

Hydrothermal Synthesis of Nanocrystalline Cerium(IV) Oxide Powders

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Nanocrystalline cerium(IV) oxide (CeO_2) powders were prepared by heating solutions of cerium(IV) salts in the presence of urea under hydrothermal conditions at 120° to 180°C. The effects of the concentration of urea and hydrothermal treatment temperature on the morphology and crystallite size of the synthesized particles were investigated. The synthesized particles were angular, ultrafine CeO_2 , with a cubic fluorite structure. Their crystallite size decreased from 20 to 10 nm with increasing urea concentration from 2 times to 8 times that of the Ce^{4+} ion. The size only slightly changed by calcining at temperatures below 600°C.

I. Introduction

CERIA (CeO_2) has been considered a useful material and attracted interest in an application for catalytic supports (for automotive exhaust systems).^{1,2} Several rare-earth-doped cerium oxides exhibit high oxygen ionic conductivity which makes them interesting materials for applications as solid electrolytes in solid oxide fuel cells.^{3,4} Ceria has a fluorite structure that is stable from room temperature to its melting point as compared with other pure oxides with oxygen ion conductivity, zirconia, and bismuth oxide, which have polymorph transformations in different temperature ranges. This material has also received attention for other various applications such as additives for glass, stabilizers for ZrO_2 , glass polishers, and so on.

There is current interest in using hydrothermal routes to synthesize materials at relatively low temperatures. The hydrothermally synthesized powder has excellent homogeneity and particle uniformity. Several techniques that include hydrothermal synthesis,⁵⁻⁸ urea-based homogeneous precipitation,⁹⁻¹² hexamethylenetetramine-based homogeneous precipitation,^{13,14} coprecipitation,^{15,16} decomposition of oxalate precursors,¹⁷ forced hydrolysis,¹⁸ and electrochemical synthesis¹⁹ have been developed for the production of ceria or cation-doped ceria particles and their precursors. The sintering behavior of CeO_2 and Y_2O_3 -doped CeO_2 particles that were hydrothermally synthesized from $\text{Ce}(\text{NO}_3)_3$ solution and ammonium hydroxide solution has been reported by Zhou and Rahaman.⁶ Tani *et al.*⁵ studied the effect of mineralizers on the crystal growth of CeO_2 under hydrothermal conditions at 500–600°C and 100 MPa. It was also shown that controlling the growth of CeO_2 particles was possible, and ultrafine ceria particles could be hydrothermally prepared from $\text{Ce}(\text{IV})$ sources.^{7,8} Studies on the synthesis of Y_2O_3 - ZrO_2 powders by the hydrothermal technique in the presence of urea have also been reported.^{20,21} These crystalline powders had a 11.6 nm crystalline size and consisted of metastable cubic zirconia. However, few researchers have reported the hydrothermal synthesis of powders in the presence of urea except for 3 mol% Y_2O_3 - ZrO_2 powder.

The purpose of the present work is to report the synthesis of ultrafine CeO_2 powders under hydrothermal conditions in the presence of urea and investigate the effects of the concentration of urea and hydrothermal treatment temperature on the morphology and crystallite size of the synthesized particles.

II. Experimental Procedure

(1) Preparation

Cerium(IV) sulfate tetrahydrate ($\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, Kishida), cerium(IV) ammonium sulfate dihydrate ($\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$, Nacalai), and urea ($\text{CO}(\text{NH}_2)_2$, Nacalai) were of laboratory purity and used as the starting materials. A given quantity (20 cm^3) of mixed solution of the cerium salt and urea in the desired concentrations was poured into a Teflon bottle with an inner volume of 25 cm^3 held in a stainless-steel vessel. After the vessel was sealed, it was placed in a thermostatted oven, heated, and constantly rotated at 120° to 180°C for 5 h. The precipitated powders were then washed and dried in an oven with an air atmosphere. The calcination of the powders was carried out at 300° to 900°C for 1 h in a furnace with an air atmosphere.

(2) Measurements

The crystalline phase identification was performed by the X-ray diffraction (XRD) method using $\text{CuK}\alpha$ radiation. The crystallite size was estimated by line broadening analysis. The reflection from the (220) plane was used for the crystallite size determinations. The precipitate morphology and size were examined by transmission electron microscopy (TEM) (Model JEM-200CX, JEOL, Tokyo, Japan). Specific surface areas of the as-synthesized and calcined powders were determined by the BET method.

