

## Effect of aging temperature on CeO<sub>2</sub> formation in homogeneous precipitation

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Cerium oxide is a useful industrial material for applications such as solid-state electrolytes for electrochemical devices, as well as oxygen storage capacity component in three-way automotive catalysts [1–4]. For this reason, the preparation of cerium oxide powders has been investigated by a number of different techniques [5–11]. In the homogeneous precipitation method [6], cerium oxide is produced directly so that the calcination treatment can be reduced. It has recently been shown that the homogeneous precipitation at low temperature, from Ce(III)nitrate aqueous solutions in the presence of hexamethylenetetramine (HMT), produces crystalline CeO<sub>2</sub> powders. In this work, we examine the effect of the aging temperature on the homogeneous precipitation method using HMT at temperatures of 60–95 °C.

Preliminary experiments in our laboratory [11, 12] showed that the condition for the formation of spherulic and dispersed CeO<sub>2</sub> was limited by several factors, especially the concentration of HMT and Ce precursors. Two aqueous solutions of 0.3 M hexamethylenetetramine (HMT, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>) and 0.05 M cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>) were separately prepared with distilled water by mixing for 1 h. The solutions were mixed, and stirred for 0.5 h, then heated at a heating rate of 10 K/min and aged at temperatures of 60–95 °C for 1 h. The precipitate was separated from the solution by centrifugation and washed with water, then dried at 120 °C for 10 h. The yield was measured by the amount (in weight) that could be extracted if all the cerium nitrate in the solution precipitated during the reaction. We examined the influence of the operation temperature on the phase and the morphological characteristics i.e., crystalline size and shape of the particles. The phase identification was determined by powder X-ray diffraction (XRD; Rint2000, Rigaku Co., Ltd., Tokyo, Japan). The morphology of powders was characterized by scanning electron microscopy (SEM; Jeol, JMS6100, Tokyo, Japan). The surface area was measured by the Brunauer-Emmett-Teller (BET) method using N<sub>2</sub> absorption at 77 K (Quantachrome, Autosrp 3b, Boyton Beach, FL, USA).

In the precipitation method described earlier [6], HMT in the aqueous cerium nitrate solution decomposes homogeneously into ammonia, which then causes the precipitation of cerium oxide. A particular advantage of this synthesis method, when applied to cerium nitrate solution, is the direct precipitation of cerium oxide in the cubic fluorite structure. This feature was evident in this work, as shown in the diffraction patterns,

(a)–(d) in Fig. 1. All the precipitate was crystalline cubic cerium dioxide as the final oxide but without a hydroxide or carbonate. The XRD patterns of all powders looked similar to one another, despite the different aging temperature in the synthesis process; however, a slight difference of peak widths was observed. Generally, the broadness in XRD peaks is caused by the small size of the particles. The crystalline size, calculated by peak broadness, versus the aging temperature, is shown in Fig. 2. The crystalline size increased as the temperature increased, for example, 7.9 nm for a powder produced at 60 °C and 10.5 nm at 95 °C.

Fig. 3 shows the SEM micrograph of the powder produced at 95 °C. The powder was aggregate, but the agglomeration force seemed to be weak, since the ultrasonic treatment of the suspension easily produced the isolated spherulic particles. The secondary particle size of around 0.1–0.2 μm, from SEM observation, seemed to show a slight increase as the operation temperature increased. The surface area of powders is shown in Fig. 4. The primary (crystallite) and the secondary particle size should affect the surface area. In this experimental batch, the surface area was distributed in the range between 21 and 28 m<sup>2</sup>/g.

