Low-Temperature Direct Synthesis of Nanoparticles of Fluorite-Type Ceria–Zirconia Solid Solutions by "Forced Cohydrolysis" at 100°C

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Nanometer-sized particles ranging from 2 to 3 nm of CeO_2 (ceria)–ZrO_2 (zirconia) solid solutions with cubic and/or tetragonal fluorite-type structure in the wide composition range from 20 to 100 mol% CeO_2, without a trace of monoclinic ZrO_2 phase, could be directly synthesized at low temperature of 100°C from acidic aqueous solutions of $ZrOCl_2$ and $(NH_4)_2Ce(NO_3)_6$ by forced simultaneous hydrolysis, i.e., "forced cohydrolysis." Analytical values of CeO_2/ZrO_2 ratio in the as-precipitated solid solutions showed fairly good agreement with starting compositions in the solutions. The proceeding of the hydrolysis and formation rate of fluorite-type solid solutions tended to slow down at near median composition. Any change in crystalline phase of as-precipitated solid solutions was not observed by powder X-ray diffractometry after heat treatment in air below 1000°C. Ceria–zirconia solid solutions with fluorite structures containing large amount of ZrO_2 maintained high surface area after heat treatment at 1000°C. © 2001 Academic Press

Key Words: hydrolysis; hydrothermal treatment; cerium oxide; zirconium oxide; solid solution.

1. INTRODUCTION

Recently, ceria–zirconia solid solutions are of considerable interest as catalytic supports for automotive exhaust, and a large amount of ZrO_2-doped cubic ceria with high surface area is sought for improving their performance (1–3). In general, heat treatment in air above 300°C was reported to be necessary to make solid solutions between ceria and zirconia, even if active precursor was prepared through chemical solution routes (4). From mixed fine powders of ceria and zirconia, a temperature of 1400°C or higher was necessary to obtain the solid solutions (5, 6). Forced hydrolysis of cerium and zirconium salt solutions and the hydrothermal method are the most common preparation techniques for pure ceria (7–13) and pure zirconia (13–26). Although pure zirconia (i.e., hydrous monoclinic zirconia)

could be directly precipitated from acidic solutions, synthesis of solid solutions of zirconia, e.g., stabilizer-doped zirconia, was difficult in acidic solution by forced hydrolysis. Therefore, almost all zirconia solid solutions doped with stabilizing agents (e.g., MgO (27, 28), CaO (27), Y_2O_3 (27–29), and CeO_2 (30, 31)) were conducted at high pH range under hydrothermal conditions. There are a few reports on the formation of ceria–zirconia solid solution particles rich in CeO_2, only that by emulsion combustion (32) and mechanical milling (33, 34). In our previous work (35) on the hydrothermal synthesis at high pH range over the wide concentration in the CeO_2–ZrO_2 system, single-phase solid solution particles could not be obtained at the composition rich in ceria. Synthesizing Y_2O_3-doped zirconia was not succeeded in acidic solution by hydrolysis around 100°C (36). Moreover, when the mixed solutions of $ZrOCl_2$ and $CeCl_3$ were hydrolyzed by boiling in the absence of base such as aqueous ammonia, only monoclinic pure hydrous-zirconia precipitates were reported to be formed (4). However, we could achieve the formation of ceria–zirconia solid solutions from acidic solutions by forced cohydrolysis under hydrothermal conditions at 240°C (37). To investigate on the synthesis of the ceria–zirconia solid solutions at lower temperature is important and necessary for the development of their practical applications. Whether the solid solutions are directly formed or not in the acidic mixed solutions at the boiling temperature as low as the formation temperature of monoclinic pure hydrous zirconia is interesting.

In the present study, forced cohydrolysis of mixed solutions of $ZrOCl_2$ and $(NH_4)_2Ce(NO_3)_6$ was carried out at 100°C in a low pH range to clarify the possibility of direct synthesis of the ceria–zirconia solid solutions with fluorite-type structure at the low temperature.

