NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Synthesis of ZrO_2–TiO_2 solid solutions by various synthetic methods in the region of high zirconium contents

Koichi Kubo · Saburo Hosokawa · Satoshi Furukawa · Shinji Iwamoto · Masashi Inoue

Abstract Zirconia samples and ZrO_2–TiO_2 solid solutions were synthesized from zirconium and titanium alkoxides with the Zr/Ti molar ratios of 1:0, 9:1, 6:1, and 3:1 by various methods, i.e., glycothermal method using 1,4-butanediol or ethylene glycol, alkoxide method, and solvothermal treatment of the alkoxide-derived hydroxide sol. The samples were characterized by XRD, TG-DTA, Raman spectroscopy, and nitrogen adsorption isotherm. In all the samples, ZrO_2–TiO_2 solid solutions were obtained in which Ti was incorporated into the ZrO_2 lattice. The ZrO_2–TiO_2 solid solutions had higher thermal stabilities and much larger surface areas than ZrO_2.

Introduction

The ZrO_2–TiO_2 solid solutions attract much attention in recent years, because they are used as catalysts and catalyst supports for a variety of reactions such as dehydrogenation [1, 2], isomerization [3, 4] and photocatalysis [5–7]. Therefore, they have been synthesized by various methods such as coprecipitation [8, 9], sol–gel [10, 11] and polymer gel templating methods [12]. High surface area ZrO_2 has low thermal stability, and when ZrO_2 is calcined at high temperatures, phase transition from tetragonal to monoclinic phase occurs accompanying a drastic decrease in surface area. Therefore, attempts have been made to improve the thermal stability of ZrO_2 by incorporation of another element into the ZrO_2 lattice [13, 14].

Solvothermal methods have been widely studied for the synthesis of a variety of inorganic materials [15]. We have been studying "glycothermal reaction," which uses glycol as a solvent in solvothermal reaction. This method gives a convenient way to synthesize crystalline oxides at relatively low temperatures and samples having high thermal stability can be synthesized [16].

In this article, the ZrO_2–TiO_2 solid solutions were synthesized by various methods, i.e., the glycothermal method in 1,4-butanediol (1,4-BG) or ethylene glycol (EG) as the solvent, the alkoxide method, and solvothermal treatment of the alkoxide-derived hydroxide sol, and effects of synthetic methods on the properties of the products were investigated.

Experimental

Reaction

Five methods were applied for the synthesis of ZrO_2 and ZrO_2–TiO_2 mixed oxides from zirconium and titanium alkoxides with the Zr:Ti molar ratios of 1:0, 9:1, 6:1, and 3:1.

Synthesis of Zr–Ti mixed oxides by the glycothermal methods (Methods A and B)

Desired amounts of zirconium *n*-propoxide (Mitsuwa Chemicals Co., Ltd.) and titanium isopropoxide (Nakalai Tesque) were suspended in 100 mL of 1,4-BG (Method A) or EG (Method B) in a test tube serving as an autoclave

K. Kubo · S. Hosokawa · S. Furukawa · S. Iwamoto ·
M. Inoue (✉)
Department of Energy and Hydrocarbon Chemistry, Graduate
School of Engineering, Kyoto University, Katsura,
Kyoto 615-8510, Japan
e-mail: inoue@scl.kyoto-u.ac.jp

liner and the test tube was placed in a 300 mL autoclave. An additional 40 mL of the solvent 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 powder was washed with methanol repeatedly by vigorous mixing and centrifuging, and then air-dried.

Synthesis of Zr–Ti mixed oxides by the sol–gel method (Method C)

Desired amounts of zirconium n-propoxide and titanium isopropoxide were dissolved in 100 mL of toluene. Hydrolysis of the alkoxide solution was carried out by keeping the solution in a constant humidity box (RH = 76%). Water dissolved from the gas phase into the toluene solution slowly hydrolyzes the alkoxides yielding hydroxide sol. The solution was kept standing in the humidity box until no further change was observed. The thus-obtained hydroxide sol was washed with water repeatedly by vigorous mixing and centrifuging, and then dried in an 80 °C oven.

Synthesis of Zr–Ti mixed oxides by the solvothermal treatment of the alkoxide-derived hydroxide sol in toluene (Method D)

The hydroxide sol obtained by the alkoxide method (Method C) was transferred into a test tube and it was set in a 300 mL autoclave. An additional 50 mL of toluene was added to 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, and held at that temperature for 2 h under the autogenous pressure of toluene. The resulting precipitate was washed with methanol repeatedly by vigorous mixing and centrifuging, and then air-dried.

