Glycothermal synthesis of zirconia–rare earth oxide solid solutions

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The reactions of mixtures of zirconium alkoxide and cerium or yttrium acetate in 1,4-butanediol at 300 °C (glycothermal reaction) yielded microcrystalline tetragonal zirconia–rare earth oxide solid solutions. The products maintained large surface areas even after calcination at high temperatures. The surface area of the products with low rare earth contents strongly depended on the drying conditions because of compaction at the drying stage, and the product dried by microwave irradiation had the highest surface area.

Keywords: tetragonal zirconia, stabilized zirconia, rare earth oxide, solid solution, surface area, glycothermal method

1. Introduction

Zirconia exhibits interesting specific catalytic actions for isomerization of olefins [1] and epoxides [2], dehydration of alcohols [3,4], hydrogenation of olefins [5–7] and carboxylic acids [8], and so on [9,10]. Much attention is also being devoted to the use of zirconia as a support material for a variety of catalysts [11–13].

Specific surface area is one of the important factors for catalysts and catalyst supports. Precipitation from solutions of zirconium (or zirconyl) salts and hydrolysis of zirconium alkoxides afford amorphous zirconia having a large surface area (200–300 $m^2\,g^{-1}$) [14,15]. However, the initial surface area abruptly decreased at around 450 °C due to crystallization of the monoclinic and/or the metastable tetragonal phase(s), and calcination at higher temperatures (for example, at above 800 °C) causes crystal growth of the phase(s) remaining only few square meters per gram of surface area. Because the decrease in the surface area of a support during the reaction causes an enormous effect on the supported metal particles [16], improvement of the thermal stability of the catalyst support is desired for the practical use, and various methods for the synthesis of zirconias having improved thermal stabilities have been developed [17–22]. The effect of additives has also been investigated and partial success has been achieved by the addition of sulfate [23], potassium [24,25], or rare earth ions [25–31].

In a series of our works on the use of organic media in inorganic synthesis [17,18,32–37], we reported that thermal decomposition of zirconium alkoxides in organic solvents yielded tetragonal zirconia having a large surface area and a fairly high thermal stability [17]. On the other hand, we also reported that the reaction of two starting materials such as alkoxides, acetylacetonate, or acetate in 1,4-butanediol (glycothermal reaction) affords crystalline binary oxides such as yttrium aluminum garnet [33], aluminum zinc oxide (spinel structure) [34], and rare earth niobate (illumenite structure) [35]. In the present work, we will report the formation of large surface area zirconia–rare earth oxide solid solutions by the glycothermal reaction.

2. Experimental

2.1. Reaction

Zirconium n-propoxide (12.5 g, Mitsuwa) and a desired amount of a rare earth (RE) acetate hydrate (Wako) with the charged RE/Zr ratio of 3/100–1/2 were suspended in 130 ml of 1,4-butanediol (1,4-BG) in a test tube serving as an autoclave liner, and the test tube was then set in a 300 ml autoclave. An additional 30 ml of the glycol was added in the gap between the test tube and the autoclave wall. The autoclave was purged with nitrogen, heated to 300 °C at a rate of 2.5 °C min^{-1}, and held at that temperature for 2 h under the autogenous pressure of the glycol. After the mixture had been cooled, the resulting powders were washed repeatedly with methanol and air-dried. Calcination of the product was conducted in a box furnace for 1 h.

2.2. Characterization

Powder X-ray diffraction (XRD) was measured on a Shimadzu XD-D1 diffractometer using Cu Kα radiation and a carbon monochromator. Crystallite size was calculated from the half-height width of the 111 diffraction peak of tetragonal zirconia using the Scherrer equation; the value of the shape factor, K, was arbitrary taken to be 0.9. The specific surface area was calculated using the BET single-point method on the basis of nitrogen uptake measured at 78 K using a gas chromatograph. The products were dried *in situ* at 300 °C for 1 h to remove the adsorbed species and, therefore, the reported surface areas of "the products"

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are actually those of the samples that had suffered from the thermal effect at that temperature. Simultaneous thermogravimetric and differential thermal analyses (TGA and DTA) were performed on a Shimadzu TG-50 thermal analyzer at a heating rate of 10 °C min^{-1} in a 40 ml min^{-1} flow of dried air. Morphology of the products was observed on a transmission electron microscope (TEM), Hitachi H-800, operated at 200 kV.

