Pore-Structure-Controlled Coagulates of CeO$_2$ Nanoparticles for Supporting Ru Catalysts in Liquid Phase Oxidation of Benzyl Alcohol

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CeO$_2$ colloidal particles with a mean crystallite size of 2 nm synthesized by a solvothermal reaction were coagulated with 1 mol/L solutions of various bases: NaOH, NH$_3$OH, Na$_2$CO$_3$, (NH$_4$)$_2$CO$_3$, NaHCO$_3$, and NH$_3$HCO$_3$. The CeO$_2$ powders obtained by calcination of the coagulated products at 300°C had almost the same crystallite sizes in a range of 4–5 nm, while their BET surface areas were considerably different. The CeO$_2$ powders coagulated with Na$_2$CO$_3$ and NH$_3$OH had large surface areas due to micropores, and the powders obtained using NaHCO$_3$ and (NH$_4$)$_2$CO$_3$ had large pore-volumes derived from macropores. A series of Ru/CeO$_2$ catalysts were prepared by a precipitation-deposition method, and characteristics of the Ru species supported on these CeO$_2$ powders having different pore structures were examined in the liquid phase oxidation of benzyl alcohol. The Ru species having well-crystallized RuO$_2$ bulk showed only low activities. On the other hand, well dispersed Ru species exhibited high activities. The pore structure of CeO$_2$ affected the states of the Ru species loaded, and, consequently, affected their activities for the oxidation. Ruthenium species were not loaded on the surface inside the micropores by the preparation method adopted in this work. Accordingly, the Ru/CeO$_2$ catalysts with large surface areas derived from meso- and macro-pores had well-dispersed Ru species and showed high activities, which were much higher than that of the Ru/CeO$_2$ catalyst prepared by a conventional co-precipitation method.

Key-words : CeO$_2$, Ru/CeO$_2$, Pore structure, Colloidal solution, Oxidation, Benzyl alcohol, Solvothermal reaction

1. Introduction

Recently, remarkable progress is made in the syntheses of metal oxide nanoparticles. It is expected that the properties of metal oxide nanoparticles differ from those of bulk particles. New properties of nano-sized metal oxide particles are derived from the defect structure in the crystals, their size distribution, morphology of the primary particles, etc. Rare earth (RE) oxide nanoparticles exhibit extraordinary properties; for example, Sharma et al. have reported that the luminescence intensity of Y$_2$O$_3$:Eu$^{3+}$, used as a red light-emitting material in fluorescence lamps, is stronger for smaller particles (10 nm).$^5$ The RE oxides can be used as catalysts or catalyst supports.$^{21–25}$ It is, therefore, very interesting to develop methods for synthesizing nano-sized RE oxides with large surface areas. There are various methods of synthesizing RE oxide nanoparticles; reverse micelle method,$^6$ combustion method,$^7$ etc.

Ceria shows unique functions different from other RE oxides.$^{8,11–13}$ Interaction of ceria with noble metals is important and improves the activities of various noble metals for many reactions such as detoxification of vehicle exhaust gas,$^{12–15}$ methane oxidation (Rh/CeO$_2$),$^{16}$ and CO oxidation (Pt/CeO$_2$).$^{17}$ The Ru/CeO$_2$ catalyst is remarkably effective for oxidation of organic pollutants in waste water,$^{18,19}$ liquid-phase oxidation of alcohols,$^{20}$ and N$_2$O decomposition with C$_2$H$_4$.$^{21}$ The catalytic activity of Ru/CeO$_2$ is affected by the state of CeO$_2$ before Ru loading.$^{22}$

Previously, we found that the reaction of RE metals in 2-methoxyethanol at 200–300°C yielded transparent colloidal solutions of ultrafine particles of RE oxides (CeO$_2$, Sm$_2$O$_3$, and Yb$_2$O$_3$) with diameters of 2–3 nm.$^{23–25}$ As the RE colloidal particles have high-surface energy, the particles are strongly coagulated with addition of alkaline solutions, and micropore systems are formed in the void between the small particles; for example, CeO$_2$ powder was obtained by the coagulation of CeO$_2$ colloidal particles with a NH$_3$OH solution.$^{24}$

