

## Preparation of Er<sub>2</sub>O<sub>3</sub> Nanorod Catalyst without Using Organic Additive and Its Application to Catalytic Dehydration of 1,4-Butanediol

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Er<sub>2</sub>O<sub>3</sub> nanorods were successfully prepared with hydrothermal treatment without using organic additives such as surfactant, fatty acid, or alcohol. Er<sub>2</sub>O<sub>3</sub> nanorods were obtained under high temperature and/or long reaction times. Er<sub>2</sub>O<sub>3</sub> nanorods mainly exposed {440} and {400} facets on the surface. Er<sub>2</sub>O<sub>3</sub> nanorods showed excellent catalytic activity compared to commercial Er<sub>2</sub>O<sub>3</sub> nanoparticles in the dehydration of 1,4-butanediol to produce 3-buten-1-ol.

It is well known that rare earth oxides (REOs) with cubic phase, such as CeO<sub>2</sub> and Er<sub>2</sub>O<sub>3</sub>, consist of ordinary spherical or octahedral nanocrystals, which are usually called nanoparticles. Several groups have recently prepared unusually shaped CeO<sub>2</sub> nanocrystals such as nanorods,<sup>1–3</sup> nanocubes,<sup>2,4</sup> nanoplates,<sup>3</sup> triangular microplates,<sup>5</sup> nanotubes,<sup>6</sup> and nanotadpoles<sup>7</sup> by hydrothermal (HT) treatment or solvothermal methods. These nanocrystals expose specific crystal facets on the surface. For example, CeO<sub>2</sub> nanorod mainly exposes both {220} and {200} facets on the surface and CeO<sub>2</sub> nanocube exposes only {200} facet, whereas CeO<sub>2</sub> nanoparticles mainly expose {111} facet.<sup>1,2,4</sup> In the oxidation of carbon monoxide, Au deposited on CeO<sub>2</sub> nanorod is more active than Au on CeO<sub>2</sub> nanoparticle.<sup>8</sup> Nguyen et al. prepared Er<sub>2</sub>O<sub>3</sub> nanorods and nanocrystals with several shapes via solvothermal reaction in water, ethanol, and decanoic acid.<sup>9</sup> Other REO nanorods are also prepared with organic additives.<sup>10</sup> There is only one report on CeO<sub>2</sub> nanorods prepared without organic substance but with sodium hydroxide.<sup>2</sup> Unfortunately, organic additives and residual metal cations often work as catalytic poison. It is desired that oxide catalysts are prepared without organic additives and metal-containing bases.

In our previous work,<sup>11</sup> 1,4-butanediol was dehydrated to 3-buten-1-ol with selectivity higher than 90% over commercial Er<sub>2</sub>O<sub>3</sub> nanoparticles, and it was speculated that active sites of this reaction exist on {222} facet. Much more data, however, are required to discuss active crystal facets on the catalysis. The purpose of this work is to prepare Er<sub>2</sub>O<sub>3</sub> nanorods without organic additives and to investigate catalytic activity of Er<sub>2</sub>O<sub>3</sub> nanorods in order to ascertain whether the active sites exist on {440} and {400} facets.

Commercial Er<sub>2</sub>O<sub>3</sub> nanoparticles, supplied by Kanto Chemical Co., Ltd., Japan, were calcined at 500, 650, 800, and 1000 °C, which have specific surface areas of 33.5, 26.8, 21.5, and 13.6 m<sup>2</sup> g<sup>−1</sup>, respectively. Er<sub>2</sub>O<sub>3</sub> nanoparticle or nanorod catalyst was prepared with a HT method. Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (4.64 g, as 2.0 g of Er<sub>2</sub>O<sub>3</sub>, Sigma-Aldrich, USA) was dissolved in 50 mL of distilled water. Then, the pH of the solution was adjusted to 10 with 25 wt % aqueous ammonia (Wako, Japan) with stirring. No additives such as amine, fatty acid, or alcohol were added. The solution was transferred into a 100-cm<sup>3</sup> Teflon-lined autoclave. Hydrothermal treatment was carried out at a prescribed temperature for a prescribed period. The resulting precipitate was

filtered, washed, dried at 110 °C for 12 h, and calcined at 400 °C for 3 h. Here, commercial Er<sub>2</sub>O<sub>3</sub> is named as “CM-(calcination temperature (°C)),” and the prepared Er<sub>2</sub>O<sub>3</sub> is named as “HT-(HT temperature (°C))-(HT time (h)).”

