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Preparation of monodispersed cerium(IV) oxide particles by thermal hydrolysis: influence of the presence of urea and Gd doping on their morphology and growth

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Monodispersed cerium(IV) oxide (CeO_2) particles composed of an agglomeration of primary nanocrystalline particles with a cubic fluorite structure could be synthesized from relatively concentrated cerium(IV) sulfate solutions up to 0.5 mol dm^{-3} by thermal hydrolysis at 120 to 240 °C. The influences of the presence of urea and its concentration on their crystallite size and morphology were investigated. Upon the addition of urea and increasing its concentration, the morphology gradually changed from monodispersed particles to dispersed ultra-fine particles that had no definite shape and tight agglomeration. The mechanisms for the growth and agglomeration of the particles formed by thermal hydrolysis were discussed. The existence of a dopant such as Gd was effective for suppressing the grain growth of the ceria particles during the calcining and sintering.

Introduction

Cerium(IV) oxide (CeO_2, ceria) is one of the highly refractory oxides and has the fluorite structure which is stable from room temperature up to its melting point. Ceria, either undoped or doped with zirconium or several rare earth elements, is of considerable interest as catalytic supports for automotive exhaust systems[1,2] and as solid electrolytes for solid-oxide fuel cells.[3,4] Its performance as a solid electrolyte is similar to that of zirconium oxide (ZrO_2)[5,6] because of its high oxygen ion conductivity and relatively low operating temperature. The preparations of fine CeO_2 particles or cation-doped ceria particles and their precursors have been examined using several techniques such as hydrothermal synthesis,[7–10] urea-based homogeneous precipitation,[11–14] hexamethylenetetramine-based homogeneous precipitation,[15,16] coprecipitation,[17,18] decomposition of oxalate precursors,[19] forced hydrolysis,[20] electrochemical synthesis,[21] the use of hydrazin monohydrate,[22] and solvothermal synthesis.[23]

The method of precipitation from solution under hydrothermal conditions, which is one of the soft solution routes, is of current interest and is attractive for the direct synthesis of crystalline ceramic particles at relatively low temperatures. Hydrothermal reactions in general are carried out in an autoclave at temperatures between the boiling and critical points of water (100 to 374 °C) at elevated pressure (up to *ca.* 15 MPa). This hydrothermal route has been used for the synthesis of fine powders of various oxide ceramics[24] because the synthesized powder has excellent homogeneity and particle uniformity. The hydrothermal synthesis of CeO_2 particles has been the subject of several investigations. Zhou and Rahaman[8] synthesized fine CeO_2 and Y_2O_3-doped CeO_2 particles by the hydrothermal treatment of a gelatinous precipitate from cerium(III) nitrate solution and excess aqueous ammonia. The effect of mineralizers on the crystal growth of CeO_2 from cerium(III) nitrate solution and excess aqueous ammonia under hydrothermal conditions at 500–600 °C and 100 MPa was reported.[7] In a series of our studies, the preparation of nanocrystalline CeO_2 particles from different cerium salt solutions and excess aqueous ammonia was studied to determine their effects on the crystallinity, crystallite size, and crystal growth of the synthesized CeO_2 particles. Ultra-fine ceria particles could be hydrothermally prepared from Ce(IV) sources.[9,10] On the other hand, it is well known that uniform particles of metal (hydrous) oxides are generated by the hydrolysis of acidified solutions of the metal salts. The synthesis of monodispersed ceria particles by thermal hydrolysis was successfully carried out at very low cation concentrations (below 5×10^{-4} mol dm^{-3}).[20] However, this route was not practical for powder production. Meanwhile, urea has been used as the ligand source for ammonia in a homogeneous precipitation method, but the hydrothermal technique in the presence of urea has rarely been used except for the synthesis of 3 mol% Y_2O_3–ZrO_2 powders.[25,26] In our previous work, the applicability of this method for the preparaton of CeO_2 powders was shown by the synthesis of nanocrystalline ceria particles from cerium(IV) sulfate solution,[27] but there was no comparison of results obtained in the presence and the absence of urea.

