Synthesis of porous yttrium aluminium oxide templated by dodecyl sulfate assemblies

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An yttrium aluminium oxide dodecyl sulfate mesophase with a hexagonal structure has been synthesized by a homogeneous precipitation method using urea and was converted into a porous material with a specific surface area of 662 m^2 g^{-1} by anion exchange of the surfactant with acetate ion.

Increasing attention has been paid to mesoporous materials, mainly because of their great applicabilities as catalysts, molecular sieves and host materials based on their large internal surface areas and narrow pore size distributions. The first examples of such materials, MCM-41[1] and FSM-16[2] silicas, were synthesized by calcining their mesostructured precursors formed in the presence of a cationic surfactant. This approach has been applied to the preparation of niobium, zirconium and other binary metal oxide-based mesophases.[3,4] Much less study, however, have been reported concerning similar but ternary metal oxide-based materials such as those containing $AlPO_4$[5] and $AlBO_3$[6] as their skeleton.

Our previous studies demonstrated the synthesis of aluminium-based dodecyl sulfate mesophases by the homogeneous precipitation method using urea, in which the surfactant mesophases occurred initially in the layer structure and grew into their hexagonal form with versatile morphologies such as winding-rod, spherical, tubular and funneled shapes depending on the urea concentration.[7,8] A similar observation was made for the gallium-based dodecyl sulfate system.[9] Coincorporation of dodecyl sulfate and alkyl alcohols in the aluminium-based system also led to a lamellar structure with biomimetic surface patterns such as cone-shaped or terraced hollows and domed scales.[10] Recently, we also succeeded in the synthesis of a mesoporous yttrium oxide by the anion exchange method with acetate anion.[11]

Yttrium aluminium oxide is useful as hosts for solid-state lasers such as YAG ($Y_3Al_5O_{12}$) or YALO ($YAlO_3$) and luminescence systems and window materials for a variety of lamps. Therefore, if we could obtain a ordered mesoporous yttrium aluminium mixed oxide, it would be useful not only for adsorbing or separating agents and catalytic bodies but also as a host for the homogeneous dispersion of optically functional species, followed by its post-sintering. The aluminium component combined with yttrium oxide units would also be effective for increasing the solid acidity of the resulting oxide. Here, we report the synthesis of an yttrium aluminium oxide mesophase templated by dodecyl sulfate assemblies with a hexagonal structure and its conversion into a porous material by anion exchange of the surfactant species with acetate ion.

The yttrium aluminium oxide surfactant mesophases with lamellar and hexagonal structures were synthesized by the homogenous precipitation method using urea. Yttrium nitrate hexahydrate [$Y(NO_3)_3 \cdot 6H_2O$] was used as the yttrium source and 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. Yttrium nitrate, aluminium nitrate, SDS, urea and water were mixed at a molar ratio of 0.375 : 0.625 : 2 : 30 : 60 and stirred at 40 °C for 1 h to obtain a transparent mixed solution. The nominal Y to Al molar ratio of 3 : 5 corresponds to that for YAG. Urea was used to gradually raise the pH of the reaction mixture since on heating at above 60 °C it is hydrolyzed and releases ammonia. The mixed solution was heated at 80 °C and then kept at that temperature. The pH of the reaction mixture increased from an initial value of 3.6, due to hydrolysis of urea, and precipitation occurred. Immediately after 3 or 20 h, the resulting mixtures were cooled to room temperature to prevent further hydrolysis of urea. After centrifugation, the resulting solids were washed with water a few times and then dried at 60 °C. Powder X-ray diffraction (XRD) measurements were made on a Simadzu XD-D1 diffractometer with Cu-Kα radiation. X-Ray microanalysis (XMA) was conducted with a HORIBA EMAX-5770 instrument. Transmission electron microscopy (TEM) was carried out using a Hitachi H-800MU instrument.

Precipitation at 80 °C commenced when the pH of the reaction mixture reached 6.1 after 1.5 h. Two white solid samples, **1** and **2**, were separated after 3 and 20 h, respectively. The XRD pattern of **1** is characterized by three diffraction peaks at $2\theta = 1$–$7°$, along with a halo band near $2\theta = 20°$ [Fig. 1(a)]. The former three peaks are attributable to the 001, 002 and 003 reflections for a lamellar phase with an interlayer spacing of 3.9 nm and the halo band suggests that the short-range arrangement of constituent atoms is completely disordered. According to XMA, the dodecyl sulfate (S) to metal (Al + Y) mole ratio was 0.63, and the Y to Al mole ratio was 0.18. In contrast to the layered mesophase **1**, the XRD pattern of **2** is characterized by a major peak located at $2\theta \approx 2.3°$ and two weak peaks at $2\theta = 3$–$5°$ along with a halo at $2\theta \approx 20°$[Fig. 1(b)]. On the basis of a hexagonal unit cell with a = 4.3 nm, these three peaks can be assigned to the 100, 110 and 200 reflections. Thus, these two XRD patterns indicate that the

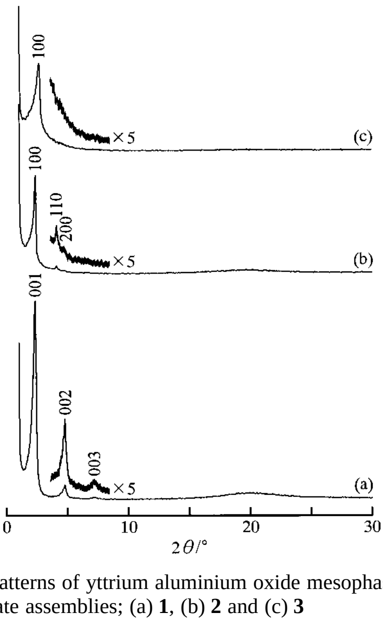

Fig. 1— XRD patterns of yttrium aluminium oxide mesophases templated by dodecyl sulfate assemblies; (a) **1**, (b) **2** and (c) **3**