3. Results and discussion

As reported previously, the glycothermal reaction of zirconium alkoxide alone yields tetragonal zirconia [17]. The XRD patterns of the products obtained by the reaction of the mixture of zirconium alkoxide and yttrium acetate are given in figure 1 (b)–(f). All the products exhibited similar XRD patterns indicating that tetragonal (and/or cubic) zirconia was formed for all the samples with the Y/Zr ratio of 0–1/2. The glycothermal reaction of rare earth acetate alone yielded two morphs of rare earth acetate oxide ($RE(OCOCH_3)O$), rare earth acetate dihydroxide ($RE(OCOCH_3)(OH)_2$), or rare earth diacetate hydroxide ($RE(OCOCH_3)_2(OH)$) depending on the ionic size of the RE element [35]. These phases can be easily detected because each of them shows quite a strong diffraction peak at the low-angle region. Absence of these phases in the present product suggests that the zirconium species facilitated the cleavage of the bond between the RE and acetate ions. As shown in figure 1, the diffraction peaks gradually shifted toward the low-angle side as the amount of rare earth acetate in the starting mixture increased, suggesting that the zirconia solid solutions were directly formed by the glycothermal reaction.

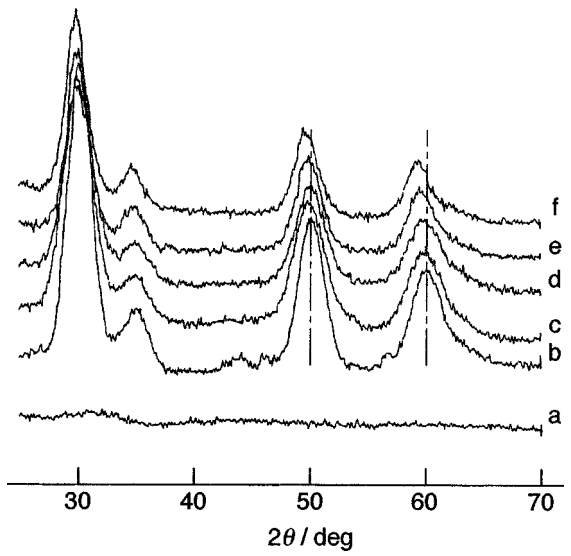

Figure 1. XRD patterns of the products obtained by the reaction of zirconium *n*-propoxide and yttrium acetate with the Y/Zr charged ratio of 3/100 (a) and (c), 0/100 (b), 6/100 (d), 12/100 (e), 25/100 (f) in ethylene glycol (a) and 1,4-butanediol (b)–(f) – each at 300 °C for 2 h.

Danièle et al. [38] reported that the reaction of lanthanide acetate with zirconium isopropoxide in toluene at the reflux temperature yielded heterometallic alkoxides having a formula of $RE_2Zr_6(\mu_4\text{-}O)_2(\mu_4\text{-}OAc)_{10}(\mu\text{-}OPr^i)_6(\mu\text{-}OPr^i)_{10}$, which indicates that the bonds between RE and acetate ions are not cleft at that temperature. However, it seems to be reasonable to consider that similar heterometallic alkoxide, formed as an intermediate of the present reaction, contributes to the direct formation of the solid solution.

The use of 1,4-BG was essential to obtain the zirconia solid solution and the use of ethylene glycol in place of 1,4-BG resulted in formation of amorphous products (figure 1(a)). A similar medium effect was observed for the synthesis of a variety of binary oxides by the glycothermal method [32,33,37] and was explained by that the electron withdrawing effect of the intramolecular hydroxyl group at the β-position of the glycoxide formed by the reaction of metal alkoxide and ethylene glycol retards the cleavage of the C–O–M bond yielding the carbenium ion [32,37].

A number of papers have reported the synthesis of powders of the zirconia solid solution by various processes such as the co-precipitation method [25,27–30], the alkoxide process [31], and the polymerized citrate-complex method [39]. However, most of these processes require the calcination step, where transformation of the amorphous phase into the tetragonal phase takes place accompanying the decrease in surface area. On the other hand, the tetragonal solid solution was directly crystallized in the organic media in the present method, and the product did not suffer from the phase transformation.

