Hydrothermal Synthesis and Characterization of Nanocrystalline Ceria Powders

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Abstract: Nanocrystalline ceria powders were prepared by hydrothermal treatment of cerium(IV) ammonium nitrate solutions at 120–200 °C in the absence of a precipitating agent. We have conducted a systematic investigation of the effects that the hydrothermal temperature and reaction time have on the physical properties of the product powders. When the hydrothermal temperature was increased, the product ceria powders exhibited larger crystallite sizes and higher yields. Increasing the reaction time produced a greater yield of crystalline ceria powder as a result of further hydrothermal reactions and structural rearrangement. The physical properties of these ceria powders can be controlled by adjusting the hydrothermal conditions.

Keywords: ceria, nanocrystalline, hydrothermal treatment, crystallite size

Introduction

Ceria (CeO₂) has attracted much attention because of its various applications, such as chemical mechanical polishing media, automobile exhaust catalysts and their supports, dense ceramic membranes for oxygen separation, and solid electrolytes in solid oxide fuel cells [1-4]. Ultratine ceria powders are particularly important for many of these applications, because of their small particle size, high surface area, and improved sintering properties. Therefore, the preparation of nanocrystalline ceria powders without hard agglomeration has been investigated intensively.

Recently, the hydrothermal process has attracted a lot of attention for the direct synthesis of crystalline ceramic powders at relatively low temperatures. The hydrothermal process is generally performed in an autoclave at temperatures between the boiling and critical points of water (100 to 374 °C) at autogeneous pressure [5]. This method has been used for the synthesis of fine powders of various oxide ceramics because the product powders have excellent homogeneity and particle uniformity [5]. In addition, the product powders can be controlled in size and shape by changing the preparation conditions, such as the hydrothermal temperature, reaction time, solute concentration, and precursor types [6].

Several research groups have reported the synthesis of ceria powders under hydrothermal conditions. Tani and coworkers [7] studied the effect that mineralizers have on the hydrothermal synthesis of ceria powders from a cerium(III) nitrate solution with excess ammonia at 500 to 600 °C and 100 MPa. Zhou and Rahaman [8] investigated the sintering behavior of ceria powders produced by hydrothermal process from cerium(III) nitrate solution with excess ammonia. Hirano and Kato [9] synthesized ultratine ceria powders from cerium(III) nitrate, cerium (IV) sulfate, and cerium(IV) ammonium sulfate under hydrothermal conditions at 120–200 °C for 5–40 h. They reported that the particles synthesized from the cerium(IV) compounds showed significant coarsening, while those synthesized from the cerium(III) salt did not coarsen. Djuricic and Pickering [10] synthesized weakly agglomerated ceria powders by precipitating cerium(III) nitrate with hydrogen peroxide and ammonia, followed by hydrothermal treatment at 180 °C. They reported that the function of hydrogen peroxide was to slowly oxidize the cerium cation to a higher valence state and thereby initiate homogeneous precipitation with the formation of dense spherical agglomerates. Most of methods for preparing ceria powders under hydrothermal conditions, including those mentioned above, consist of two steps.

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The first step is the precipitation of the cerium salt using ammonia or urea, followed by conditioning of the precipitates. The second step is hydrothermal treatment of the precipitates.

Recently, Hirano and coworkers [11] reported the direct synthesis of nanocrystalline pure ceria and ceria/zirconia powders through hydrothermal treatment of cerium(IV) ammonium nitrate solution or a mixed solution of cerium(IV) ammonium nitrate and zirconium oxychloride in a total cation concentration of 0.005 M without the need for a precipitating step. They kept the concentration very low to prepare ultra-fine monodisperse particles. Although they produced nanocrystalline ceria and ceria/zirconia powders at a relatively low temperature of 100 °C, this method was not practical for powder production because of the low concentration. In addition, the authors did not investigate the effects of the hydrothermal conditions. In this work, nanocrystalline ceria powders were synthesized in the absence of a precipitating agent through the hydrothermal treatment of cerium(IV) ammonium nitrate solution at a relatively high concentration of 0.1 M. The effects that the hydrothermal temperature and reaction time have on the physical properties and crystal growth of the product ceria powders were systematically investigated.