2. EXPERIMENTAL PROCEDURE

2.1. Sample Preparation

Cerium(IV) diammonium nitrate $((NH_4)_2Ce(NO_3)_6$, reagent grade, Kishida Chemical, Osaka, Japan) and

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zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$, reagent grade, Kishida Chemical) were used as the starting materials. A given quantity (1000 cm^3) of a mixed solution of the cerium salt and the zirconium salt in a total cation concentration (Ce + Zr) of 0.005 mol dm^{-3} was poured into a polypropylene bottle. After the lid was put on the bottle, it was heated at 100°C for 168 h in a thermostatted oven. The precipitates formed after heat treatment were separated with ultrafiltration (UK-50, Advantec, Toyo Roshi Kaisha, Ltd., Tokyo, Japan), washed with distilled water, and dried in an oven at 60°C in air atmosphere. The precipitates thus obtained were heat treated in alumina crucibles at 300 to 1000°C in air.

2.2. Sample Characterization

Phase identification was performed by powder X-ray diffractometry (XRD) using Cu$K\alpha$ radiation. The crystallite size was estimated from line broadening of the 220 diffraction peak according to the Scherrer equation. The lattice parameters were measured from the 220 diffraction line using a silicon as the internal standard. The precipitate morphology and size were examined using a transmission electron microscope (TEM) (Model JEM-2010, JEOL, Japan). The overall CeO_2/ZrO_2 molar ratio (mol%) in the precipitates was estimated by analysis of the concentration of unreacted Ce and Zr existing in the ultrafiltrated solution using an inductively coupled plasma (ICP) emission spectrometer (Model ICP575II, Nippon Jarrell-Ash, Japan). The specific surface area of the prepared samples was measured from adsorption isotherm of nitrogen at 77 K using a gas adsorption instrument (Model QS-10,Quantasorb, Yuasa Ionics, Japan), based on the Brunauer–Emmit–Teller (BET) method.

3. RESULTS AND DISCUSSION

3.1. Low-Temperature Synthesis of Solid Solution Precipitates

Experimental conditions and unreacted Ce and Zr constituents existing in the solutions after the treatment at 100°C for 168 h are shown in Table 1. The ratio (mol%) of cerium and zirconium constituents formed as solid precipitates was calculated on the basis of the analytical results of unreacted Ce and Zr remained in the solution after hydrolysis, respectively. Figure 1 shows compositional dependence of hydrolysis ratio after heat treatment for 168 h at 100°C (which is also considered the rate of hydrolysis) of $ZrOCl_2$ and $(NH_4)_2Ce(NO_3)_6$ in the CeO_2–ZrO_2 system. By heat treatment for 168 h at 100°C, either pure $ZrOCl_2$ or pure $(NH_4)_2Ce(NO_3)_6$ solutions were almost thoroughly hydrolyzed, and precipitation of hydrous zirconia and ceria was at high yield (99 and 95%, respectively (specimens(a) and (f))). Whereas, with increases of either the amount of CeO_2 intro-

TABLE 1
Treatment Time at 100°C, Starting Concentration, and Concentration After Hydrolysis

Specimen	Treatment time (h)	Starting concentration ($\times 10^{-3}$ mol dm^{-3})		Concentration after hydrolysis ($\times 10^{-3}$ mol dm^{-3})	
		Zr	Ce	Zr	Ce
a	168	5	0	0.036	0
b	168	4	1	0.045	0.047
c	168	3	2	0.77	0.54
d	168	2	3	0.91	1.5
e	168	1	4	0.066	0.47
f	168	0	5	0	0.27

duced into ZrO_2 or the amount of ZrO_2 introduced into CeO_2, decreases in the ratio of the hydrolysis (i.e., decrease in the hydrolysis rate) was clearly observed. The hydrolysis ratio tended toward minimum value near the medium composition (i.e., 60 mol% CeO_2). The analytical results also suggest that the hydrolysis reaction of $ZrOCl_2$ and $(NH_4)_2Ce(NO_3)_6$ occurs almost simultaneously, even en route and before completion of the reaction, though it is found that there exists a very little difference in hydrolysis ratio between $ZrOCl_2$ and $(NH_4)_2Ce(NO_3)_6$ in the mixed solutions.

