

Synthesis of CeO₂ Spherical Fine Particles by Homogeneous Precipitation Method with Polyethylene Glycol

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(Received May 21, 2002; CL-020441)

CeO₂(IV) fine particles were prepared by heating a polyethylene glycol solution of Ce(NO₃)₃·6H₂O at 383 K for 3 h. When a polyethylene glycol whose molecular weight was 7500 or 20000 was used for the preparation, the obtained CeO₂ particles were almost monodispersed.

Cerium (IV) oxide (CeO₂) is an oxygen ion conductor which has many potential applications. It can be applicable to solid oxide fuel cells and oxygen sensors, and can also be used for shielding materials from ultraviolet light.^{1,2} For these applications, however, it is of critical importance to regulate both the particle size and morphology of the particles.

In recent years, several novel methods of preparing CeO₂ particles have been reported. Hirano et al. synthesized CeO₂ powder by hydrothermal treatment of cerium hydroxide precipitate at 453 K.³ This method makes it possible to obtain particles whose diameter ranges from 3 nm to 16 nm. Nakane et al. prepared CeO₂ nanoparticles by adding hydrazine monohydrate to an aqueous solution of cerium nitrate hydrate at 343 K.⁴ A preparation process by the homogeneous precipitation method with urea was also reported by Chen et al.⁵ In some studies, we noted that polyethylene glycol (PEG HO-(CH₂CH₂O)_n-H) can be used as a solvent for inorganic salts and also that the ether oxygen in the PEG acts as base.^{6,7} Therefore, in the present study, we examined a novel homogeneous precipitation method for the preparation of CeO₂ fine particles using PEG.

The cerium oxide fine particles were prepared as follows: 5 g of cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) was added to 10 g of PEG having a molecular weight of 1000 (hereafter referred to as "PEG1000") and stirred at 333 K with no added water. A homogeneous clear solution was obtained. The PEG solution of the cerium (III) nitrate hydrate was kept in a pyrex glass beaker at 383 K for 3 h. The evolution of NO_x gas and the turbidity of the solution were observed during the heating process. The solution obtained after heat treatment was a composite of cerium oxide, unreacted cerium nitrate hydrate, and PEG. In order to separate the obtained oxide, this product was homogeneously dispersed in distilled water to dissolve the unreacted cerium nitrate hydrate and PEG. The cerium oxide was separated by centrifugation, followed by drying at 333 K for 3 h. This procedure was also carried out using one of the following in each preparation: ethylene glycol (EG), a PEG with an average molecular weight of 7500 (PEG7500), and a PEG with an average molecular weight of 20000 (PEG20000). All of the chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries, Ltd., Osaka, Japan). For the purposes of this study, EG is considered to be PEGs. The structure of the obtained

powder was characterized by means of X-ray diffraction (XRD) (Cu K α 40 kV, 200 mA, Mac Science MXP-18, Mac Science Co., Ltd., Kanagawa, Japan). The particle shape was observed by field emission-SEM (FE-SEM, JSM-6330, JEOL, Inc., Tokyo, Japan). The FT-IR spectra of the PEG solution of cerium nitrate hydrate were measured using a JASCO FT/IR-350 spectrometer (Jasco, Inc.). After pretreatment at 383 K in 1 mPa for 2 h, the N₂ adsorption isotherm was measured at 77 K by the volumetric method.

Figure 1 shows the XRD patterns of the obtained powder. All XRD patterns in Figures 1a-d can be identified as pure CeO₂(IV). Crystallite size was calculated using Scherrer's equation and the half width of the diffraction peak of the CeO₂ (111) plane. The crystallite size of the samples ranged from 7 nm to 9 nm. We believe that the CeO₂ was obtained by hydrolysis reaction of the aquo complex of cerium ions (Ce(H₂O)_n³⁺) in the PEG solution. Here, the aquo complex of cerium ions was derived from crystal water of cerium nitrate hydrate. We did not add any reagent for precipitation to the PEG solution, and CeO₂ powder was formed by heat treatment of the PEG solution alone. Therefore, we can classify this method as a homogeneous precipitation method. Conventional methods of preparation of CeO₂ by solution process usually require a base; while this homogeneous precipitation method with PEG did not require any inorganic base.

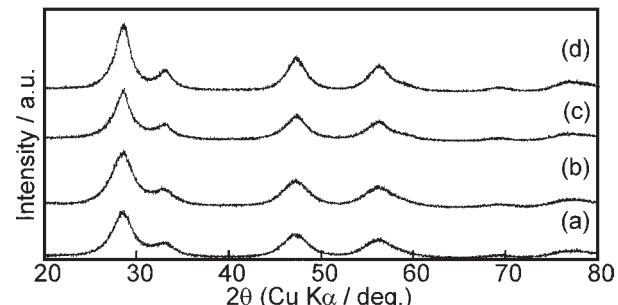


Figure 1. X-ray diffraction patterns of the powders prepared by the homogeneous precipitation method with PEG and Ce(NO₃)₃·6H₂O at 383 K. The PEGs used for the preparation were (a) EG, (b) PEG1000, (c) PEG7500, and (d) PEG20000.