**Experimental**

Cerium(IV) ammonium nitrate [(NH₄)₂Ce(NO₃)₆, 98.5%, Aldrich] was used as the starting material. The appropriate quantity of a cerium salt was dissolved in double-distilled water at a concentration of 0.1 M and then stirred vigorously for 0.5 h. The well-dissolved solution was poured into an autoclave and treated hydrothermally at various conditions. To investigate the effect of hydrothermal temperature, the solution was treated hydrothermally at 120, 160, 200, and 240 °C for a reaction time of 4 h. In addition, the reaction time was varied from 4 to 24 h at a hydrothermal temperature of 200 °C. The precipitates formed after hydrothermal treatment were separated by centrifugation, washed with distilled water, and dried in an oven at 80 °C under an air atmosphere. We label each product ceria powder as xHTy, where x represents the hydrothermal temperature in °C and y represents the reaction time in hours.

An X-ray diffractometer (Model M18XHF-SRA, Mac Science Co., Yokohama, Japan) was used for phase identification with Ni-filtered CuKα radiation over the range of 2θ from 25 to 60°; the intensity data for each point was collected at 4-s intervals. The crystallite size was estimated from line broadening of the (111) diffraction peak according to the Scherrer equation [12]. The powder morphology and size were examined using a transmis-

![Figure 1. Evolution of XRD patterns of the product ceria powders prepared through hydrothermal treatment at 120 to 240 °C for 4 h.](image)

sion electron microscope (Model JEM-2010, JEOL, Tokyo, Japan). The specific surface area (SSA) of the prepared samples was obtained through N₂ adsorption/desorption at 77 K (Model ASAP2020, Micromeretics Instrument Co., Norcross, GA). All samples were degassed at 150 °C prior to measurement. The SSA was determined using the multipoint Brunauer-Emmett-Teller (BET) method and the adsorption data in obtained the relative pressure (P/P₀) range of 0.05–0.25. The powders were analyzed using a thermogravimetric analyzer (Model TGA-7, Perkin Elmer Co., Norwalk, CT) at a heating rate of 10 °C/min in flowing air.

**Results and Discussion**

Figure 1 shows the XRD patterns of the product powders that were formed from 0.1 M (NH₄)₂Ce(NO₃)₆ solution under hydrothermal conditions at 120–240 °C for 4 h. All of the powders showed the presence of CeO₂ with distinguishable peaks indicating dominant (111), (200), (220), and (311) diffraction lines, suggesting a fluorite structure. It is noteworthy that the powders prepared at 120 °C already exhibited all of the major reflections of CeO₂ having a fluorite structure and relatively good crystallinity. From the evolution of these XRD patterns, it is apparent that the peaks become sharper upon increasing the hydrothermal temperature, indicating larger crystallite sizes. We attribute this result to more-rapid development into larger ceria crystals at higher hydrothermal temperatures.

Hydrolysis refers to the reactions of metal cations with water that liberate protons and produce hydroxyl or oxy complexes in solution and precipitate hydroxide or oxide solids [13]. Ce(III) and Ce(IV) salts have cations that display different characteristics. When dissolved in water,
Ce$^{4+}$ ions have lower basicity and higher charge than do Ce$^{3+}$ ions [14]. Therefore, Ce$^{4+}$ ions are more easily hydrolyzed and readily form many different complex ions. Upon deprotonation at elevated temperatures, the hydrated Ce$^{4+}$ ions in acidified solutions are hydrolyzed to form complexes with H$_2$O molecules or OH ions, in the form of [Ce(OH)$_x$(H$_2$O)$_y$]$^{(4-x^3)+}$, where x+y is the coordination number of Ce$^{4+}$ [14]. In aqueous solution, H$_2$O, a polar molecule, tends to take protons away from the hydroxide, forming CeO$_2$·nH$_2$O as follows:

$$Ce(OH)_x(H_2O)_y^{(4-x^3)+} + H_2O \rightarrow CeO_2 \cdot nH_2O + H_3O^+ \quad (1)$$