In the present study, thermal hydrolysis was performed at 120 to 240 °C to synthesize monodispersed ceria particles from a relatively concentrated cerium(IV) sulfate solution (*ca.* 0.5 mol dm^{-3}). The effects of the hydrolysis temperature (*ca.* 240 °C), time, and concentration of the starting cerium(IV) sulfate on the crystal phase of the solid products and the crystallite size and morphology of the obtained ceria particles were examined. The influences of the presence of urea and its concentration on the crystallite size and morphology were also investigated. The mechanisms for the growth and agglomeration of the primary particles of ceria were discussed. In order to clarify the effect of dopant on the grain growth of ceria upon heat treatment and sintering, the doping of 20 mol% $GdO_{1.5}$ into the CeO_2 particles was also examined.

Experimental

Sample preparation

Cerium(IV) sulfate ($Ce(SO_4)_2 \cdot 4H_2O$, Kishida Chemical Co., Ltd., Japan) and urea ($CO(NH_2)_2$, Nacalai Tesque, INC., Japan) were of laboratory purity and used as the starting materials. A given quantity (20 cm^3) of a mixed solution of the cerium salt with urea in the desired concentration was poured into a Teflon bottle with an inner volume of 25 cm^3, held in a stainless-steel vessel. After the vessel was sealed, it was placed in a thermostatted oven, heated with constant rotation at 150 to 240 °C for 5 h to 48 h. The precipitated particles were separated by centrifuging, washed (distilled water), and then dried in an oven at 60 °C under an air atmosphere. The addition of Gd_2O_3 to CeO_2 was carried out by homogeneous precipitation as follows. The precipitated ceria particles before drying were then dispersed in a solution of 0.01 mol dm^{-3} gadolinium chloride ($GdCl_3 \cdot 6H_2O$, Kishida Chemical Co., Ltd., Japan) to make a suspension. The suspension, after the addition of 0.5 mol dm^{-3} urea, was heated and kept at 90 °C with stirring. The composition of the solid solution was adjusted to 20 mol% $GdO_{1.5}$–80 mol% CeO_2. The resultant homogeneous precipitates were filtered, washed (distilled water), dried, pulverized, and calcined at 300 to 900 °C in air. The doped and undoped ceria powders calcined at 600 °C were ball-milled in ethanol, dried, and then uniaxially cold-pressed under a pressure of 98 MPa to form pellets. The green compacts thus prepared were sintered at 1200 to 1600 °C for 1 h in air.

Sample characterization

Phase identification was performed by X-ray powder diffraction (XRD) using Cu-Kα radiation. The crystallite size was estimated from line broadening of the 220 diffraction peak according to the Scherrer equation. The precpitate morphology and size were examined by transmission electron microscopy (TEM; model JEM-200CX, JEOL, Tokyo, Japan). The bulk density of the sintered bodies was measured using the Archimedes technique. The microstructure of the poloished and thermally etched surfaces of the sintered samples was observed using a scanning electron microscope (SEM).

Results and discussion

Synthesis of monodispersed ceria particles

The thermal hydrolysis of $Ce(SO_4)_2$ solutions with concentrations of 0.05 to 0.5 mol dm^{-3} was performed in the temperature range of 120 to 240 °C for different periods of time. In Fig. 1 is shown a TEM photograph of the solid products obtained from the 0.1 mol dm^{-3} solution by thermal hydrolysis at 180 °C for 5 h, proving that they are uniform and spherical particles with diametres of 85 to 105 nm. The XRD data of the solid products were characteristic of CeO_2 with the fluorite structure. Hsu *et al.*[20] investigated the hydrolysis of very dilute Ce(IV) salt solutions in the presence of dilute sulfuric acid at 90 °C for 12 h and showed that monodispersed CeO_2 particles were formed from the solutions with Ce(IV) ion concentrations ranging from 2.5×10^{-4} to 2×10^{-3} mol dm^{-3}, but irregular rod-like or cylindrical particles were formed in the solutions with higher ceric sulfate concentrations ($> 5 \times 10^{-4}$ mol dm^{-3}). In the present work, it is obvious that the monodispersed particles, which are composed of an agglomeration of primary nanocrystalline ceria particles, can be prepared from the 0.1 mol dm^{-3} solution by thermal hydrolysis.

