Synthesis and deorganization of an aluminium-based dodecyl sulfate mesophase with a hexagonal structure

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An aluminium-based dodecyl sulfate mesophase with a hexagonal structure is synthesized by the homogeneous precipitation method using urea and is thermally deorganized into a hexagonal but less ordered framework structure with a *d* spacing of 3.4 nm.

Increasing attention has been focused on mesoporous materials, because of their great applicability as catalysts, molecular sieves and host matrices, based on their large internal surface areas.[1,2] Silica and silica-based mesoporous materials with a hexagonal framework structure have been synthesized utilizing the micellar assembly of cationic surfactants as a template.[3–5] The micellar assembly-based method using cationic or anionic surfactants has also been applied to the synthesis of a variety of metal oxide/surfactant composite materials containing framework elements such as Pb, Fe and W, but most attempts led to unsuccessful removal of the incorporated surfactant species.[6,7] A similar approach to alumina-based mesoporous materials also resulted only in the formation of lamellar phases.[6]

We have now found that an aluminium-based dodecyl sulfate mesostructured material with a hexagonal framework can be obtained by the homogeneous precipitation method using urea, and converted into a deorganized but less ordered form.

Aluminium nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] was used as the aluminium source and sodium dodecyl sulfate (SDS), $Me(CH_2)_{11}OSO_3Na$, was used as the templating agent. The aluminium oxide/anionic surfactant complex was prepared as follows: aluminium nitrate, SDS, urea and water were mixed in a molar ratio of 1 : 2 : 30 : 60 and stirred at 40 °C for 1 h to yield a transparent solution. This solution was heated at 80 °C and then kept at that temperature until the pH increased from its initial value of 3.6 as a consequence of the enhanced hydrolysis of urea. Upon reaching a predetermined pH, the resulting mixture was immediately cooled to room temperature, to prevent further hydrolysis of urea. After centrifugation, part of the resulting solid was washed with water a few times and then dried in air and the other part of the solid was freeze-dried without washing. Both the washed and the unwashed materials were calcined in air at 600 and 1000 °C for 10 h to remove their organic moieties. The calcined products were then re-washed with water to remove water-soluble impurities such as sodium sulfate formed during calcination. Powder X-ray diffraction (XRD) measurements were made on a Simazu XD-3AS diffractometer with Cu-Kα radiation. IR absorption spectra were measured using the KBr pellet method on a Nippon Bunko FT/IR-300 instrument. Transmission electron microscopy (TEM) was carried out using a Hitachi H-800MU instrument.

Precipitation at 80 °C occurred when the pH of the reaction mixture reached 5.5 or above. Fig. 1 shows the XRD data for the washed samples precipitated at pH 6.0 and 7.0 (**1** and **2**). The two diffraction peaks in the region 2θ 1–5° for **1** are attributable to the (100) and (200) reflections for a lamellar phase with an interlayer spacing of 3.5 nm. The XRD pattern of **2**, on the other hand, is characterized by the major peaks in the region 2θ 1–5°, along with a halo band at 2θ *ca.* 20°. These three peaks can be assigned to the (100), (110) and (200) reflections based on a hexagonal unit cell with a = 4.3 nm ($2d_{100}/\sqrt{3}$). The halo peak suggests that the short-range arrangement of constituent atoms is completely disordered. A similar hexagonal structure has been observed for MCM-41 silica/surfactant composite materials.[1]

Although the transmission electron micrograph of **2** under low magnification shows a macro morphology different from that expected from the crystallographic cell, the regular hexagonal array of channels is observed at high magnification [Fig. 2(*b*)]. The longer dimension of the channels is 3.7 nm, comparable to the *a* value of 4.3 nm obtained by XRD. The stripes observed for the same sample but in a different orientation give a spacing of 2.1 nm [Fig. 2(*c*)]. This value is in good agreement with the 2.1 nm spacing of *a*/2 expected when the sample is viewed along the [210] zone axis of the hexagonal cell (Fig. 3). The longitudinal length of the stripes in Fig. 2(*c*) also shows that the hexagonal channels extend for more than several hundred nanometers.

