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Preparation of discrete nanosize ceria powder

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Abstract

Ultrafine CeO_2 powders have been prepared from a solution of cerium(III) nitrate by a two-stage precipitation process. Precipitated cerium hydroxide gel was reacted in boiling basic solutions. Amorphous cerium hydroxide gel crystallized to $CeO_2 \cdot nH_2O$ ($n < 2$) during the low-temperature hydrothermal treatment, and this process was effective to dehydrate the adsorbed water and decrease the hydrogen bonding effect leaving a weakly agglomerated powder. The preparation was calcined at 600 °C to obtain urea. In order to avoid agglomerating during drying and calcining, sodium hexametaphosphate was introduced. The resulting powders are highly crystalline and weakly agglomerated.

Keywords: Nanocrystalline powder; Low-temperature hydrothermal; Anion surfactant; Cerium oxide

1. Introduction

Ceria (CeO_2) is a useful material for ceramics, glasses, catalysts, solid oxide fuel cells, phosphors, and for chemical applications. Production of cerium oxide powders is by no means a new research subject; however, practical methods are still needed for synthesizing high-quality ultrafine powders with required characteristics in terms of their size, size uniformity, morphology, specific surface areas, microstructure, crystallinity, etc. In a typical precipitation procedure, oxide powders or their precursors are first obtained by directly adding a ligand, for instance ammonia, etc., to a solution containing metal cations. An insoluble salt is precipitated once its solubility limit is exceeded, but this procedure has little control over the precipitate shape and size because of the rapid change of solution concentration and the localized discontinuous nature of ligand introduction and reaction. As a result of that, such powders tend to form excessively hard agglomerates.

There is an intense interest in preparing cerium oxide powders with controlled particle size and morphology. Recently, a few studies have been conducted to prepare fine ceria powders using the homogeneous precipitation based on forced hydrolysis. A key feature of homogeneous precipitation method is the controlled release of the reaction-participating ligands by another source in the solution. Urea and hexamethylenetetramine, which can slowly decompose to increase the pH of the solution, were usually used as the ligand source for ammonia as demonstrated by the original work. Aiken et al. [1] obtained an Y(III)/Ce(III) mixed compound with spherical morphology by homogeneous precipitation with urea. Matijevic and Hsu [2] prepared non-spherical ultrafine crystalline particles of $CeO(CO_3)H_2O$ through a urea solution. Chen and Chen [3] synthesized CeO_2 powders with a narrow size distribution by aging a cerium(III) nitrate solution in the presence of hexamethylenetetramine. The homogeneous precipitation results succeed in decreasing the tendency of the primary particles to agglomerate and yield powders with a narrow size distribution. However, the precipitated species are usually a precursor, e.g. hydroxide or carbonate, rather than the required oxide and a thermal decomposition treatment is needed to obtain the final product. But in precursor powders there are many points of contact between primary particles and even a low-temperature decomposition treatment allows sufficient diffusion to form hard agglomerates [4]. Dense agglomerates must therefore be avoided during the thermal decomposition if fine powders are to be obtained. In order to avoid hard agglomerates, hydrothermal treatment is an attractive method for the preparation of weakly agglomerated oxide powders. Hirano and Kato [5] obtained ultrafine ceria oxide powders (3–16 nm) from cerium(III) nitrate, cerium(IV) sulfate, and cerium(IV) ammonium sulfate under

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hydrothermal conditions at 120–200 °C for 5–40 h. Lin and Duh [6] synthesized 5.5 mol% CeO_2–2 mol% $YO_{1.5}$–ZrO_2 ultrafine powders (4.8 nm) with controlled crystallite size by coprecipitation and hydrothermal treatment. Wu et al. [7] studied the relationship between the particle size, the morphology of the ceria crystallites and the reaction conditions during the hydrothermal synthesis.