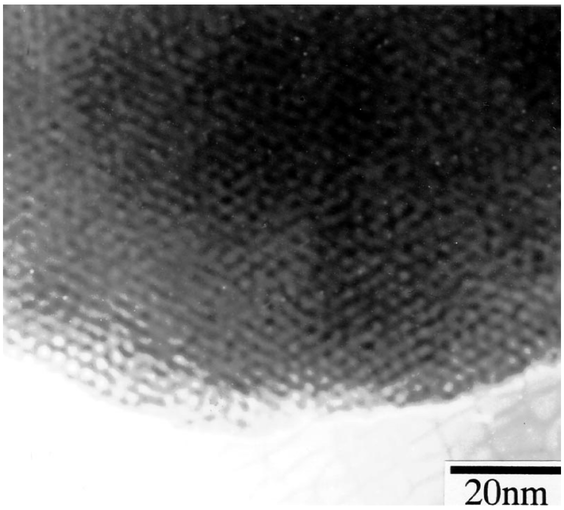

Fig. 2 TEM image of yttrium aluminium oxide mesophase **2** viewed along the axis of the hexagonal channel

yttrium aluminium mixed oxide mesophase undergoes a layer to hexagonal structural transition, as observed in the Al-, Ga- and Y-based systems.[7–11] The unit cell parameter of 4.3 nm for the Y–Al based hexagonal mesophase **2** is equal to that for the Al-based mesophase, but is much less than that for the Y-based mesophase (6.1 nm). A transmission electron micrograph of **2** showed a regular hexagonal array of channels extending for several hundred nanometers or more as shown in Fig. 2. This ordered hexagonal arrangement is similar to the atomic arrangement for the Al-based hexagonal mesophase and MCM-41, but is different from a disordered arrangement observed for the Y-based one. Furthermore, the S to metal mole ratio of 0.31 for the Y–Al based mesophase **2** is close to 0.33 and 0.28 for the Al- and Y-based analogues, indicating that nearly the same amount of surfactant per metal is incorporated in these three mesophases. The Y to Al mole ratio for the Y–Al based mesophase **2** is only 0.34, being nearly half its nominal value. Details for the control of Y to Al mole ratio in the resulting mesophases will be described elsewhere.

A further attempt was made to remove the surfactant species from the hexagonal mesophase **2** by anion exchange with acetate anions in a manner similar to that reported by Holland *et al.* for mesoporous aluminophosphate;[12] the mesophase sample (0.5 g) was mixed with a 0.05 M ethanol solution of sodium acetate (40 ml), and then stirred at 40 °C for 1 h. The centrifuged solid was then washed repeatedly with ethanol. The 100 reflection for the acetate-treated solid **3** shifted slightly to higher angle relative to that of **2**, and the 110 and 200 reflections for the former disappeared, as shown in Fig. 1(c). No sulfur species were detected by XMA of **3**, suggesting the complete removal of dodecyl sulfate species. Since the Y to Al molar ratio of 0.36 for **3** is nearly equal to 0.34 for **2**, the resulting decrease of unit cell parameter *a* from 4.3 to 3.8 nm would be attributable to partial condensation of hydroxide groups induced by the removal of surfactant. Preliminary data suggested that the solid **3** become completely disordered upon calcination at 300 °C for 5 h in air.

Fig. 3 shows an N_2 adsorption isotherm for **3**, measured after heating at 150 °C for 1 h to remove adsorbed water. The rapid adsorption in the range of P/P_0 = 0–0.25 for the sample is due to the monolayer coverage of pores and particle surface and capillary condensation in the pores. The specific surface area determined by the BET method was as large as 662 $m^2\ g^{-1}$ and the pore size determined by Clanston–Inkley method[13] was 1.6 nm. Pre-heating of **3** at 150 °C for dehydration led to a decrease of its crystallinity, as suggested from a slight shift of the 100 reflection from 2.6 to 2.9°. Upon similar acetate-treatment, the Al-based hexagonal mesophase collapsed in structure to yield a specific surface area of only 12 $m^2\ g^{-1}$, whereas the Y-based analogue was converted into a mesoporous solid with a specific surface area of as large as 545 $m^2\ g^{-1}$ without any radial contraction.[11] Thus, the pore structure change observed in the Y–Al mixed system is a result of the stabilization of the inorganic framework due to the combination of yttrium-based species with Al-based structural units.

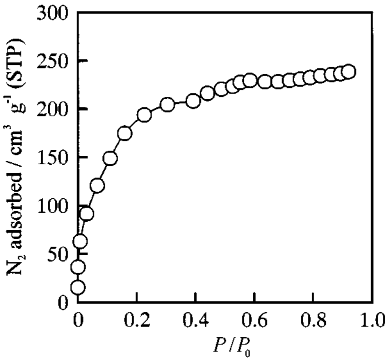

Fig. 3 N_2 adsorption isotherm for **3**

In conclusion, we have synthesized, for the first time, a hexagonal yttrium aluminium oxide mesophase by a homogeneous precipitation method using urea, and demonstrated its conversion into an acetate-exchanged porous material. The present approach and findings using the homogenous precipitation method will contribute to further development of functional mesostructured ternary or even more complex metal-based oxides.

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