The incorporation of dodecyl sulfate groups in the aluminium-based solid was confirmed by the IR spectrum of **2** in which sharp peaks at 2924 and 2854 cm^{-1} due to the $-CH_2-$ group and a peak at 2958 cm^{-1} due to the $-CH_3$ group are observed along with strong bands at 1244 and 1207 cm^{-1} associated with the $-OSO_3^-$ group. When sodium decyl sulfate was used in place of sodium dodecyl sulfate, the *a* value evaluated from XRD data for the resulting hexagonal phase decreased from 4.3 to 3.8 nm, in accordance with twice the difference of 0.25 nm in surfactant chain length. These observations indicate that the hexagonal channels in the

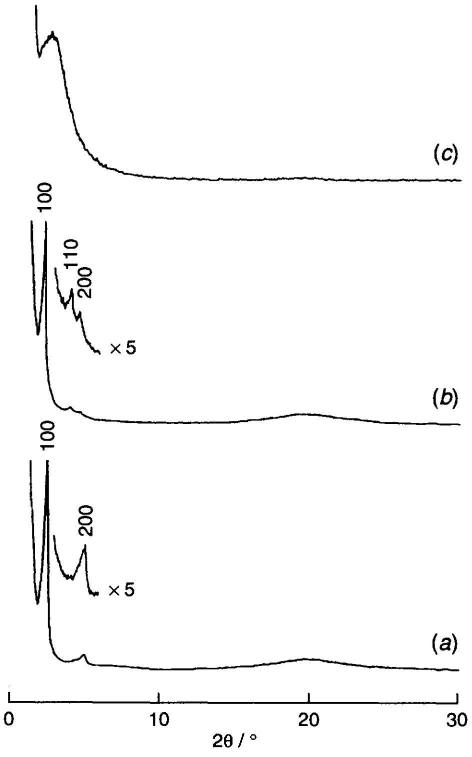

Fig. 1 XRD patterns of (*a*) **1**, (*b*) **2** and (*c*) **3** calcined at 600 °C

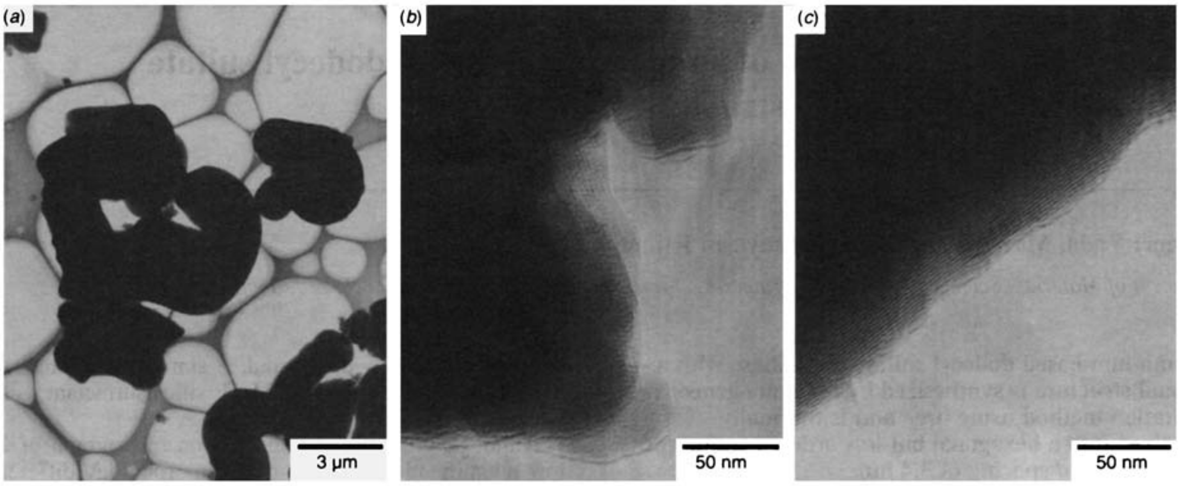

Fig. 2 Transmission electron micrographs of **2**; viewed (*a*) under low magnification, (*b*) under high magnification along the channel axis, and (*c*) perpendicular to the channel axis

