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Properties of the ceria colloidal particles prepared by the solvothermal oxidation of cerium metal

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Abstract

Solvothermal reaction of cerium metal in 2-methoxyethanol at 200–300 °C yields a transparent colloidal solution containing crystallized ultrafine (2–6 nm) ceria particles. High-surface area ceria powder (183 $m^2 g^{-1}$) is obtained by heat treatment at 100 °C of the product recovered by coagulation of ceria particles in the colloidal solution. However, the surface area of the ceria powders abruptly decreased by calcinations at high temperatures (the sample calcined at 600 °C have a surface area of 2.7 $m^2 g^{-1}$ with the crystallite size of 21 nm). When a non-ionic surfactant was added to the recovered ceria powder, it maintained a high-surface area (76 $m^2 g^{-1}$) even after calcination at 600 °C.

Keywords: Ceria; Solvothermal oxidation; Cerium metal; Colloidal solution

1. Introduction

Ceria is used as oxygen ion conductors, automotive catalysts [1], ultraviolet radiation blocking materials [2] and so on. Synthesis of fine crystals of ceria having high-surface area together with high thermal-stability is important for the practical use as catalysts.

In our laboratory, various inorganic materials were synthesized by using organic solvents at temperatures higher than their boiling points under autogenous pressure in an autoclave. This method is called solvothermal method because of the use of solvent in the place of water for the hydrothermal reaction.

Hydrothermal oxidation of metals has been examined and the obtained products were reported to have unique properties [3]. However, solvothermal oxidation of metals has been scarcely examined [4].

In the present paper, we examine solvothermal oxidation of cerium metal. This reaction yields a transparent colloidal solution of ultrafine ceria particles [5,6]. Properties of ceria powders recovered from the solution by coagulation are reported.

2. Experimental

The process for the synthesis of the ceria nanoparticles is illustrated in Fig. 1. Cerium metal (2 g) and 2-methoxyethanol (80 mL; bp, 124.6 °C; T_c, 324.5 °C [7]) were placed in a test tube, which was then set in an autoclave (200 mL). In the gap between the test tube and the autoclave wall, an additional 40 mL of 2-methoxyethanol was placed. After completely purged with nitrogen, the autoclave was heated to a desired temperature at the rate of 2.3 °C/min and kept at the temperature for 2 h under the autogeneous pressure of the solvent and evolved hydrogen (ca. 3.5 MPa at 250 °C; ca. 7.5 MPa at 300 °C). When the autoclave was cooled at room temperature, the produced mixture was centrifuged, and a dark brown transparent supernatant was obtained. To the supernatant, a small amount of aqueous ammonia was added. The solution became turbid and a yellow precipitate was formed. The product was centrifuged at 3500 rpm. The precipitate was washed with distilled water, dried in air, and calcined at various temperatures for 1 h.

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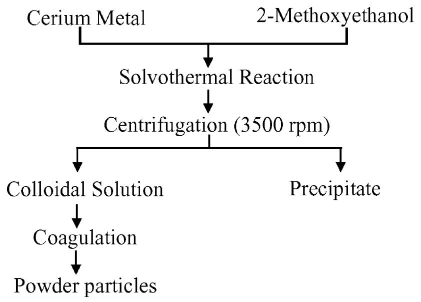

Fig. 1. Flow chart of solvothermal oxidation of cerium.

Pluronic 123 (BASF Co.), a non-ionic surfactant ($(EO)_{20}$ $(PO)_{70}(EO)_{20}$), was added to the precipitates with distilled water and stirred until the surfactant was dissolved. The mixture was calcined as mentioned above.

For comparison, a ceria sample was prepared by the precipitation method; 7.73 g of $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 400 mL of water and 30 mL of 1N NaOH was added to the solution. The precipitate was centrifuged and washed with distilled water.

X-ray powder diffraction (XRD: Model XD-D1 Shimadzu) was performed with a Cu Kα radiation. The crystallite size was estimated from line broadening of the 220 diffraction peak by Scherrer equation [8]. Specific surface area was calculated using the BET single-point method based on N_2 uptake measured at 77 K. Nitrogen adsorption isotherm was measured using a volumetric gas-sorption system, Autosorb-1 (Yuasa Ionics).

