Synthesis of Aluminum-Based Surfactant Mesophases Morphologically Controlled through a Layer to Hexagonal Transition

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The morphologically controlled synthesis of aluminum-based surfactant mesophases by the homogeneous precipitation method using urea is demonstrated, together with a model for the templating mechanism pathway. Dodecyl sulfate surfactant initially forms a layered mesophase with an interlayer spacing of 3.5 nm in which the surfactant molecules are arranged as a bilayer between the linked sheets of aluminum oxyhydroxide groups. The aluminate sheets consist mostly of octahedral Al but contain some fraction of tetrahedral Al dependent on urea concentration. On further hydrolysis of urea, the layered mesophase is transformed into a hexagonal form through the interlayer condensation and cross-linking of the Al−OH groups in any adjacent aluminate sheets. The structural transition accompanies the rearrangement of the bilayered surfactant molecules into a rodlike assembly, followed by the additional growth into enlarged particles. The hexagonal mesophase resulting from the lamellae containing comparatively large amounts of tetrahedral Al forms a ringed or curved wormlike morphology, while the phase grown from octahedral Al−enriched forms appears in versatile patterns including spherical, funneled, and tubular particles. Such morphologically versatile characteristics of the hexagonal mesophases reflect those of their precursors produced by the folding of aluminum-based flexible sheets of aluminum oxyhydroxide octahedral groups mixed with their tetrahedral ones at a fraction dependent on urea concentration.

Introduction

The discovery of MCM-41 and FSM-16 mesoporous silica materials has opened a route to mesostructured materials chemistry useful for the design of valuable inorganic solids as catalysts, molecular sieves, and host matrices.[1−3] These two mesoporous materials were synthesized by calcining their mesostructured precursors formed in the presence of a cationic surfactant. Some perturbed studies, however, have been reported on the templating mechanism pathway in the MCM-41 system. Early reports suggested that the hexagonal precursor is formed via an ion-pair complex of silicate oligomers and surfactant molecules[4] or a collection of individually silicated surfactant rods.[5] In contrast, the transition from a lamellar to the hexagonal phase was proposed on the basis of X-ray and electron microscopic observations for as-grown or calcined silica mesophases.[5,6]

For the morphological properties of mesostructured silicas, some studies revealed the growth of mesoporous silica thin films on mica substrates[7] as well as the formation of hexagonal prisms[1] and, less predominantly, curved wormlike[8] or tubular particles[9] in bulk solution. No corroborative evidence, however, has been presented to explain how closely such complex morphologies are related to the surfactant templating mechanism pathway.

Recently we reported the synthesis of an aluminum-based dodecyl sulfate mesophase with a hexagonal structure by a similar approach coupled with the homogeneous precipitation method using urea, along with the formation of a deorganized but less ordered phase upon calcination.[10] This is the first example of aluminum-based surfactant mesophases having a long-range hexagonal arrangement of surfactant-filled channels. The hexagonal framework in this system is structurally similar to that in the MCM-41 system. Hence further studies on the crystal growth patterns and morphological properties of aluminum-based mesostructures would also contribute to the elucidation of those for the MCM-41 system.

Here, we demonstrate the morphologically controlled synthesis of aluminum-based surfactant mesophases by the homogeneous precipitation method using urea, as well as a model for the templating mechanism pathway. The mesostructured materials initially appear in a layer structure and grow into a hexagonal phase in versatile morphologies such as curved wormlike, funneled, and tubular particles. The morphologically characteristic patterns reflect primarily those of their precursors which are formed by the folding of the flexible sheets of aluminum oxyhydroxide octahedral units mixed with their tetrahedral ones at a fraction dependent on urea concentration.

Experimental Section

The aluminum oxide/anionic surfactant mesophases were prepared as in a previous report[10] but with varying urea concentrations. Aluminum nitrate, sodium dodecyl sulfate (SDS), urea, and water were mixed at varying molar ratios of 1:2:x:60 (x = 10, 20, 30, and 40) and stirred at 40 °C for 1 h. The transparent mixed solution obtained was heated at 70 or 80 °C and then kept at that temperature until the pH of the reaction mixture increased from its initial value of 3.2−3.6 due to