It is believed that hydrothermal treatment enhances the crystallization and crystal growth of CeO$_2$ from these hydrated CeO$_2$·nH$_2$O or [Ce(OH)$_x$(H$_2$O)$_y$]$^{(4-x^3)+}$ species, according to the solution-precipitation mechanism, in which the gelatinous precipitate dissolves in the liquid and re-precipitates on the nuclei formed initially [15]. When Ce(IV) salts are used as precursors, the starting precipitates consist of very fine crystals, resulting in notable crystal growth upon increasing the hydrothermal temperature. The XRD data presented in Figure 1 indicate that, relative to the results obtained at reaction temperatures of 120 and 160 °C, significantly larger crystals formed at 200 and 240 °C.

Figure 2 shows the crystallite sizes and values of SSA of the product powders as a function of the hydrothermal temperature. The powders prepared at 120 °C have the smallest crystallite size (3.0 nm). Upon increasing the hydrothermal temperature to 160, 200, and 240 °C, the crystallite sizes grew to 3.9, 5.4, and 9.0 nm, respectively. It is apparent that lower hydrothermal temperatures produced poorly crystallized powders that might include uncrystallized amorphous materials, whereas higher hydrothermal temperatures produced more-crystalline powders and less amorphous material. The SSA of the product powders agrees well with the XRD crystallite sizes. The 120HT4 powders have the largest SSA (175 m$^2$/g) and smallest crystallite size (3.0 nm), whereas the 240HT4 powders have the smallest SSA (108 m$^2$/g) and the largest crystallite size (9.0 nm).

Figure 3 shows TEM micrographs of product powders prepared under different conditions. The particle size
increased upon increasing the hydrothermal temperature. The powders prepared at 120 and 160 °C have very fine particle sizes (<4 nm). Upon increasing the hydrothermal temperature, the particle sizes of the product powders increased, as shown in Figures 3(c) and (d). The particle sizes observed by TEM roughly corresponded to the crystallite sizes estimated by Scherrer equation in Figure 2.

Figure 4 shows XRD patterns of the product powders obtained after calcination at 450 °C for 3 h of the samples prepared at various hydrothermal temperatures. When compared with the XRD patterns of the uncalcined powders (Figure 1), it is interesting that the powders prepared at 200 and 240 °C maintained similar full widths at half maximum (FWHM), indicating their similar crystallite sizes. In contrast, the 120HT4 and 160HT4 powders showed increased intensities and reduced peak widths, indicating significant crystal growth. The amorphous materials remaining after hydrothermal treatment were not as stable as the crystalline polymorphs during calcinations. With further heat treatment, therefore, the powders produced at lower hydrothermal temperatures showed rapid crystallization of the amorphous materials upon further heat treatment at the elevated temperature. The values of SSA of the product powders agree well with the XRD crystallite sizes. Upon calcination at 450 °C for 3 h, the SSAs of the 120HT4 and 160HT4 powders decreased rapidly from 175 to 108 m²/g and from 164 to 145 m²/g, respectively, whereas the 200HT4 and 240HT4 powders maintained almost the same SSA values.

Table 1. Autogeneous Pressures and Yields of the Product Powders with Respect to the Hydrothermal Temperature

<table>
<thead>
<tr>
<th>Hydrothermal Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Yield (%)</th>
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</thead>
<tbody>
<tr>
<td>120</td>
<td>6.8</td>
<td>82.3</td>
</tr>
<tr>
<td>160</td>
<td>9.5</td>
<td>85.9</td>
</tr>
<tr>
<td>200</td>
<td>16.3</td>
<td>90.8</td>
</tr>
<tr>
<td>240</td>
<td>36.1</td>
<td>92.3</td>
</tr>
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Figure 5. TGA traces of the product ceria powders prepared through hydrothermal treatment at 120 to 240 °C for 4 h.

Figure 6. Evolution of XRD patterns of the product ceria powders prepared through hydrothermal treatment at 200 °C. The reaction times varied from 4 to 24 h.

