Sonochemical Synthesis of Layered and Hexagonal Yttrium−Zirconium Oxides

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Layered and hexagonal mesostructures of yttrium−zirconium oxides have been synthesized using a sonochemical method. Sodium dodecyl sulfate is used as the templating agent and urea as the precipitant agent. There is a transformation from layered to hexagonal mesostructure with a prolonged sonication time of 6 h. The surface areas of the sample with hexagonal mesostructure before and after extraction with sodium acetate were 98 and 245 m^2/g, respectively. Low-angle X-ray diffraction, transmission electron microscopy, Brunauer−Emmett−Teller, energy-dispersive X-ray analysis, thermogravimetric analysis, and Fourier transform infrared were used to characterize these mesostructures.

Introduction

Since the discovery of the ordered mesoporous silica M41S,[1] a variety of ordered mesoporous materials have been synthesized using the supramolecular assembly of surfactant molecules as a template. These materials have a range of framework compositions, morphologies, and porous structures. This approach to mesostructured materials has been extended to non-silica oxides,[2−16] which might promise applications involving electron transfer, magnetic interactions, photocatalysis, and catalyst support. In particular, mesoporous oxides of yttrium and zirconium have been synthesized using a variety of surfactant template molecules and transition-metal precursors.[5−7,14−16] Only a few papers have appeared on the synthesis of mesoporous yttria-stabilized zirconia, although yttria-stabilized zirconia is the material of choice for use in solid oxide fuel cells (SOFC).[17] Ozin et al.[18] used cetyltrimethylammonium bromide as a template to synthesize mesoporous yttria−zirconia with a high surface area (116 m^2/g) and a high thermal stability. However, the zirconia precursor must be modified with ethylene glycol for the synthesis of mesoporous yttria−zirconia, and the process requires an extended period of time (as long as 5 days). Yada et al.[16,19−21] reported on the synthesis of mesoporous aluminum, gallium, yttrium, and rare-earth oxides using homogeneous precipitation of inorganic salts in the presence of sodium dodecyl sulfate (SDS). With this method, surfactant templates can be removed easily by extraction while the mesoporous structure can be maintained.

Sonochemical processing has been proven to be a useful technique for generating novel materials with unusual properties.[22,23] Recently, we reported on the synthesis of mesoporous TiO_2 with a high surface area, using a sonochemical method; we proposed that the high temperature in the interface of the gas phase and bulk solution can accelerate the condensation of titanium hydroxide and shorten the synthesis time.[24]

In the present work, we have tried to synthesize layered and hexagonal yttria−zirconia, especially the hexagonal structure, with ultrasound irradiation in order to obtain good mesostructures and shorten the synthesis time.

Experimental Procedure

Synthesis. In this method, SDS was used as the surfactant template, urea was used as the precipitant agent, and

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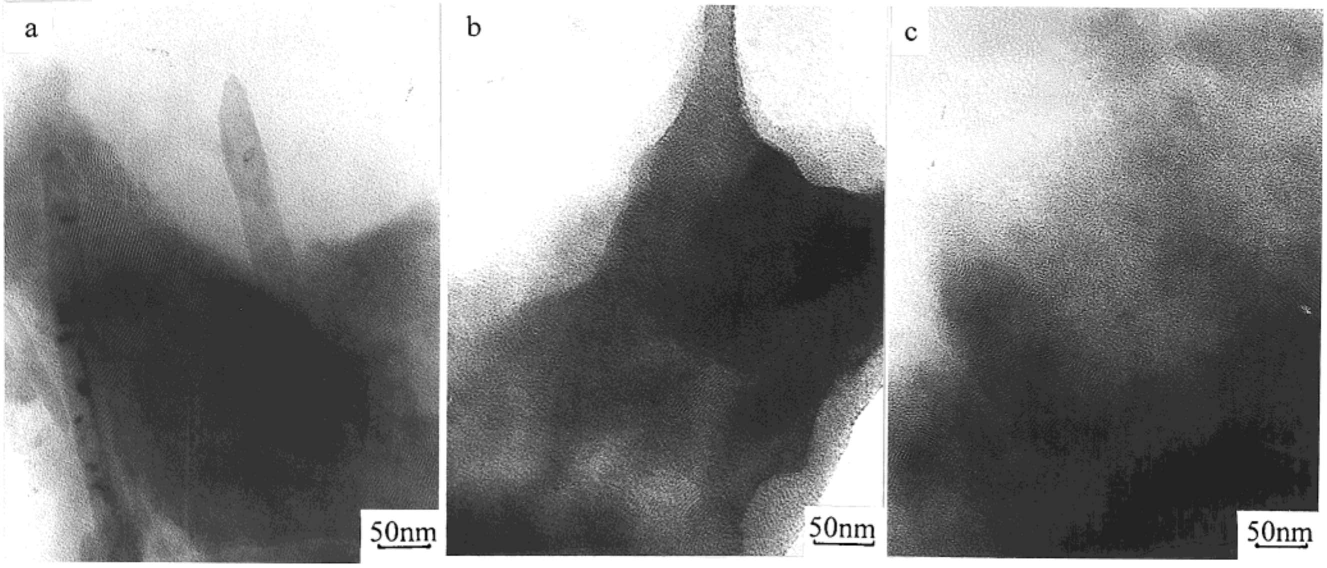

