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# Rapid Synthesis of Mesoporous Yttrium–Zirconium Oxides with Ultrasound Irradiation

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## Introduction

Increasing attention has been paid to mesoporous materials since the discovery of the ordered mesoporous M41S,<sup>1</sup> primarily because of their applications as catalysts, molecular sieves, and host materials based on their large internal surface areas and narrow pore size distributions. Mesophase oxides of titanium, niobium, zirconium, and other metals have been prepared.<sup>2–5</sup> However, there have been very few reports on the synthesis of micro- and mesoporous yttrium–zirconium oxides, although yttria-stabilized zirconia is the material of choice for use in solid oxide fuel cells (SOFC).<sup>6</sup> It may be used as the electrolyte<sup>7</sup> or in the anode (mixed with NiO<sup>7</sup>) or in the cathode (mixed with LSM<sup>7</sup>).

Ozin et al.<sup>8,9</sup> used CTAB as a template to synthesize mesoporous yttria–zirconia with a high surface area (260 m<sup>2</sup>/g, calcined at 450 °C) and high thermal stability, but the zirconium precursor must be modified with ethylene glycol and a long time was also required (as long as 5 days).<sup>8</sup> In their more recent report,<sup>9</sup> the reaction time was cut drastically to only 1 day.

Sonochemical processing has been proven to be a useful technique for generating novel materials with unusual properties.<sup>10,11</sup> We have recently reported the synthesis of mesoporous TiO<sub>2</sub> with high surface area using a sonochemical method. It was proposed that the high temperature created in the sonochemical process at the gas–solution interface could accelerate the condensation of titanium hydroxyl and further shorten the synthesis time.<sup>12</sup> Recently, Antonelli<sup>13</sup> reported a new method for the synthesis of micro- and mesoporous zirconia, using carboxylic acids of various chain lengths as templates. High surface area

was obtained, but it required a very long time (25 days). In the work that we report below, we have attempted to synthesize mesoporous yttria–zirconia with high thermal stability and to shorten the synthesis time. Octanoic acid (C<sub>7</sub>H<sub>15</sub>COOH) and  $\omega$ -undecenoic acid (C<sub>10</sub>H<sub>19</sub>COOH) were used as the templating agents in these sonochemical reactions.

## Experimental Procedure

**Synthesis.** The molar ratio of Y/Zr in solution was always 1/1, and the molar ratio of (Y + Zr)/carboxylic acid in solution was 1/0.7. Typically, 0.28 g of Y<sub>2</sub>O<sub>3</sub> was dissolved in a minimum amount of HNO<sub>3</sub> and the solution was heated to dryness; then, 40 mL of distilled water was added. In another bottle, 1.0 g of Zr(*i*-OPr)<sub>4</sub> was mixed with 1.0 g of octanoic acid and this mixture was heated to form a homogeneous solution. The previously prepared solution of yttrium salt in water was then added to this solution with stirring. The pH of the mixture was adjusted to 5.0 with ammonium hydroxide, and the mixture was allowed to age overnight. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (0.1 g) was added to the above suspension, and the mixture was then sonicated for 6 h, as reported elsewhere.<sup>12</sup> The as-prepared sample was obtained by centrifugation, washed with distilled water and ethanol, and dried at 110 °C overnight. For the removal of carboxylic acid, the as-prepared sample was calcined at 400 °C for 1 h (ramp 1 °C/min). A similar procedure was used when  $\omega$ -undecenoic acid was employed as the template molecule.  $\omega$ -Undecenoic acid was dissolved in 10 mL of 2-propanol before the addition of Zr(*i*-OPr)<sub>4</sub> because an amorphous product was obtained when  $\omega$ -undecenoic and Zr(*i*-OPr)<sub>4</sub> were mixed together in the absence of 2-propanol.

**Characterization.** Low-angle (2–10°) and wide-angle X-ray powder diffraction (XRD) patterns were obtained using a Bruker D8 diffractometer, with Cu K $\alpha$  irradiation. Transmission electron microscopy (TEM) studies were carried out on a JEOL 2000 electron microscope. Energy-dispersive X-ray analysis (EDXA) was carried out using a JEOL-JSM-840 electron microscope to ascertain the elemental content of Y and Zr in the mesophases. The elemental analysis was carried out using an Eager 200 instrument to ascertain the content of sulfur in the sample before and after calcination. The thermogravimetric analysis (TGA) measurements were carried out on a Mettler Toledo TGA/SDTA 851<sup>e</sup>, to estimate the amount of surfactant incorporated in the mesostructure. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics Gemini 2375 instrument, after the samples were dried at 170 °C for 1 h. Brunauer–Emmett–Teller (BET) surface areas were calculated from the linear part of the BET plot.