3. Results and discussion

3.1. Properties of the colloidal solution

After the reaction, a pale yellow precipitate and a dark brown transparent solution were obtained. The XRD pattern of the precipitates showed characteristic peaks of ceria and the crystallite size of the precipitates calculated by the XRD line broadening was over 100 nm. The precipitate was derived from the ceria superficial layer on the cerium metal chips, because the property of the precipitate was not altered by the reaction conditions.

Addition of distilled water to the transparent solution obtained as the supernatant after centrifugation of the product did not lead any change except for dilution of the color of the solution. When laser beam was irradiated to the colloidal solution, Tyndall phenomenon was observed (Fig. 2).

When cerium metal was kept in 2-methoxyethanol for 10 days at room temperature, the solvothermal reaction gave ceria powders with a crystallite size of 11 nm (bigger than colloidal particles) and colloidal solution was not obtained. These results indicate that the superficial layer on the cerium metal chips slowly reacts with 2-methoxyethanol and that the burst nucleation of ceria caused by reaction of cerium metal with the solvent at high temperature is essential for the formation of the colloidal solution.

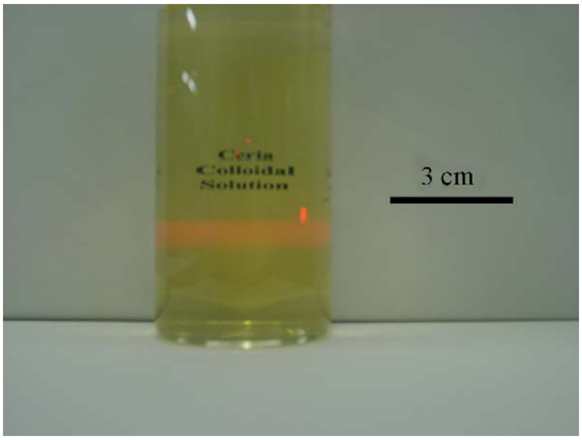

Fig. 2. Transparent colloidal solution of ceria (6.3 g ceria/L) obtained by solvothermal reaction of cerium metal.

When the colloidal solution was kept standing for several weeks with slow evaporation of the solvent, gelation took place and the gel gradually shrank while remaining transparent. On the other hand, when the solution was kept in a closed bottle, it was stable for at least several months.

Addition of salt solutions such as aqueous NaCl to the transparent solution caused the formation of gelatinous precipitates.

3.2. Properties of the colloidal particles

The colloidal particles were coagulated by addition of aqueous NH_3 to the colloidal solution. The precipitate separated by centrifugation and dried in air was obtained as yellow powder. The XRD patterns of the powder obtained by the reaction at various temperatures are shown in Fig. 3.

Although these powders exhibited broad peaks, the XRD profile coincided with the fluorite type structure of ceria. The crystallite size of the particles was about 2 nm (Fig. 3(a)), which is in agreement with the particle size observed by

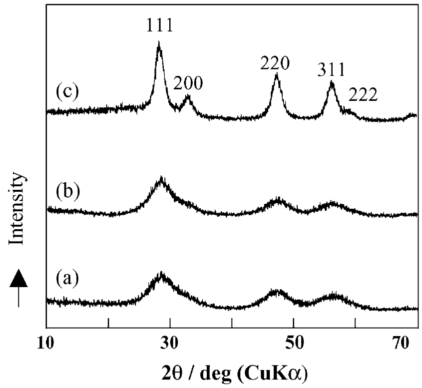

Fig. 3. XRD patterns of the powders prepared by the reaction at (a) 200 °C, (b) 250 °C and (c) 300 °C.