Hydrolysis refers to those reactions of metallic ions with water that liberate protons and produce hydroxy or oxy complexes in soluton and precipitate hydroxide or oxide solids.[28] Ce^{4+} ions, which have a low basicity and high charge, undergo strong hydration. Upon deprotonation at elevated temperatures for a definite period of time, the hydrated Ce^{4+} ions in acidified solutions are hydrolyzed and form complexes with H_2O molecules or OH^- ion, in the form of $[Ce(OH)_x(H_2O)_y]^{(4-x)+}$, where $x+y$ is the coordination number of Ce^{4+}, to give polymeric species, which are intermediates for the precipitation of the hydrous oxide. Further polymerization is likely, and both can serve as precursors for the final oxide. Since H_2O as polar molecules tend to take protons away from the hydroxide in aqueous solution, the hydroxide reacts with H_2O to form $CeO_2 \cdot n(H_2O)$ and H_3O^+, whereas there was a large difference in basicity between the Ce^{4+} and Ce^{3+} ions, which was indirectly proved. By treatment under the same hydrothermal conditions as in the present work, there was no or very little solid precipitate from the Ce(III) sulfate solutions, showing that hydrolysis in Ce(III) salt solutions hardly occur. It is well known that the hydroxylation of metal ions and the deprotonation can be greatly accelerated by raising the solution temperature. In the present work, to accelerate the reactions and enable one to produce the particles from the solution with a high Ce(IV) ion concentration, the thermal hydrolysis was carried out at 120 to 240 °C.

The effect of the treatment temperature and time on the crystal phase of the solid products obtained by the thermal hydrolysis of 0.5 mol dm^{-3} $Ce(SO_4)_2$ solutions is shown as the XRD profiles in Fig. 2. Upon thermal hydrolysis at 150 °C for 5 h, $CeOSO_4 \cdot H_2O$ was formed as the main solid product together with CeO_2. It is evident that treatment at higher temperature and for a longer holding time is required for the completion of hydrolysis. In the present work, it was found that CeO_2 particles in a single crystalline phase could be prepared from 0.5 mol dm^{-3} $Ce(SO_4)_2$ solutions by thermal hydrolysis at 240 °C for 48 h, as shown in Fig. 2. A similar effect of the hydrolysis temperature was observed in the preparation of ultra-fine particles of monoclinic ZrO_2 by the hydrolysis of $ZrOCl_2$.[29]

The crystallite sizes of the CeO_2 particles obtained from the

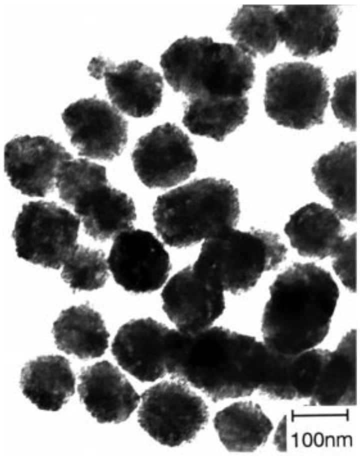

Fig. 1 TEM photograph of monodispersed CeO_2 particles prepared from 0.1 mol dm^{-3} $Ce(SO_4)_2 \cdot 4H_2O$ solution by thermal hydrolysis at 180 °C for 5 h.

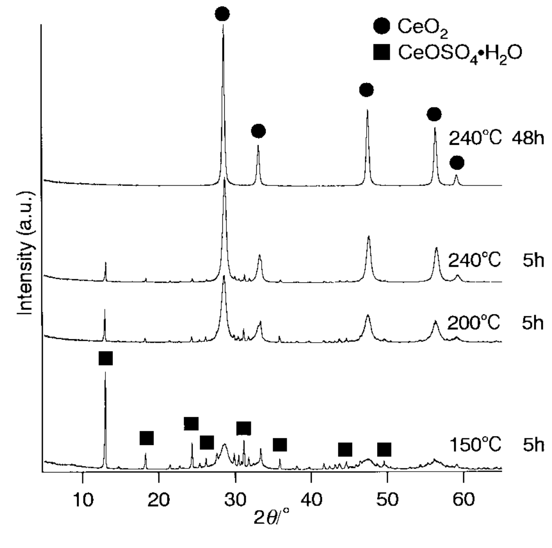

Fig. 2 X-Ray diffraction patterns of the solid products prepared from 0.5 mol dm^{-3} $Ce(SO_4)_2 \cdot 4H_2O$ solutions by thermal hydrolysis at different temperatures for 5 h or 48 h.

