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Mesostructured gallium oxides templated by dodecyl sulfate assemblies

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A gallium-based dodecyl sulfate mesophase with a hexagonal structure was synthesized by the homogeneous precipitation method using urea. The hexagonal phase has a unit-cell parameter *a* of 4.4 nm and appears as winding-rod shaped particles with hexagonal-shaped transverse surfaces. On removal of the incorporated surfactants by chemical or thermal treatment the mesophase structure collapses. On calcination at 700 °C or above it is totally converted into normal gallium oxide particles keeping the as-grown morphology. Precipitation in the presence of both dodecyl sulfate and lauryl (dodecyl) alcohol leads to the formation of a layered structure with an interlayer spacing of 4.0 nm which is so stable as to hamper the transition from layer to hexagonal structure.

Introduction

The discovery of MCM-41[1] and FSM-16[2] silicas has triggered increasing attention on a novel family of porous materials, because of their wide applicability as catalysts, molecular sieves and host materials based on their large internal surface areas. Mesoporous titanium,[3] zirconium[4] and other metal oxides with a hexagonal structure have been synthesized by the removal of surfactants from their mesostructured precursors templated by surfactant assemblies. Some studies in this field have been also devoted to the biomimetic formation of complex morphologies in such templating systems, as reported for the silica–surfactant mesophases.[5–7] Recently, we synthesized aluminium-based dodecyl sulfate mesophases by the homogeneous precipitation method using urea and found that the mesophases occur initially in the layer structure and grow into their hexagonal form with versatile morphologies such as winding-rod, spherical, tubular and funneled shapes depending on the urea concentration.[8,9] This structural and morphological transformation behavior in the aluminium–surfactant system suggested that polynuclear aluminium cations are likely responsible for the formation of hexagonal mesophases. According to Bradley *et al.*,[10] the hydrolysis of aqueous gallium(III) salt solutions also yields a gallium polymeric species analogous to the Keggin cation of aluminium $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. These facts aroused our interest in a gallium-based templating reaction.

Gallium oxide is known to act as a functional material in catalytic carriers and hosts for an alkali-metal ion conductor with the β-alumina structure. If mesostructured or mesoporous gallium oxides were to be obtained, they would extend the applicability of gallium oxide as a functional material. An attempt was thus made to apply the urea-based homogeneous precipitation approach to a gallium–surfactant system. In this paper, we report the synthesis of gallium oxide-based mesophases with hexagonal and lamellar structures templated by dodecyl sulfate assemblies.

Experimental

The gallium-based surfactant mesophases with a hexagonal structure were synthesized by the homogenous precipitation method using urea as follows. Gallium chloride ($GaCl_3$) was used as the gallium source and sodium dodecyl sulfate [sds, $CH_3(CH_2)_{11}OSO_3Na$] as the templating agent. Urea was used to increase the pH of the solution because it gradually releases ammonia through its hydrolysis on heating at above 60 °C. Gallium chloride, sds, urea and water were mixed at a molar ratio of 1 : 2 : 30 : 60 and stirred at 40 °C for 1 h to yield a transparent solution. This was heated at 80 °C and then kept at that temperature. The pH increased from 2.6 initially to 7.0 after 4 h, due to the enhanced hydrolysis of urea. Upon reaching different pHs (pH 4.2, 5.0, 6.0 and 7.0, solids obtained at pH 4.2 and 7.0 only are described), the reaction mixture was immediately cooled to room temperature to prevent further hydrolysis of urea. The resulting solid was centrifuged and washed with water a few times and then dried in air. Powder X-ray diffraction (XRD) measurement was made on a Shimadzu XD-D1 diffractometer with Cu-Kα radiation. Infrared spectra were measured by the KBr pellet method using a Nippon Bunko FT/IR-300 spectrometer, transmission electron microscopy (TEM) was carried out using a Hitachi H-800MU and scanning electron microscopy (SEM) was performed on a Hitachi H-4100 instrument. X-Ray microanalysis (XMA) was done using a Horiba EMAX-5770. Thermogravimetric and differential thermal analyses (TG-DTA) were conducted on a Seiko TG/DTA320U apparatus with a heating rate of 10 °C min^{-1} in air.