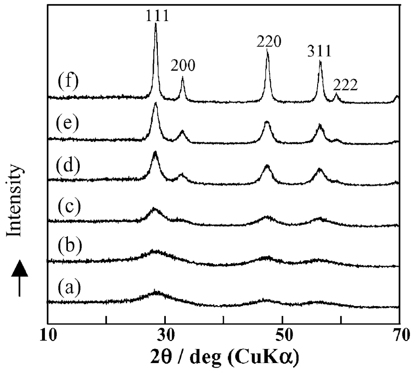

Fig. 4. XRD patterns of the powders prepared by coagulation of colloidal particles formed by the reaction at 250 °C. Calcination temperatures are (a) 25 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, (e) 400 °C and (f) 600 °C.

TEM. It is noted that a spherical ceria particle with a diameter of 2 nm contains about 200 cerium atoms. The size of ceria nanoparticles increases at a reaction above 250 °C (6 nm by the reaction at 300 °C). When the particles were calcined, the XRD peaks became gradually sharp (Fig. 4), but no other phases appeared.

Fig. 5 shows the change in the crystallite size of the ceria by calcinaton. In comparison with the ceria powder prepared by precipitation, the crystal growth of the ceria powders prepared by solvothermal method easily took place by calcination at relatively low temperatures. It must be noted that the crystallite size sharply increased when the ceria powder was calcined at a temperature above 600 °C.

Surface area and crystallite size of the ceria powders prepared by the solvothermal method are summarized in Table 1. High-surface area ceria powders (183 $m^2 g^{-1}$) were obtained by the heat treatment of the coagulated ceria particles at 100 °C. When ceria powder was calcined at high temperatures, surface area decreased and crystallite size increased. The surface area of ceria powders calcined at 600 °C was 2.7 $m^2 g^{-1}$ and the crystallite size was about 21 nm.

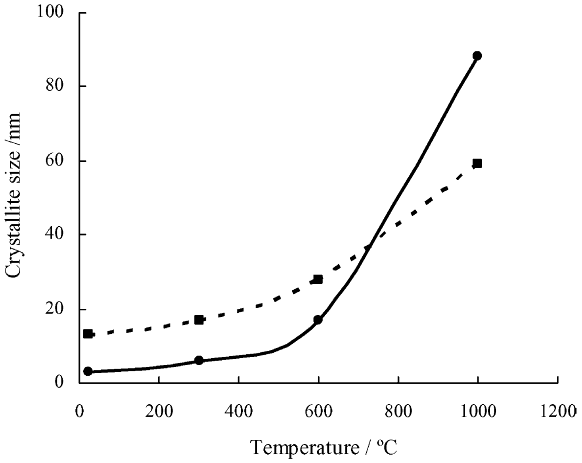

Fig. 5. Effect of the calcination temperature on the crystallite size of the ceria powder prepared by a precipitation from $Ce(NO_3)_3 \cdot 6H_2O$ (■) and by coagulation of colloidal particle formed by the solvothermal reaction (●).

Table 1
Surface area and crystallite size of the ceria powders prepared by the solvothermal oxidation

Reaction temperature (°C)	Calcination temperature (°C)	Crystallite size (nm)	BET surface area ($m^2 g^{-1}$)
200	Room temperature	2.4	–
	100	2.5	183
	200	3.8	126
	300	5.8	79
	400	6.7	42
	600	19	1.7
250	Room temperature	2.8	–
	100	2.9	152
	200	3.5	131
	300	5.8	85
	400	7.4	50
	600	21	2.7
300	Room temperature	4.5	–
	100	4.5	150
	200	4.9	147
	300	5.1	140
	400	6.4	124
	600	9.4	88

3.3. *Effect of surfactant*

The surface area and crystallite size of the ceria powders calcined after Pluronic 123 was added to the coagulated gel are shown in Table 2. The ceria powder calcined with the surfactant maintained smaller crystallite size and higher surface area than that without the surfactant.

Fig. 6 shows N_2 adsorption isotherms and *t*-plots [9]. The latter plot provides conclusive evidence for the presence or absence of micro- or meso-pore systems. From Fig. 6(a), it is evident that the ceria powders directly calcined has micropores. The average pore size was calculated to be 8 Å. Because fine particles have high-surface energy, the ceria particles are strongly coagulated and micropore systems are formed in the void between the small ceria particles. Consequently, this coagulation facilitates the crystal growth of ceria particles.