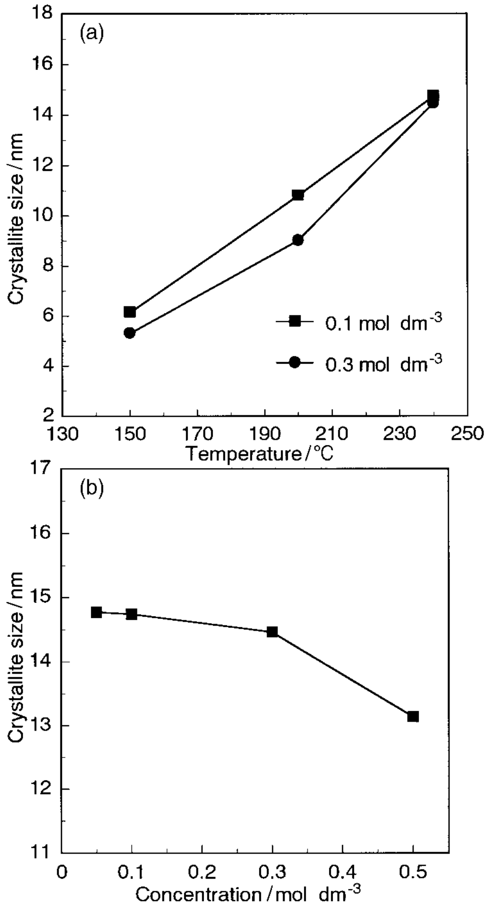

Fig. 3 (a) Effect of thermal hydrolysis temperature on the crystallite growth of CeO_2 particles prepared from 0.1 and 0.3 mol dm^{-3} $Ce(SO_4)_2 \cdot 4H_2O$ solutions for 5 h. (b) Crystallite size of CeO_2 particles prepared from $Ce(SO_4)_2 \cdot 4H_2O$ solutions by thermal hydrolysis at 240 °C for 5 h *versus* the concentration of the solution.

XRD line-broadening of the 220 peak are plotted as functions of the hydrothermal treatment temperature and the concentration of Ce(IV) ions in Fig. 3. Monodispersed ceria particles, which were synthesized from 0.1 to 0.3 mol dm^{-3} $Ce(SO_4)_2$ solutions at 150 to 240 °C for 5 h, were composed of an agglomeration of primary nanocrystalline ceria particles, and their crystallite size was in the range 5 to 15 nm. It is evident that the higher the treatment temperature, the larger the crystallite size. There was a tendency that the crystallite size decreased slightly with increasing cation concentration of the solution as shown in Fig. 3(b). In Fig. 4(a) and (b) are shown the effects of the cation concentration on the size and morphology of the synthesized particles as viewed by the TEM photographs in contrast to Fig. 1. The particle size of the agglomeration, *i.e.*, the secondary particle size of the formed precipitates, is plotted *versus* the cation concentration of the solution in Fig. 5. The XRD data of all these samples were characteristic of CeO_2 without any other crystal phase. It is clear that the secondary particle size increases upon increasing the cation concentration of the solution. The secondary particle size depended on the treatment temperature and time, as well as on the cation concentraton of the solution. It was possible to control the size of the monodispersed particles by adjusting the concentration of the cerium sulfate.

Influence of the presence of urea on the morphology

Since the hydroxylation process can sometimes be accelerated by the homogeneous generation of hydroxide ion, such as by the decomposition of urea, hydrothermal treatment in the presence of urea was performed and the influence of the urea concentration was examined. The dependence of the crystallite size of the synthesized CeO_2 particles and the pH value of the solutions after the treatment on the concentration of urea is indicated in Fig. 6. Up to the addition of 0.1 mol dm^{-3} urea, although the pH of the solution was increased very slightly, the value of the crystallite size scarcely changed and little influence of the addition of urea could be observed. As the urea concentration was increased from 0.1 to 0.2 mol dm^{-3}, the crystallite size suddenly increased from about 7 to 20 nm, together with a gradual increase of the solution pH. Although a urea concentration of 0.2 mol dm^{-3} was not enough to supply sufficient hydroxide ion for neutralization, the rate of both crystal growth and nucleation must be accelerated by the generation of hydroxide ion supplied by the decomposition of urea. However, it seems reasonable to suppose that the increase