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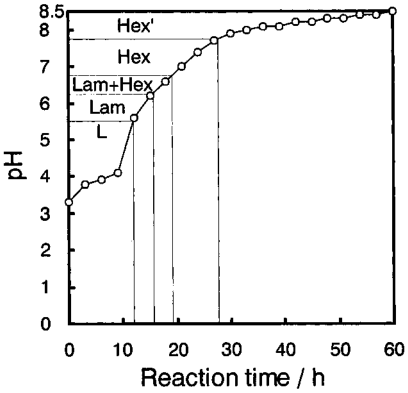

Figure 1. Variation of pH with time for the reaction mixture at 70 °C. The phases separated at different pHs are also indicated. Key: L, liquid; Lam, lamellar phase; Hex, hexagonal phase; Hex′, disordered hexagonal phase.

the enhanced hydrolysis of urea. Upon reaching a predetermined pH, the resulting mixture was immediately cooled to room temperature. After centrifugation, the resulting solid was washed with water a few times and then dried at 60 °C in air. XRD patterns were obtained on Simadzu XD-3AS and XD-D1 diffractometers with Cu Kα radiation. SEM observations were made on a Hitachi H-4100 instrument. NMR spectra were measured on a Bruker AC-250 spectrometer with an MAS frequency of 3 kHz.

Results and Discussion

The pH of the reaction mixture at 70 °C increased in two steps with time as urea was hydrolyzed into ammonia, as exemplified in Figure 1. The first inflection at pH ~4.0 is probably due to the formation of polynuclear aluminum oxy-hydroxide clusters in solution. Precipitation at 70 °C was initiated by a further increase in pH up to a critical value or 5.5−8.5 dependent on the [urea]/[Al] ratio (=x). Figure 2A summarizes the XRD patterns for the resulting solids separated at pH 6.0−8.5 at 70 °C when $x = 20$. At the initial stage of precipitation, a layered mesophase with an interlayer spacing of 3.5 nm appeared, as indicated by the 100 and 200 reflections located at $2\theta = 1{-}5°$ for the pH 6.0 product (Figure 2A(a)). In the pH range 6.5−7.0, the layered phase indicated a tendency to coexist with a second phase, as shown in Figure 2A(b). With further increase in pH with time up to 7.0, the layered phase disappeared, while only a second mesophase was obtained in much higher yield. The second phase exhibited XRD patterns characterized by their major peaks attributable to the 100, 110, and 200 reflections based on a hexagonal unit cell with $a =$ 4.3 nm ($2d_{100}/3^{1/2}$) (Figure 2A(c)), as previously described.[10] It should be noted that the hexagonal mesophase was produced by the structural conversion of the initial layered mesophase with an accompanying additional crystal growth. At pH 8.0 or above, the hexagonal phase decreased in crystallinity (Figure 2A(d)), indicating that the hexagonal mesophase undergoes decrystallization in basic solution. The reaction diagram at 70 °C thus obtained is shown in Figure 1. The incorporation of dodecyl sulfate species in either the aluminum-based layered or hexagonal mesophase was spectroscopically confirmed by their infrared spectra indicating strong bands at 1244 and 1207 cm^{-1} concerned with the $-OSO_3-$ groups along with the C−H stretching bands at 2924 and 2854 cm^{-1} due to the $-CH_2-$ groups.