## Results and Discussion

When octanoic acid (C<sub>7</sub>H<sub>15</sub>COOH) was used as a templating agent and Zr(*i*-OPr)<sub>4</sub> and Y<sub>2</sub>O<sub>3</sub> were used as precursors, mesoporous yttria–zirconia was obtained. The molar ratio of Y/Zr was 16.5/83.5 after sonication (from EDXA), which is much lower than the initial solution Y/Zr ratio of 1/1. This is because the precipitation process was done in a weakly acidic environment (pH  $\approx$  5) and the required pH for the precipitation of Y<sup>3+</sup> ions is  $\sim$ 7, so yttrium ions cannot precipitate completely.

Figure 1a shows the low-angle XRD pattern for the as-prepared sample. It can be seen that there is one broad peak, with a *d* spacing of 2.2 nm. Owing to the broadness of this reflection, it is difficult to index the patterns of any particular phase, but the TEM picture provides further information. Figure 2a is the TEM picture of the as-prepared sample, which shows the wormholelike structures. After calcination at 400 °C for 1 h, the mesostructure is still maintained. The low-angle XRD pattern is shown

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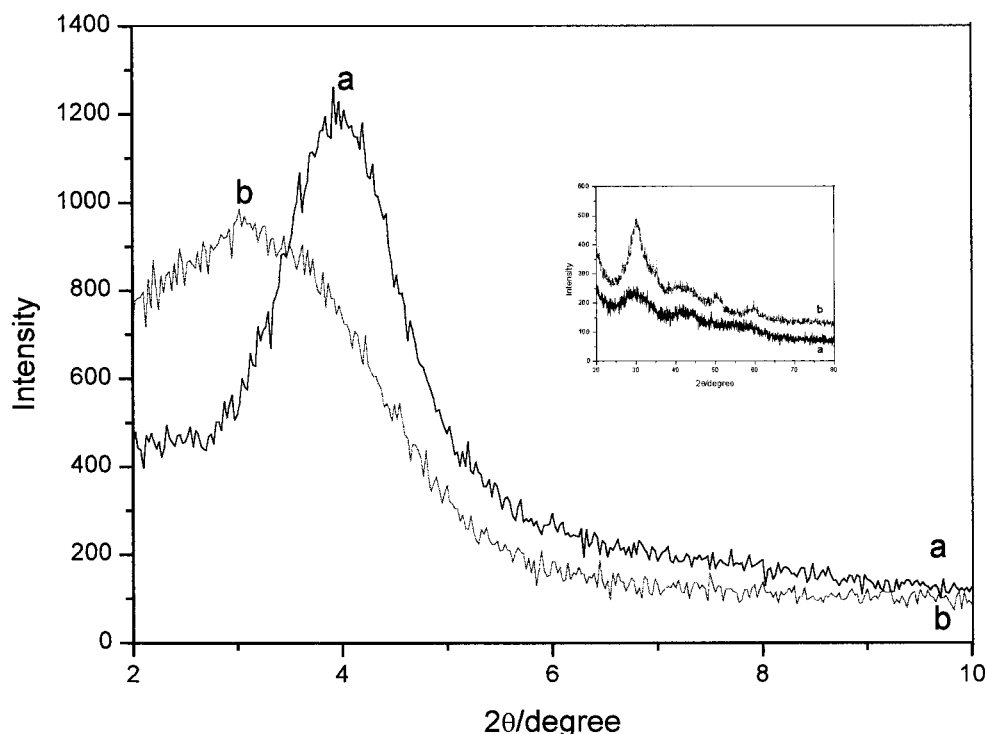
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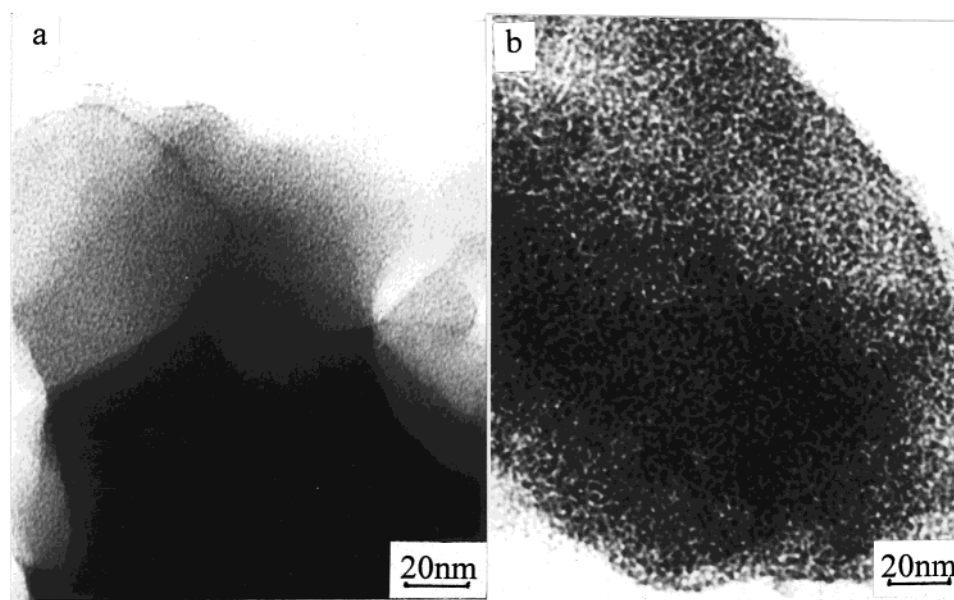
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**Figure 1.** Low-angle XRD patterns of the sample prepared using octanoic acid as the templating agent: (a) as-prepared sample and (b) after calcination at 400 °C. (Inset) Wide-angle XRD: (a) as-prepared sample and (b) after calcination at 400 °C.