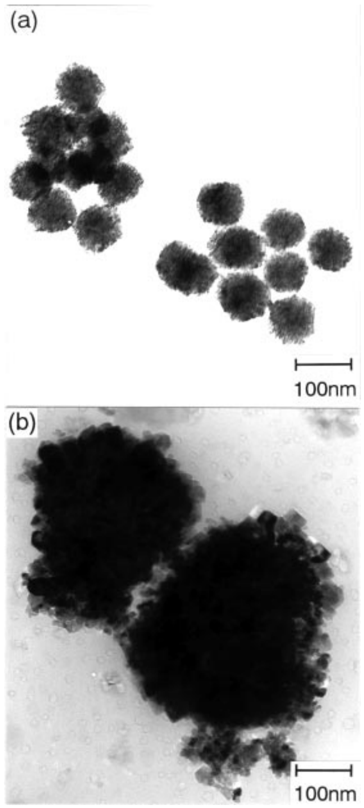

Fig. 4 TEM photographs of monodispersed CeO_2 particles prepared from (a) 0.05 mol dm^{-3} $Ce(SO_4)_2 \cdot 4H_2O$ solution by thermal hydrolysis at 150 °C for 5 h and (b) 0.3 mol dm^{-3} $Ce(SO_4)_2 \cdot 4H_2O$ solution by thermal hydrolysis at 240 °C for 5 h.

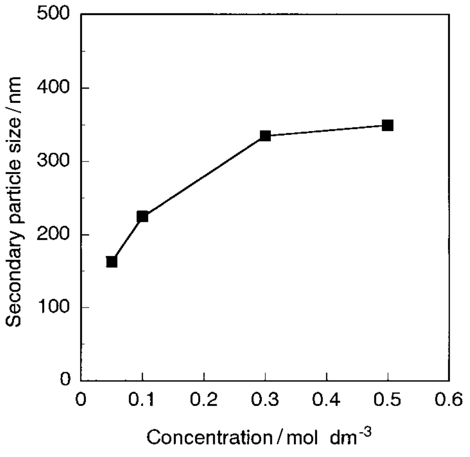

Fig. 5 Particle size of agglomeration, secondary particle size, prepared from $Ce(SO_4)_2 \cdot 4H_2O$ solutions by thermal hydrolysis at 240 °C for 5 h *versus* the concentration of the solution.

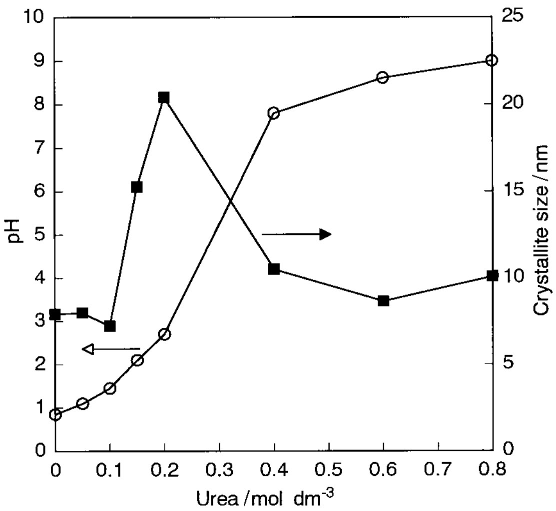

Fig. 6 Effect of urea concentration on the pH of the solution after synthesis and on the crystallite size of CeO_2 particles prepared from 0.1 mol dm^{-3} $Ce(SO_4)_2{\cdot}4H_2O$ solution at 180 °C for 5 h.

in the rate of crystal growth was more than that for the rate of nucleation, because of a rapid rate of increase in the crystallite size. With the increase in the pH of the solution upon the further addition of urea and supplying enough hydroxide ion, cerium hydroxide was formed in the solution, and the crystallite size decreased as shown in Fig. 6. We can be fairly certain that the crystallization and crystal growth of CeO_2 from the hydroxide proceeded by aging under hydrothermal conditions according to the solution and precipitation mechanism. One explanation for the decrease in the crystallite size upon the further addition of urea may be as follows. In neutral or basic solutions, the rate of crystal growth must be low due to insufficient supply of the solute by diffusion, because the concentration of the solute in the solution without a precipitate must be low as a result of the formation of large amounts of cerium hydroxide, nuclei for the crystallization of CeO_2, in contrast with hydrolysis in acidified solution. The hydrolysis reaction of cerium(III) salt solutions could hardly be advanced by hydrothermal treatment in the acidified solution without urea at up to 240 °C, though two types of cerium carbonate particles were formed by hydrothermal treatment in the presence of urea, depending on the treatment conditions.[30]