Synthesis of Zr–Ti mixed oxides by the solvothermal treatment of the alkoxide-derived hydroxide sol in mineral oil (Method E)

Desired amounts of zirconium n-propoxide and titanium isopropoxide were hydrolyzed as Method C and the hydroxide sol was separated from toluene by centrifugation. Then, the hydroxide gel was added to mineral oil (100 mL) and dispersed in it. The resulting sol was solvothermally treated in the similar fashion as Method D. The precipitate was washed with methanol and air-dried.

Calcination of the product was conducted in a box furnance at a desired temperature for 30 min.

Characterization

Powder X-ray diffraction (XRD) pattern was recorded on a diffractometer, Shimadzu XD-D1, using CuK$_\alpha$ radiation and a carbon-monochromator. Specific surface area of the sample was calculated by the BET single-point method on the basis of the nitrogen uptake measured at 77 K using a Micromeritics Flowsorb II 2300 sorptionmeter. Nitrogen adsorption isotherm was measured using a Quantachrome Autosorb-1 volumetric gas-sorption system. Raman spectra were recorded on a Jobin-Yvon T64000 spectrometer at room temperature using a 514.5 nm line of argon laser. Simultaneous thermogravimetric and differential thermal analyses were performed on a Shimadzu DTG-50 thermal analyser at a rate of 10 °C/min in a 40 mL/min flow of dried air. The elemental analyses were performed using a Shimadzu ICPS-1000 IV, inductively coupled plasma (ICP) emission spectrometer, after the ZrO$_2$–TiO$_2$ solid solutions were dissolved in H$_2$SO$_4$.

Results and discussion

The XRD patterns of the products obtained by the various synthetic methods are shown in Fig. 1. The XRD patterns of the products obtained by Methods B and C indicate that they were amorphous irrespective of the Zr/Ti ratio. Tetragonal ZrO$_2$ was crystallized by Method D, but the addition of titanium isopropoxide to the reaction mixture resulted in formation of amorphous products. On the other hand, the products synthesized by Method A were directly crystallized, and exhibited the XRD pattern due to tetragonal zirconia. As the Ti ratio charged for the glycothermal reaction increased, the diffraction peaks of the products shifted toward the higher angle side, indicating that ZrO$_2$–TiO$_2$ solid solutions were directly crystallized by the glycothermal reaction. In the case of Method E, the samples with the Zr/Ti molar ratios of 9:1 and 1:0 were crystallized, and higher-angle shift of the diffraction peaks indicates that the ZrO$_2$–TiO$_2$ solid solution was formed for the sample with the Zr/Ti molar ratio of 9:1. Since the materials charged for the solvothermal treatment were amorphous as shown in Fig. 1c, crystallization took place during the solvothermal treatment. This result shows a clear contrast against the result for method D: Whereas the solvothermal treatment in toluene yielded amorphous products (except for pure ZrO$_2$), solvothermal treatment in mineral oil facilitated the crystallization of the product. These results can be explained by the fact that the affinity of mineral oil
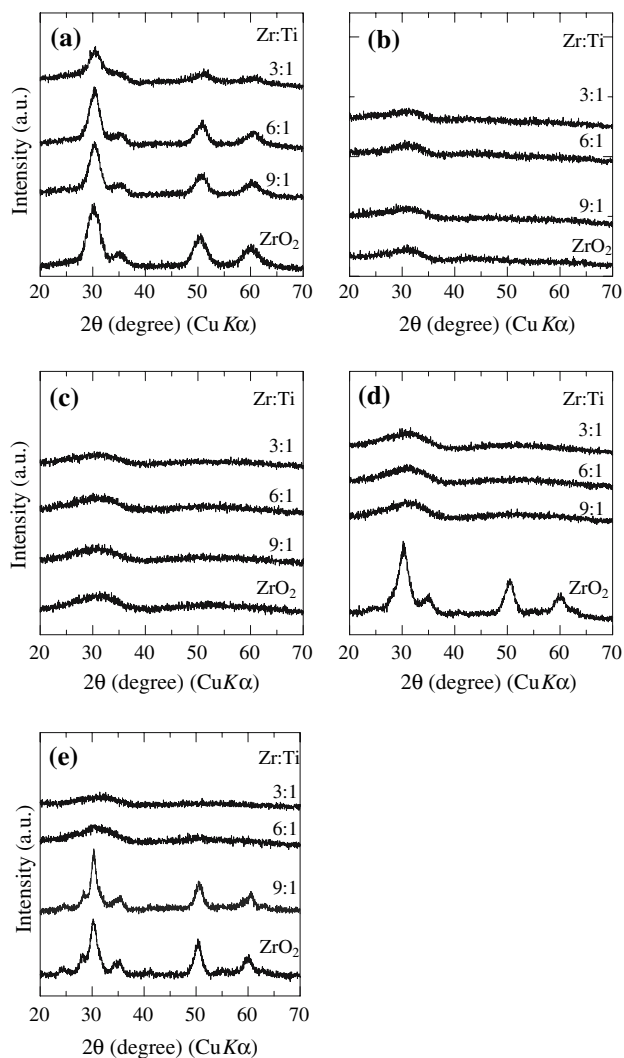
Fig. 1 XRD patterns of the products obtained by: (**a**), Method A; (**b**), Method B; (**c**), Method C; (**d**), Method D; (**e**), Method E