III. Results and Discussion

$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ solution (0.1 $\text{mol} \cdot \text{dm}^{-3}$) was hydrothermally treated in the presence of urea (0.3 $\text{mol} \cdot \text{dm}^{-3}$) at 180°C for 5 h. The XRD data of the synthesized particles were characteristic of CeO_2 with a fluorite structure. Similar CeO_2 particles were also synthesized from $\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ solutions under the same conditions. Figure 1 shows the morphology of the synthesized CeO_2 particles as viewed by TEM. It reveals that the particles are angular and very fine. They appear to be cubic or octahedral and ranged in size from 10 to 25 nm. They must be single CeO_2 crystals based on the fact that their particle size is in good accordance with the crystallite size determined by the XRD line broadening analysis. Their particle size is coarser than those (3 nm in size) hydrothermally prepared from the same cerium(IV) salt solution with an excess amount of ammonia solution for the same treatment temperature and holding time.^{7,8} The number of nucleations of the hydroxide from the solution using urea may be fewer than those from the solution using an excess amount of ammonia. The morphology and size of the particles obtained in this study are similar to those hydrothermally prepared from the cerium(III) salt solution with an excess amount of ammonia solution rather than those from the cerium(IV) salt solution.⁸ It is noteworthy that there is a large difference in the size of the

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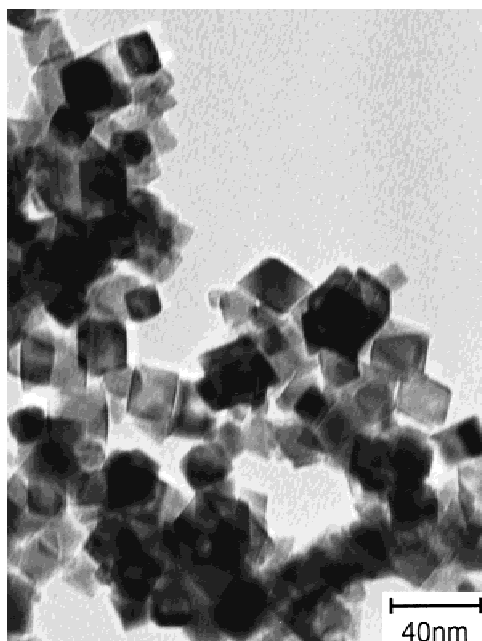
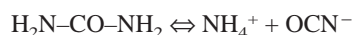


Fig. 1. TEM photographs of CeO₂ particles prepared from 0.1 mol·dm⁻³ Ce(SO₄)₂·4H₂O solution in the presence of 0.2 mol·dm⁻³ urea under hydrothermal conditions at 180°C for 5 h.

particles prepared from the same cerium(IV) salt solution between ammonia and urea which is used as the ligand source for ammonia.

In the present study, the precipitate formed by heating the solutions of cerium(IV) salts in the presence of urea under hydrothermal conditions was not cerium carbonate but CeO₂. Urea produces ammonium and cyanate ions:



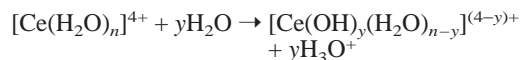
In an acidic solution, cyanate ions rapidly react according to



In neutral and basic solutions, carbonate ions and ammonia are formed:



Because of their lower basicity and higher charge, Ce⁴⁺ ions usually undergo strong hydration and form hydroxide at low pH (PH 1,²² 3.0²³). The hydrated Ce⁴⁺ ions can form complexes with H₂O molecules or OH⁻ ions.



Further polymerization is likely, and both can serve as precursors for the final oxide. In aqueous solution, H₂O as polar molecules tend to take protons away from the hydroxide.



In this way, Ce⁴⁺ ions precipitate as CeO₂ before reacting with the CO₃²⁻ ions. On the other hand, Ce³⁺ ions precipitated as two types of cerium carbonate particles.²⁴

The effect of hydrothermal treatment temperature on the crystallite size of the CeO₂ particles based on the XRD line-broadening analysis of the (220) peak of the powder hydrothermally synthesized for 5 h from 0.1 mol·dm⁻³ cerium(IV) sulfate solution in the presence of 0.4 mol·dm⁻³ urea is summarized in Fig. 2. The crystallite size increased with the hydrothermal treatment temperature. It appeared that the hydrothermal treatment at higher temperature promoted the crystallization and crystal growth of CeO₂ from those hydrated Ce(OH)_y(H₂O)_x^{(4-y)+} or CeO₂·n(H₂O) species according to the dissolution-precipitation mechanism.

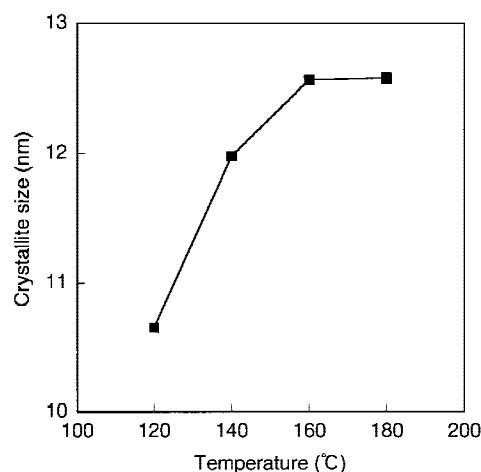


Fig. 2. Effect of hydrothermal treatment temperature on the crystallite size of CeO₂ precipitates prepared from 0.1 mol·dm⁻³ Ce(SO₄)₂·4H₂O solution in the presence of 0.4 mol·dm⁻³ urea under hydrothermal conditions for 5 h.

