Solution phase synthesis of t-ZrO$_2$ nanoparticles in ZrO$_2$-SiO$_2$ mixed oxide

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A solution phase synthesis is used to prepare tetragonal zirconia nanoparticles. Ammonia solution and zirconia precursor solution were prepared separately and then mixed together to get colloidal hydroxide precipitate. The colloidal hydroxide was treated with silica sol and then the precipitate was separated and dried. The dried powder was then calcined at different temperatures for 2 and 6 h. The mean particle size of the powder calcined at 1000°C was found to be around 8–10 nm. The thermal analysis of dried powder indicates the formation of bulk tetragonal zirconia phase at 780°C. X-ray diffraction (XRD) and infrared spectroscopic analyses confirm the presence of 100% tetragonal zirconia phase in the powder calcined at 1000°C. The addition of silica stabilised the tetragonal zirconia phase. It is advantageous to use this powder as catalyst or catalyst support that operates at high temperatures.

Keywords: chemical synthesis; nanoparticle; ZrO$_2$; SiO$_2$; X-ray diffraction; differential thermal analysis; thermogravimetric analysis; transmission electron microscopy; infrared spectroscopy

1. Introduction

Zirconia has been shown to be effective both as a catalyst and a support [1]. It has been found that zirconia has high catalytic activity for the isomerisation of olefins [2] and epoxides [3]. Zirconia is an important promoter in the catalytic converter system for automobile emission control and has been shown to regulate the redox reaction of the ceria catalyst support. Several methods have been developed to increase the surface area and stabilise the tetragonal phase of zirconia (t-ZrO$_2$). These include the addition of additives such as sulphate [4], potassium [5,6], rare earth ions [7–13] and silica [14,15]. It has been reported that the surface area of zirconia is increased by the presence of a small amount of silica [16,17]. However, the effect of these additives varies with the preparation

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method and the amount of additives. Recently, Chandradass et al. [18] prepared ZrO_2–SiO_2 particle by oxalate processing and reported that the size of zirconia nanoparticle decreased with the increase in silica content. This investigation is focusing on the development of a zirconia catalyst with fine particle size and high thermal stability.

2. Experimental procedure

Zirconium oxychloride $ZrCl_2O \cdot 8H_2O$ (Junsei chemical, South Korea) was dissolved in distilled water taken in a beaker to 0.8 M concentration. The hydrogel was obtained by the dropwise addition of ammonium hydroxide (Dae Jung, South Korea) until the pH reaches 10. The silica sol was prepared by the following process as reported elsewhere [19]: tetraethoxysilane (TEOS) and aqueous solution of ethanol (C_2H_5OH) were mixed with magnetic stirring in a beaker; then 0.01 M HCl (1 ml) was added as a catalyst for hydrolysis reaction. The volume ratio of $TEOS : C_2H_5OH : H_2O$ was maintained at 1 : 5 : 5. The silica sol is formed after 1.5 h stirring. The required amount of silica sol was added to the colloidal hydroxide such that the final composition contains 10 wt% SiO_2. It was then stirred for 1 h. The precipitate was centrifuged, washed and redispersed in water for three times. The centrifuged cake was oven dried. The dried cake was crushed and calcined in air in a muffle furnace at different temperatures for 2 and 6 h.

X-ray diffraction (XRD) analysis of the calcined powders was carried out in an X-ray diffractometer (Philips X'pert MPD 3040) over a 2θ range of 10–80° at a rate of $3° \, min^{-1}$. The samples were continuously scanned with a step size of 0.05° (2θ) and a count time of 1 s per step. The volume fraction of monoclinic phase in the mixture of both monoclinic and tetragonal phases was determined by the relative intensity relationship of the XRD [20]:

$$\text{Percentage of monoclinic phase} = \frac{I_m(111) + I_m(\overline{1}11)}{I_m(111) + I_m(\overline{1}11) + I_t(111)} \times 100, \quad (1)$$

where the subscripts m and t refer to the monoclinic and tetragonal phases, respectively, and I refers to the intensity of the corresponding peak. The thermal decomposition behaviour of the dried powder was studied by thermogravimetric–differential thermal (TG–DT) analysis (SCINCO, STA 1500). The average size of the particles was estimated from the transmission electron microscopy (TEM) micrographs using standard software (ImageJ). The morphology of the calcined powder particles was observed using TEM (JEM 2100F). Fourier transform infrared spectral (FTIR) analysis was made on a Nicolet Impact 410 digital signal processing (DSP) spectrophotometer using the KBr pellet made with the powder sample.