The most important influence of temperature appeared in the resultant yield of powders, as in Fig. 5. The yield drastically decreased as the operation temperature decreased. When the reaction was performed at 60 °C, the yield was only 25%, but at 95 °C it increased to 100%. The reason is that the reaction kinetics

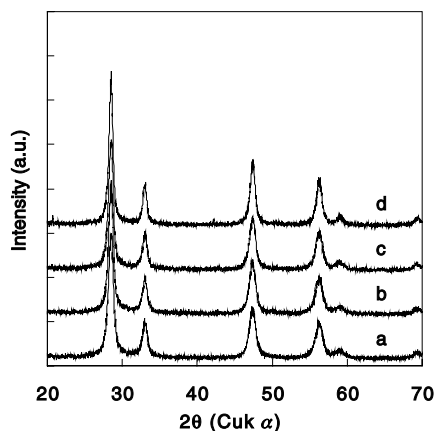


Figure 1 Powder X-ray diffraction pattern of cerium oxide from homogeneous precipitation using HMT at aging temperature of: (a) 60 °C, (b) 70 °C, (c) 80 °C, and (d) 95 °C for 24 h in air.

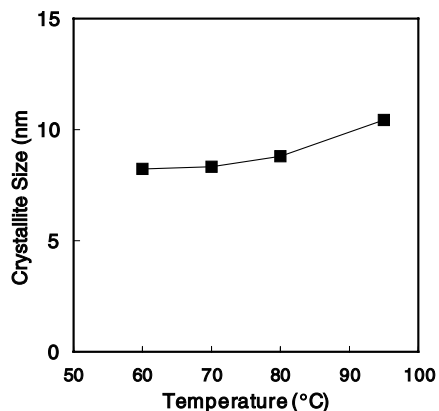


Figure 2 Crystalline size of CeO<sub>2</sub> powders versus aging temperature (60–95 °C).

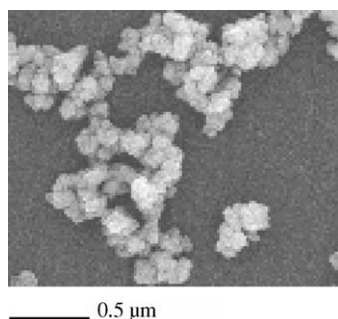


Figure 3 SEM image of CeO<sub>2</sub> powders produced at 95 °C.

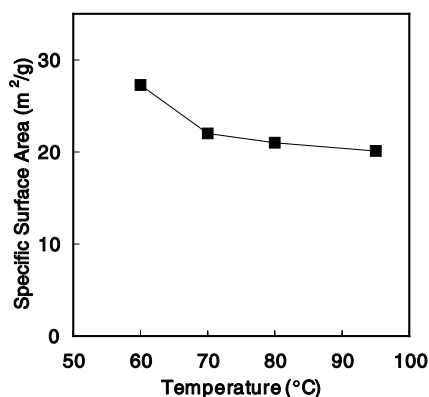


Figure 4 Specific surface area of CeO<sub>2</sub> powders versus aging temperature (60–95 °C).

is dependent on the temperature, such that a longer time for reaction is required for the lower-temperature operation. The difference in yield is important for practical production control using homogeneous precipitation with HMT, because the precursor cerium, which

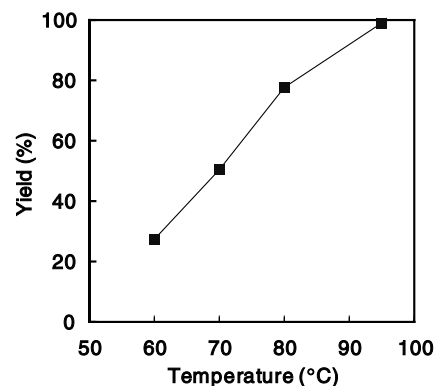


Figure 5 Yield of CeO<sub>2</sub> powders versus aging temperature (60–95 °C) for 24 h in air.

is one of the rare earth elements, is rather expensive. Despite the small differences, such as surface area, between these powders, the yield decreases as the temperature decreases.

Since the characteristics of obtained powders, such as the phase, surface area, crystalline size and agglomeration, are similar for all aging temperatures from 60 to 95 °C in the present work, we may select these operation temperatures to produce CeO<sub>2</sub>. These results are useful for the practical synthesis procedure of CeO<sub>2</sub> by homogeneous precipitation with HMT for ceramic and catalysis research.

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