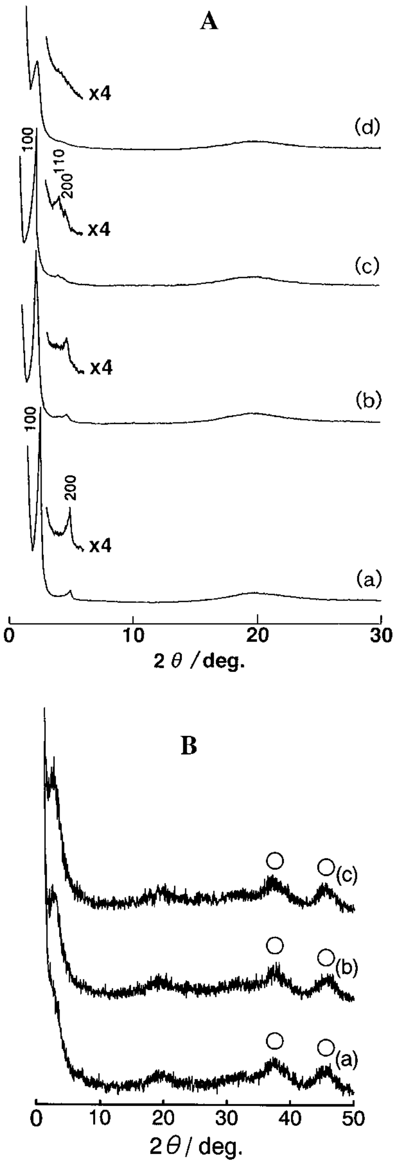

Figure 2. Powder X-ray diffraction (XRD) patterns of (A) as-grown samples of aluminum-based dodecyl sulfate mesophases separated at different pHs ($x = 20$) and (B) precalcined samples of its hexagonal mesophases separated at pH 7.0 ($x = 30$). Panel A: lamellar phase (pH 6.0) (a), mixed phases (pH 6.5) (b), hexagonal phase (pH 7.0) (c), and hexagonal but poorly crystalline phase aged at pH 8.5 for 108 h (d). Panel B: precalcined at 600 °C for 10 h after heating at a rate of 5 °C·min^{-1} (a) and for 3 h after heating up at a rate of 1 °C·min^{-1} (b, c). See text for (c) in panel B. The phase of γ-alumina is designated by open circles.

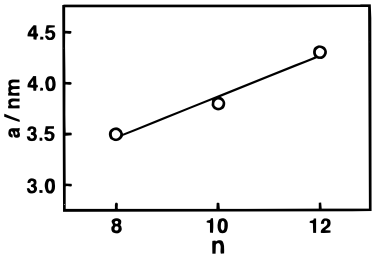

Figure 3. Plot of unit cell parameter a against carbon number of surfactant main chain for the hexagonal mesophases obtained at 80 °C.

The precipitation at 80 °C also yielded a similar layered mesophase at pH 5.5 when $x = 10$ and at the pH 6.0 when $x =$ 20, 30, and 40. With further increase in pH up to 7.0, the layered mesophases formed at different [urea]/[Al] ratios were all transformed into a hexagonal phase. A similar reaction at 80 °C in the $x = 30$ system using sodium decyl or octyl sulfate in place of SDS gave a hexagonal phase at pH 7.0. The plots of cell parameter a in nanometers against the number of CH_2 units (n) in the surfactant main chain gave a straight line with