The crystallite size and BET surface area of the present product are summarized in table 1. All of the products had relatively small crystallite sizes, which aligned in a relatively narrow range, suggesting that the nucleation frequency of the product is scarcely affected by the RE ions. As expected from the small crystallite sizes, the products with large RE contents had large surface areas, which were much larger than those of the zirconia solid solutions prepared by the co-precipitation method [25,27–30] or the alkoxide process [31] (40–100 $m^2\,g^{-1}$). Transmission electron micrographs of the products (figure 2) showed that the products were comprised of agglomerates of primary particles having diameters of 3.4–3.8 nm. Since this particle size was quite close to the crystallite size determined by the XRD line broadening technique, each primary particle observed in TEM is a single crystal of the zirconia solid solution. Note that TEM images of the products gave no indication of the presence of the amorphous phases.

When one assumes that the product was composed of spherical particles with a diameter of 4.0 nm, similar to the crystallite size, the surface area of the product was calculated to be 260 $m^2\,g^{-1}$. This value is in good agreement with the observed surface areas of the products with large RE contents, suggesting that each crystallite of these products exposes its outer surface to the adsorbate molecules.

Table 1
Crystallite size and BET surface area of the tetragonal zirconia solid solution obtained by the glycothermal method and of the samples prepared by calcination thereof.[a]

RE	RE/Zr	Product					
		As-synthesized		Calcined at 500 °C		Calcined at 700 °C	
		d_{111}[b] (nm)	S_{BET}[c] ($m^2\,g^{-1}$)	d_{111}[b] (nm)	S_{BET}[c] ($m^2\,g^{-1}$)	d_{111}[b] (nm)	S_{BET}[c] ($m^2\,g^{-1}$)
	0/100	3.4	92	5.8	24	11.6	3.8
Y	6/100	3.1	82	4.9	48	–	25
	12/100	4.0	215	4.9	151	7.1	92
	25/100	4.0	262	4.8	214	5.8	128
	50/100	3.8	232	5.0	217	7.7	131
Ce	3/100	4.0	187	5.2	103	8.7	42
	6/100	4.1	151	5.3	103	8.2	45
	12/100	4.1	202	5.0	123	7.1	81
	25/100	3.4	201	–	143	–	–

[a] Products were obtained by the reaction of zirconium n-propoxide and rare earth acetate in 1,4-butanediol at 300 °C for 2 h.
[b] Crystallite size of zirconia calculated from the (111) diffraction peak.
[c] BET surface area.

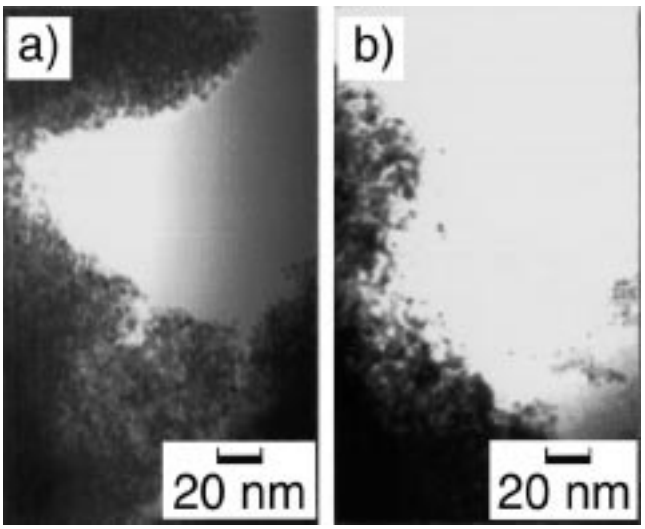

Figure 2. Transmission electron micrographs of the products obtained by the glycothermal reaction of zirconium n-propoxide and rare earth acetate at 300 °C for 2 h: (a) Y/Zr = 3/100 and (b) Ce/Zr = 25/100.

Table 2
BET surface area of the tetragonal zirconia–yttria solid solution (Y/Zr = 3/100) dried under various conditions.[a]

Drying conditions	S_{BET} ($m^2\,g^{-1}$)
Washed with methanol and air-dried	124
Washed with acetone and air-dried	80
Washed with water and air-dried	110
Washed with methanol and dried by microwave irradiation[b]	161

[a] Synthesis conditions: zirconium n-propoxide and yttrium acetate in 1,4-butanediol at 300 °C for 2 h.
[b] 2.45 GHz, 600 W microwave was used. Care was taken not to explode the powders: after 1 min microwave irradiation, the product was pulverized and cooled and this cycle was continued five times.