In this work, we analyzed the pore structure of CeO$_2$ powders obtained by coagulation of the CeO$_2$ colloidal particles with various alkaline solutions. Ruthenium was supported on these CeO$_2$ powders, and the activities of the Ru/CeO$_2$ catalysts were evaluated by the liquid-phase oxidation of benzyl alcohol. The CeO$_2$ powders and Ru/CeO$_2$ catalysts were characterized by temperature-programmed reduction (TPR), X-ray diffraction analysis (XRD), thermogravimetric and differential thermal analyses (TG–DTA), transmission electron microscopy (TEM), and N$_2$ adsorption isotherm measurement.

2. Experimental

2.1 Synthesis of ceria colloidal particles by the solvothermal reaction

Cerium metal purchased from Wako Pure Chemical Industries, Ltd. was used without further purification. Cerium metal (5 g; the size of the chips of cerium metal of ca. 3.5 mm $\times$ 2.0 mm $\times$ 1.0 mm) and 2-methoxyethanol (80 mL) were placed in a test tube, which was then set in an autoclave (200 mL). In the gap between the test tube and the autoclave wall, an additional 40 mL of 2-methoxyethanol was placed. After completely purged with nitrogen, the autoclave was heated to 250°C at a rate of 2.5°C/min and kept at that temperature for 2 h. After the autoclave was cooled to room temperature, the product was centrifuged at 3000 rpm for 15 min to remove coarse particles originating from the superficial layer of the Ce metal chips; a transparent solution containing colloidal particles was obtained.

2.2 Coagulation of the colloidal particles

The ceria colloidal particles were coagulated by the addition of 200 mL of 1 mol/L solutions of the following bases to 100 mL of the transparent product solution: NaOH, NH$_3$OH, Na$_2$CO$_3$, (NH$_4$)$_2$CO$_3$, NaHCO$_3$, and NH$_3$HCO$_3$. The coagulated products were washed with deionized water repeatedly.

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until the pH of the supernatant became below 8, and with methanol in the final washing. The products were dried at room temperature in air, followed by calcination at 300°C for 3 h in air.

2.3 Preparation of Ru/ CeO₂ catalysts

The CeO₂ powder obtained by calcination at 300°C of the product coagulated with one of the alkaline solutions was dispersed in 500 mL of deionized water. A desired amount of RuCl₃·3H₂O was dissolved in the suspension and 5 mL of 37% formic acid was then added. The suspension was stirred at 80°C for 0.5 h, and then, 3 mol/L NaOH was added until the pH of the suspension became about 11. The resultant precipitate was separated by centrifugation and washed with deionized water repeatedly with confirmation of the final pH of the supernatant below 8. The precipitate was dried at 80°C in air overnight and, then, calcined at 500°C for 3 h in air. The Ru loadings were adjusted to 2 wt% on metal basis.

2.4 Liquid phase oxidation of benzyl alcohol

The catalyst (0.5 g, Ru: 0.1 mmol) and acetonitrile (10 mL) were placed in a glass vessel equipped with a reflux condenser. After the vessel was filled with oxygen, benzyl alcohol (1 mmol) in acetonitrile (5 mL) was added. The reaction mixture was vigorously stirred at 50°C for 6 h under atmospheric pressure of oxygen. Benzyl alcohol conversion and benzaldehyde yield were determined with a FID gas chromatograph (Shimadzu, GC–14A) by an internal standard method (standard substance: diphenyl ether).