to water is lower than that of toluene, and the activity of water in mineral oil is much higher than that in toluene, when the same amount of water is present in two solvents. Therefore, when the solvothermal treatment of the hydroxide sol was conducted in mineral oil, the sol reacts just as under hydrothermal reaction because of water present in the hydroxide sol. Note that prolonged reaction time in the solvothermal treatment facilitated the crystallization of the ZrO_2–TiO_2 solid solutions. For example, the solid solution with the Zr/Ti charged ratio of 6/1 was crystallized by Method D with the solvothermal treatment for 4 h.

The results for thermal analysis of the products are shown in Fig. 2. In the case of the products synthesized by Method A, an exothermic peak due to combustion of organic moieties remaining on the product surface was observed at around 300 °C, but the exothermic peak due

to crystallization was not observed. This result is in accordance with the XRD results which showed that the products were crystallized. For the products obtained by Method E, an exothermic peak due to combustion of mineral oil was observed at around 350 °C. The exothermic peak due to crystallization was observed for the sample with the Zr/Ti molar ratio of 3:1. However, a slight intensity of the peak suggests that the as-synthesized product was partially crystallized. In the case of the other samples, the exothermic peaks due to crystallization were observed at the temperature range of 400–700 °C. The crystallization temperature increased gradually with increasing the Ti content. Similar results were reported by Xu and Anderson [13] and Zou and Lin [14].

The pure ZrO_2 synthesized by Method D was crystallized by the effect of water present in toluene and in the hydroxide gel. With increasing the amount of titanium
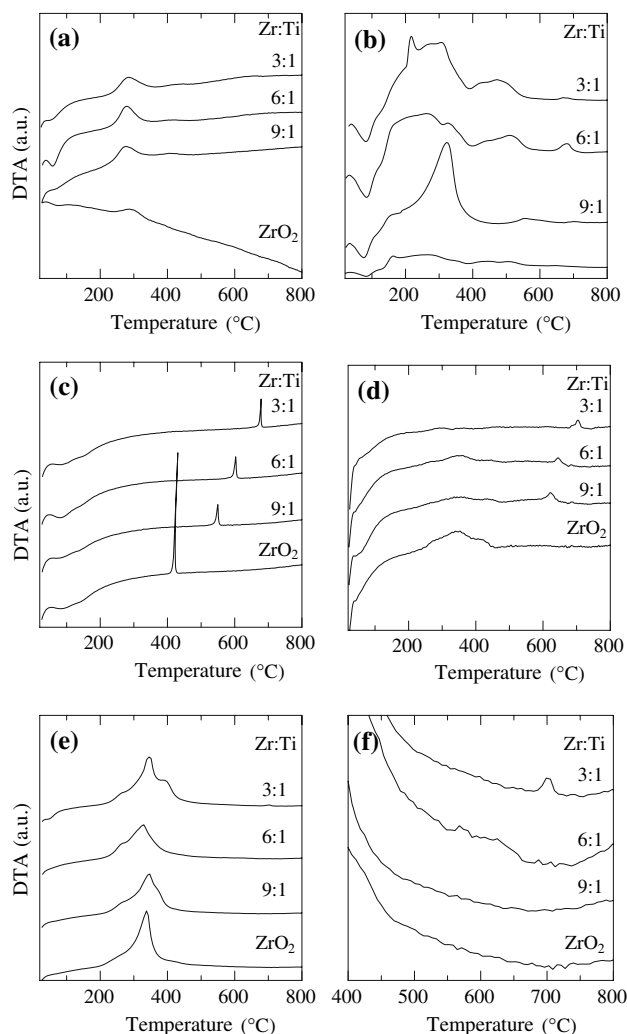

Fig. 2 DTA curves of the products obtained by: (**a**), Method A; (**b**), Method B; (**c**), Method C; (**d**), Method D; (**e**), Method E; (**f**), Method E, with 15 times expansion in the Y-axis

alkoxide in the starting material, the crystallization of the ZrO_2–TiO_2 solid solution was inhibited, as is shown by the XRD patterns in Fig. 1. This result suggests that crystallization of the ZrO_2–TiO_2 solid solution proceeds more slowly as compared with crystallization of ZrO_2. The increase in the crystallization temperature of the products synthesized by Methods C and D shown in Fig. 2 can also be explained along the same line.