The influence of the starting composition in the CeO_2–ZrO_2 system on the crystal phase of the precipitates is shown as XRD patterns in Fig. 2. In the precipitates from pure $ZrOCl_2$, a small broad peak besides monoclinic ZrO_2
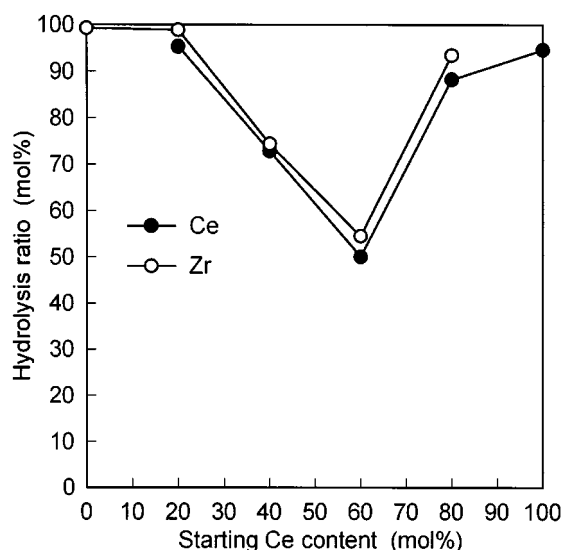

FIG. 1. Ratio of hydrolysis (mol%) of aqueous solutions of $ZrOCl_2$ and $(NH_4)_2Ce(NO_3)_6$ by heat treatment at 100°C for 168 h versus content of Ce in total cation (Ce + Zr) of starting mixed solutions.
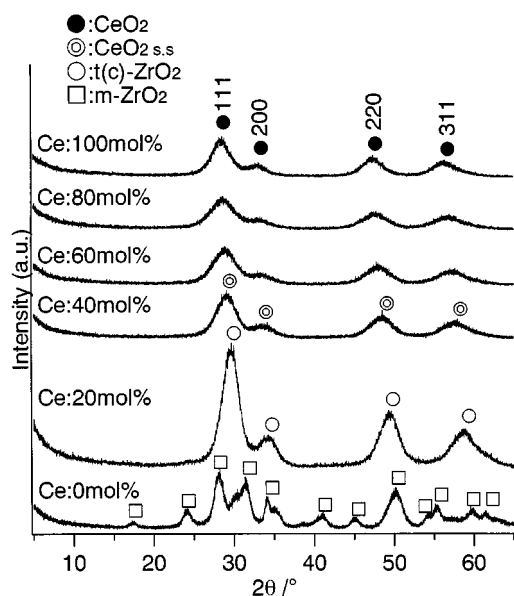
FIG. 2. X-ray diffraction patterns of the precipitates obtained by forced hydrolysis at 100°C for 168 h.