2.5 Characterization

The X-ray powder diffraction (XRD) analysis was performed with a Shimadzu XD-D1 X-ray diffractometer with a CuKα radiation. The crystallite size of ceria was calculated from the half-height width of the 220 diffraction peak (47.5° 2θ) by the Scherrer equation. Simultaneous thermogravimetric and differential thermal analyses were performed on a Shimadzu DTA–50 thermal analyzer at a rate of 10°C/min in a 40 mL/min flow of dried air. Nitrogen adsorption isotherms were measured using a volumetric gas-sorption system (Quantachrome Autosorb–1) and the pore-size distribution was calculated by the BJH method; the data for CeO₂ powders obtained by temperature-programmed reduction (TPR) analysis was carried out with a flow-type reactor. Hydrogen (2 vol.% in Ar; 30 mL/min) was passed through a reaction tube containing the catalyst at atmospheric pressure. The catalyst was heated with an electric furnace at 2°C/min, and the amount of H₂ consumed was monitored with a TC detector (Shimadzu 4CPT gas chromatograph). The morphology of the products was observed with a transmission electron microscope (TEM), Hitachi H–800, operated at 200 kV.

3. Results and discussion

3.1 Properties of the coagulated CeO₂ particles

Figure 1 shows the XRD patterns of CeO₂ particles obtained by calcining at 300°C the products coagulated with various alkaline solutions. All the XRD profiles coincided with the fluorite type structure of CeO₂. Table 1 shows crystallite sizes and BET surface areas of the CeO₂ powders. The crystallite sizes were almost the same and were in a range of 4–5 nm. As the mean crystallite size of the colloidal particles before coagulation was about 2 nm, crystal growth of the CeO₂ nanoparticles occurred by the calcination at a low temperature of 300°C. The BET surface areas were considerably different from sample to sample. The surface area calculated assuming that each CeO₂ particle is spherical with a diameter of 5 nm (crystallite size) should be 166 m²/g, which is significantly larger than the observed surface areas. Therefore, the coagulation states of the CeO₂ particles were different, depending upon the coagulants used.

Figures 2 and 3 show the N₂ adsorption isotherms, and Fig. 4 and 5 the pore-size distribution curves calculated by the BJH method; the data for CeO₂ powders obtained by

Table 1. Characterization of the Coagulated CeO₂ Particles and Performance of the Ru Catalysts Supported on the Particles

<table>
<thead>
<tr>
<th>Coagulant</th>
<th>Crystallite size (nm)</th>
<th>BET surface area (m²/g)</th>
<th>Total surface area (m²/g)</th>
<th>Surface area of micropores (m²/g)</th>
<th>Surface area due to meso- and macro-pores (m²/g)</th>
<th>Benzyl alcohol Conversion (%)</th>
<th>Benzaldehyde yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH⁵⁺</td>
<td>2</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>53.0</td>
<td>35.5</td>
</tr>
<tr>
<td>NH₄HCO₃</td>
<td>5.2</td>
<td>90</td>
<td>92</td>
<td>44</td>
<td>48</td>
<td>81.4</td>
<td>57.8</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>4.2</td>
<td>75</td>
<td>79</td>
<td>6</td>
<td>73</td>
<td>81.2</td>
<td>58.3</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>4.8</td>
<td>123</td>
<td>152</td>
<td>91</td>
<td>61</td>
<td>79.6</td>
<td>58.0</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>4.6</td>
<td>61</td>
<td>67</td>
<td>63</td>
<td>4</td>
<td>16.8</td>
<td>8.6</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>5.2</td>
<td>92</td>
<td>111</td>
<td>95</td>
<td>11</td>
<td>32.5</td>
<td>28.4</td>
</tr>
<tr>
<td>NaOH</td>
<td>5.2</td>
<td>122</td>
<td>132</td>
<td>82</td>
<td>40</td>
<td>42.3</td>
<td>37.1</td>
</tr>
</tbody>
</table>

a) Prepared by a coprecipitation method from Ce(NO₃)₂·6H₂O; denoted as Ru/CoO₂-A.

b) Surface area calculated by BET equation.

c) Surface area calculated by the t-plot.