3. Results and discussion

The thermal behaviour of the as-synthesised zirconia precursor powder with 10 wt% silica is shown in Figures 1 and 2. There is an endothermic peak at 100°C, with a corresponding weight loss of 6.3%, due to the evaporation of water, solvent and other residuals. A second weight loss of 10.6% occurred between 100°C and 400°C is associated with sample dehydroxylation. The initial formation of tetragonal zirconia is indicated in the
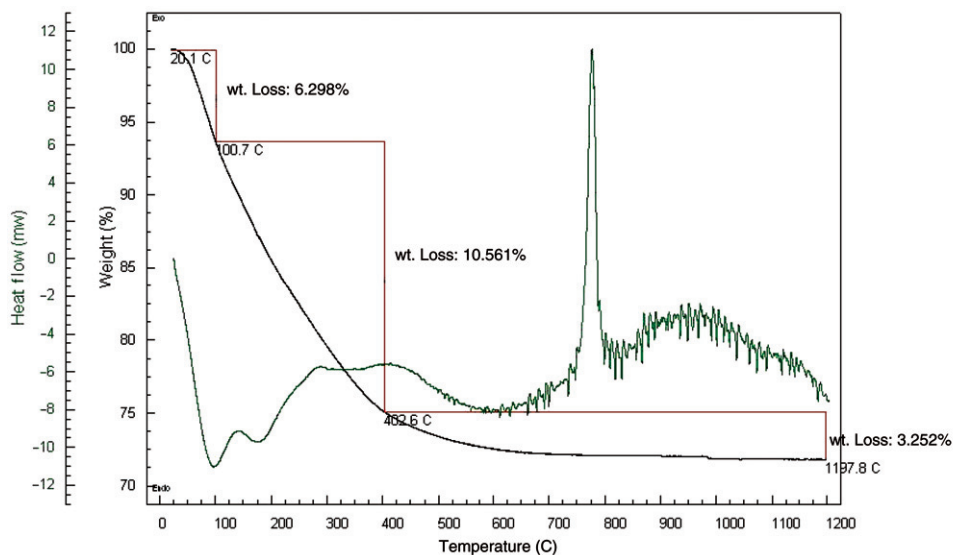
Figure 1. DTA and TGA of as-synthesized zirconia precursor with 10 wt% silica.
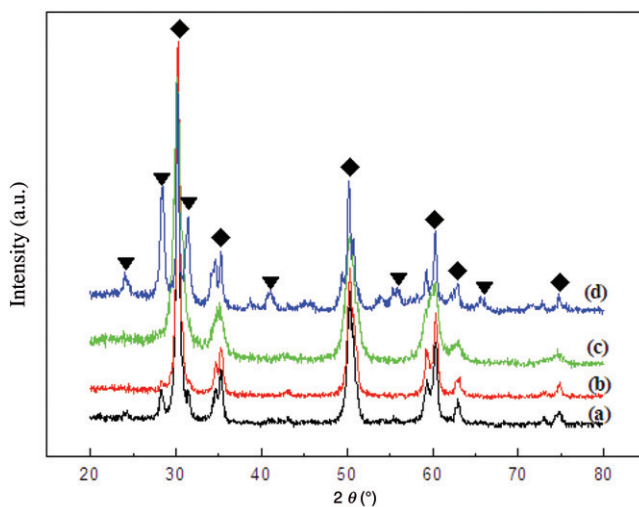
Figure 2. XRD patterns of the zirconia powder with 10 wt% silica calcined for 2 h at (a) 600°C; (b) 800°C; (c) 1000°C; and (d) 1200°C (▼ – monoclinic: ◆ – tetragonal).

thermogram by a wide exothermic peak at approximately 405°C [21]. A second exothermic peak located at 780°C is ascribed to the bulk crystallisation of tetragonal zirconia [22].

The XRD patterns of the powders calcined at different temperatures are shown in Figures 3 and 4. The powders composed mainly of tetragonal phase after calcination at

Figure 3. XRD patterns of the zirconia powder with 10 wt% silica calcined for 6 h at (a) 600°C; (b) 800°C; (c) 1000°C; and (d) 1200°C (▼ – monoclinic: ◆ – tetragonal).