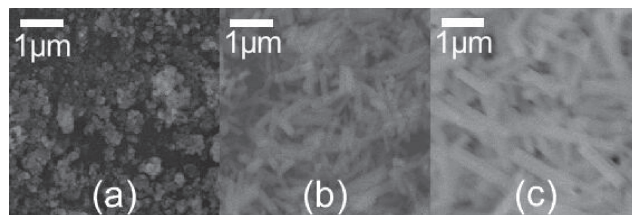
Specific surface area (SA) of the sample was calculated by the Brunauer–Emmett–Teller (BET) method using the N<sub>2</sub> adsorption isotherm at −196 °C. Scanning electron microscope (SEM) and high-resolution transmission electron microscope (TEM) images were taken on a JEOL JSM-6510 microscope operated at 20–30 kV and on a Hitachi HF-2200 microscope operated at 200 kV, respectively.

Vapor-phase catalytic dehydration of 1,4-butanediol to produce 3-buten-1-ol was performed at 350 °C in a fixed-bed down-flow reactor under atmospheric pressure of N<sub>2</sub> at a flow rate of 30 cm<sup>3</sup> min<sup>−1</sup>. After 0.3 g of catalyst was preheated at 400 °C for 1 h, 1,4-butanediol was fed into the reactor at a liquid flow rate of 1.8 cm<sup>3</sup> min<sup>−1</sup>. A reaction mixture recovered every hour was analyzed by gas chromatography (GC-2014, Shimadzu, Japan) with a 30-m capillary column (Rtx-Wax, RESTEK, USA).

SEM images in Figure 1 show changes in shape of Er<sub>2</sub>O<sub>3</sub> prepared by hydrothermal synthesis at 150 °C as HT time increases. In the images, nanoparticles were first formed (Figure 1a) and then they were converted to nanorods. The average length and width of Er<sub>2</sub>O<sub>3</sub> nanorods were increased from 0.8 × 0.2 to 1.6 μm × 0.3 μm with increasing HT time from 24 to 48 h. The same behavior was observed at HT temperature of 200 °C. It was found neither organic additives nor organic solvents were essential to prepare Er<sub>2</sub>O<sub>3</sub> nanorods.

Figure 2 shows TEM image of HT-200-24. The Er<sub>2</sub>O<sub>3</sub> nanorod exposed {440} and {400} facets on the surface parallel to the longitudinal edge. However, it was not clear that {222} facet was exposed. The orientation of crystal facets on the surface is in good harmony with CeO<sub>2</sub> nanorods reported previously.<sup>1,2</sup> Several SEM and TEM images of Er<sub>2</sub>O<sub>3</sub> prepared under HT conditions are displayed in Figure S1.<sup>12</sup>

Figure 3 summarizes morphology of HT-prepared Er<sub>2</sub>O<sub>3</sub> nanomaterials, together with the SA values. At HT temperature of 100 °C, Er<sub>2</sub>O<sub>3</sub> nanoparticles were first formed after 6 h (Figure S1<sup>12</sup>). The nanoparticles were converted to nanorods after 24 h, and surface area was decreased from 18.2 to 8.5 m<sup>2</sup> g<sup>−1</sup> with increasing HT time from 24 to 48 h. However, the morphology



**Figure 1.** SEM images of Er<sub>2</sub>O<sub>3</sub> prepared under HT conditions. (a) HT-150-1; (b) HT-150-24; (c) HT-150-48.

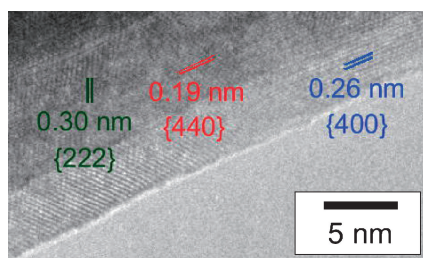


Figure 2. High-resolution TEM image of HT-200-24.

|                     |           | HT time (h) |        |       |
|---------------------|-----------|-------------|--------|-------|
| HT temperature (°C) | Particles |             |        |       |
|                     | Rods      | 6           | 24     | 48    |
|                     | 100       | (26.2)      | (18.2) | (8.5) |
|                     | 150       | (10.3)      | (14.0) | (5.6) |
| 200                 | (13.5)    | (12.6)      | (11.8) |       |

Figure 3. Physical properties of HT  $\text{Er}_2\text{O}_3$  nanomaterials. The number in parenthesis indicates specific surface area ( $\text{m}^2 \text{g}^{-1}$ ).