As shown in Fig. 6(b), on the other hand, *t*-plot of the ceria powders calcined after addition of the surfactant exhibited a straight line going through the origin, indicating that the powders have not apparent pore systems. This result shows that addition of the surfactant prohibits the strong coagulation of the ceria particles and the powders are only loosely floccu-

Table 2
Surface area and crystallite size of the ceria powders calcined after addition of Pluronic 123 to the coagulated gel

Calcination temperature (°C)	Crystallite size (nm)	Surface area ($m^2 g^{-1}$)
300	5.0	137
400	6.7	98
600	11	76

The ceria powders were obtained by coagulation of ceria particles in the colloidal solution prepared by the solvothermal oxidation of cerium metal at 250 °C.

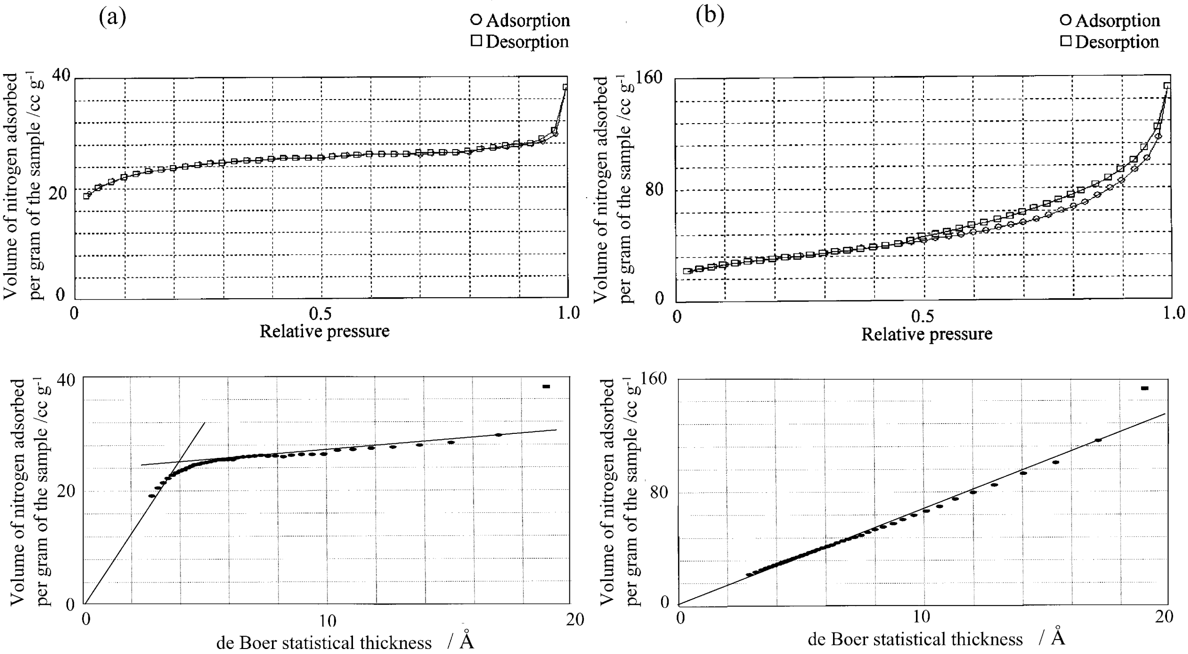

Fig. 6. N_2 adsorption isotherm (upper) and *t*-plot (lower) of ceria powders calcined at 300 °C without the surfactant (a) and ceria powders calcined at 300 °C with the surfactant (b).

lated. Since long diffusion path is required for sintering and crystal growth, the ceria particles prepared by addition of the surfactant maintained smaller crystallite size and higher surface area than those prepared without the surfactant.

4. Conclusion

Solvothermal oxidation of cerium metal in 2-methoxyethanol at 200–300 °C yielded a transparent colloidal solution containing crystallized ultrafine (2–6 nm) ceria particles. Ceria particles were recovered by addition of aq. NH_3.When a surfactant was added to the coagulated gel, ceria powders maintained high-surface area even after the calcination at high temperatures.

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