Figure 5 shows the thermogravimetric analysis (TGA) traces of the 120HT4, 160HT4, 200HT4, and 240HT4 powders after they had been dried at 80 °C. For the 120HT4 and 160HT4 powders, two main zones of weight loss are apparent. The first zone (from 50 to 250 °C) corresponds to the removal of physically adsorbed water. The second zone (from 250 to 450 °C) corresponds to the crystallization and removal of chemically adsorbed water. For the 200HT4 and 240HT4 powders, however, the total weight decreased slowly until 450 °C without any distinct stages.

The chemical composition of the product powders can be deduced from the TGA data by comparing the measured values with the theoretical weight losses for plausible decomposition reactions. During hydrothermal treatment, cerium ions are hydrated with water, resulting in either a hydrated oxide or oxide precipitate at the end of the hydrolysis reaction [16]. As hydrothermal treatment proceeds, the hydrated oxide is crystallized further. The XRD spectra indicated that CeO₂ was present in all of the powders, but the additional presence of amorphous Ce(OH)ₓ/CeO₂·nH₂O cannot be excluded.

The 120HT4 and 160HT4 powders showed weight losses of 17.0 and 13.5 %, respectively. Most of these weight losses are attributed to the decomposition of either a partially hydrated form of ceria, i.e., CeO₂·nH₂O, or a mixture of phases, e.g., CeO₂·CeO₃·2H₂O. In contrast, the 200HT4 and 240HT4 powders showed smaller weight losses (7.0 and 3.5 %, respectively). Table 1 shows the autogeneous pressures and yields of the product ceria powders with respect to the hydrothermal temperature. The autogeneous pressure at a hydrothermal temperature of 120 °C was 6.8 atm. Upon increasing the hydrothermal temperature to 160, 200, and 240 °C, the autogeneous pressures increased to 9.5, 16.3, and 36.1 atm, respectively. Higher pressures during the hydrothermal process
enhanced crystallization reactions, resulting in larger crystallite sizes and higher yields of the product powders.

The reaction time of the hydrothermal process also influences the properties of the product powders. Figure 6 shows the XRD patterns of the ceria powders prepared at 200 °C for different reaction times. The XRD patterns indicate that all of the product powders possessed fluorite structures. From the evolution of these XRD patterns, the (111) diffraction line became sharper upon increasing the reaction time. This finding indicates that the crystallite size grows through further hydrothermal reactions and structural rearrangement. However, the effect of the hydrothermal temperature was more critical than that of the reaction time.

Figure 7 shows the crystallite sizes and values of SSA of the product powders as a function of the reaction time. The powders prepared at 200 °C for 4 h have the smallest crystallite size (5.4 nm). Upon increasing the reaction time to 8, 12, and 24 h, the crystallite sizes grew to 6.0, 6.7, and 7.7 nm, respectively. It is clear that shorter reaction times produced smaller crystallites and a smaller number of crystals. This result indicates that the reaction is not complete after 4 h at 200 °C. The values of SSA of the product powders are in good agreement with the XRD crystallite sizes. The 120HT4 powders have the largest SSA (174.8 m²/g) and the smallest crystallite size (3.0 nm), whereas the 240HT4 powders have the smallest SSA (107.5 m²/g) and the largest crystallite size (9.0 nm). This result confirms that the crystallite sizes and values of SSA of the product ceria powders can be controlled by the hydrothermal conditions.

Conclusions

Nanocrystalline ceria powders having cubic fluorite structures were obtained by hydrothermal treatment of cerium(IV) ammonium nitrate without the use of a precipitating agent. The physical properties of the product powders were strongly influenced by the hydrothermal temperature and reaction time. In general, increasing the hydrothermal temperature and reaction time produced a greater yield of crystalline powders. The powders prepared at a hydrothermal temperature of 120 °C had the largest SSA (174 m²/g) and the smallest crystallite size (3.0 nm), whereas the powders prepared at 240 °C had the smallest SSA (108 m²/g) and the largest crystallite size (9.0 nm). Thus, hydrothermal synthesis is an effective means of preparing nanocrystalline ceria powders.

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References