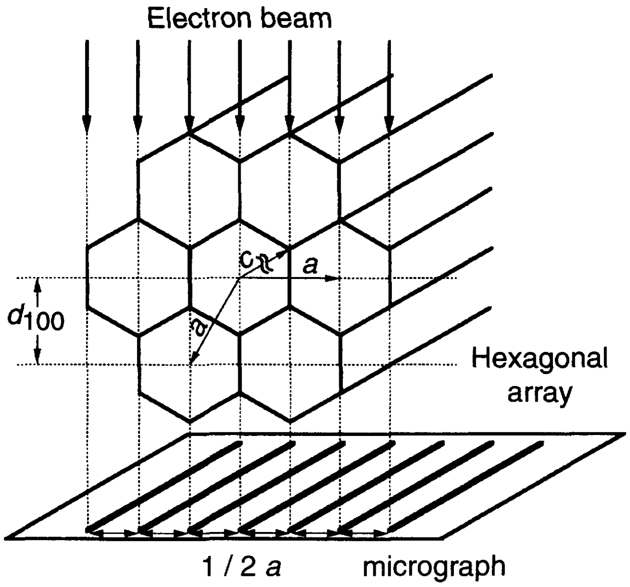

Fig. 3 Schematic model of the stripes shown in Fig. 2(*c*)

aluminium-based solid are likely to be occupied by rod-like assemblies of extended chain surfactant molecules. It is thus concluded that the aluminium-based dodecyl or decyl sulfate mesostructured materials obtained in the present study are structurally similar to the MCM-41 silica mesophase.[1]

The XRD peaks for **2** disappeared when the sample was calcined at 600 °C, whereas peaks characteristic of α- and γ-alumina appeared upon calcination at 1000 °C. This indicates that the washed composite solid with hexagonal structure is deorganized into a completely disordered form at 600 °C and totally converted into α- and γ-alumina at 1000 °C. The anionic surfactant could not be removed by washing with ethanol or acetone without collapse of the hexagonal structure.

In contrast to the washed products, the unwashed sample precipitated at pH 7.0 showed a slight shoulder in the region 2θ 1–3° in its XRD pattern even after calcination at 600 °C and washing with water. One explanation for this behaviour may be that the unreacted sodium dodecyl sulfate species coexisting within the mesostructured phase would prevent the rapid desorption or degradation of incorporated surfactant groups so that the principal framework of the aluminium-based structure is retained even upon condensation of the remaining aluminium hydroxide groups. On the basis of the above data, an additional sample was prepared by a procedure in which the reaction mixture was aged at 50 °C for 3 days immediately after its pH had reached 7.3 at 80 °C. After washing with water and calcination at 600 °C, the aged product showed an XRD pattern similar to that for **2**. Upon heating at 600 °C, the aged but unwashed product, **3**, showed a broad but distinct diffraction peak at 2θ = 2.6° corresponding to a *d* spacing of 3.4 nm and some additional weak bands assignable to alumina (Fig. 1). This fact suggests that the aged product was deorganized into a mesoporous alumina with some structural disorder but with the hexagonal structure retained in its principal framework. It is therefore likely that the ageing of the precipitated product in the mother liquor is effective in preventing the collapse of the hexagonal framework structure. This is probably because the aluminium-based framework is strengthened by the partial condensation of aluminium hydroxide groups prior to the major heat treatment at elevated temperature. The slight contraction of 0.3 nm in *d* spacing relative to 3.7 nm for the uncalcined form would be due to the thermal condensation of the remaining aluminium hydroxide groups during calcination.

In conclusion, we have synthesized an aluminium-based dodecyl sulfate mesophase with a hexagonal structure by homogeneous precipitation and suggested a promising route to convert this mesostructured phase into a mesoporous alumina of similar structure to the MCM-41 silica mesophase.

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