doi:10.1246/cl.2012.593

Preparation of Er_2O_3 Nanorod Catalyst without Using Organic Additive and Its Application to Catalytic Dehydration of 1,4-Butanediol

Fumiya Sato, Yasuhiro Yamada, and Satoshi Sato*
Graduate School of Engineering, Chiba University, 1-33 Yayoi, Inage-ku, Chiba 263-8522

(Received March 5, 2012; CL-120188; E-mail: satoshi@faculty.chiba-u.jp)

Er_2O_3 nanorods were successfully prepared with hydrothermal treatment without using organic additives such as surfactant, fatty acid, or alcohol. Er_2O_3 nanorods were obtained under high temperature and/or long reaction times. Er_2O_3 nanorods mainly exposed {440} and {400} facets on the surface. Er_2O_3 nanorods showed excellent catalytic activity compared to commercial Er_2O_3 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_2 and Er_2O_3, consist of ordinary spherical or octahedral nanocrystals, which are usually called nanoparticles. Several groups have recently prepared unusually shaped CeO_2 nanocrystals such as nanorods,[1–3] nanocubes,[2,4] nanoplates,[3] triangler microplates,[5] nanotubes,[6] and nanotadpoles[7] by hydrothermal (HT) treatment or solvothermal methods. These nanocrystals expose specific crystal facets on the surface. For example, CeO_2 nanorod mainly exposes both {220} and {200} facets on the surface and CeO_2 nanocube exposes only {200} facet, whereas CeO_2 nanoparticles mainly expose {111} facet.[1,2,4] In the oxidation of carbon monoxide, Au deposited on CeO_2 nanorod is more active than Au on CeO_2 nanoparticle.[8] Nguyen et al. prepared Er_2O_3 nanorods and nanocrystals with several shapes via solvothermal reaction in water, ethanol, and decanoic acid.[9] Other REO nanorods are also prepared with organic additives.[10] There is only one report on CeO_2 nanorods prepared without organic substance but with sodium hydroxide.[2] 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,[11] 1,4-butanediol was dehydrated to 3-buten-1-ol with selectivity higher than 90% over commercial Er_2O_3 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_2O_3 nanorods without organic additives and to investigate catalytic activity of Er_2O_3 nanorods in order to ascertain whether the active sites exist on {440} and {400} facets.

Commercial Er_2O_3 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 $m^2\,g^{-1}$, respectively. Er_2O_3 nanoparticle or nanorod catalyst was prepared with a HT method. $Er(NO_3)_3 \cdot 5H_2O$ (4.64 g, as 2.0 g of Er_2O_3, 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^3 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_2O_3 is named as "CM-(calcination temperature (°C))," and the prepared Er_2O_3 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_2 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_2 at a flow rate of 30 $cm^3\,min^{-1}$. 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 $cm^3\,min^{-1}$. 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_2O_3 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_2O_3 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_2O_3 nanorods.

Figure 2 shows TEM image of HT-200-24. The Er_2O_3 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_2 nanorods reported previously.[1,2] Several SEM and TEM images of Er_2O_3 prepared under HT conditions are displayed in Figure S1.[12]

Figure 3 summarizes morphology of HT-prepared Er_2O_3 nanomaterials, together with the SA values. At HT temperature of 100 °C, Er_2O_3 nanoparticles were first formed after 6 h (Figure S1[12]). The nanoparticles were converted to nanorods after 24 h, and surface area was decreased from 18.2 to 8.5 $m^2\,g^{-1}$ with increasing HT time from 24 to 48 h. However, the morphology

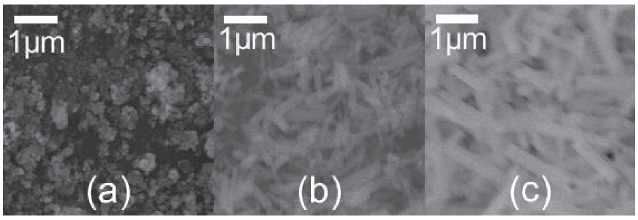

Figure 1. SEM images of Er_2O_3 prepared under HT conditions. (a) HT-150-1; (b) HT-150-24; (c) HT-150-48.

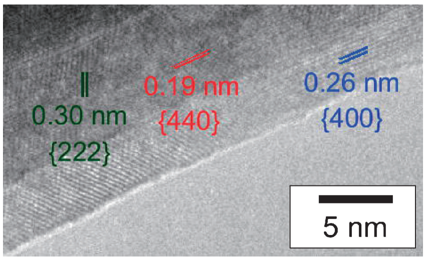

Figure 2. High-resolution TEM image of HT-200-24.

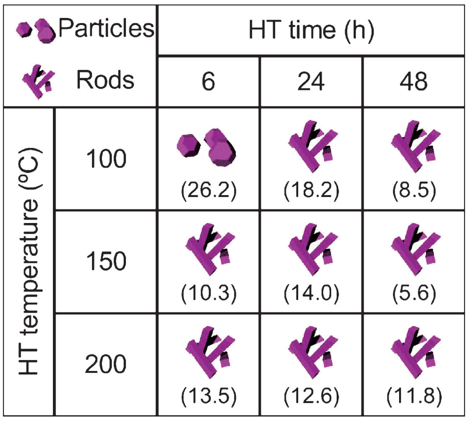

Figure 3. Physical properties of HT Er_2O_3 nanomaterials. The number in parenthesis indicates specific surface area ($m^2\,g^{-1}$).

