Synthesis and Morphology Control of SBA-1 Mesoporous Silica with Surfactant of Cetyltrimethylammonium Bromide (CTMABr)

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The 3d-cubic $Pm\bar{3}n$ SBA-1 mesoporous silica synthesized under highly acidic conditions using cetyltrimethylammonium bromide exhibited a distinct octadecahedron crystal shape in contrast to the material synthesized in the presence of cetyltriethylammonium bromide under less acidic conditions, which showed a highly isotropic morphology with fifty-four or more crystal faces.

The 3d-cubic $Pm\bar{3}n$ SBA-1 phase possesses a three-dimensional channel system with a uniformly sized cage type pore structure with open windows.[1] It has been reported that SBA-1 can be synthesized from a combination of surfactant, halogen anion and silica framework ($S^+X^-I^+$), and that the large head-group surfactants such as alkyltriethylammonium $C_nH_{2n+1}(C_2H_5)_3N^+$ ($n = 12, 14, 16, 18$) favor this cubic $Pm\bar{3}n$ phase.[2] The materials with three-dimentional channel network are much more desirable than MCM-41 or SBA-3 with mono-dimentional channel system because of their promising applicability to adsorbents and catalysts. Up to now, however, few researches have been reported on SBA-1, compared to other mesoporous materials such as MCM-41, FSM-16 or SBA-3. One of the reasons might be that the large head-group surfactants are not commercially available.

Kim and Ryoo[3] have briefly mentioned that the 3d-cubic $Pm\bar{3}n$ SBA-1 mesophase can be synthesized under a highly acidic condition using cetyltrimethylammonium chloride (CTMACl) as a surfactant.

Here, we present the procedure for synthesizing 3d-cubic $Pm\bar{3}n$ silica using CTMABr, the surfactant for SBA-3 and MCM-41, as a template, tetraethyl orthosilicate (TEOS) as a silica source, and hydrochloric acid. The mesostructure formation greatly depended on the concentration of acid. The 3d-cubic $Pm\bar{3}n$ SBA-1 mesoporous silica was formed at an extremely high HCl concentration, and the resultant material exhibited not only an excellent structural order but also the distinct crystalline morphology of octadecahedron.

Synthesis of the samples was performed as follows: The surfactant CTMABr, distilled water, and hydrochloric acid were mixed to obtain a homogeneous solution, which was allowed to react at a desired temperature prior to the addition of the silica source, TEOS. After the addition of TEOS, the mixture was stirred for 10 min and then the reaction was continued at 0 °C under a static condition for a desired period. The resultant white precipitates were filtered (without washing) and dried at 100 °C overnight. The as-synthesized samples were calcined in air under a static condition at 600 °C for 4 h. The molar composition of the reaction mixture was 0.20 : 1 : x : 125 CTMABr : TEOS : HCl : H_2O, where x was varied in the range of 32–0.375.

Figure 1 shows the powder X-ray diffraction (XRD) patterns of as-synthesized mesoporous silica prepared with H_2O/HCl molar ratios of 4.7 and 12.5 for 80 min and 120 min, respectively. The material prepared from the synthetic gel with the H_2O/HCl molar ratio of 4.7 ($x = 27$) showed an XRD pattern with three well-resolved sharp diffraction peaks in the region of $2\theta = 1.5$–3.0 ° (Figure 1a), which are indexed to the 200, 210, and 211 reflections based on the cubic structure system.[1–3] Additional weak peaks in the range of 3.5–6 ° corresponding to the 220, 310, 222, 320, 400, 420 and 421 reflections indicated that the as-synthesized SBA-1 had a high degree of cubic mesoscopic organization.[1,2] With decreasing H_2O/HCl molar ratio to less 4.7 ($x > 27$) the regularity of SBA-1 structure decreased. The materials synthesized in the H_2O/HCl molar ratio of 5.6 ($x = 22$) proved to be a mixed phase of SBA-1 and SBA-3, and in the range of 6.25 to 300 the 2d-hexagonal *p6mm* SBA-3 mesostructure was formed.

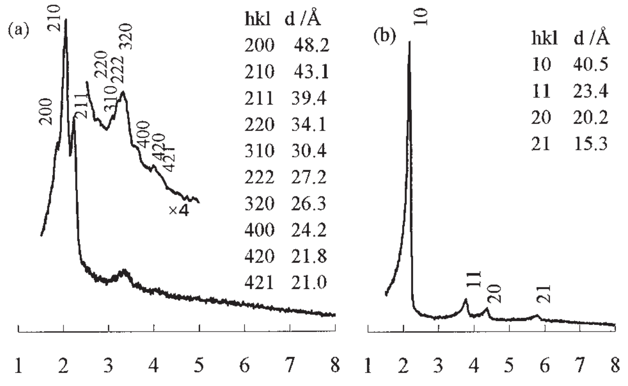

Figure 1. XRD patterns of as-synthesized SBA-1(a) and SBA-3(b) prepared with different H_2O/HCl molar ratios at 0 °C. Synthesis molar composition : 1 TEOS : 0.2 CTMABr : x HCl : 150 H_3O. H_3O/HCl = (a) 4.7 (80 min), (b) 12.5 (120 min).