d) Reaction conditions: benzyl alcohol (1 mmol), Ru/CoO₂ (0.5 g Ru: 0.1 mmol), 50°C, 4 h
using coagulants containing Na⁺ cation are shown in Figs. 2 and 4, and the data for those obtained by using coagulants with NH₄⁺ cation, in Figs. 3 and 5. As large amounts of nitrogen were adsorbed at the low $P/P_0$ ($<0.03$) region on the powders coagulated with Na₂CO₃ and NH₄OH, large surface areas due to micropores were suggested to be present. On the other hand, large amounts of nitrogen were adsorbed at the high $P/P_0$ ($>0.8$) region for the powders coagulated with NaHCO₃ and NH₄OH₂CO₃, indicating that macropores with large pore volumes were formed. The powders coagulated with NaOH and NH₄HCO₃ exhibited hysteresis loops, identified as E type according to de Boer classification, indicating the presence of ink-bottle shaped voids or tubular pores of narrow constrictions. The latter explanation is more feasible because coagulation of spherical primary particles gives this type of pores between primary particles. Figures 4 and 5 indicate that these powders had mesopores with relatively narrow pore-size distributions centered at ~4 nm.

The CeO₂ powder coagulated with Na₂CO₃ had an essentially identical morphology to that coagulated with NaOH (Fig. 6). The particles were closely packed each other. However, the CeO₂ powders coagulated with NaHCO₃ were composed of loosely packed aggregates of primary particles and voids between the aggregates were clearly observed.

The XRD patterns of the as-coagulated CeO₂ particles are shown in Fig. 7. The powders coagulated with (NH₄)₂CO₃ and NaHCO₃ exhibited peaks at 10°, 20°, 30°, etc., which were not due to CeO₂. These peaks coincided with those for Ce₂(CO₃)₃·8H₂O, which was formed probably by the reaction...
between CO$_3^{2-}$ and Ce ions remaining in the solution after the solvothermal reaction. The TG profiles of the samples coagulated with (NH$_4$)$_2$CO$_3$ and NaHCO$_3$, however, were not so different from those of the samples coagulated with NaOH and NH$_3$OH (Fig. 8); the amounts of Ce$_2$(CO$_3$)$_3$·8H$_2$O present in the former samples seem to be relatively small.

Only the CeO$_2$ powders containing Ce$_2$(CO$_3$)$_3$·8H$_2$O formed macropores after calcination at 300°C (Figs. 2 and 3). The result shown in Fig. 8 indicates that Ce$_2$(CO$_3$)$_3$ was transformed to CeO$_2$ by calcination at 300°C. Therefore, CO$_2$ gas evolved from contaminated Ce$_2$(CO$_3$)$_3$ during calcination at 300°C partially destructed micropore structures, leaving the aggregates and macropores. For the reason why NH$_3$HCO$_3$ and Na$_2$CO$_3$ did not form Ce$_2$(CO$_3$)$_3$·8H$_2$O, the pH of the solution of the former compound is so low that the concentration of carbonate ions seems to be too low for the formation of Ce$_2$(CO$_3$)$_3$·8H$_2$O. On the other hand, the pH of the latter solution is so high that cerium species seem to have tendency to form cerium hydroxide, preventing the formation of Ce$_2$(CO$_3$)$_3$·8H$_2$O.

The coagulation of CeO$_2$ nanoparticles can be affected by complex balance between the ionic strength and pH of the coagulant solutions. Moreover, only a minor change of the drying conditions possibly affects the pore structure of the coagulated particles because of surface tension of water remaining between particles. Therefore, a systematic work is in progress to elucidate the prime factor controlling the pore structure of CeO$_2$ powders.

### 3.2 Effect of pore structure of the CeO$_2$ support on the activity of Ru/CeO$_2$

The results for benzyl alcohol oxidation over Ru/CeO$_2$ catalysts are also given in Table 1. The Ru/CeO$_2$ catalyst whose performance is shown at the top line of Table 1 (Ru/CeO$_2$-A) was prepared by the co-precipitation method employed in the previous work. The activity of Ru/CeO$_2$ catalysts differed depending upon CeO$_2$ supports. It must be noted that the activities of the Ru catalysts supported on the CeO$_2$ samples coagulated with (NH$_4$)$_2$CO$_3$, NaHCO$_3$ and NH$_3$HCO$_3$ were much higher than that of Ru/CeO$_2$-A; the conversion of benzyl alcohol was about 80% and benzaldehyde yields about 58%.