The products synthesized by Method B showed complicated DTA peaks and total weight loss was about 50%, much larger than those for the other four products. The IR spectra of the samples synthesized by Method B are shown in Fig. 3 together with that of liquid EG. The IR spectrum of the as-synthesized sample resembled that of EG, although high-wavenumber shifts of the bands were apparently observed. The EG networks were not completely removed by washing, remaining in the amorphous product.

The N_2 adsorption isotherm of the sample with the Zr/Ti molar ratio of 6:1 synthesized by Method B followed by calcination at 400 °C is shown in Fig. 4. Large N_2 uptake at the region of low relative pressure clearly shows the presence of the micropores in the sample. The t-plot

derived from the adsorption branch of the isotherm showed an abrupt decrease in the slope suggesting the presence of a micropore system in the sample.

These results suggest that diffusion of organic molecules through micropores proceeds slowly; thus, organic molecules were converted into carbonaceous matter and hydrogen, which easily diffused out from the particles. Furthermore, the diffusion of oxygen into the matrix seems to be difficult, and therefore the organic species are not burnt easily, remaining carbonaceous matter in the matrix, which combusted at higher temperatures. Therefore, exothermic peaks were complicated. The color of the sample calcined at 400 °C was brown, which also suggests the presence of carbonaceous matter in the sample.

The XRD patterns of the products calcined at 800 °C are shown in Fig. 5. All the samples were crystallized by
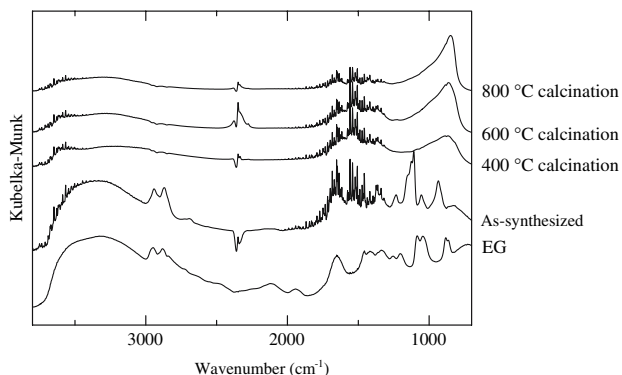

Fig. 3 FTIR spectra of the product with Zr/Ti molar ratio of 6:1 synthesized by Method B and of the samples obtained by calcination thereof. For comparison, FTIR spectrum of liquid EG is also given
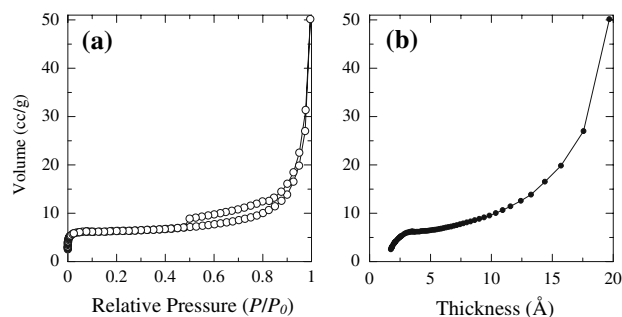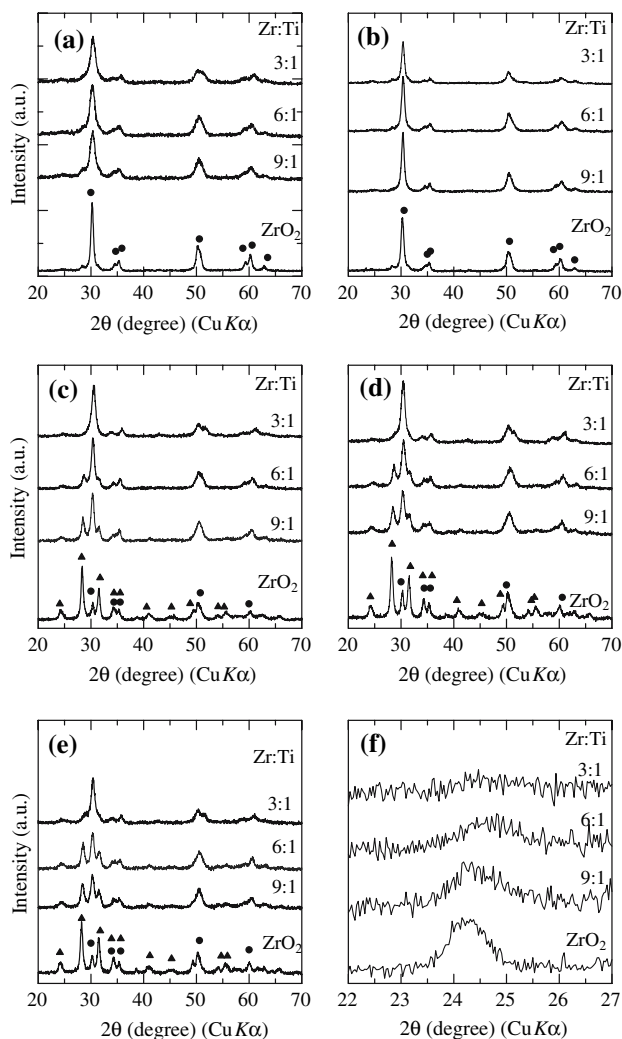