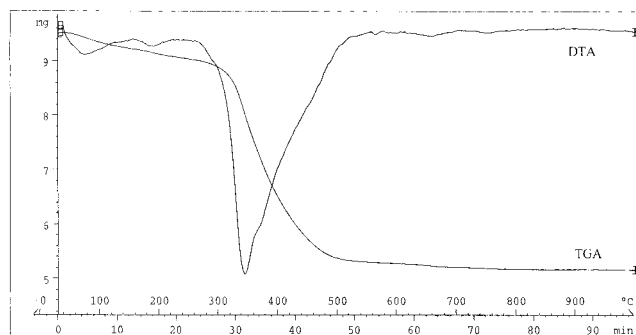


**Figure 2.** TEM pictures of the samples described in Figure 1: (a) as-prepared sample and (b) after calcination at 400 °C.

in Figure 1b. It can be seen from Figure 1 that after calcination, the diffraction peak shifts to lower angle with the  $d$  spacing becoming larger, ca. 2.8 nm. The increased  $d$  spacing is consistent with the collapse of walls between neighboring pores leading to materials with larger pore sizes. Figure 2b also shows the TEM picture of the calcined sample; it still shows the wormholelike structures. The larger  $d$  spacing after calcination is different from that reported by Antonelli.<sup>13</sup> In his work, the  $d$  spacing became smaller after calcination at 400 °C. This indicates that the mesoporous yttria–zirconia prepared sonochemically is more stable than mesoporous zirconia prepared by his method (involving heating at different temperatures for 25 days). The enhanced stability and the shortened

synthesis time (25 days vs 6 h) are two advantages of our sonochemical approach.

The inset in Figure 1 depicts the wide-angle XRD patterns of the as-prepared sample and the sample after calcination. The as-prepared sample has a crystalline wall with an nc-YZ structure, which is very different from the samples synthesized by Ozin.<sup>8,9</sup> (In Ozin's work,<sup>8,9</sup> the wall begins to crystallize at 400 °C). After calcination at 400 °C for 1 h, the diffraction peaks become sharper, indicating the growth of the wall particles under calcination. Elemental analysis shows that the sulfur content before and after calcination is 8.7 and 0%, respectively. This result is different from that reported by Antonelli.<sup>13</sup> In his report, the content of sulfur after calcination is 2%. The incor-