In comparison with Fig. 1, the effect of urea concentration on the morphology of the synthesized CeO_2 is shown in Fig. 7 as TEM photographs corresponding to Fig. 6. The morphology of the synthesized particles gradually changed from monodispersed particles to dispersed ultra-fine particles having no definite and tight agglomeration as the pH of the solutions increased and approached neutralization upon the addition of urea and with its increasing concentraton. The particle size observed by TEM agreed fairly well with the crystallite size determined by the XRD line broadening. It is found that the hydrolysis in acidified solution (such as sulfuric acid) is important and necessary for the formation of monodispersed ceria particles from cerium(IV) salt solutions.

Solid solution with gadolinium and grain growth

The effect of doping on the particle and grain growth of ceria during the course of the heat treatment and sintering was estimated. In the present work, using the monodispersed ceria particles, 20 mol% $GdO_{1.5}$ was doped into the CeO_2 by homogeneous precipitation and calcination. The crystallite sizes determined from the 220 reflection are plotted *versus* the heat treatment temperature in Fig. 8. As can be seen, the crystallite sizes of both the undoped and doped ceria changed very little when the calcination temperature was below 500 °C. At this point, the average crystallite sizes of the undoped and the doped ceria were 9.3 nm and 7.7 nm, respectively. The crystallite size of the undoped ceria was slightly larger than that of the doped ceria, and its behavior with respect to the increase in the crystallite size showed a tendency similar to that of the doped ceria up to around

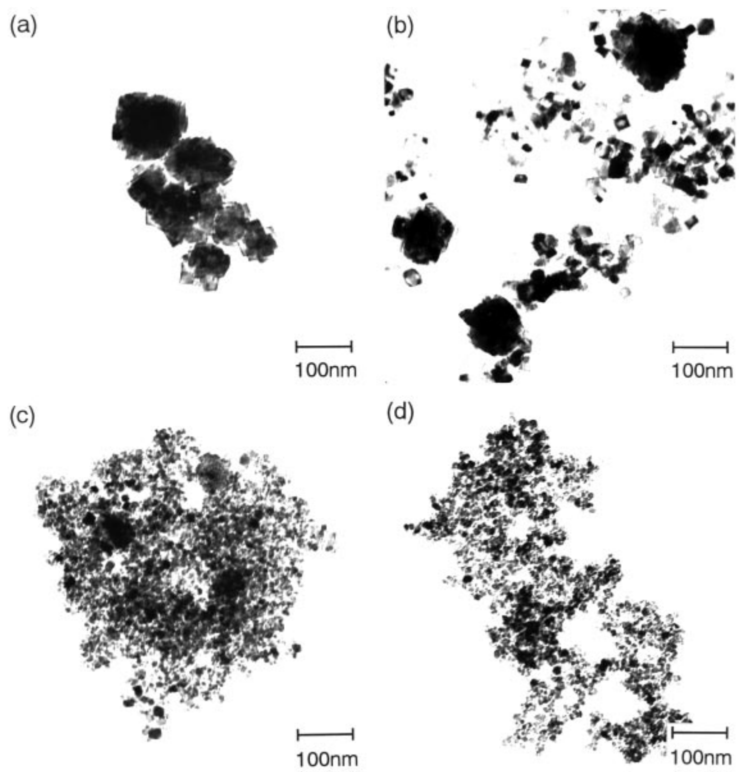

Fig. 7 TEM photographs of CeO_2 particles prepared from 0.1 mol dm^{-3} $Ce(SO_4)_2{\cdot}4H_2O$ solutions in the presence of (a) 0.15 mol dm^{-3} urea, (b) 0.2 mol dm^{-3} urea, (c) 0.4 mol dm^{-3} urea, and (d) 0.8 mol dm^{-3} urea at 180 °C for 5 h.