Figure 1. TEM pictures of the as-prepared samples sonicated at different times (h): (a) 1.5; (b) 3.0; (c) 6.0.

$ZrO(NO_3)_2$ and Y_2O_3 were used as the sources of zirconium and yttrium, respectively.

The molar ratio of Y/Zr was 1/1, and the molar ratio of (Y + Zr)/SDS/urea was 1/2/30. Typically, 0.28 g of Y_2O_3 was dissolved in a minimum amount of HNO_3 and heated until dry. A total of 60 mL of distilled water was then added to this mixture. To this solution were added under stirring 0.57 g of $ZrO(NO_3)_2$, 2.88 g of SDS, and 9.0 g of urea. The pH of this mixture was ca. 4.5. The mixture was sonicated at room temperature for 1.5, 3, or 6 h by a high-intensity ultrasonic probe (Misonix XL sonifier, 1.13 cm diameter Ti horn, 20 kHz, 100 W/cm^2). During sonication, the temperature of the reaction mixture rose to ca. 80 °C. After sonication, the suspension was centrifuged, washed with deionized water and ethanol, and dried in a vacuum. For the removal of the surfactant, sodium acetate was used, following Yada's method.[16]

Characterization. Low-angle (2−10°) X-ray powder diffraction (XRD) patterns were obtained using a Bruker D8 diffractometer, with Cu Kα irradiation. Transmission electron microscopy (TEM) studies were carried out on a JEOL 2000 electron microscope. The samples for TEM were prepared by dispersing the final powders in ethanol, which was dropped onto carbon−copper grids. Energy-dispersive X-ray analysis (EDAX) was carried out using a JEOL-JSM-840 electron microscope to ascertain the elemental content of Y and Zr in the mesophases. After the samples were dried at 170 °C for 1 h, nitrogen adsorption and desorption isotherms at 77 K were measured using Micromeritics (Gemini 2375). Surface areas were calculated from the linear part of the Brunauer−Emmett−Teller (BET) plot. Thermogravimetric analysis (TGA) was carried out on TGA/SDTA851^e to estimate the amount of surfactant incorporated in the mesophases. Infrared spectra were recorded by employing a Nicolet (impact 410) FT-IR spectrometer and the KBr disk method.

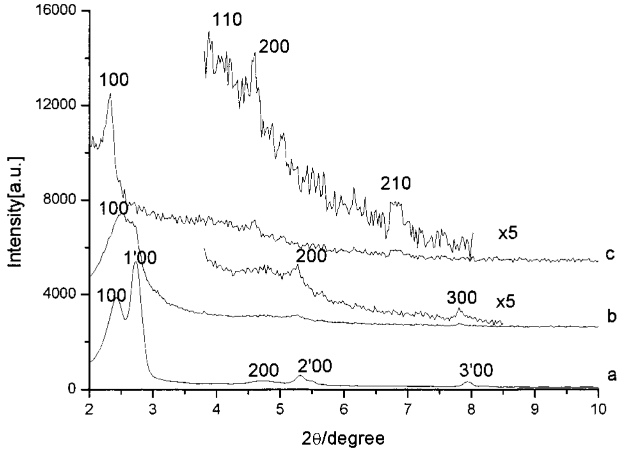

Figure 2. Low-angle XRD patterns of the as-prepared samples sonicated at different times (h): (a) 1.5; (b) 3.0; (c) 6.