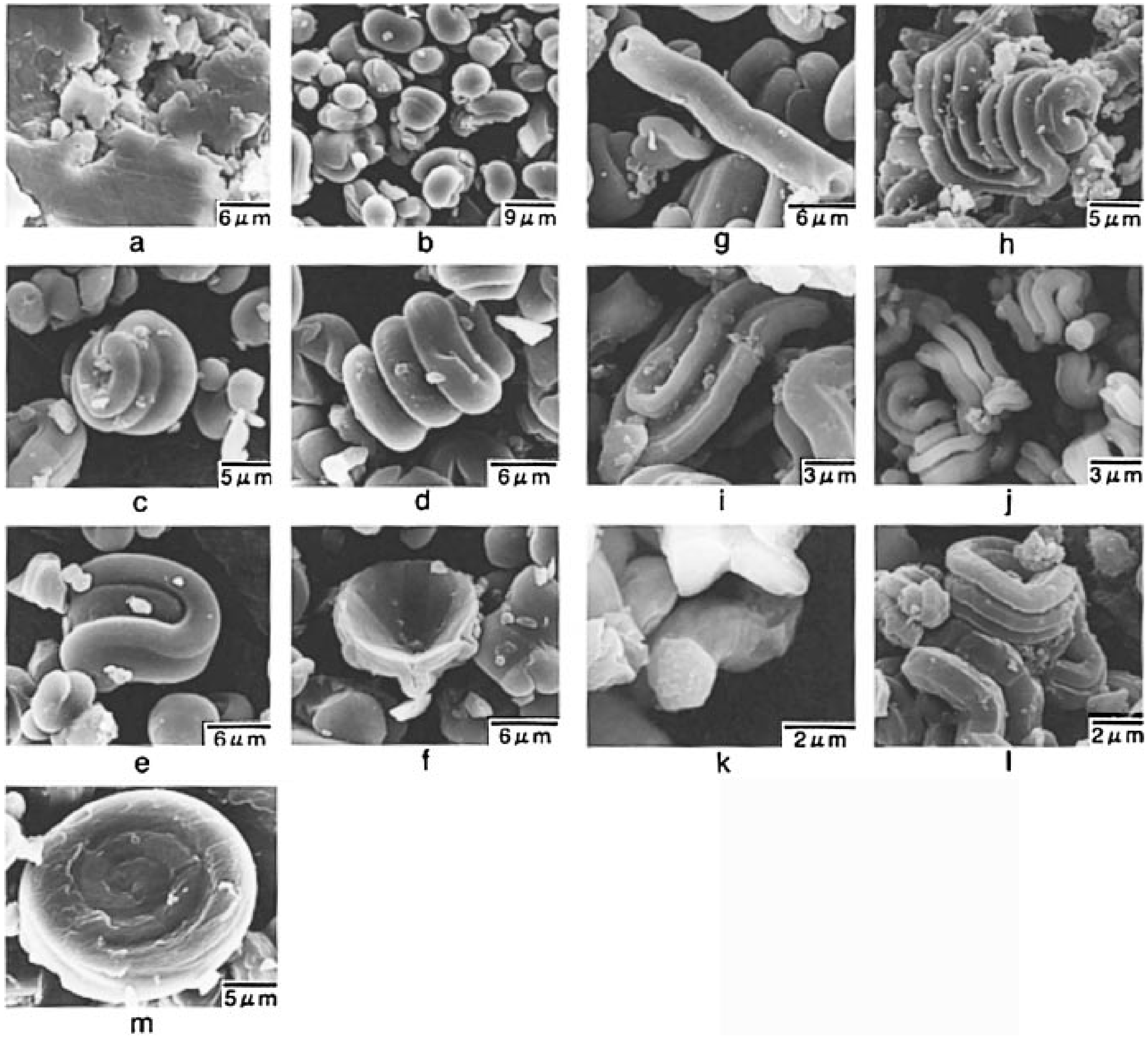

Figure 4. Scanning electron micrographs of aluminum-based lamellar and hexagonal mesophases with morphologically different shapes separated at pH 6.0 (a), 7.0 (b−k), and 7.5 (l) at different urea addition levels: (a) lamellar ($x = 30$), (b) spherical or ellipsoidal ($x = 10$), (c) snailed ($x = 10$), (d) multiringed ($x = 10$), (e) horseshoe shaped with a flat stage ($x = 10$), (f) funneled ($x = 10$), (g) tubular ($x = 10$), (h) winding rod-shaped ($x = 20$), (i) ringed rods appearing at the critical stage of structural transition from layer to hexagonal ($x = 20$), (j) winding rod-shaped ($x = 30$), (k) hexagonal-shaped transverse surface and edges ($x = 30$), (l) winding and ringed rod-shaped ($x = 40$), and (m) spiral (see text).

a slope of ~0.2 nm/CH_2, in close agreement with twice the increase of 0.127 nm/CH_2 for an extended alkyl chain (Figure 3). It is therefore most likely that the hexagonal channels in the aluminum-based mesophases are occupied by rodlike assemblies as observed in the MCM-41 silica system.[1,2] Another marked effect of surfactant chain length on precipitation was that the minimum pH to give a layered mesophase decreased from 6.8 for $n = 8$ down to 5.5 for $n = 12$ via 6.7 for $n = 10$. This finding indicates that the longer the alkyl chain of the surfactant molecule, the more easily the surfactant micelles aggregate together with aluminum species to form a mesophase, due to an increase of their aggregation energy with an increase in the surfactant chain length.

Scanning electron microscopic (SEM) images were taken on the dodecyl sulfate mesostructured solids obtained by the reaction at 80 °C. The initially precipitated mesophases were characterized by the appearance of macroscopically lamellar particles (Figure 4a), in harmony with those expected from their crystallographic structure. In contrast, the morphological properties of the hexagonal mesophases showed a marked dependence on the urea concentration x. When x was as low as 10, the resulting hexagonal phase appeared mostly in spherical or ellipsoidal particles and partly in snailed, multiringed, funneled, or tubular particles (Figure 4b−g). When $x = 20$, the hexagonal phase crystallized mainly in single or multiringed and winding hexagonal rods with a length as long as more than several micrometers (Figure 4h). The image shown in Figure 4i, in connection with the X-ray observations on the same sample, clearly reveals the critical stage at which the lamellar sheet is folded on the micron scale to grow into morphologically ringed and crystallographically hexagonal rod crystals. At higher addition levels of $x = 30$ and 40, well-defined winding or curved wormlike rods occurred and some of the rods sharply exhibited their hexagonal-shaped transverse surface and edges, as shown in Figure 4j−l. This distinct crystal habit definitely reflects a highly ordered hexagonal arrangement of aluminum oxide and surfactant species, in keeping with the sharp XRD peaks observed for the same sample. The spiral growth of the