Homogeneous precipitation, based on decomposition of urea and hexamethylenetetramine, and the high-temperature hydrothermal treatment are effective methods to prepare ultrafine cerium oxide powders, but the high production cost and the low productivity limit their commercialization. Therefore, it's necessary to develop a powder fabrication method to control the characteristics of CeO_2 powder and to fabricate it economically. Woodhead [8,9] reported another chemical approach for colloidal cerium oxide, cerium(IV) hydroxide was precipitate from Ce(III) nitrate using a mixture of hydroxide peroxide and ammonia, but this was not a homogeneous precipitation. Djuricic and Pickering [10] reported a new approach to prepare ultrafine CeO_2 powders. Nanocrystalline powders of cerium oxide were prepared from Ce(III) nitrate solution by a precipitation process, the synthesis was completed by hydrothermal treatment at 180 °C to yielded weakly agglomerated cerium oxide powders; and calcination process of precursor was also studied, in comparison with hydrothermal method, there was considerable grain coarsening and the agglomerates were hard and non-dispersible.

The goal of this research is to investigate an economically feasible method that is suitable for mass production of powders. This approach involves a two-step precipitation process based on the research of Djuricic and Pickering [10], and a low-temperature hydrothermal treatment (evaluated at ≤100 °C) [11–13]. The decomposition of the precursor is completed by calcination to prepare the cerium oxide powders. In order to make the CeO_2 powders easy to be redispersed after drying and calcining, an anion surfactant was introduced [14–16].

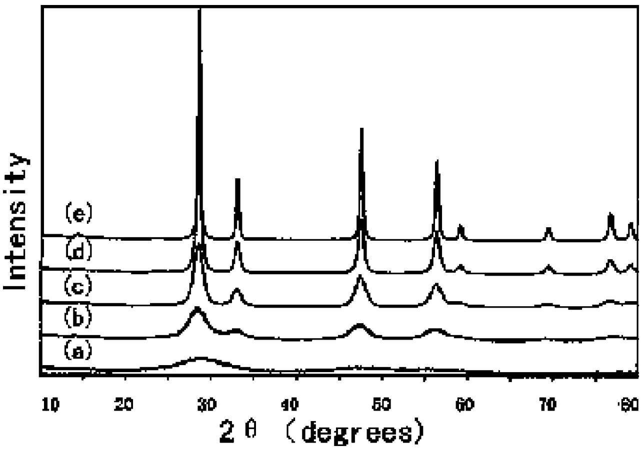


Fig. 1. X-ray diffraction patterns for CeO_2 powders: (a) freshly-prepared precipitate, (b) powder after hydrothermal treatment for 2 h at 100 °C, (c) calcined at 450 °C for 2 h, (d) calcined at 600 °C for 2 h, (e) calcined at 800 °C for 2 h.

2. Experiment procedure

2.1. Powder preparation

Cerium nitrate hexahydrate ($Ce(NO_3)_3\cdot 6H_2O$, >99.99%), ammonium hydroxide (NH_4OH, 25 vol.%), and hydrogen peroxide (H_2O_2, 30 vol.%) were used as starting materials. Sodium hexametaphosphate (SHMP, >99%) was used