Results and Discussion

Precipitation of $Y_2O_3-ZrO_2$ occurs when urea decomposes under ultrasound irradiation and releases NH_3. Layered and hexagonal mesophases with the molar ratio of Y/Zr at ca. 1/1 (from EDAX) were obtained after sonication for 1.5 and 6 h, and the pH of the suspension was 7.3 and 7.8, respectively. In the homogeneous precipitation,[16,18−21] the layered and hexagonal structures were obtained after heating for 4 and 10 (or 20) h, and the pH was ca. 7.3; only after heating for 78 h did the pH of the suspension reach 7.8. This indicates that ultrasound irradiation can accelerate the decomposition of urea, by creating localized hot spots through adiabatic compression. The high temperature at the interface of the collapsing bubble and the bulk solution also accelerates the condensation of yttrium and zirconium hydroxide, further shortening the synthesis time.

Figure 1 shows the TEM pictures of the as-prepared samples at different reaction times. It can be seen from Figure 1a that a straight-extended layered structure was obtained, with the interlayer spacing of ca. 3.5 nm and a wall thickness of ca. 1.0 nm. This spacing can be rationalized by assuming that SDS molecules are arranged as a bilayer between the inorganic layers. This straight-extended layered structure is similar to those obtained for most of silica/surfactant[25] and zirconia/surfactant[26] systems but is different from those obtained from homogeneous precipitation under heating.[16,19−21] In homogeneous precipitation under heating, the curled or "fingerprint" layered structure was obtained after 4 h. Yada[16] attributed the structure to the partial defect of YO_6 octahedra, enabling the surfactant molecules to occupy interlayer space. We thus attribute the straight-

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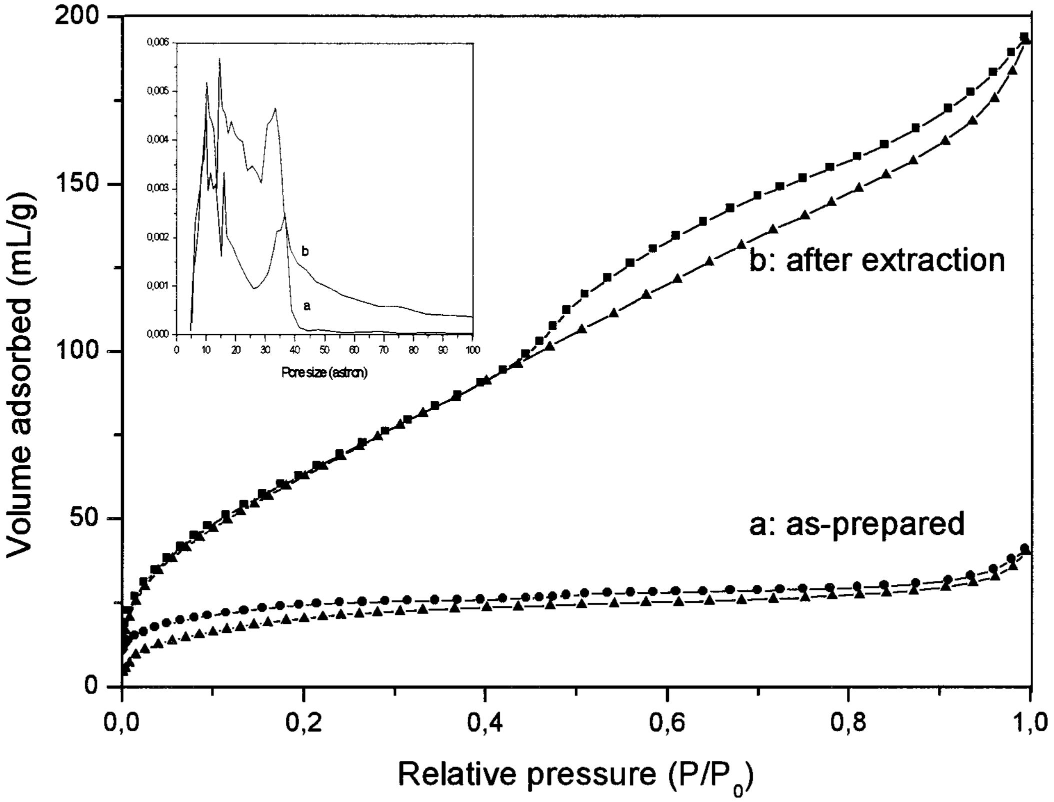