On the other hand, the products with low RE contents had relatively smaller surface areas. However, these values had relatively poor reproducibility, and varied from lot to lot. Since the increase in surface area with the increase in the amount of RE ions suggested that surface energy of the particles of the zirconia solid solution increases with the decrease in RE content so that the product particles with low RE/Zr ratios coagulated by the surface energy, a new lot of the product (Y/Zr = 3/100), after thoroughly being washed with methanol, was divided into four parts and each part was dried by a different method. As summarized in table 2, the surface area of the product varied by the drying conditions, whereas the crystallite size did not change (3.0 ± 0.1 nm). This result suggests that compaction of particles of the product, originally having had a large surface area, took place during the drying stage owing to the surface tension of fluid between the particles. Under theses conditions, large surface energy of the ultrafine particles created tight agglomerates and the surface area around the point of contact between two particles cannot be accessed by the nitrogen molecules. Moreover, closed voids (voids where nitrogen molecules are not accessible) among the particles were possibly formed, resulting in a decrease in apparent surface area. When the product was dried by microwave irradiation, the fluid between the particles was rapidly evaporated, which avoided the compaction of particles, resulting in the formation of the dried product with a large surface area.

Thermal analyses of the products (figure 3) showed that two weight decrease processes took place, at 70 °C and at around 350 °C. The former process was associated with endothermic response in DTA and is attributed to the desorption of physisorbed species (water, methanol or 1,4-BG). On the other hand, the latter process was highly exothermic and is due to combustion of surface alkyl groups. Small amounts of alkyl (i.e., 4-hydroxybutyl) groups covalently

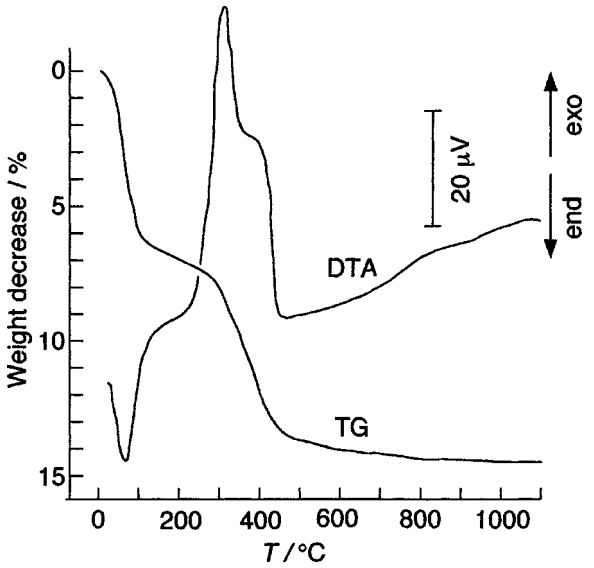

Figure 3. Thermal analyses of the zirconia–yttria solid solution (Y/Zr = 12/100) obtained by the glycothermal method: heating rate 10 °C min^{-1} in a 40 ml min^{-1} flow of dried air; reference sample, α-alumina.

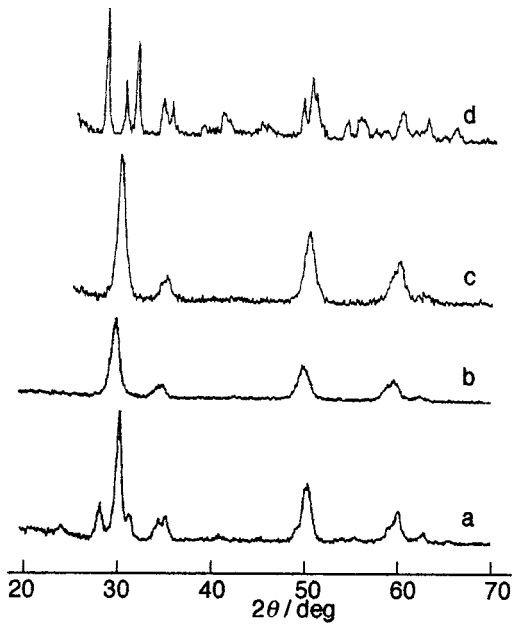

Figure 4. XRD patterns of the calcined product obtained by the glycothermal reaction of zirconium n-propoxide and yttrium acetate: (a) unmodified zirconia calcined at 700 °C, (b) zirconia–ceria solid solution (Ce/Zr = 6/100) calcined at 700 °C, (c) and (d) zirconia–yttria solid solution calcined at 700 and 1300 °C, respectively.

bonded to the surface oxygen atoms of the particles are always detected in the product obtained by the glycothermal method [32,33,35,37].