Fig. 4 The N_2 adsorption isotherm (a) and t-plot (b) of the sample with Zr/Ti molar ratio of 6:1 synthesized by Method B followed by calcination at 400 °C

Fig. 5 XRD patterns of the products calcined at 800 °C (●, t-ZrO_2; ▲, m-ZrO_2): (a), Method A; (b), Method B; (c), Method C; (d), Method D; (e), Method E; (f), Method D, with 4 times expansion in the intensity
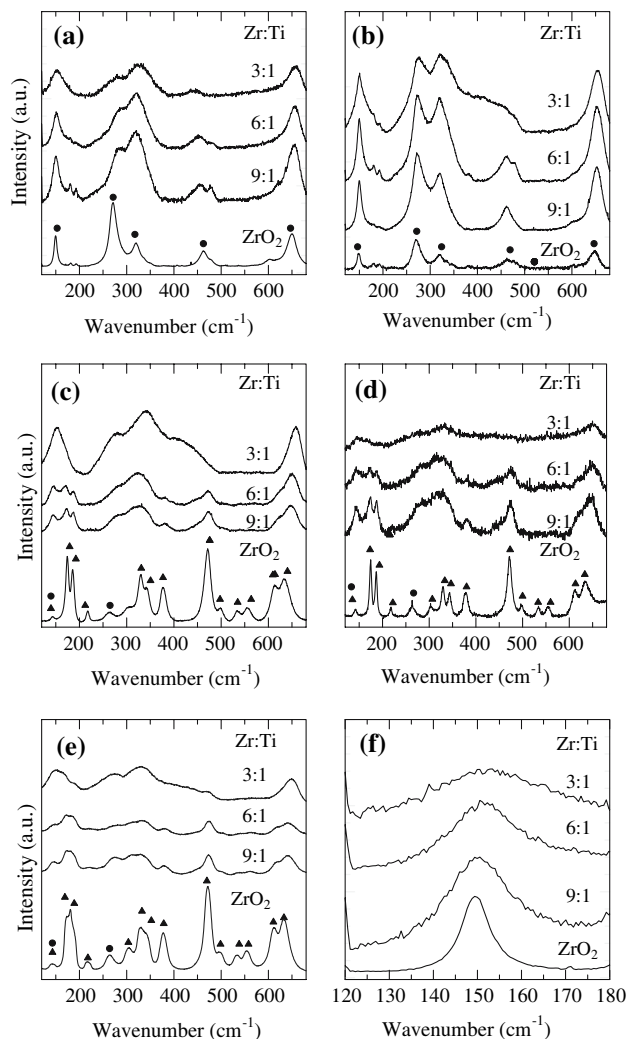
Fig. 6 Raman spectra of the products calcined at 800 °C (●, t-ZrO$_2$; ▲, m-ZrO$_2$): (a), Method A; (b), Method B; (c), Method C; (d), Method D; (e), Method E; (f), Method A, with 2 times expansion in the Y-axis

Fig. 7 SEM images of pure ZrO$_2$ calcined at 500 °C: (a), Method A; (b), Method B; (c), Method C; (d), Method D; (e), Method E

calcination. The XRD patterns due to the tetragonal and monoclinic phases were observed and those of zirconium titanate (ZrTiO$_4$) were not (See, however, the discussion on the Raman spectra). It must be noted that for the mono-clinic phase, higher-angle side shift of the diffraction peaks with the increase in the Ti content was also observed (Fig. 5f), indicating the formation of the monoclinic solid solutions. Xu and Anderson [13] and Troitzsch and Ellis [17] showed that the solid solutions of both the tetragonal and monoclinic phases were obtained by heat treatment of the products synthesized by the sol–gel and solid-phase methods.