Figure 3. Adsorption/desorption isotherm of the hexagonal sample before and after extraction with sodium acetate.

extended layered structure to a small number of defects in the mesophases, because the high temperature at the gas/bulk interface favors condensation of yttrium and zirconium oxides. It can be seen from Figure 1c that a hexagonal array of channels with a short-range ordered structure was obtained after 6 h. This structure can also be detected clearly from the low-angle XRD pattern. Figure 2 shows the low-angle XRD patterns for the as-prepared samples at different reaction times. Figure 2a is the low-angle XRD pattern of the sample sonicated for 1.5 h. Unlike the normal layered structure which reveals one set of diffraction peaks, this shows two sets of diffraction peaks, and the interlayer spacings of the layered structures are 3.65 and 3.20 nm, respectively. Yada mentioned the same phenomenon. Figure 2c is the low-angle XRD pattern of the sample sonicated for 6 h. It shows that there is a strong peak in low-angle diffraction and three weak peaks in higher angle diffraction, which can be attributable to 100, 110, 200, and 210 reflections, indicating the formation of hexagonal structure after sonication for 6 h. The *d* spacing from the lowest angle diffraction peak is 3.8 nm, and the unit cell parameter is 4.4 nm.

This lamellar to hexagonal transition can be explained in terms of interlayer condensation and subsequent rearrangement of the surfactant. The increase in pH caused by the decomposition of urea would result in interlayer condensation and cross-linking between adjacent oxides or hydroxides. This would proceed cooperatively with partial release of the surfactant molecules and their rearrangement into a more stable, rodlike assembly. This transformation can already be seen after sonication for 3 h. The low-angle XRD pattern after sonication for 3 h, in Figure 2, shows one strong peak in the low-angle diffraction region and two weak peaks in the high-angle diffraction region, indicating transformation from layered to hexagonal structure. The TEM picture in Figure 1b shows the coexistence of layered and hexagonal mesostructures, indicating that this is a transition state.

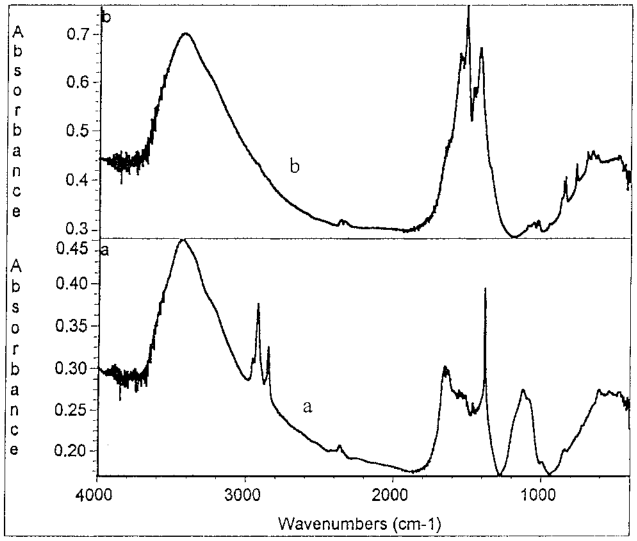

Figure 4. FTIR spectra of the sample before (a) and after extraction (b).

The lamellar and hexagonal structures have both collapsed after extraction with sodium acetate or upon calcination at 400 °C for 4 h, but the surface area of the hexagonal sample after extraction is still high. Figure 3 shows the N_2 adsorption/desportion isotherms of the as-prepared samples with hexagonal mesostructure before and after extraction with sodium acetate. For the as-prepared samples, the adsorption/desorption isotherms are open curves, indicating that there should