is observed near $2\theta = 30°$ between monoclinic ZrO_2 111 and $\bar{1}11$ diffraction peaks. Only monoclinic phase is reported to appear in the hydrous zirconia obtained from 0.05 to 0.4 mol dm^{-3} $ZrOCl_2$ solutions (38). The observed small broad peak appears to be due to a small amount of cubic or tetragonal ZrO_2 phase which may be formed by hydrolysis of a very dilute $ZrOCl_2$ solution. To make clear whether it is a cubic or tetragonal phase is not the aim of the present work. The crystalline phase of the precipitates correspond-
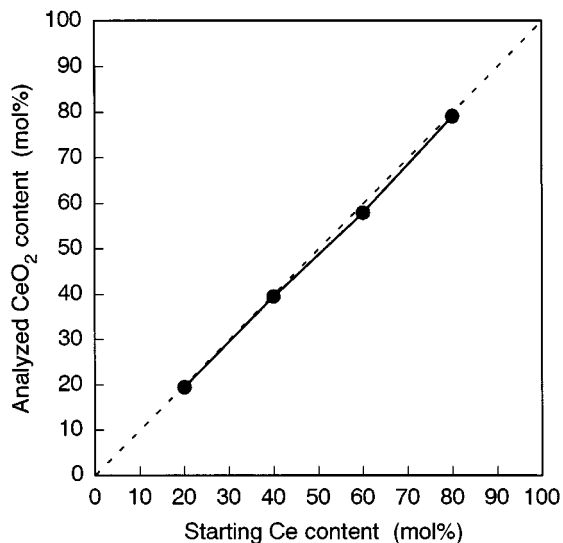
ing with 100 mol% CeO_2 was the single phase of cubic CeO_2.

At the composition range from 100 to 20 mol% CeO_2, the crystalline phase of the precipitates is proved to be cubic and/or tetragonal fluorite structure. No peaks for monoclinic phase and no trace of other crystalline phase were detected in the XRD, though the diffraction peaks were pretty broad. With increasing ZrO_2 content up to 40 mol% CeO_2, shifting of 111, 200, 220, and 311 diffraction peaks of cubic CeO_2 to a higher theta angle is clearly observed in Fig. 2, certainly proving that the precipitates directly formed at 100°C from acidic aqueous solutions were ceria–zirconia solid solutions with fluorite-type structure with the composition corresponding to the starting solution. Though it is noticed that solid solutions with good crystallinity that are considered to be mostly tetragonal were directly synthesized at 20 mol% CeO_2 in this acidic condition, Raman spectroscopy studies may be desired for strict discussion on slight distortions of structure to the tetragonal phase, particularly for the samples containing large amounts of ZrO_2.

3.2. Characterization of Solid Solution Precipitates

CeO_2 contents in the solid solution precipitates, which were calculated for the analytical results of the concentrations of unreacted Ce and Zr constituents existing in the ultrafiltrated solutions after hydrolysis, are plotted as a function of the starting composition as shown in Fig. 3. Chemical composition of the solid solution precipitates well agrees with starting composition. From the results of Figs. 2 and 3, it is reconfirmed that ceria–zirconia solid solution with cubic and/or tetragonal fluorite structure can successfully and directly synthesize from acidic aqueous solutions at 100°C over the wide composition range from 20 to 100 mol% CeO_2. Matsui and Ohgai reported that the fine particles, which were synthesized from the mixed aqueous solutions of $ZrOCl_2$ and $CeCl_3$ by hydrolysis at 100°C for 170 h, were pure ZrO_2 with monoclinic structure without any cerium(4). To synthesize Y-doped ZrO_2 in acidic solution was also reported to be difficult at boiling temperature because of the high solubility of Y^{3+} in this pH region (36). In the present study, direct formation of ceria–zirconia solid solutions at a low temperature of 100°C may be considered to be mainly achieved by the acceleration of the hydrolysis reaction by use of the cerium (IV) salt with low basicity, instead of cerium(III) salt, together with control of the concentration (i.e., use of dilute solution).