The ICP emission spectrometric analyses showed that the Ti contents were 31.5, 24.5, 30.4, 30.8, and 31.1 mol% for the 800 °C-calcined products synthesized with the Zr:Ti charged ratio of 3:1 by methods A, B, C, D, and E,
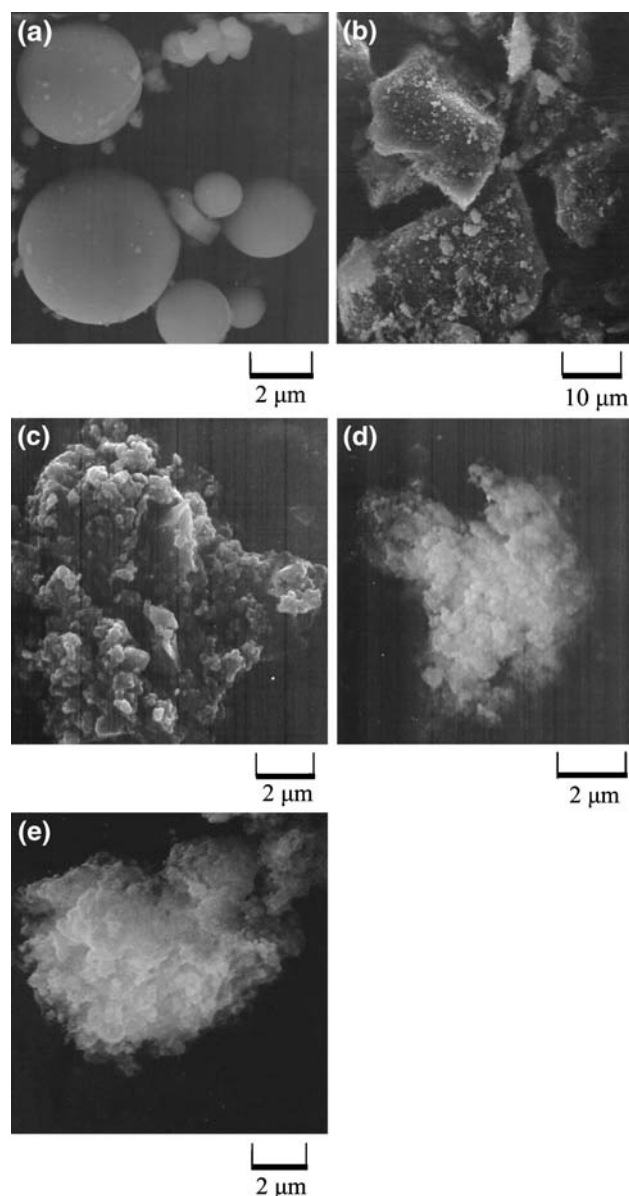
respectively. The Ti contents were slightly higher than those in the starting materials (Ti = 25 mol%) for the products obtained by methods A, C, D, and E, suggesting that a small amount of Zr alkoxide did not react or was not hydrolyzed during the glycothermal reaction or the sol–gel process. On the other hand, the Ti content in the product obtained by method B was essentially identical with that in the starting mixture charged for the reaction, indicating that all the starting materials were incorporated into the EG networks by the alkoxy-exchange reaction.

The Raman spectra of the samples calcined at 800 °C are shown in Fig. 6. For pure ZrO$_2$ prepared by Methods C, D, and E, the Raman spectra clearly showed the major
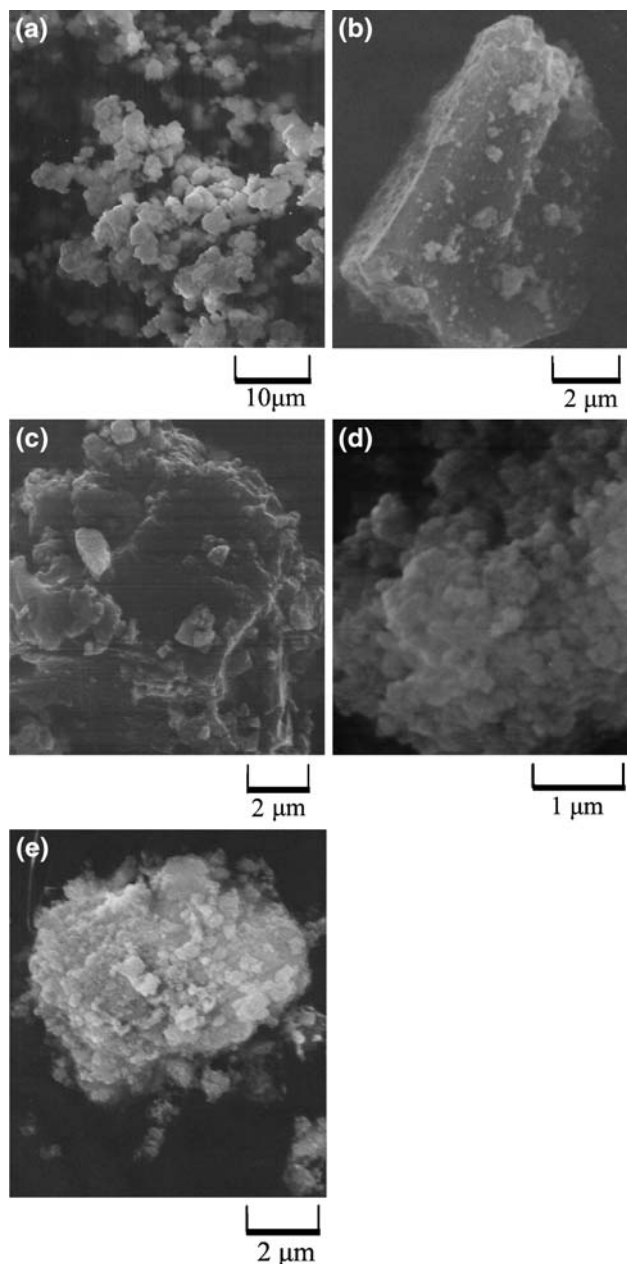
Fig. 8 SEM images of ZrO_2 solid solution with Zr/Ti molar ratio of 6:1 calcined at 500 °C: (**a**), Method A; (**b**), Method B; (**c**), Method C; (**d**), Method D; (**e**), Method E