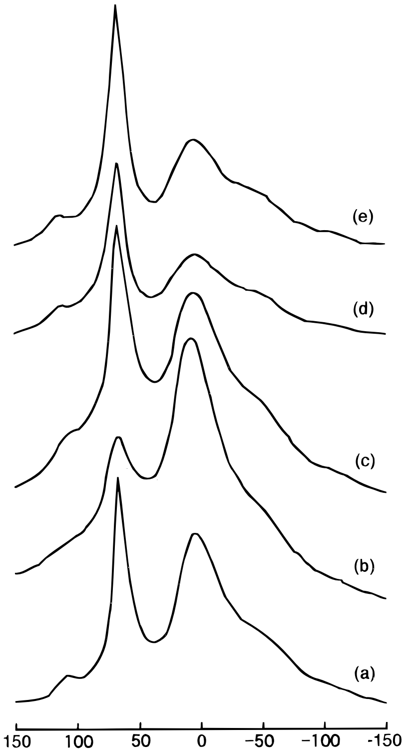

Figure 5. ^{27}Al MAS NMR spectra of aluminum-based dodecyl sulfate mesophases separated at pH 6.0 (a) and 7.0 (b−e) at different urea addition levels: lamellar phase ($x = 20$) (a), hexagonal phases obtained when $x = 10$ (b), 20 (c), 30 (d), and 40 (e).

hexagonal mesophase was also observed for the solid obtained when the mixing ratio of Al, SDS, urea, and water was 1:1: 10:30 (Figure 4m).

The short-range structural properties of the resulting mesophases were studied by ^{27}Al MAS NMR spectroscopy. The NMR data indicated that the 4-coordinate Al peak near 61 ppm increases in intensity remarkably with an increase in urea concentration, while the 6-coordinate Al peak near 1 ppm becomes broad (Figure 5b−e). It is also noted that the ratio of 4-coordinate Al to 6-coordinate Al for the layered mesophase is little changed by the layer to hexagonal transition, since both phases for $x = 20$ give nearly the same NMR patterns (Figure 5a,c).

In general, aluminum oxyhydroxide compounds consist mostly of their octahedral units, as observed for aluminum-based Keggin cations and $Al(OH)_6$ layers in smectites. Taking into further consideration the broadened 6-coordinate Al peaks, it may be reasonable to assume that the inorganic layers in the layered mesophase are composed of octahedral Al as the predominant component and tetrahedral Al as the secondary one. The fraction of the latter Al would increase with an increase in urea concentration, as expected from the NMR results for the hexagonal mesophases.

On the basis of the above X-ray, SEM, and NMR observations, we can propose that the layer to hexagonal transition in the present system would occur through the interlayer condensation and cross-linking of Al−OH groups in any adjacent aluminate sheets, accompanying the rearrangement of bilayered surfactant molecules into a rodlike assembly (Figure 6a). A similar mechanism was suggested by Monnier et al. for the MCM-41 silica mesophase[5,6] and by Inagaki et al. for the FSM-16 silica system.[11] The considerable increase in yield of precipitate during the layer to hexagonal transition also means that the structural transition would be followed by the subsequent growth into enlarged particles through an additional supply of aluminum cations, hydroxyl anions, and surfactant species from solution. Furthermore, the present data suggest that the aluminum-based hexagonal mesophase resulting from the lamellae having an increased fraction of tetrahedral Al forms a ringed or curved wormlike morphology, whereas the mesophase grown from those much less substituted with tetrahedral Al exhibits more numerous patterns including spherical, funneled, and tubular particles. Such morphologically versatile characteristics of the hexagonal mesophase appear to reflect primarily those of their precursors which would be produced by the folding of aluminum-based flexible layers accompanied by the layer to hexagonal transition, as illustrated in Figure 6b. The increased tetrahedral Al groups for the $x \geq 20$ products may increase the flexibility of lamellae available for the uniform development of interlayer cross-linking or transition into a hexagonal structure, leading to a straight, ringed or curved wormlike morphology characterized by their hexagonal crystal habit. The