Crystallite size of the ceria–zirconia solid solution estimated from the Scherer equation is plotted as a function of analyzed CeO_2 content in the solid solutions in Fig. 4. Synthesized ceria–zirconia solid solutions were nanometer-sized ultrafine particles in the range of 2 to 3 nm, and these values are very small in comparison with those of the solid
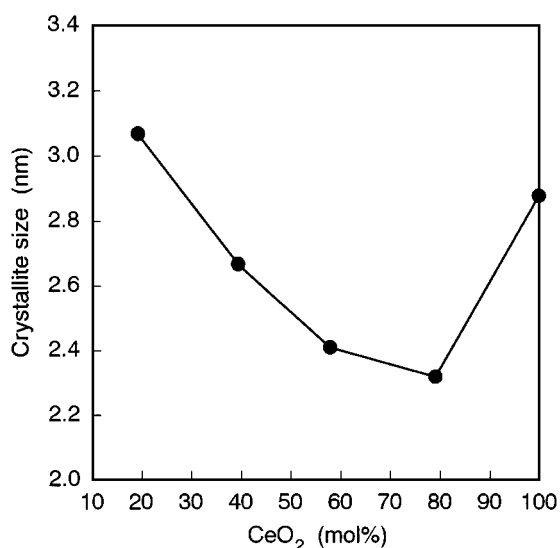

FIG. 3. Analyzed CeO_2 content (mol%) in the CeO_2–ZrO_2 solid solutions precipitated by forced hydrolysis at 100°C for 168 h versus Ce content (mol%) in the starting solution.

FIG. 4. Crystallite size of the CeO_2–ZrO_2 solid solutions versus analyzed CeO_2 content (mol%) in the precipitates.

with each other and simultaneous hydrolysis of Zr(IV) and Ce(IV) salt occurs around 100°C, complex polynuclear species of hydrolysis products (e.g., $Ce_XZr_Y(OH)_{2(X+Y)}^{2(X+Y)+}$) in
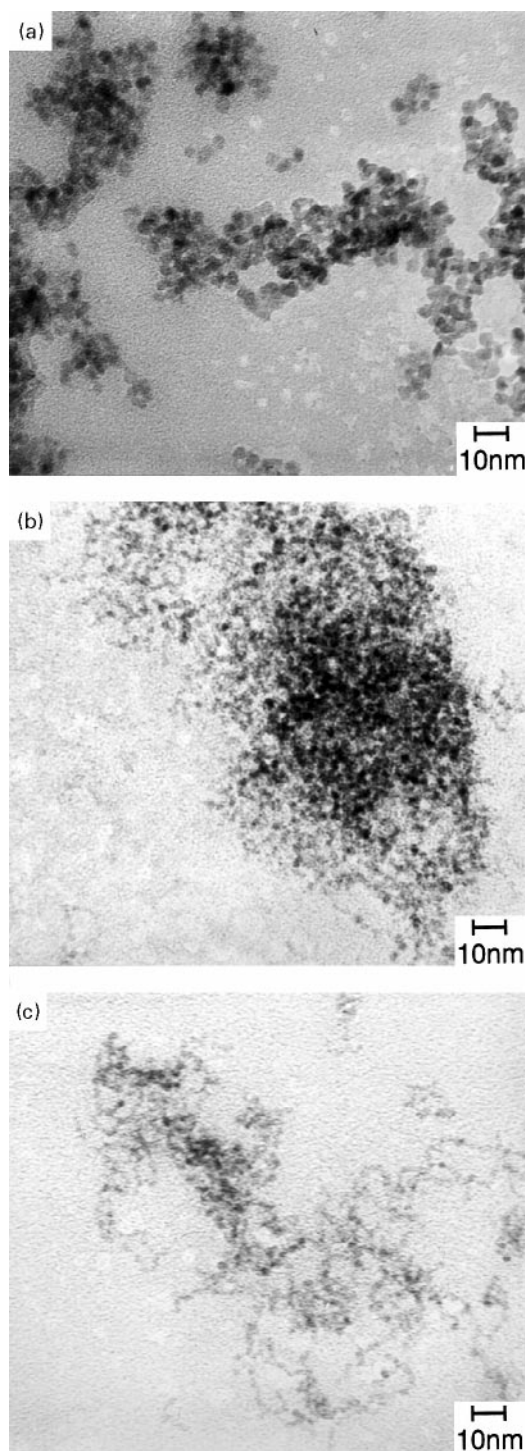