Figure 9 shows the XRD patterns of the Ru/CeO$_2$ catalysts. The catalysts with the CeO$_2$ supports coagulated with NaOH, NH$_3$OH, and Na$_2$CO$_3$, had a peak at 35° due to RuO$_2$, indicating that the Ru species on these CeO$_2$ supports were well-crystallized. These catalysts showed only low oxidation activities. The TPR profiles (Fig. 10) show that the Ru species on these CeO$_2$ supports had two reduction peaks at 75°C and 90°C (NaOH and NH$_3$OH samples) or one peak at 90°C (Na$_2$CO$_3$ sample). On the other hand, the Ru species on the CeO$_2$ supports coagulated with (NH$_4$)$_2$CO$_3$, NaHCO$_3$, and NH$_3$HCO$_3$ had only one peak at 75°C, and the RuO$_2$ peak was not detected by the XRD analysis (Fig. 9). The latter three catalysts were highly active for the oxidation of benzyl alcohol. It was clarified previously that the TPR peak at the lower temperature (~75°C) is due to well-dispersed Ru species on CeO$_2$, with the RuO$_2$ peak in addition to the Ru-O-Ce bonds. The TPR peak at the higher temperature (~90°C) was attributed to well-crystallized RuO$_2$ on CeO$_2$, which has only the Ru-O-Ru bonds. The Ru species well-dispersed on CeO$_2$ showed high activity for oxidation reactions such as propylene oxidation, but the activity of the bulk RuO$_2$ well-crystallized on CeO$_2$ was low.

The surface areas of the CeO$_2$ supports calculated by the $V$-$t$ plots are also shown in Table 1. The total surface area was calculated from the slope of the first segment of the $V$-$t$ plot and surface area due to meso- and macro-pores was estimated...
loading the Ru species on the surface inside the micropores of CeO₂. The Ru species supported on the CeO₂ samples, coagulated with (NH₄)₂CO₃, NaHCO₃, and NH₄HCO₃ and, accordingly, having large surface areas due to meso- and macro-pores, exhibited high activities for oxidation of benzyl alcohol because most of the Ru species were highly dispersed. Their activities were much higher than that of the Ru/CeO₂ catalyst prepared by the conventional co-precipitation method.

4. Conclusions
The CeO₂ colloidal particles were synthesized by a solvothermal reaction of Ce metal in 2-methoxyethanol, and the CeO₂ powders were obtained by coagulation of the resultant colloidal particles with various alkaline solutions. The CeO₂ powders had different pore structures depending on the various alkaline solutions. Ru was loaded on these CeO₂ powders by a precipitation-deposition method, which did not allow from the slope of the second segment. The catalyst activity was correlated well with the surface area originating from meso- and macro-pores and the catalysts with large surface areas had high activities. In other words, even if a catalyst has high total surface area, its activity is low when most part of the surface area comes from micropores. Although the two CeO₂ samples had different pore structures depending on the variation of NaOH modified surface properties of CeO₂ powders, the catalysts supported on these two samples exhibited far different activities. One possible explanation for this result is that the highly basic solution of NaOH modified surface properties of CeO₂ particles thereby preventing the deposition of highly dispersed Ru species. The results of N₂ adsorption measurement and TPR analysis suggested that well-crystallized RuO₂ particles were formed on the CeO₂ supports whose surface areas due to meso- and macro-pores were small. It is, therefore, deduced that the catalyst preparation method adopted in this work cannot load Ru on the surface of micropores. When the support has a small meso- and macro-pore surface area, a large part of the Ru species had to be loaded on the surface outside the micropores, making the RuO₂ particles grow large. The Ru species supported on the CeO₂ with a large meso- and macro-pore surface area have high activity, because most of the Ru species are highly dispersed.

References

Fig. 10. TPR profiles for Ru species supported on CeO₂ samples coagulated with various alkaline solutions.