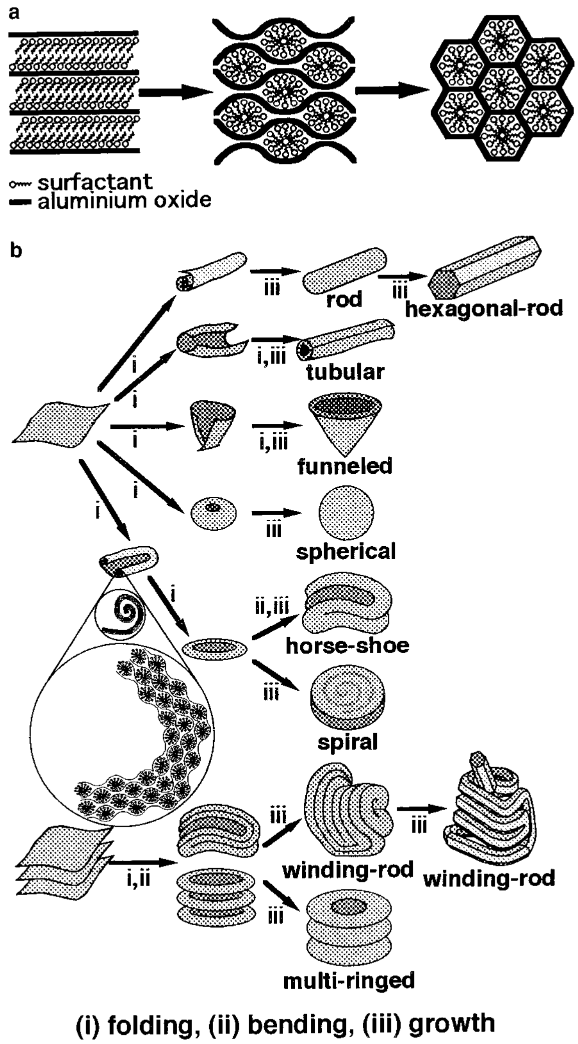

Figure 6. Schematic representation of a model proposed for the formation of aluminum-based surfactant mesophases: (a) the pathway for the transition from the layer to hexagonal structure via a transient intermediate through the interlayer cross-linking of Al−OH groups in any adjacent aluminate sheets, accompanying the rearrangement of bilayered surfactant molecules into a rodlike assembly and (b) possible routes for the morphologically versatile growth of hexagonal mesophases from their precursors which are formed by the folding of single or stacked flexible lamellae accompanying the layer to hexagonal transition.

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predominant octahedral Al groups for the $x = 10$ products, on the other hand, would make the aluminate lamellae much more rigid to triggering the geometrically heterogeneous development of interlayer cross-linking, leading to various morphologies unexpected from the crystal structure. The absence of such structurally rigid groups in the layered silicas composed of only SiO_4 tetrahedral units may be responsible for limited kinds of morphologies of hexagonal silica mesophases.[1,7-9] We can thus suggest that the morphologically versatile growth of the aluminum-based hexagonal mesophase is controllable through the tetrahedral to octahedral Al ratio determined by the urea concentration in the reaction mixture.

The viscosity of the starting solution with SDS was extremely high when $x = 10$, but it decreased rapidly with further addition of urea. This means that urea acts not only as a source of hydroxyl anions but also as a dispersing agent for the surfactant micelles. Urea further acts as a stabilizer for aluminum hydroxide-based polynuclear clusters formed during the hydrolysis of urea itself. This effect, in combination with the dispersing effect of urea, would increase the pH for the initial precipitation due to the polymerization of octahedral aluminum hydroxide monomers, resulting in the increase of the tetrahedral Al content with an increase in urea concentration. These two effects would also contribute to copious nucleation leading to a decrease in particle size at high urea concentration of $x = 20$ or above. Urea is also essential for the layer to hexagonal transition because the reaction at 80 °C using aqueous ammonium solution in place of urea yields only a mixture of a layered mesophase and aluminum hydroxide even at pH as high as 7.0−8.0.