Fig. 9 TEM images of the products synthesized by Method A and calcined at 500 °C: (**a**), pure ZrO_2; (**b**), Zr/Ti molar ratio of 9:1; (**c**), Zr/Ti molar ratio of 6:1; (**d**), Zr/Ti molar ratio of 3:1

component was the monoclinic phase, which accords with the XRD results. The ZrO_2 samples synthesized by the glycothermal methods in 1,4-BG and EG (Methods A and B) contained much smaller amounts of the monoclinic phase. Whereas tetragonal ZrO_2 was directly crystallized without formation of the hydroxide phase by the glycothermal reaction of zirconium alkoxide alone, Methods C, D, and E yielded the hydroxide gel containing water, from which both the tetragonal and monoclinic ZrO_2 phases were crystallized. High thermal stability of the tetragonal
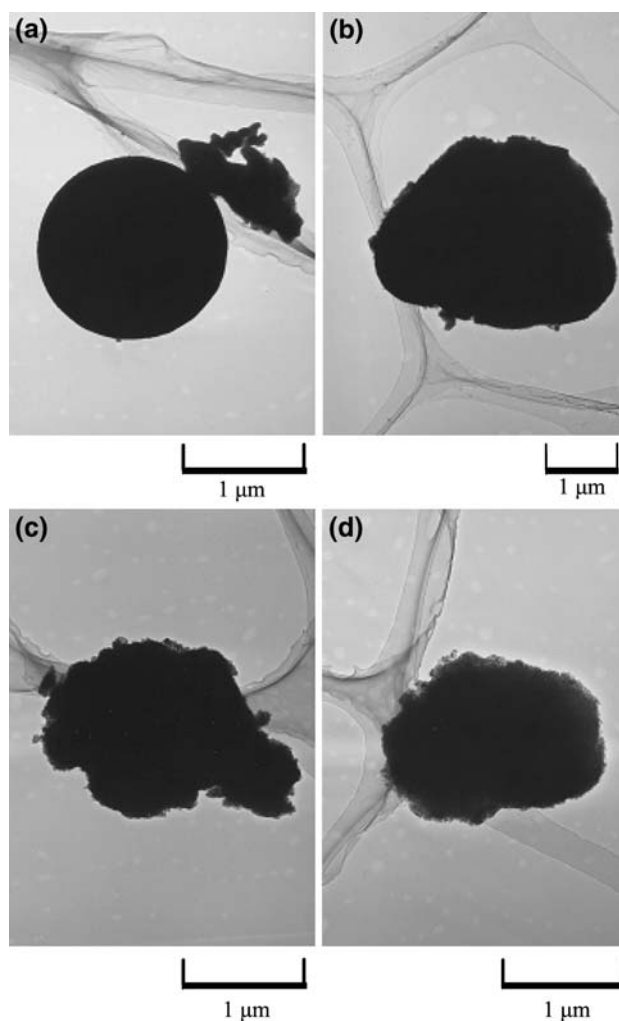
ZrO_2 phase synthesized by the glycothermal method seems to connect with these histories of the samples.