Figure 3 shows the effect of urea concentration on the morphology and the particle size of the CeO₂ formed from the 0.1 mol·dm⁻³ Ce(SO₄)₂ solution under hydrothermal conditions at 180°C in contrast with Fig. 1. It was observed that the crystallinity and particle size of the synthesized ceria decreased with an increase in the urea concentration as seen from these examples. Figure 4 indicates the dependence of the crystallite size of the synthesized CeO₂ particles on the concentration of urea. The pH of the solutions after hydrothermal treatment containing 0.2 mol·dm⁻³ and 0.4 mol·dm⁻³ urea was 2.7 and 7.8, respectively. It is likely that the increase in crystallite size is due to a decrease in the nucleation in the acidic solution as the solution becomes acidic by a decrease in the urea concentration.

The effects of calcining temperature on the specific surface area and crystallite size of the CeO₂ particles are shown in Fig. 5. The crystallite size of the as-prepared CeO₂ particles was

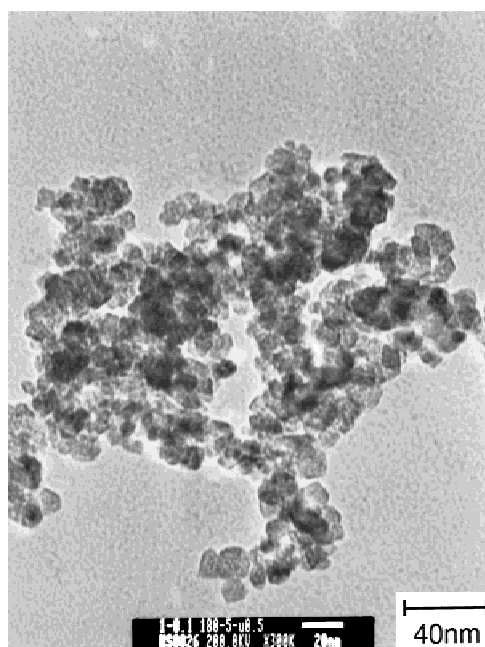


Fig. 3. TEM photographs of CeO₂ particles prepared from 0.1 mol·dm⁻³ Ce(SO₄)₂·4H₂O solution in the presence of 0.5 mol·dm⁻³ urea under hydrothermal conditions at 180°C for 5 h.

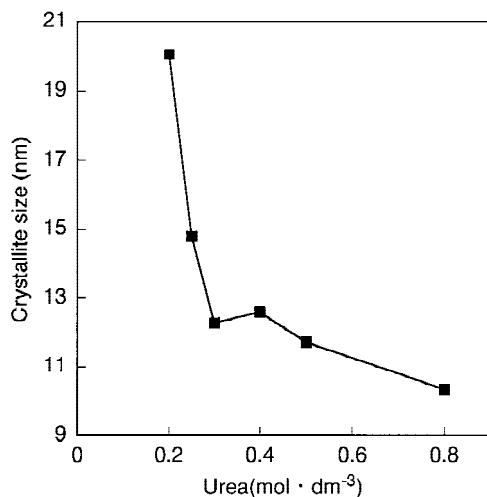


Fig. 4. Effect of urea concentration on the crystallite size of CeO_2 precipitates prepared from $0.1 \text{ mol} \cdot \text{dm}^{-3}$ $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ solution in the presence of urea under hydrothermal conditions for 5 h.

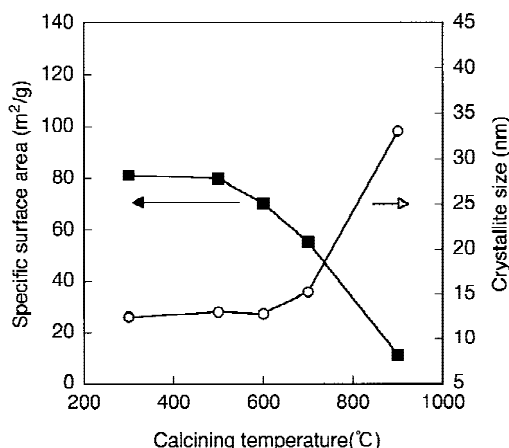


Fig. 5. Calcining temperature dependence of specific surface area and crystallite size of CeO_2 powder prepared from $0.1 \text{ mol} \cdot \text{dm}^{-3}$ $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ solution in the presence of $0.4 \text{ mol} \cdot \text{dm}^{-3}$ urea under hydrothermal conditions at 180°C for 5 h.

12.5 nm, and it scarcely changed by calcining at a temperature below 600°C . A significant increase in the crystallite growth of the particles occurred at temperatures above 700°C . The specific surface area of the as-synthesized powder was $80 \text{ m}^2/\text{g}$, and the change with heat treatment temperature showed good agreement with the change in the crystallite size.

IV. Conclusions

Nanocrystalline CeO_2 powders, with a particle size of 10–25 nm, were synthesized by heating solutions of cerium(IV) salts in the presence of urea under hydrothermal conditions at 120° to 180°C . The particle size was controlled by adjusting the concentration of urea and the hydrothermal treatment tempera-

ture. The crystallinity and particle size of the synthesized ceria decreased with an increase in the urea concentration. Their crystallite size only slightly changed by calcining at temperatures below 600°C .

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