Results and Discussion

Precipitation occurred at pH 3.9 after 2.7 h. Two solids **1** and **2** were separated at pH 4.2 after 2.8 h and at pH 7.0 after 4 h, respectively. The incorporation of surfactant in both mesophases was confirmed by their IR spectra indicating sharp peaks at 2920 and 2852 cm^{-1} [$\nu(CH_2)$] as well as peaks at 1259 and 1213 cm^{-1} [$\nu(OSO_3^-)$].

The XRD pattern of solid **1** indicated three diffraction peaks at $2\theta = 1–5°$ along with a halo band at $2\theta \approx 20°$, as shown in Fig. 1. The former three peaks can be assigned to the 100, 110 and 200 reflections on the basis of a hexagonal unit cell with $a = 4.4$ nm and the halo band suggests that the short-range arrangement of constituent atoms is almost completely disordered. The *a* value of 4.4 nm for this phase is close to the 4.3 nm observed for the aluminium-based hexagonal mesophase with dodecyl sulfate.[8,9] The transmission electron micrograph of **1** showed a regular hexagonal array of channels extending for several hundred nanometers or more [Fig. 2(a)]. This periodic structure was substantiated by an additional image viewed along the [100] zone axis of the hexagonal cell indicating stripes the spacing of which, 3.4 nm, is comparable to the d_{100} value (3.8 nm), as shown in Fig. 2(b). For the hexagonal phase the thickness of the inorganic wall estimated from the dark width in the stripe image is *ca.* 1 nm, similar to the 0.82–1.07 nm of

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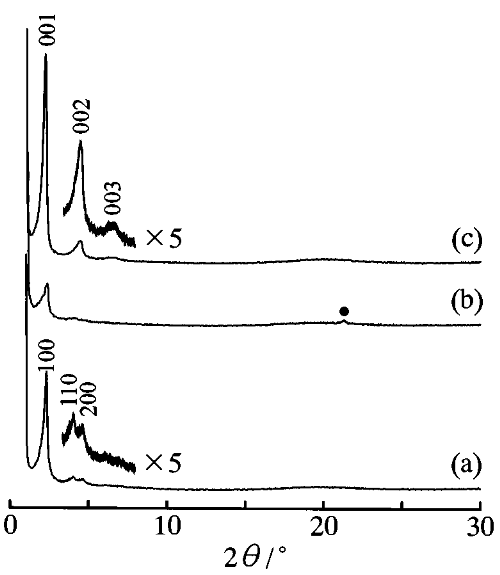
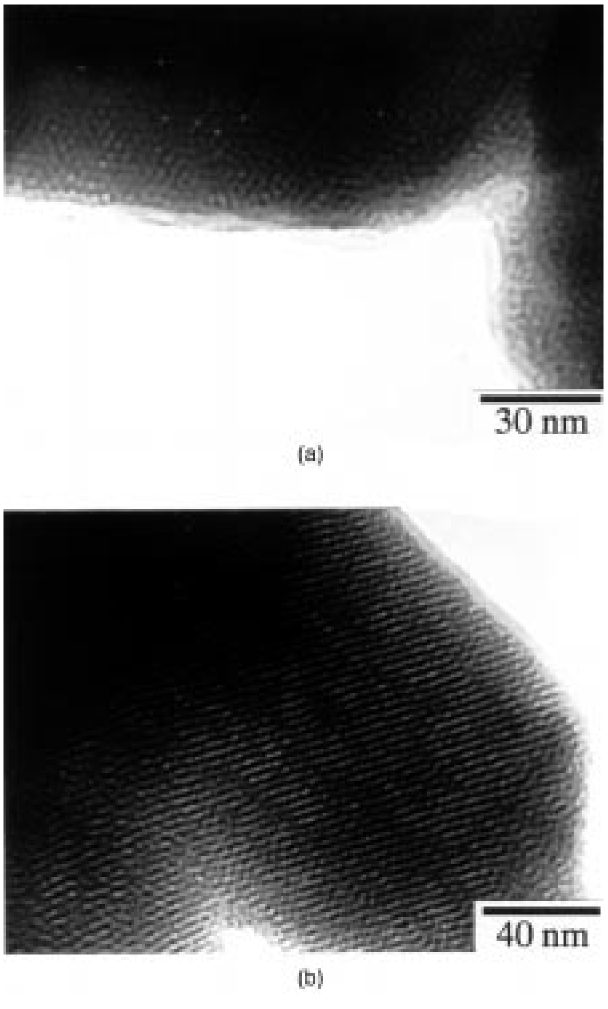