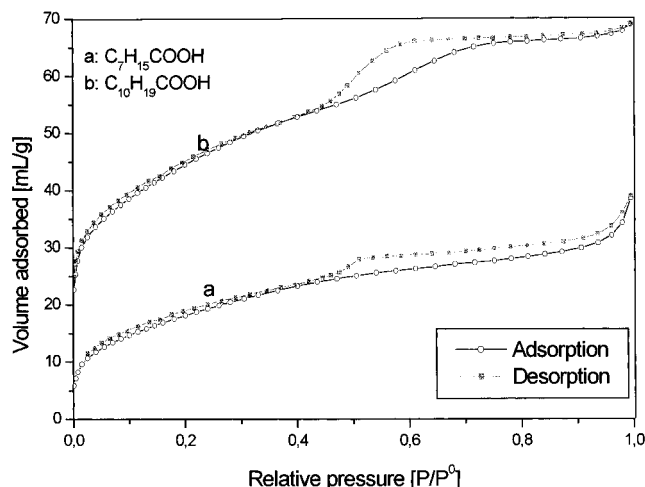
**Figure 3.** TGA and DTA profiles of the as-prepared sample synthesis with octanoic acid as the templating agent.

poration of sulfur in the structure of mesoporous  $\text{ZrO}_2$  is considered important for the thermal stability.<sup>14</sup> In the current experiment, the thermal stability of the mesoporous yttria–zirconia is determined by the effect of yttrium. This is due to the stabilization effect of yttrium on the zirconia structure. Another possible explanation for the crystalline wall of the as-prepared sample is related to the sonication process. Further calcination just increases the particle size, rather than destroying the porous structure.

The formation of the mesostructures by using carboxylic acid templates is explained by Antonelli,<sup>13</sup> based on a new mechanism, in which the self-assembly step and the condensation step occur simultaneously with the propagation of the growing polymer chain; the heating process makes the pre-existing ordered structure interconnected with the more highly ordered mesostructure. In the sonochemical process, the high temperature at the interface of the gas phase and the bulk solution can accelerate the condensation of metal hydroxyl and further shorten the synthesis time.

The removal of the carboxylic acid from the mesophase is estimated by TGA measurements. The TGA weight loss in Figure 3 is ca. 43.5%. The weight loss which occurs in the temperature range of 0–300 °C is attributed to the desorption of the solvent. On the other hand, the weight loss in the temperature range of 300–460 °C originates from the removal of the carboxylic acid. The sharp endothermic peak at 380 °C in the DTA profile confirms this result.

If  $\omega$ -undecenoic acid ( $\text{C}_{10}\text{H}_{19}\text{COOH}$ ) was used as a templating agent and mixed with  $\text{Zr}(i\text{-OPr})_4$  in the absence of 2-propanol, an amorphous material is obtained. This is because  $\omega$ -undecenoic acid has a long alkyl chain, leading to its insolubility in water. However, when  $\omega$ -undecenoic acid ( $\text{C}_{10}\text{H}_{19}\text{COOH}$ ) was dissolved in 2-propanol and mixed with  $\text{Zr}(i\text{-OPr})_4$ , mesoporous yttria–zirconia with the molar ratio of  $\text{Y}/\text{Zr} = 13/87$  was also obtained; the  $d$ spacing



**Figure 4.** The adsorption/desorption isotherms of the samples after calcination at 400 °C: (a) octanoic acid and (b) undecenoic acid used as templates.

was 2.4 nm (a little larger than that with an octanoic acid template). In the two cases, the  $d$  spacings are smaller than the length of the fully stretched two carboxylic acids (octanoic acid length = 11.8 nm, undecenoic acid length = 15.2 nm). This can be attributed to the curving of the alkyl chain.

Figure 4 is the adsorption/desorption isotherm of the samples calcined at 400 °C. It shows a strong hysteresis loop, consistent with partial degradation of the walls of the structure leading to an extended network of pores. The surface areas are 80 and 203  $\text{m}^2/\text{g}$  for octanoic and undecenoic acids. These values are smaller than those reported by Antonelli.<sup>13</sup> Mesoporous zirconia is usually yielding relatively low surface areas compared with the silicas, titanias, and niobias. Any explanation for the low surface area obtained by the sonochemical method is speculative at this stage. The calculated pore sizes are 1.5 and 1.7 nm (using the BJH method) for the octanoic acid and undecenoic acid, respectively. The pore size distributions are wide.

Sonochemistry is a novel route for the synthesis of micro- and mesoporous materials. In this work, the mesoporous yttrium–zirconium oxides with thermal stability were obtained after sonication of 6 h, much shorter than the general sol–gel method for the synthesis of mesoporous zirconium oxide (25 days).

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