Table 1. Dehydration of 1,4-butanediol over  $\text{Er}_2\text{O}_3$  catalysts<sup>a</sup>

| Code      | Conv. /% | Selectivity/mol % |                  |                  |
|-----------|----------|-------------------|------------------|------------------|
|           |          | 3-Buten-1-ol      | THF <sup>b</sup> | GBL <sup>b</sup> |
| CM-800    | 49.3     | 75.3              | 6.7              | 1.9              |
| CM-1000   | 48.2     | 83.9              | 5.9              | 1.0              |
| HT-100-24 | 71.0     | 81.3              | 6.6              | 0.8              |
| HT-150-24 | 51.5     | 81.8              | 3.9              | 2.0              |
| HT-200-24 | 55.5     | 77.9              | 3.0              | 1.7              |

<sup>a</sup>Conversion and selectivity were averaged in the initial 5 h. <sup>b</sup>THF: tetrahydrofuran, GBL:  $\gamma$ -butyrolactone.

transformation at high temperatures is faster than that at 100 °C. According to X-ray diffraction profiles of  $\text{Er}_2\text{O}_3$  nanomaterials (Figure S2<sup>12</sup>), all the HT-prepared  $\text{Er}_2\text{O}_3$  nanomaterials as well as commercial  $\text{Er}_2\text{O}_3$  samples had cubic bixbyite phase. There is no clear difference in the peak intensity among the  $\text{Er}_2\text{O}_3$  samples.

Table 1 compares conversion and selectivity between HT-prepared and commercial  $\text{Er}_2\text{O}_3$  samples. The HT-prepared  $\text{Er}_2\text{O}_3$  showed high conversion of 1,4-butanediol with high selectivity to 3-buten-1-ol. In the dehydration of 1,4-butanediol over commercial  $\text{Er}_2\text{O}_3$ , the conversion was maximized at 54.8% at calcination temperature of 650 °C (Table S1<sup>12</sup>). In contrast, the selectivity to 3-buten-1-ol was increased from 58.9 to 83.9% with increasing calcination temperature from 500 to 1000 °C. The results show a similar tendency to a previous report.<sup>11</sup> In the dehydration over the HT-prepared  $\text{Er}_2\text{O}_3$ , the 1,4-butanediol conversion was in the range between 42.2 and 71.0% (Table S2<sup>12</sup>). The conversion values are quite high irrespective of the small specific surface area. The selectivity to 3-buten-1-ol was higher than 74.5%, and it is as high as the selectivity of CM-800 and CM-1000.

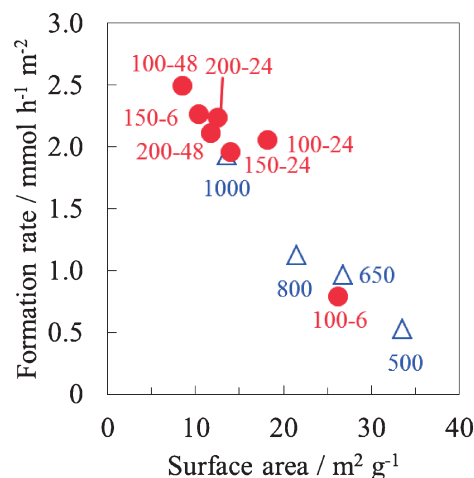


Figure 4. Dehydration of 1,4-butanediol over  $\text{Er}_2\text{O}_3$  catalysts: (filled circle) HT synthesis and (open triangle) commercial. Reaction temperature, 350 °C; reaction time, 5 h.

Since specific surface area of each catalyst is different, Figure 4 compares formation rate of 3-buten-1-ol per unit surface area as an intrinsic catalytic activity. The intrinsic catalytic activity of commercial  $\text{Er}_2\text{O}_3$  was increased from 0.52 to  $1.93 \text{ mmol h}^{-1} \text{ m}^{-2}$  with increasing calcination temperature. The intrinsic catalytic activity of HT-prepared  $\text{Er}_2\text{O}_3$  nanorods except HT-100-6 was higher than that of CM-1000, while the exposed surface of  $\text{Er}_2\text{O}_3$  nanorod was different from those of  $\text{Er}_2\text{O}_3$  nanoparticles. This illustrates active sites for the dehydration of alkanediol probably exist not only on {222} facet but also on {440} and/or on {400} facets. In contrast, HT-100-6 is less active, which is as low as CM-500 and CM-650. As shown in SEM and TEM images of HT-100-6 nanoparticle,<sup>12</sup> this catalyst does not grow each crystal plane on the surface.

In conclusion,  $\text{Er}_2\text{O}_3$  nanorods were prepared without using organic additives, and exposed {440} and {400} facets on the surface.  $\text{Er}_2\text{O}_3$  nanorods show high catalytic activity in the dehydration of 1,4-butanediol to produce 3-buten-1-ol. The nanorod structure of  $\text{Er}_2\text{O}_3$  is maintained during the catalytic dehydration (Figure S3<sup>12</sup>).

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