Fig. 1 The XRD patterns of gallium-based dodecyl sulfate mesophases (a) **1**, (b) **2** and (c) **3**. Peak assignment: ●, GaO(OH)



(a)

(b)

Fig. 2 The TEM images of the mesophase **1** viewed (a) along the axis of the hexagonal channel and (b) perpendicular to the hexagonal channel

the gallium-based Keggin cation.[10] It is therefore most likely that the framework of the gallium-based mesophase is composed of Keggin-type cation species formed during the gradual hydrolysis of urea. The SEM observations showed that the mesophase **1** is formed mostly of winding-rod or curved worm-like particles [Fig. 3(a) and 3(b)] and some of the rods sharply exhibited hexagonal-shaped transverse surface and edges. This distinct crystal habit definitely reflects a highly ordered hexagonal arrangement of gallium oxide and surfactant species. A similar observation was made for the aluminium-based surfactant mesophase.[9] On the other hand, although the XRD pattern of the mesophase **2** was essentially similar to that of **1**, the former showed a remarkably decreased 100 peak as well as poorly resolved 110 and 200 peaks, and some additional peaks assignable to GaO(OH) appeared. In keeping with this crystallographic change, the SEM image of **2** displayed the formation of indefinite-shaped particles. These data mean that at pH around neutrality the mesostructured particles are partly degraded to form inorganic extra phases such as GaO(OH).

The above XRD, TEM and SEM observations indicate that at the initial stage of precipitation the gallium-based mesophase occurs in the hexagonal form and grows with an increase of pH, in striking contrast to the aluminium-based hexagonal mesophases formed through the structural transition of the initially precipitated layered phase.[8,9] The layer to hexagonal transition in the latter system was verified to occur through the partial condensation and cross-linking of aluminium hydroxide oxide layers interleaved with dodecyl sulfate bilayers, accompanied by the rearrangement of the bilayered surfactant molecules into a rod-like assembly.[9] It is therefore reasonable to assume that the gallium-based hexagonal mesophase is precipitated directly from solution or formed through an extremely fast layer to hexagonal transition. The latter process is more likely because the resulting solid partly contains morphologically lamellar particles, as shown in Fig. 3(c). Such a fast structural transition is plausible because the metal hydroxide oxide layers initially formed in the gallium-based system would undergo condensation much more rapidly than those in the aluminium-based system, as expected from the fact that gallium salt solutions are hydrolysed to yield GaO(OH) without forming $Ga(OH)_3$.[10]

The TG-DTA curve for solid **1** showed four weight losses until the mesostructured solid was totally converted into normal gallium oxide at 700 °C (Fig. 4). The first endothermic weight loss at below 130 °C is due to desorption of adsorbed water. The second at *ca.* 130–250 °C is due to the endothermic desorption of water formed by condensation of gallium hydroxide groups as well as the partial exothermic combustion of incorporated surfactants and the endothermic desorption of it. The third weight loss in the range of *ca.* 250–550 °C is due to the markedly exothermic carbonization and/or combustion of the residual surfactant moiety. The XMA analysis showed that the sulfur species remains in the 600 °C product, but that it is completely lost from the 800 °C product. Therefore, the fourth exothermic weight loss near 665 °C is assignable to the complete desorption of sulfated groups. The composition of **1** determined on the basis of the TG data is $Ga_2O_3\cdot0.35CH_3(CH_2)_{11}OSO_3H\cdot3.8H_2O$. In contrast, the S to Ga molar ratio for **1** obtained by XMA analysis is 0.31 : 1, being more than the thermogravimetric value of 0.18 : 1. This is probably because dodecyl sulfate species are partially decomposed by the action of acidic gallium hydroxide species. On calcination at 400 °C or above or treatment with an ethanol solution of sodium acetate, the mesophase was observed to collapse in structure. Calcination of the mesophase **1** at 800 °C yielded gallium oxide particles similar in shape to the as-grown ones. Thus, although the gallium-based mesophase with a hexagonal structure is not useful for the synthesis of mesoporous materials, it would be applicable to the synthesis of gallium oxide with complex morphologies.