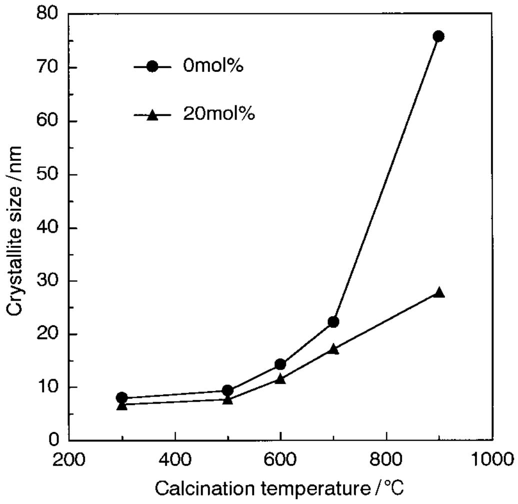

Fig. 8 Average crystallite sizes of undoped CeO_2 particles synthesized from 0.3 mol dm^{-3} $Ce(SO_4)_2 \cdot 4H_2O$ solutions at 200 °C for 5 h and 20 mol% $GdO_{1.5}$-doped CeO_2 powders *versus* calcination temperature.

700 °C. However, calcining at 900 °C made its crystallite size increase approximately threefold to 76 nm in contrast to the doped ceria. It was proved that the undoped ceria showed a sudden coarsening by calcination at temperatures above 700 °C. The microstructure and grain sizes of the sintered ceria polycrystals are considered to be strictly dependent on the existence of dopants such as Gd, Y and so on. In Fig. 9 is shown the typical microstructure of the polished and thermally etched surfaces of the undoped and the 20 mol% $GdO_{1.5}$-doped ceria ceramics sintered at 1500 °C. The average grain sizes of the undoped and the 20 mol% $GdO_{1.5}$-doped ceria ceramics wree 14.7 µm and 1.3 µm, respectively. We could obtain $GdO_{1.5}$-doped ceria ceramics having a dense body with a relatively uniform microstructure. The above data showed that the grain size and microstructure were governed by the existence of the dopant, and the addition of the Gd dopant to ceria was very effective for suppression of its grain growth during the course of calcining and sintering.

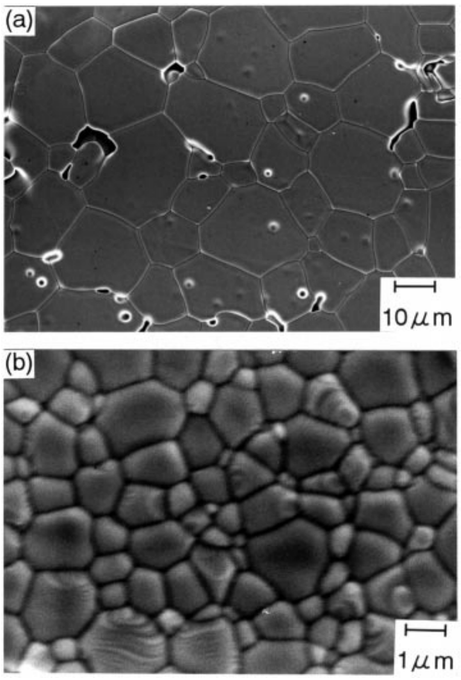

Fig. 9 SEM photographs of the polished and thermally etched surfaces of (a) undoped and (b) 20 mol% $GdO_{1.5}$-doped ceria polycrystals sintered at 1500 °C for 1 h.

Summary

We have successfully prepared spherical and monodispersed CeO_2 particles composed of an agglomeration of primary nanocrystalline particles with a cubic phase from a cerium(IV) sulfate solution with a relatively high concentration of 0.5 mol dm^{-3} cerium(IV) by thermal hydrolysis at 240 °C. It was possible to control the size of the monodispersed particles by adjusting the concentration of the cerium sulfate. The change in the crystallite size depending on the urea concentration was mainly explained in terms of the effect of the concentration of hydroxide ion, generated by the decomposition of urea, on the supply of the solute by diffusion and the amount of nucleation. The present work showed that the morphology of the synthesized particles gradually changed from spherical and monodispersed particles to dispersed nanocrystalline particles having no definite and tight agglomeration upon the addition of urea and with its increasing concentration. The presence of the Gd dopant was very effective for the suppression of grain growth of the ceria particles during the course of calcining and sintering. The 20 mol% $GdO_{1.5}$-doped ceria ceramics prepared by sintering the powder synthesized by the thermal hydrolysis exhibited a dense body having a relatively uniform microstructure.

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