FIG. 5. TEM photographs of solid solutions obtained at the compositions of (a) 20 mol% CeO_2–80 mol% ZrO_2, (b) 60 mol% CeO_2–40 mol% ZrO_2, and (c) 80 mol% CeO_2–20 mol% ZrO_2 by forced hydrolysis at 100°C for 168 h.

solution particles formed by forced cohydrolysis under hydrothermal conditions at 240°C (37). The crystallite size showed the lowest values at the composition of 60 to 80 mol% CeO_2. In Fig. 5, TEM photographs of the solid solution precipitates are shown, in which cannot be observed so much clear microstructure as those reported in the case of hydrothermal treatment at 240°C (37), but suggesting that nanosized ulirafine particles are existed without making appreciable secondary particles. The nanoparticles in Fig. 5 probably appear to be faceted, e.g., with (100) and/or (111) facetes. Solid solution precipitates at the composition of 60 and 80 mol% CeO_2 with cubic fluorite structure (Figs. 5b and 5c) are observed to be smaller in size than stabilized zirconia precipitates with cubic and/or tetragonal structure at the composition of 20 mol% CeO_2 (Fig. 5a). Particle sizes observed by TEM were well corresponded to the results of crystallite size estimation in Fig. 4 and the sharpness of the XRD profiles in Fig. 1.

3.3. Formation Process of Solid Solution Precipitates

Based on the experimental results, a formation process of the solid solution is considered as follows. The principal species of Zr(IV) existing in solid zirconium oxychloride and in its aqueous solutions is known to be tetramer, $Zr_4(OH)_8^{8+}$, which has a square planar structure of $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ (39). Depending on cation concentration and kind of anion in the solution, on the other hand, the species of Ce(IV) are reported to change from mononuclear species to hexamer, the principal hydrolysis products which first appear being $Ce_2(OH)_4^{4+}$ and probably $C_6(OH)_{12}^{12+}$ (40). If hydrolysis rates of two salts coincide

proportion to the composition in the starting solutions are thought to be formed. At 100°C, these complexes react to produce polymeric species and polymerization occurs. When the concentration of the polymeric species reaches a supersaturation level, nuclei of hydrous ceria–zirconia solid solutions are generated, and their primary particles are formed by the growth of the crystal nuclei.