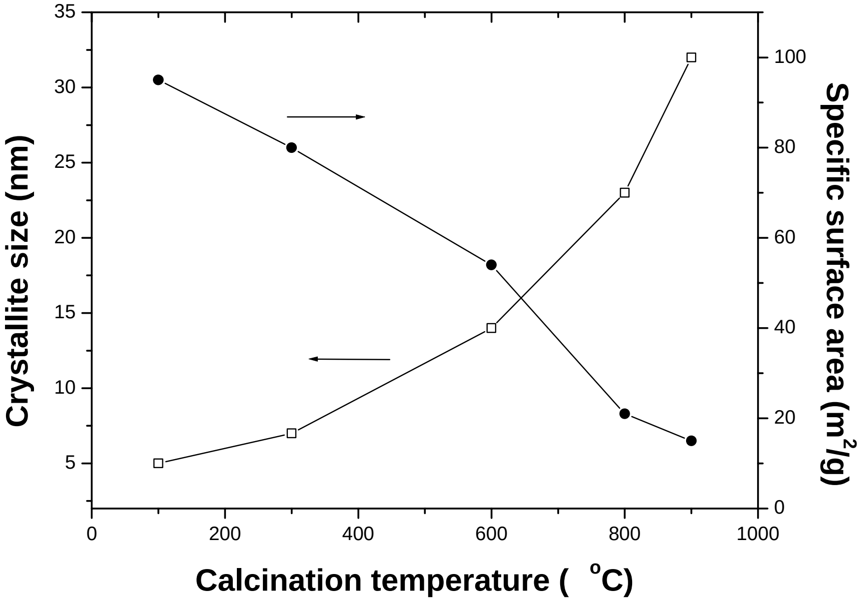


Fig. 2. Effects of calcination temperatures on the crystallite size and the specific surface area.

as anion surfactant in this study. When needed, dilute nitric acid or ammonia were used to adjust the pH. A solution of 0.1 mol l^{-1} Ce(III) nitrate in water was mixed with 30 vol.% hydrogen peroxide under constant stirring in a volume ratio of 3:1 at 5 °C. After 10 min the solution turned orange–yellow, but remained transparent. Ammonium hydroxide solution was then added dropwise to increase the pH to 10 [10]. The solution was transferred into a glass beaker and was refluxed at 100 °C for 2 h in an oil bath. After this hydrothermal treatment, the solution were cooled, filtered and washed with deionized water until the supernatant showed neutral pH. The washed precipitates (20 g) were dispersed in 1000 ml deionized water by high-speed agitation for 0.5 h, and the pH of the slurry was adjusted to 6. Then a homogeneous solution (100 ml) of SHMP (0.2 g) was slowly added to the precursor slurry with continuous stirring for 1 h. The resulting products were filtered and oven-dried overnight at 80 °C. Calcination was carried out for 2 h at 600 °C under flowing air atmosphere.

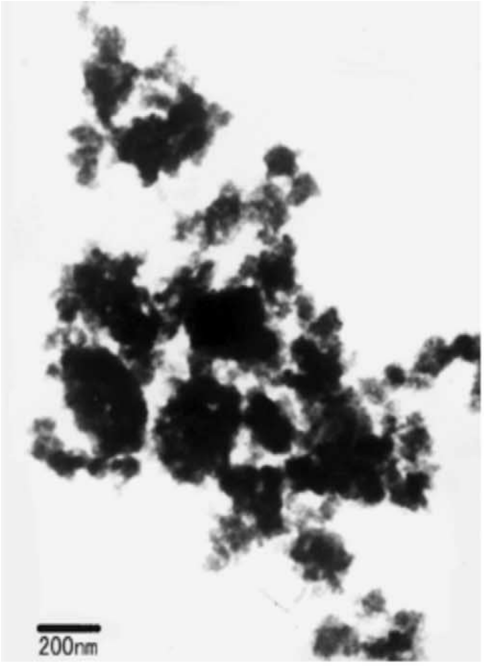
2.2. Characterization

The reaction products were characterized by XRD (3 kW/V; D/Max-IIIC, Rigaku, Tokyo, Japan) with CuKα radiation. Crystallite size was calculated from XRD peaks using the Scherrer formula. The morphology, particle size and size distribution of particles were investigated with a Jeol 100CXII electron transmission microscopy (TEM), while the powder's surface area was measured by the multipoint BET nitrogen adsorption technique. Powder samples were analyzed by thermogravimetric analysis (TG, Mettler Toledo 5202) in dry-air using a heating rate of 20 °C min^{-1}. Zeta potentials of cerium hydroxide were measured in the deionized water with a Laser Zee Meter 501 (Pen Kem Co., Ltd.) electrophoresis apparatus.