Figure 2 shows the FE-SEM images of the obtained CeO₂ particles. When EG was used for the preparation, the obtained CeO₂ consisted of aggregated particles of irregular sizes as shown in Figure 2a. When PEG1000 was used, the diameter of the obtained particles ranged from 40 nm to 300 nm (Figure 2b). Figure 2c, d show that, when PEG7500 and PEG20000 were used, almost monodispersed spherical CeO₂ particles whose average

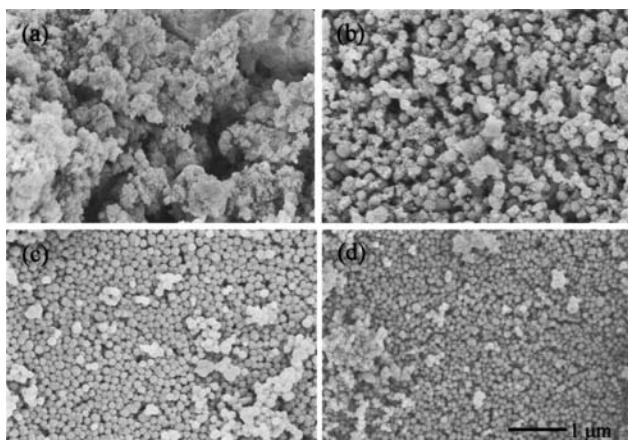


Figure 2. FE-SEM images of the obtained CeO_2 powders. The PEGs used for the preparation were (a) EG, (b) PEG1000, (c) PEG7500, and (d) PEG20000.

diameters were 140 nm and 105 nm, respectively, were obtained. Thus, when the homogeneous precipitation method with PEGs whose molecular weight is 7500 or more is employed, the particle size distribution of the obtained CeO_2 particles is almost uniform. According to the crystallite size, the resulting spherical particles were secondary particles consisting of the primary particles whose diameter ranged from 7 nm to 9 nm.

In order to investigate the formation process of the CeO_2 particles in the PEG solution, we examined FT-IR spectra of the PEG solution of cerium nitrate hydrate before heat treatment. Figure 3a, b show the FT-IR spectra of the EG solution and the PEG20000 solution, respectively. Absorption peak A, from 3600 cm^{-1} to 3000 cm^{-1} , can be assigned to the stretching vibration of the hydrogen-bonded OH groups derived from the crystal water of cerium nitrate hydrate and the terminal group of PEG; absorption peak B, around 2800 cm^{-1} , can be assigned to the stretching vibration of the CH_2 group; absorption peak C, at 1628 cm^{-1} , can be assigned to the angular vibration of H_2O molecules; and absorption peak D, around 1400 cm^{-1} , can be assigned to the stretching vibration of NO_3^- . The peak position of absorption A corresponds to the strength of the hydrogen bond of OH groups. The positions of absorption peak A of the EG solution and the PEG20000 solution were 3363 cm^{-1} and 3413 cm^{-1} , respectively. These peak positions were lower than that of liquid-state water molecules, whose peak position is 3450 cm^{-1} .⁸ This means that the strength of the hydrogen bond between water molecules and the PEG's ether oxygen and also that the terminal

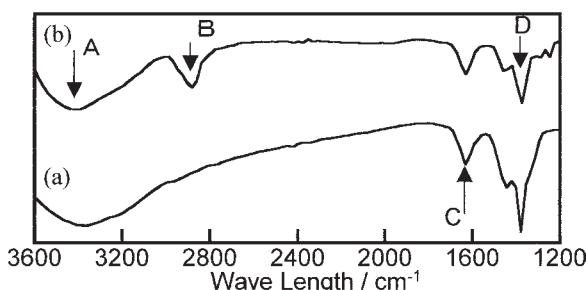


Figure 3. FT-IR spectra of the PEG solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. The PEGs used for the preparation of the solution were (a) EG and (b) PEG20000.

OH group is stronger than that found in liquid-state water. The oxygen atoms of the ether group and the terminal OH group in PEG act as a base by accepting H^+ . Therefore, the hydroxylation and oxolation processes of the aquo complex of cerium ion due to the strong hydrogen bond in the PEG solution forms CeO_2 particles.⁹ The oxidation of Ce^{3+} in cerium nitrate hydrate to Ce^{4+} in CeO_2 occurs by the following reaction of nitrate ion: $\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$. Furthermore, the wave number of peak A of the EG solution was lower than that of the PEG20000 solution. The hydrogen bond in the EG solution is therefore stronger than that in the PEG20000 solution. The formation process of CeO_2 particles by hydroxylation and oxolation of aquo complex of cerium ions depends on the strength of the hydrogen bond between water molecules and the PEG and the obtained particle size and shape thus depend on the molecular weight of the PEG. Furthermore, the viscosity of the solution depends on the molecular weight of PEG. This fact also affects the dependence of the obtained CeO_2 particle shape and size on the molecular weight of PEG.

The pore size distribution of the CeO_2 particles was obtained by analyzing the N_2 adsorption isotherm using the Cranston-Inkley method. Figure 4 shows the pore size distribution of the CeO_2 particles. The BET specific surface area (S_{BET}) of the particles prepared using the EG solution and the PEG20000 solution was $79.6\text{ m}^2/\text{g}$ and $103\text{ m}^2/\text{g}$, respectively. Compared with the pore size distribution of the particles prepared by using the EG solution, the particles prepared with the PEG20000 solution had a greater number of pores whose diameter was 4 nm. Thus, pore size distribution also depends on the molecular weight of the PEG used for the preparation.

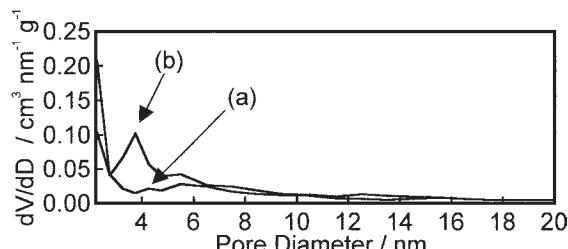


Figure 4. Pore size distribution of the CeO_2 powder obtained by the homogeneous precipitation method with PEG. The PEGs used were (a) EG and (b) PEG20000.

In summary, CeO_2 fine particles were prepared by a novel homogeneous precipitation method using PEG at 383 K for 3 h.

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