With the increase in the Ti content in the starting materials, the intensities of the peaks due to the monoclinic phase decreased. Slight shift of the band due to the tetragonal phase toward higher wavenumber side was also noted (Fig. 6f), which accords with the shrinkage of the unit cell (higher angle side shift of the diffraction peaks) of the tetragonal ZrO_2 lattice by incorporation of Ti^{4+} having smaller ionic size. The Raman spectrum of the sample with the Zr/Ti molar ratio of 3:1 synthesized by Method C was slightly different from those of the other samples with the same molar ratio in that the band at 340 cm^{-1} had a high intensity with a shoulder peak at about 410 cm^{-1}. Since the Raman spectrum of $ZrTiO_4$ has strong bands at 338 and 412 cm^{-1} [18], the intense peak at about 340 cm^{-1} observed in the Raman spectrum of the former sample can be explained by overlap of the peaks due to the tetragonal
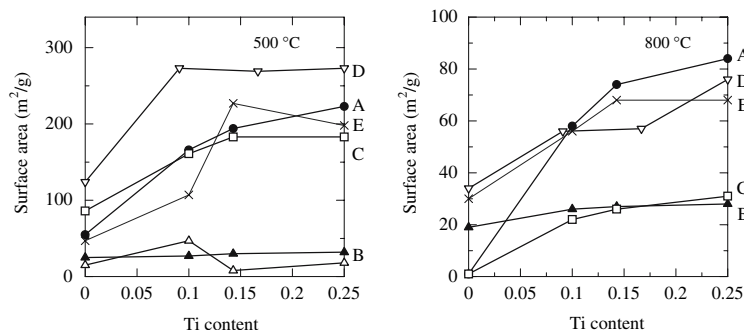
Fig. 10 BET surface area of the products synthesized by: ●, Method A; □, Method C; ▽, Method D; ×, Method E; followed by calcination at the temperatures specified in the figure. For the products

synthesized by Method B, data after calcinations at: Δ, 400 °C; ▲, 600 °C; are shown since the product exhibited an exothermic peak at around 500 °C in DTA

and $ZrTiO_4$ phases. Since the XRD pattern of the tetragonal phase resembles that of the $ZrTiO_4$ phase, the sample seems to be composed of the mixture of the tetragonal and monoclinic ZrO_2 solid solutions and the $ZrTiO_4$ phase.

The SEM images of the ZrO_2 samples and the ZrO_2 solid solutions with the Zr/Ti molar ratio of 6:1 synthesized by the five methods are shown in Figs. 7 and 8, respectively. When the samples synthesized by the glycothermal methods (Methods A and B) were compared, clear difference was observed: In the case of method A, spherical ZrO_2 particles were observed, while the Ti-doped ZrO_2 sample was composed of well-dispersed particles having ~1 μm size (Fig. 9). The morphologies of pure ZrO_2 and doped ZrO_2 synthesized by Method B were irregularly-shaped large masses comprised of densely-packed primary particles. When the morphologies of the samples synthesized by methods C and D were compared, surface morphology was different: In the case of Method C, pure ZrO_2 had jagged edges, while the surface of pure ZrO_2 synthesized by Method D were rounded off. The surface-morphological change suggests that the hydroxide gel produced by hydrolysis of the alkoxides was partially dissolved in the water layer adsorbed on the particles under the solvothermal conditions.

The BET surface areas of the samples calcined at 500 and 800 °C are shown in Fig. 10. For the product synthesized by Method B, the data of the sample calcined at 400 and 600 °C are shown in Fig. 10, since the product exhibited an exothermic peak at around 500 °C due to combustion of carbonaceous matter. Among the samples calcined at 500 °C, the sample synthesized by Method D had the largest surface area (273 m²/g). On the other hand, the sample synthesized by Method A had the largest surface area (84 m²/g) among the samples calcined at 800 °C, while the samples prepared by method E also possessed large surface areas. For the products synthesized by Methods C and D, calcination at 500 °C did not cause the crystallization and therefore their surface areas were very

large. When the products were crystallized by calcination, surface area was dramatically decreased. In contrast, the products synthesized by Method A were directly crystallized by the glycothermal reaction, and therefore high surface areas were maintained after calcination at high temperatures.

Conclusions

The ZrO_2–TiO_2 solid solutions were synthesized from zirconium and titanium alkoxides with the Zr/Ti molar ratios higher than 3 by five different methods. The ZrO_2–TiO_2 solid solutions were directly synthesized by the glycothermal reaction of zirconium n-propoxide and titanium isopropoxide in 1,4-BG as a solvent. The solvothermal treatment of the alkoxide-derived hydroxide gel also caused crystallization of the product, although prolonged reaction time was required for the samples with higher Ti content. This process was, however, hydrothermal reaction caused by water adsorbed on the particles. When the amorphous products were calcined, the ZrO_2–TiO_2 solid solutions were crystallized. When pure ZrO_2 samples calcined at 800 °C were compared, the samples synthesized by the glycothermal method (Methods A and B) had higher thermal stability in terms of the phase transition. The ZrO_2–TiO_2 solid solutions had much larger surface areas than that of ZrO_2, and the samples synthesized by the glycothermal method maintained higher surface areas ever after calcination at higher temperatures.

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