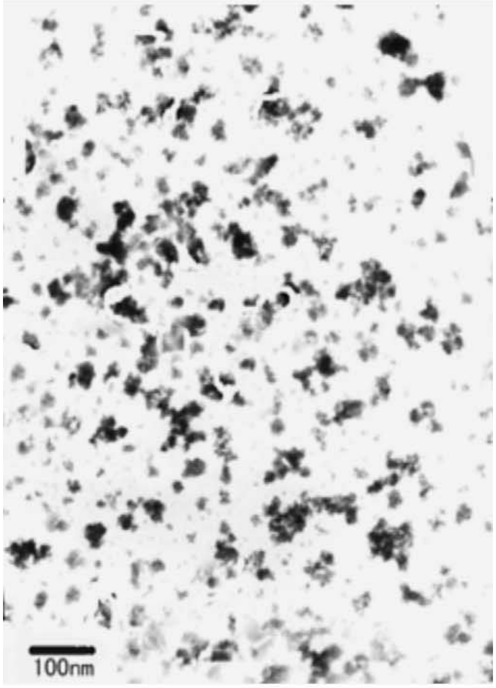
3. Results and discussion

Fig. 1 shows XRD of powders after various heat treatments. It is noteworthy that a very weak and broad peak around 30° was observed for the freshly prepared precipitate. After aging the precipitate for 2 h at 100 °C, the XRD (Fig. 1b) shows that the precipitated gel was crystallized and the spectra already displayed all of the major reflections of CeO_2 with a fluorite structure. However, the weak but distinct reflection peaks indicated the gels were not fully crystallized. After drying, heating, and calcination, the characteristic peaks of CeO_2 became sharper, and the higher the heat treatment temperature, the sharper the peaks. Fig. 2 summarizes the data obtained from line-broadening analysis of the peak in XRD as a function of heat treatment temperatures. At 600 °C, the average crystallite size is about 14 nm. However, the average crystallite size increased to about 32 nm after calcination at 900 °C. The BET specific surface area of the powders after 600 °C calcination was 55 $m^2 g^{-1}$ and after 900 °C calcination was 15 $m^2 g^{-1}$, and the change with heat treatment temperature showed good agreement with the change in the crystallite size.

TG of the precursors exhibited three weight lose steps from 0 to 500 °C and only a small mass change between 500 and 600 °C. The weight loss up to 600 °C is about 17.5%, and beyond this temperature it is negligible. The total weight loss



(a)



(b)

Fig. 3. TEM micrographs of precipitates: (a) freshly-prepared precipitate, (b) powder after hydrothermal treatment for 2 h at 100 °C.

corresponds well with that expected for $Ce(OH)_4$ decomposition (17.29%). $Ce(OH)_4$ is a hydrous oxide which can also be described as $CeO_2{\cdot}nH_2O$, which dehydrates progressively, i.e. $CeO_2{\cdot}nH_2O$ where $n \leq 2$. Therefore, the decomposition of the precursor can be described as a dehydration process of the $CeO_2{\cdot}nH_2O$. After the low-temperature hydrothermal treatment, the TG weight loss was 15.1%, which does not correspond to the decomposition of any single compound. It should be ascribed to the complete decomposition of the initial phase to $CeO_2{\cdot}nH_2O$ ($n < 2$).