Figure 4 shows XRD patterns of the samples obtained by calcination of the products. When the RE content in the product was small, the product partly transformed into the monoclinic phase, but the products with large RE contents maintained the tetragonal (and/or cubic) phase (table 3). In any cases, no other phases were detected. With the increase in the calcination temperature, the diffraction peaks

Table 3
Phases detected in the glycothermal products and samples obtained by calcination thereof.[a]

RE	RE/Zr	As-synthesized	Samples calcined at		
			700 °C	1100 °C	1300 °C
	0/100	T	T, M	T, M	M
Y	3/100	T	T	–	T, M
	6/100	T	T	T	–
	12/100	T	T	T	–
	25/100	T	T	T	–
	50/100	T	–	–	–
Ce	3/100	T	T	T, M	–
	6/100	T	T	T, M	–
	12/100	T	T	T	–
	25/100	T	T	T	–

[a] Products were obtained by the reaction of zirconium n-propoxide and rare earth acetate in 1,4-butanediol at 300 °C for 2 h. T – tetragonal or cubic phase, M – monoclinic phase.

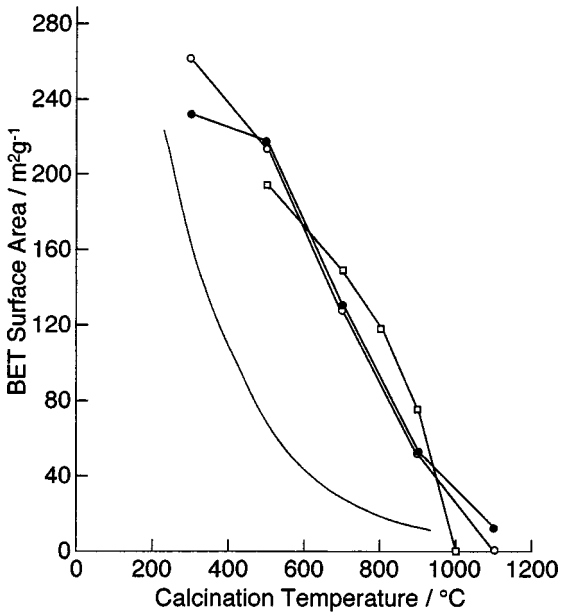

Figure 5. Surface area of zirconia samples calcined at various temperatures: (○) and (●) zirconia–yttria solid solutions with Y/Zr ratios 25/100 and 50/100, respectively, (□) potassium-modified zirconia reported by Chuah et al. [24], curved line, general tendency for the decrease of surface area of unmodified zirconia prepared by various methods, which was summarized by Cimino et al. [15].

became progressively sharp, the crystallite size being enlarged. In accordance with this result, the BET surface area (see table 1) of the calcined products gradually decreased. However, the products maintained relatively large surface areas even after calcination at higher temperatures and the surface area increased with the increase in the amount of RE ions. In figure 5, the surface area of the product is plotted against the calcination temperature. For comparison, the surface area of potassium-modified zirconia reported by Chuah et al. [24] is also plotted, and a general tendency for the decrease of surface area of unmodified zirconia with the calcination temperature, summarized by

Cimino et al. [15], is also shown in the figure. Although the potassium-modified zirconia had larger surface area than the present product when calcined at lower temperatures, the surface area of the former sample was reported to decrease abruptly by calcination at $>900\,^{\circ}C$, and the product with Y/Zr = 1/2 had larger surface area than the potassium-modified zirconia after calcination at $>900\,^{\circ}C$.

In conclusion, the thermal decomposition of mixtures of zirconium alkoxide and rare earth acetate in 1,4-BG at $300\,^{\circ}C$ yielded a zirconia–rare earth oxide solid solution with 4 nm crystallite size, which showed a high thermal stability and seems to have potential use as catalyst or catalyst support.

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