Table 1. Dehydration of 1,4-butanediol over Er_2O_3 catalysts[a]

Code	Conv. /%	Selectivity/mol %		
		3-Buten-1-ol	THF[b]	GBL[b]
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

[a] Conversion and selectivity were averaged in the initial 5 h. [b] THF: tetrahydrofuran, GBL: γ-butyrolactone.

transformation at high temperatures is faster than that at 100 °C. According to X-ray diffraction profiles of Er_2O_3 nanomaterials (Figure S2[12]), all the HT-prepared Er_2O_3 nanomaterials as well as commercial Er_2O_3 samples had cubic bixbyite phase. There is no clear difference in the peak intensity among the Er_2O_3 samples.

Table 1 compares conversion and selectivity between HT-prepared and commercial Er_2O_3 samples. The HT-prepared Er_2O_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 Er_2O_3, the conversion was maximized at 54.8% at calcination temperature of 650 °C (Table S1[12]). 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.[11] In the dehydration over the HT-prepared Er_2O_3, the 1,4-butanediol conversion was in the range between 42.2 and 71.0% (Table S2[12]). 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.

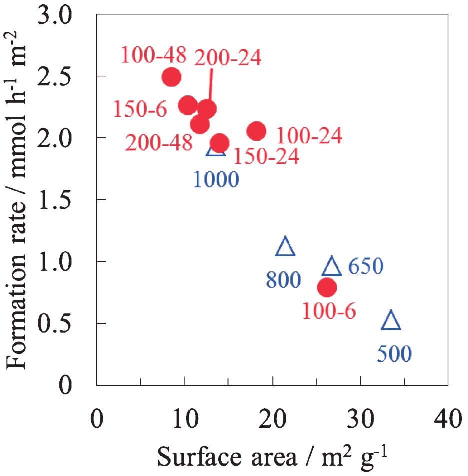

Figure 4. Dehydration of 1,4-butanediol over Er_2O_3 catalysts: (filled circle) HT synthesis and (open triangle) commercial. Reaction temperature, 350 °C; reaction time, 5 h.

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 Er_2O_3 was increased from 0.52 to 1.93 mmol h^{-1} m^{-2} with increasing calcination temperature. The intrinsic catalytic activity of HT-prepared Er_2O_3 nanorods except HT-100-6 was higher than that of CM-1000, while the exposed surface of Er_2O_3 nanorod was different from those of Er_2O_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,[12] this catalyst does not grow each crystal plane on the surface.

In conclusion, Er_2O_3 nanorods were prepared without using organic additives, and exposed {440} and {400} facets on the surface. Er_2O_3 nanorods show high catalytic activity in the dehydration of 1,4-butanediol to produce 3-buten-1-ol. The nanorod structure of Er_2O_3 is maintained during the catalytic dehydration (Figure S3[12]).

References and Notes

1 K. Zhou, X. Wang, X. Sun, Q. Peng, Y. Li, *J. Catal.* **2005**, *229*, 206.
2 H.-X. Mai, L.-D. Sun, Y.-W. Zhang, R. Si, W. Feng, H.-P. Zhang, H.-C. Liu, C.-H. Yan, *J. Phys. Chem. B* **2005**, *109*, 24380.
3 C. Pan, D. Zhang, L. Shi, *J. Solid State Chem.* **2008**, *181*, 1298.
4 S. Yang, L. Gao, *J. Am. Chem. Soc.* **2006**, *128*, 9330; J. Lv, Y. Shen, L. Peng, X. Guo, W. Ding, *Chem. Commun.* **2010**, *46*, 5909.
5 Z. Guo, F. Du, G. Li, Z. Cui, *Inorg. Chem.* **2006**, *45*, 4167.
6 K. Zhou, Z. Yang, S. Yang, *Chem. Mater.* **2007**, *19*, 1215.
7 T. Yu, J. Joo, Y. I. Park, T. Hyeon, *Angew. Chem., Int. Ed.* **2005**, *44*, 7411.
8 X.-S. Huang, H. Sun, L.-C. Wang, Y.-M. Liu, K.-N. Fan, Y. Cao, *Appl. Catal., B* **2009**, *90*, 224.
9 T.-D. Nguyen, C.-T. Dinh, T.-O. Do, *ACS Nano* **2010**, *4*, 2263.
10 N. Zhang, R. Yi, L. Zhou, G. Gao, R. Shi, G. Qiu, X. Liu, *Mater. Chem. Phys.* **2009**, *114*, 160; Q. Mu, Y. Wang, *J. Alloys Compd.* **2011**, *509*, 396.
11 S. Sato, R. Takahashi, M. Kobune, H. Inoue, Y. Izawa, H. Ohno, K. Takahashi, *Appl. Catal., A* **2009**, *356*, 64.
12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.