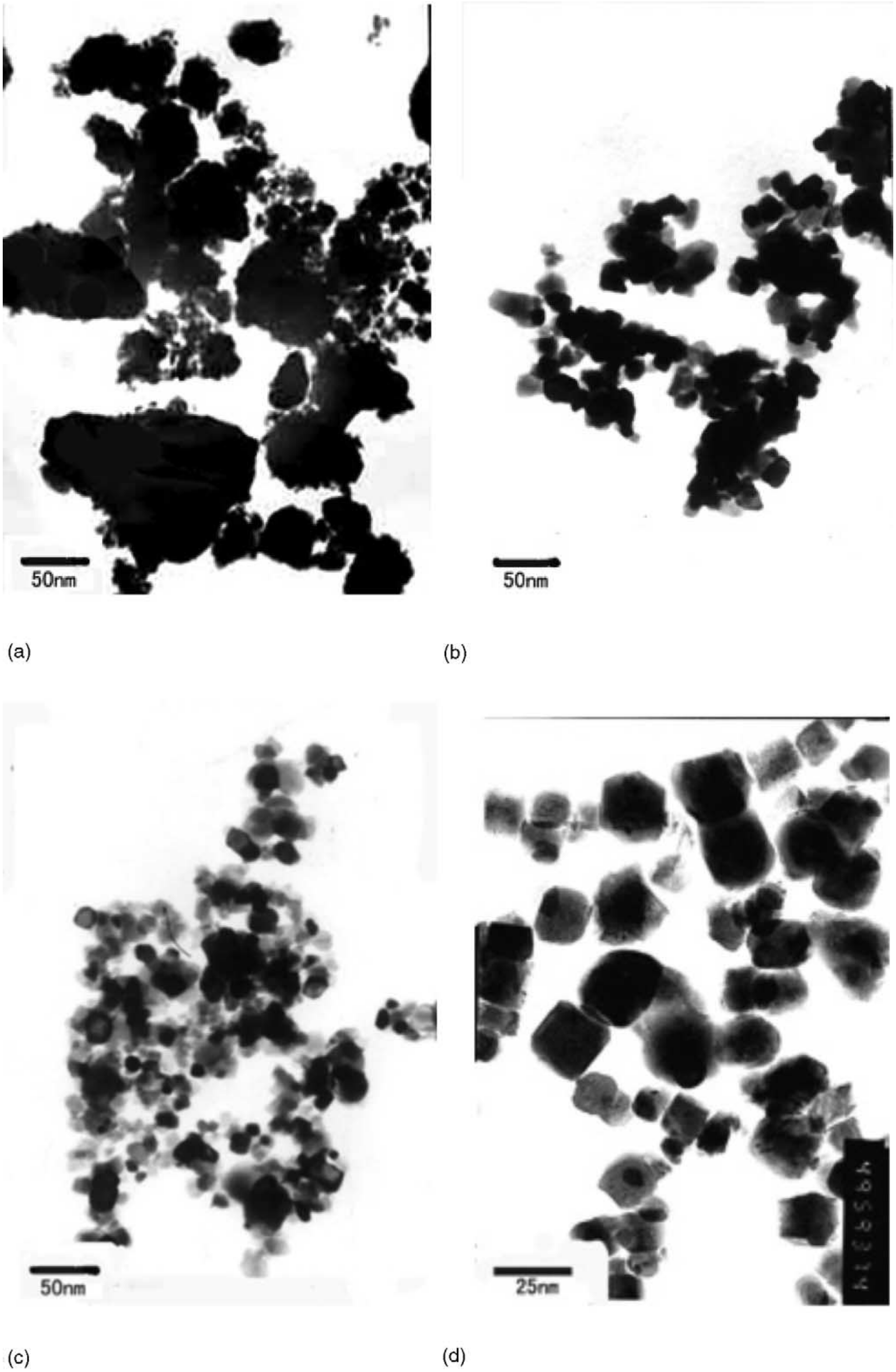


Fig. 4. TEM micrographs of cerium oxide: (a) freshly-prepared precipitate calcined for 2 h at 600 °C, (b) hydrothermally treated powder after calcination for 2 h at 600 °C. Hydrothermally treated powder with anion surfactant after calcination at 600 °C (c) and 800 °C (d) for 2 h.

The precipitate without hydrothermal treatment confirmed the Scherrer X-ray line-broadening estimate for the 5 nm size. The crystallite sizes for the powders after boiling at 100 °C for 2–4 h were around 5–7 nm. There was no difference in the crystallite size among these specimens, but the average secondary particle size and size distribution show an obvious change during the low-temperature hydrothermal treatment. Fig. 3 shows TEM micrographs of the CeO_2 precursor particles with and without low-temperature hydrothermal treatment. The large non-uniform agglomerates with the maximum particle size about 1.5 μm (Fig. 3a) is a partially amorphous phase as identified in Fig. 1a. After aging at the boiling temperature for 2 h, the large agglomerates disappeared and became smaller isometric ones and the maximum particle size decreased sharply attaining a value of 120 nm. With further aging for 4 h, there was not obvious change in the particle size and morphology.