3.4. Characteristics of Solid Solutions after Heat Treatment

Variation of the crystalline phase of the as-prepared samples (Table 1, specimen b, 20 mol% CeO_2, and specimen d, 60 mol% CeO_2) with heat treatment in air are shown in Fig. 6 as XRD patterns around 111 and 200 diffraction lines of fluorite structure. Change in crystallinity by heat treatment at 500°C is not conspicuous, but obvious improvement in crystallinity and growth in crystallite size are observed by heat treatment at 1000°C. Remarkable changes in crystalline phases, such as appearance of a monoclinic phase, is not observed by heat treatment below 1000°C. As-precipitated solid solution containing 60 mol% CeO_2 was proved to consist with almost cubic fluorite-type structure from the diffraction line 200 after heat treatment at 1000°C. It was not clear whether the crystalline phase is tetragonal or cubic structure in the XRD pattern of as-precipitated solid solution containing 20 mol% CeO_2. After the heat treatment at 1000°C, however, the structure was clarified to be mostly tetragonal zirconia doped with CeO_2
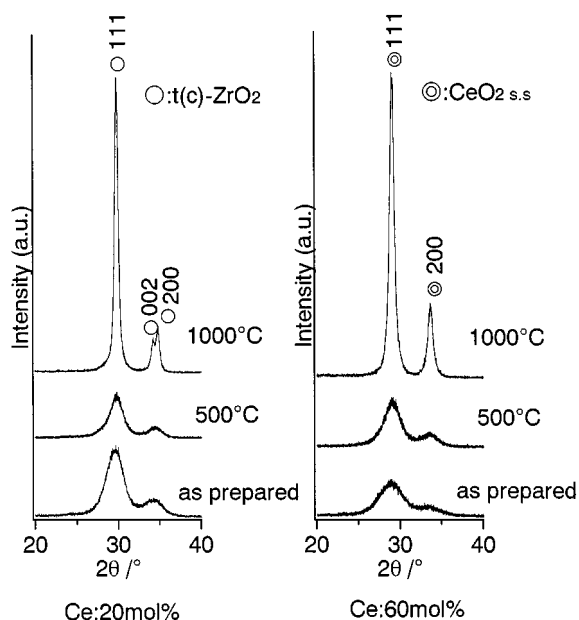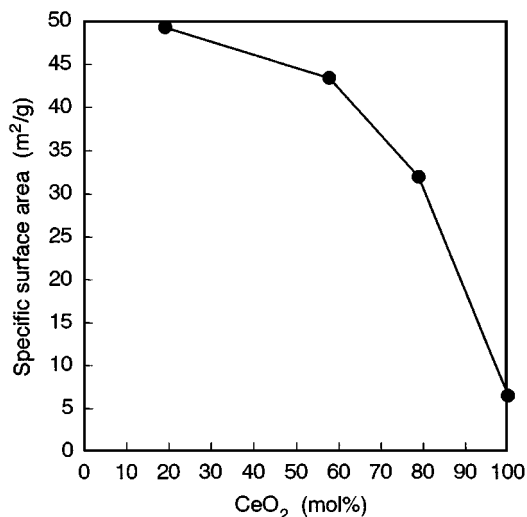
FIG. 7. Effect of CeO_2 content on the specific surface area of CeO_2–ZrO_2 solid solutions heat treated at 1000°C in air.

because separation of 200 diffraction line to 002 plus 200 lines was clearly observed.

Since doping of Gd to CeO_2 was very effective for suppression of the grain growth of CeO_2 and for maintaining surface activity of CeO_2 powder up to high temperature (8), it is also anticipated that making solid solutions with ZrO_2 will have similar influence on the surface activity of CeO_2. Specific surface areas of the solid solutions after being heat treated at 1000°C are plotted as a function of CeO_2 content in Fig. 7, showing that the surface area of CeO_2 increases by making solid solutions with ZrO_2 and with increase of ZrO_2 content. The ceria–zirconia solid solutions containing a large amount of ZrO_2 showed fairly high surface area, which maintained its high surface activity as 50 m²/g even after heat treatment at 1000°C.

4. SUMMARY

Direct precipitation of ceria–zirconia solid solutions by forced cohydrolysis from acidic dilute solutions of $ZrOCl_2$ and $(NH_4)_2Ce(NO_3)_6$ at 100°C was investigated, and the following facts were clarified.

(i) At 100°C, direct synthesis of nanoparticles ranging from 2 to 3 nm of ceria–zirconia solid solutions with cubic and/or tetragonal fluorite structure containing no trace of monoclinic phase in the wide composition range from 20 to 100 mol% CeO_2 was successfully performed.

(ii) The analytical value of CeO_2/ZrO_2 ratio in as-precipitated solid solutions well coincided with the starting composition in the aqueous solution. The proceeding of the hydrolysis reaction and the rate of direct precipitation of the solid solutions tended to slow down at near median composition.

FIG. 6. X-ray diffraction patterns of as-precipitated and heat treated solid solutions obtained at starting compositions of 20 mol% CeO_2–80 mol% ZrO_2 and 60 mol% CeO_2–40 mol% ZrO_2.

(iii) Obvious change in crystalline phase of the precipitates was not observed by XRD after heat treatment below 1000°C. Ceria–zirconia solid solutions containing a large amount of ZrO_2 maintained their surface activity even after heat treatment at 1000°C.

ACKNOWLEDGMENT

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