The sample synthesized with the H_2O/HCl molar ratio of 12.5 (Figure 1b) showed the four peaks 10, 11, 20, and 21 attributed to the 2d-hexagonal *p6mm* structure system. The samples obtained from the H_2O/HCl molar ratio of 6.25–12.5 showed the highest peak intensity and the narrowest widths, suggesting that they had higher crystallinity than the others. With further increasing the H_2O/HCl molar ratio up to 400 the XRD peak intensity decreased and the lines merged to a single broad peak.

Both SBA-1 and SBA-3 mesostrctures were maintained after

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calcination with decreasing unit cell parameters from 96.3 Å to 84.7 Å and from 46.8 Å to 37.8 Å, respectively. All of the samples having high periodicity of the cubic and hexagonal structures showed a type IV N_2 adsorption-desorption isotherm.

Scanning electron microscope (SEM) images (Figure 2a) revealed that the SBA-1 sample synthesized with the H_2O/HCl molar ratio of 4.7 was composed of the particles that are uniform in shape and with well-defined external morphologies. (Figure 2a) The SBA-1 sample consisted of very clear octadecahedron crystal shape, similar to the recently reported SBA-1 material synthesized in the presence of cetyltriethylammonium bromide (CTEABr),[1a] which was composed of 6 squares {100}, and 12 hexagons {101} (inset of Figure 2a). The samples synthesized in the H_2O/HCl ratio range of 6.25–300 showed the spiral and gyroid topologies (not shown), which is a typical morphology of SBA-3.[4]

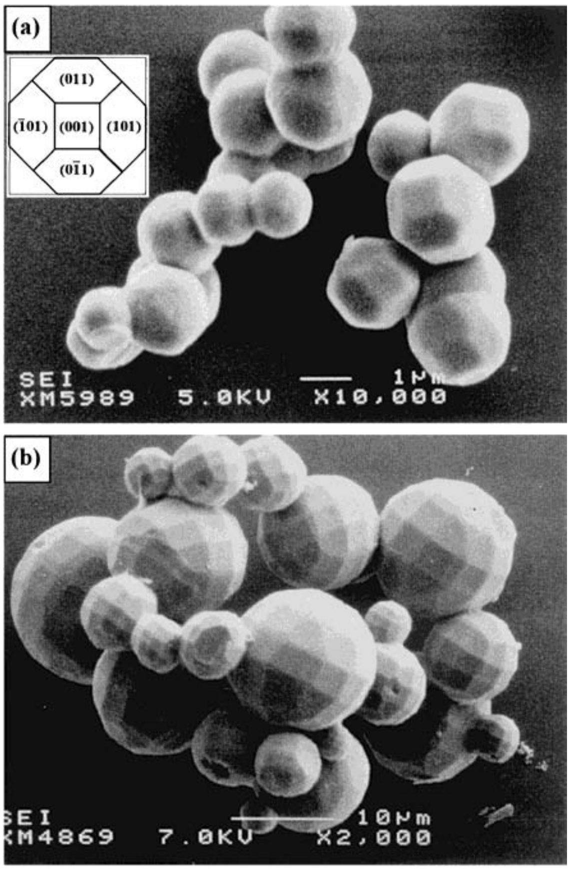

Figure 2. SEM images of SBA-1 synthesized with CTMABr (a) and with CTEABr (b) and the mutual orientation diagrams (inset of (a)) of the SBA-1 particles having decaoctahedron crystal shape.

The effect of acidity on the formation of different mesphases can be explained by the surface curvature of the micelle. The role of highly charged cationic polysilicate is an important structure directing factor, which will control the surfactant geometry through charge density matching and multidentate bonding. Silica condensation causes the positive charge density of the silicate network to decrease. Since the structure of SBA-1 corresponds to the largest surface curvature micelle of all lyotropic liquid crystals, the micellar surface has the lowest charge density. It is well known that the concentration of $[H^+]$ strongly influences the condensation reaction of silicate species. The higher the acidity the faster and the more silicate condensation proceeds so that the lower charge density of silica wall will be formed. Thus, under highly acidic synthesis conditions the organic surfactants pack to form a high surface curvature to adjust the effective headgroup area maintaining charge matching in the interface, leading to the formation of the SBA-1 mesophase. It is considered that the relatively high charge density of the silica framework resulting from insufficient silica condensation under less acidic conditions prefers to construct the SBA-3 mesophase of low surface curvature.

We have recently reported that in the presence of CTEABr the SBA-1 phase is formed via transformation of the initially formed SBA-3 mesostructure.[5] The high sensitivity of the formed mesostructure to the H_2O/HCl ratio and simultaneous formation of SBA-1 and SBA-3 phases at $H_2O/HCl = 5.6$ suggest that similar transformation is operative; however, we could not observe similar phase transformation in the CTMABr system.

In the presence of CTEABr, SBA-1 mesostructure was obtained under weakly acidic conditions, starting from a molar ratio of 0.13 : 1 : 2.5 : 125 CTEABr : TEOS : HCl : H_2O.[6] This SBA-1 sample exhibited a highly isotropic morphology with fifty-four, seventy-four or more crystal faces (Figure 2b).[6] It is considered that the crystals having a great number of crystal faces are formed through highly isotropic crystal growth and that those having fewer crystal faces reflect anisotropic crystal growth, which are due to the difference in growth rate depending on the crystal faces. Synthesis under highly acidic conditions would render crystallization more kinetically controlled, leading to more anisotropic growth as shown in Figure 2a. At lower acidity, on the other hand, the crystallization is slowed and would proceed under more thermodynamically controlled, near equilibrium conditions, leading to more isotropic growth.

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