On calcination, both the resulting hexagonal and layered mesophases were deorganized and converted into amorphous alumina at 600−700 °C, γ-alumina at 800−900 °C, and finally into α-alumina at 1100 °C or above, while keeping their as-grown morphologies. Although the apparent morphologies of mesophases such as lamellar, spherical, and wormlike shapes were little affected by heat treatment at temperatures of 600−1000 °C, calcination of the mesostructured solids at higher temperatures led to their transformation into α-alumina particles which are similar in shape but finely divided into domains and have a specific area of ca. 20 $m^2 \cdot g^{-1}$. The detailed results will be described elsewhere.[12]

Attempts to obtain mesoporous alumina by the above approach were unsuccessful, while our preliminary experiment indicated that the XRD pattern of the hexagonal mesophase freeze-dried without washing with water and calcined at 600 °C gives a discernible shoulder at $2\theta < 5°$.[10] The precalcination processing was thus applied to the series of hexagonal or lamellar mesostructured solids for $x = 10$, 20, and 30, in which the solids were heated up 600 °C at a heating rate of 5 $°C \cdot min^{-1}$ and kept at that temperature for 10 h. This revealed that the hexagonal solids for $x = 30$ yield a more distinct shoulder at $2\theta = 1-3°$ (Figure 2B(a)) in their XRD patterns than those for $x = 20$ and that no other solids show such low-angle reflections. The hexagonal $x = 30$ solid precalcined at 600 °C for 3 h after heating up at a rate of 1 $°C \cdot min^{-1}$ and the solid aged at 50 °C for 3 d prior to the same heat treatment displayed a clear diffraction peak at $2\theta = 2.4°$ ($d = 3.7$ nm) and 2.7° ($d = 3.2$ nm), respectively, along with some weak peaks assignable to γ-alumina, as shown in Figure 2B(b,c). Figure 7 shows the N_2 adsorption isotherm for the aged and precalcined product. The first rapid adsorption at low P/P_0 is due to the monolayer coverage of mesopore and particle surface, corresponding to the specific surface area of 120 $m^2 \cdot g^{-1}$. This value is more than the BET surface area of 43 $m^2 \cdot g^{-1}$ for the $x = 30$ solid postcalcined at 600 °C for 10 h after heating up at a rate of 5 $°C \cdot min^{-1}$, although it is much less than 1000 $m^2 \cdot g^{-1}$ observed for the MCM-41 mesoporous silica. The slight adsorption near $P/P_0 = 0.33$ is probably due to capillary condensation in mesopores. The BET surface area of the precalcined $x = 30$ product varied from 93 to 365 $m^2 \cdot g^{-1}$ depending on the precalcination conditions. It is thus most likely that the precalcined products are partly formed of mesoporous alumina frameworks with a hexagonal structure, in contrast to mesoporous alumina with random arrangement of pores reported by Vaudry et al.[13] and Bagshaw et al.[14] This is probably because the unreacted sodium dodecyl sulfate species remaining in the solid would prevent the rapid desorption or degradation of incorporated surfactant groups so that the principal framework of aluminum oxide is retained even upon condensation of the residual aluminum hydroxide groups. One more attempt to deorganize the hexagonal solids using methanol, ethanol, acetone, alkaline, or acid solution while keeping the inorganic framework was also unsuccessful. Further work for the advanced synthesis of hexagonal-structured mesoporous alumina is under way.

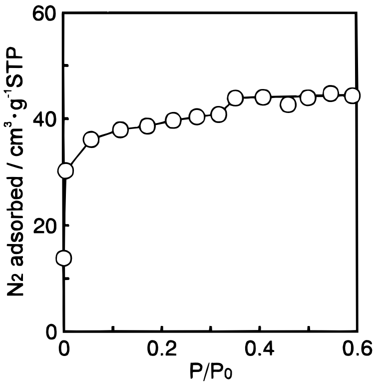

Figure 7. N_2 adsorption isotherm for the $x = 30$ hexagonal mesophase separated at pH 7.0 and aged for 3 d, followed by the precalcination at 600 °C for 3 h after heating up at a rate of 1 $°C \cdot min^{-1}$.

In conclusion, aluminum-based mesostructured phases occur initially in the layer structure, followed by growth into their hexagonal form with versatile morphologies based on the mechanism of lamellar folding depending on the urea concentration in reaction mixture. The present approach and findings contribute to the development of functional mesostructured materials. The observations for biomimetic processes may also be useful for clarifying the pathway of biomineralization in coral, shell, diatom, or other calcified tissues.

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