The low-temperature hydrothermal treatment proved to be an effective method to decrease the agglomerate. The precipitate obtained using two-stage method is a gelatinous substance, and a large amount of water existed in precipitate. Usually, grain surfaces adsorb water molecules, so that hydrogen bonds can be formed between approaching grains. Therefore, hydrogen bonding can lead to hard agglomerates of grains during the drying and calcining process. The hydrothermal process at boiling temperature is effective to dehydrate the adsorbed water and decrease the hydrogen bonding effect leaving a weakly agglomerated powder of hydrated ceria. Alternatively, if the solution was maintained at basicity, it might be due to crystallization from amorphous gel through a dissolution-precipitation, because solubility of cerium hydroxide is very high in the strong basic solution [11]. It was shown in Fig. 1b that crystallization at $\leq$100 °C is possible.

The morphology of this powder after 600 °C calcination is shown by Fig. 4. The CeO_2 powders obtained from the precursor without any hydrothermal heat treatment display excessively hard agglomerates, and the size distribution is extremely broad with the largest particles of 3 μm. In contrast, the CeO_2 powders prepared by calcining the precursor with hydrothermal treatment is weakly agglomerated, but there were still some large densely agglomerated particles (Fig. 4b). In precursor powders, there are many points of contact between primary particles and even a low temperature thermal decomposition treatment allows sufficient diffusion to occur to produce densely agglomerated nanostructure powders. In order to solve this problem, we utilized anion surfactant to decrease the agglomerate formed during the drying and calcining. According to the analysis result, the zeta potentials (ζ) of the precursor slurry change from positive to negative depending on the pH of the slurry. As the powders indicated a positive zeta potential at a pH of $<$7.2 in an acidic solution, the primary particle of hydrous ceria formed a electric double layer between the adsorbed H^+ ion on the surface hydroxyl group of the particle surface and the $NO_3{}^-$ ions that were attracted to the surface of the primary particle from the aqueous solution; this primary particle had a positive surface charge because of the formation of the electric double layer. Therefore, primary particle with a positive surface charge are thought to inhibit aggregation among particles by electrical repulsion. The effect on electrical repulsive force suggests that the secondary particle size of hydrous ceria decreased as the H^+ ion concentration increased, but the acidity great enough inclined to dissolve partially the oxide particle. As such, the pH of precipitate slurry was adjusted to 6. The zeta potentials of hydrous ceria were positive in acidic solution and the surface of hydrous ceria was thought to adsorb the anion surfactants easily due to the electrostatic force of attraction. Because of the surface adsorption of the anion surfactant, the agglomerates decreased sharply and the powders were easy to be redispersed after drying and calcining. The morphology of the CeO_2 powders obtained from the precursor coating with anion surfactant is shown in Fig. 4c. In comparison to the Fig. 4b, it displays a narrow size distribution and very weakly agglomerated nanostructure. Fig. 4d shows the morphology of cerium oxide after calcining at 800 °C for 2 h, the coarsening of crystallite was agreement with previous investigations.

4. Conclusion

The objective of this work was to develop an economically feasible precipitation method that is suitable for a large scale production of ceria oxide powders. For this purpose, a two stage homogeneous precipitation was utilized to produce the cerium hydroxide. In order to avoid agglomerating during drying and calcining, anion surfactant was introduced to solve this problem. The resulting ceria oxide powders are highly crystallite. The weakly agglomerated state of the ceria powder, the fine particle size under 30 nm, and the narrow size-distribution are characteristics which make the powder suitable for a variety of ceramic forming processes.

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