In contrast to the hexagonal mesophase, a gallium-based lamellar mesophase was obtained by the use of lauryl (dodecyl) alcohol with dodecyl sulfate similarly to the aluminium-based mixed system.[11] The XRD pattern of the resulting solid **3**, formed from a mixed solution of $GaCl_3$, sds, lauryl alcohol,

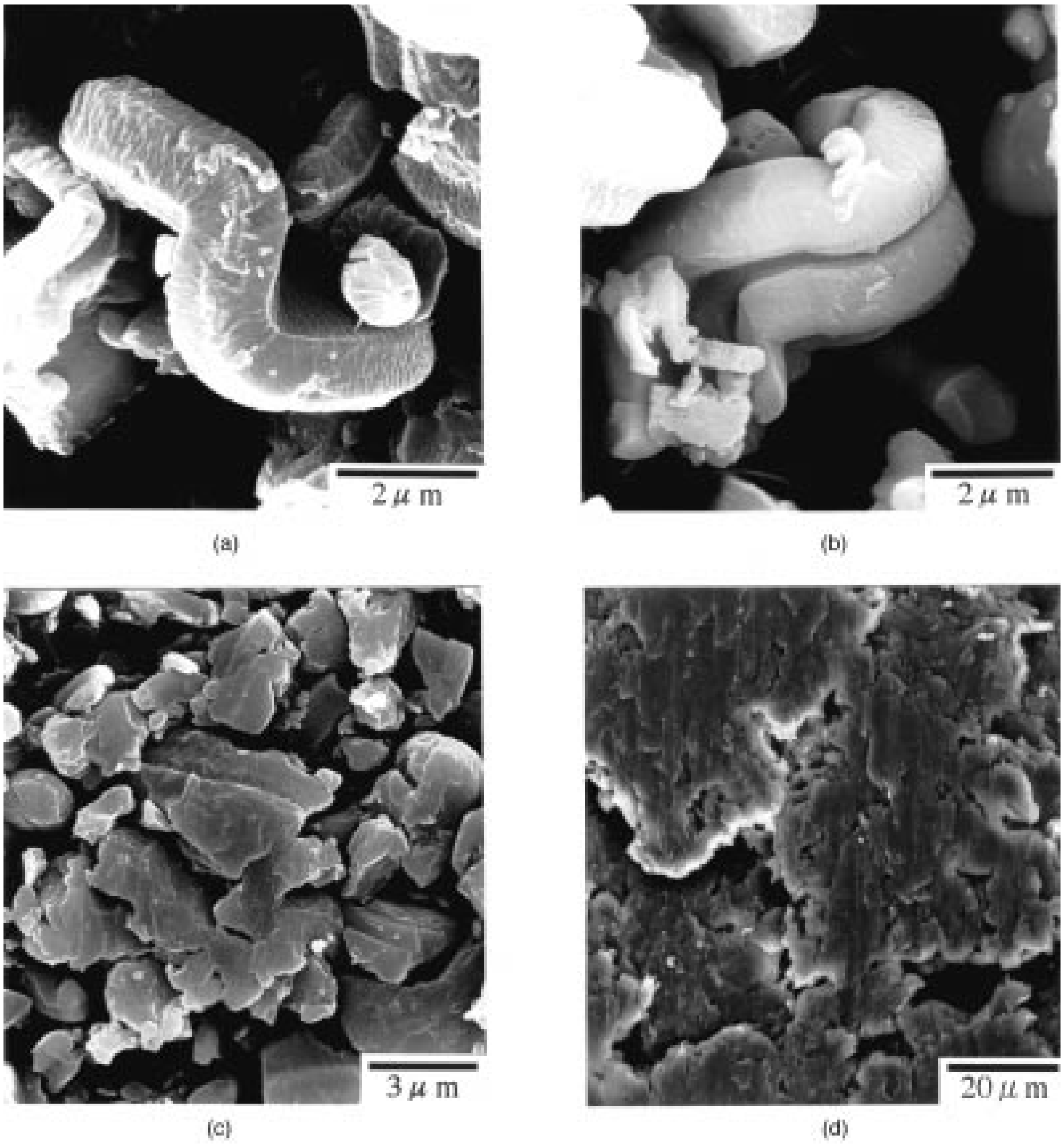


Fig. 3 The SEM photographs of the gallium-based mesophase **1** (a)–(c) and **3** (d): (a) worm-like particle with hexagonal edges, (b) worm-like particle with a hexagonal transverse section, (c) lamellar particle and (d) lamellar particle

