time of 4 days in the presence of HNO_3.

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[*] To whom correspondence should be addressed. Telephone: (81)45-339-3943. Fax: (81)45-339-3943. E-mail: ttatsumi@ynu.ac.jp.

[†] Division of Materials Science & Chemical Engineering, Faculty of Engineering, Yokohama National University.

[‡] Tohoku University.

[§] Graduate School of Environment and Information Science, Yokohama National University.

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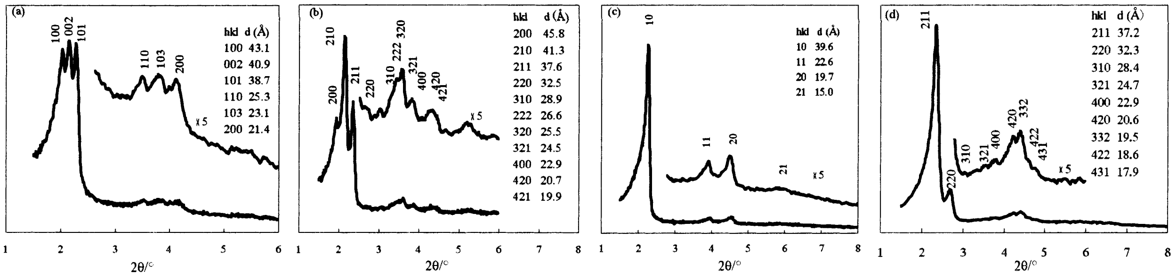

Figure 1. XRD patterns of as-synthesized materials synthesized with various acids at 0 °C for 1 day: (a) H_2SO_4, (b) HCl, (c) HBr, and (d) HNO_3.

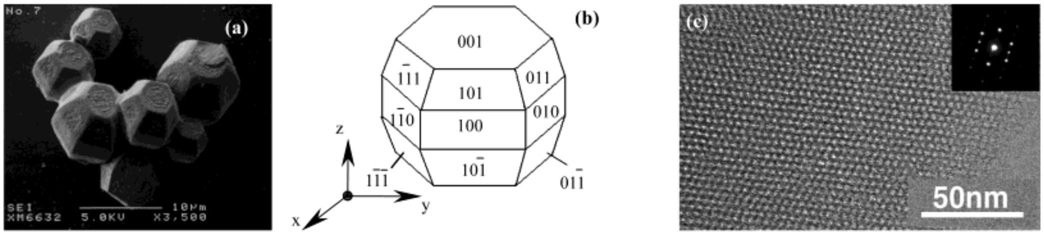

Figure 2. SEM images (a), surface index (b), and HREM image (c) of the samples synthesized with H_2SO_4.

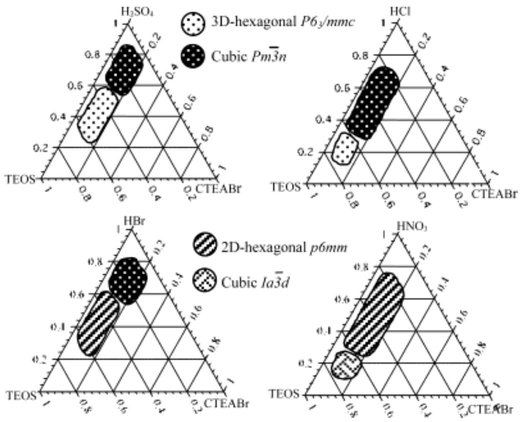

Figure 3. Synthesis-space diagram of mesophase structures established by XRD measurements. Each mixture had an H_2O/Si molar ratio of 125. The mesoporous materials were synthesized under static condition at 0 °C for 1 d.

can be explained in terms of the adsorption strength on the headgroups of the surfactant micelle. It is useful to introduce the surfactant packing parameter g; $g = v/al$, where v is the chain volume, a is the hydrophobic/hydrophilic interfacial area, and l is the chain length. The X^- ions are more or less hydrated in the surfactant solution. Less strongly hydrated ions have, in general, smaller ionic radii and bind more closely and strongly on the headgroup of the surfactant. The small anions contribute to the partial reduction in the electrostatic repulsion between the charged surfactant headgroups and the decrease in the effective area of surfactant a, therefore resulting in a significant increase in the g value. The aggregation number or the ionic radii is reported to decrease in the following order: $^1/_2SO_4^{2-} > Cl^- > Br^- > NO_3^-$.[12] Thus, it is reasonable that H_2SO_4 leads to facile formation of the 3D-hexagonal $P6_3/mmc$ mesophase with a smaller g parameter and that HNO_3 favors the formation of the $Ia\bar{3}d$ mesophase with a larger g parameter.

In Figure 3, it can be seen that the larger and smaller g parameter mesophases appear in the upper and lower parts of the diagram, respectively, in the presence of H_2SO_4 or HCl and vice versa in the presence of HBr or HNO_3. As mentioned above, the mesostructure is controlled not only by the packing of the organic surfactant but also by the charge density matching between the surfactant and the silicate. It is well known that higher counteranion concentrations[13] favor the formation of larger g parameter mesophases and the higher acidity facilitates the condensation of silicate. The composition of the lower parts should favor the formation of smaller g parameter mesophases considering the surfactant packing. However, in the presence of HBr and HNO_3, the counteranions are so small that the lamellar phases were initially formed even under the lower Br^- or NO_3^- concentration, which suggests that the surfactant packing is not profoundly affected by the concentration of counteranion; the mesophase formation is controlled predominantly by the rate of condensation, leading to results different from those obtained for H_2SO_4 and HCl. The details will be reported elsewhere.

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