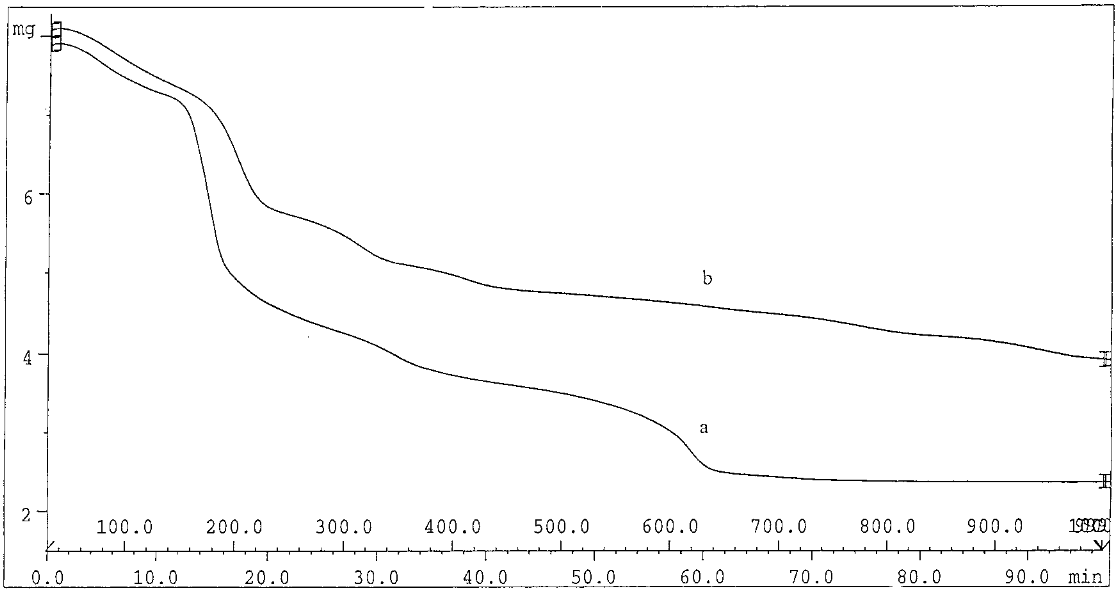

Figure 5. TGA profiles of the as-prepared samples sonicated for (a) 1.5 h and (b) 6 h.

be a strong physical adsorption of N_2 molecules at the interface of the material, and the N_2 molecules adsorbed on the interface cannot be desorbed completely at low pressure. The surface area for hexagonal material was 98 m^2/g, and the total pore volume was very low, just 0.085 mL/g. After extraction with sodium acetate, the SDS molecules were removed completely, and the surface area and pore volume were increased, reaching 245 m^2/g and 0.3 mL/g, respectively. The inset in Figure 3 shows the wide pore size distribution for the post-treated sample. This wide pore size distribution after extraction is indicative of the collapse of the ordered hexagonal structure and the formation of a bottleneck structure.

The incorporation of SDS into mesoporous structures was detected from Fourier transform infrared (FTIR) spectra. Figure 4a shows the FTIR spectrum of the as-prepared sample. The two sharp peaks at 2846 and 2916 cm^{-1} are due to $-CH_2-$ groups, and the shoulder peak at 2958 cm^{-1} is attributed to CH_3- groups. The broad peak in the range of 1300–1700 cm^{-1} is attributed to CO_3^{2-}, which comes from the decomposition of urea, along with some peaks assignable to SDS. The other broad peak in the range of 1000–1300 cm^{-1} may be attributed to $-OSO_3^-$. These bands provide evidence of the incorporation of SDS into the hydroxide. Figure 4b is the FTIR spectrum of the post-treated sample and shows that the bands of SDS disappear after extraction with sodium acetate.

The dodecyl sulfate Y/Zr ratio of the layered and hexagonal mesophase was estimated from TGA. The TGA weight losses in parts a and b of Figure 5 indicate the removal of SDS in the ranges of 0–360 °C and 0–610 °C, respectively. The weight loss was ca. 68% for the layered mesophase and ca. 29% for the hexagonal mesophase, consistent with Yada's data.[16] For the hexagonal mesophase, there is a slow weight loss at high temperatures, attributed to the loss of water that is produced by condensation of neighboring terminal hydroxyl groups.

Conclusion

The sonochemical method is a useful and simple way to synthesize layered and hexagonal yttrium–zirconium oxides. A straight-extended layered mesostucture was obtained after sonication for 1.5 h; the hexagonal mesostructure with four diffraction peaks in low-angle XRD was obtained after sonication for 6 h. In particular, successful results of mesoporous YSZ are also obtained when carboxylic acids are used as the templating agents. These attempts are reported separately.

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