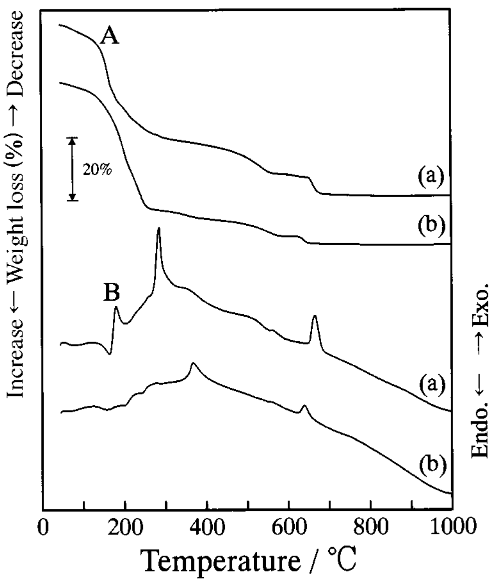


Fig. 4 The TG (A) and DTA (B) curves for the gallium-based mesophases **1** (a) and **3** (b)

water and urea at a molar ratio of 1:2:1:60:30, gave three peaks assignable to the 001, 002 and 003 reflections for a layered mesophase with an interlayer spacing of 4.0 nm, as shown in Fig. 1(c). In keeping with the structural observation, the morphology of **3** was lamellar in shape [Fig. 3(d)]. The incorporation of lauryl alcohol was verified by thermal analysis, as previously for the aluminium-based system.[11] The TG curve for **3** showed a fairly different pattern from that for **1**. The second weight loss at temperatures up to 260 °C increased from 35% for **1** to 40% for **3** and its offset temperature appeared more clearly around 260 °C. The DTA curve for **3** also gave an additional endothermic peak at *ca.* 245 °C along with the two endothermic peaks at *ca.* 160 and 205 °C observed common to both samples. It is also noted that the boiling temperature of free lauryl alcohol is as high as 255 °C. These facts mean that the rapid weight loss at below 230 °C is mainly due to desorption of water and dodecyl sulfate and that the additional weight loss in the temperature range 230–260 °C is mainly attributable to desorption of lauryl alcohol. The S to Ga molar ratio determined by XMA for **3** was also 0.28 : 1 similarly to that for the hexagonal mesophase. On the basis of the above observations it can be assumed that the lauryl alcohol molecules, together with dodecyl sulfate molecules compensating the positive charge of the gallium-based layer, are incorporated primarily through the van der Waals interaction between their alkyl chains and arranged as a bilayer interleaved with the gallium hydroxide oxide layers. The coincorporated lauryl alcohol would act to stabilize the initially formed lamellar phase against its transition into a hexagonal structure, as observed in the aluminium-based system.[11]

When 25 weight % aqueous solution of ammonia was used in place of urea in the lauryl alcohol-free system, the solid separated at pH 7.0 was only gallium hydroxide oxide, GaO(OH). This is in striking contrast to a similar reaction in the aluminium-based system yielding a lamellar mesophase.[8,9] These observations indicate that urea is essential for the formation of the hexagonal mesophase in either system. In the urea-based systems a gradual supply of hydroxide ions due to the hydrolysis of urea would contribute to the precipitation of surfactant-based mesophases.

When the chloride of indium, in the same Group as Al and Ga, was used, no mesophases were obtainable. This would be primarily because indium ions cannot form such a Keggin-type polymeric cation as formed in the Al- or Ga-based system. In harmony with this explanation, a recent study[12] also reported the synthesis of mesoporous aluminophosphate composed of Keggin cations $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. We can thus conclude that Keggin-type polymeric cation species would be essential for the formation of a class of hexagonal mesostructures.

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