Figure 4. TEM micrographs of the zirconia powder with 10 wt% silica calcined for 2 h at (a) 600°C; (b) 800°C; (c) 1000°C and (d) 1200°C.

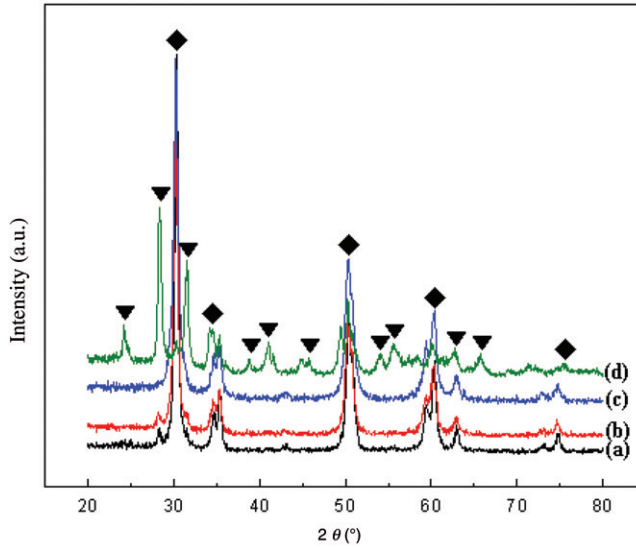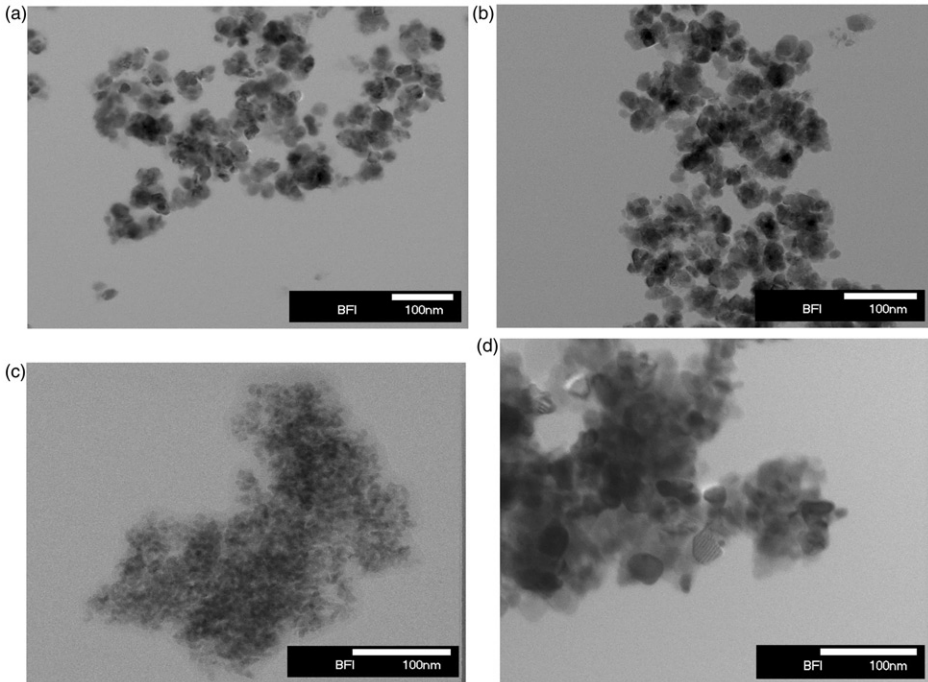600°C and 800°C. Interestingly, the monoclinic phase content decreased on increasing calcination temperature, and 100% tetragonal phase is retained at 1000°C. But, calcination at 1200°C leads to the transformation of some amount of tetragonal phase to monoclinic phase. The amounts of monoclinic phase present after calcination at different temperatures are given in Table 1. Diffraction peaks ascribed to crystalline silica (quartz) were not observed in the samples at the temperature range studied. The crystallite size of the calcined particle was calculated from full width at half maximum (FWHM) using Scherer's formula [23]

$$D = k\lambda/B\cos\theta, \tag{2}$$

where k is a constant equal to 0.9; λ is the wavelength of Cu-Kα (0.15406 nm) and B is the integral breadth (radians) at half maximum intensity. The calculated crystallite sizes are given in Table 2. The crystallite size decreases after calcination up to 1000°C and then increases after calcination at 1200°C. As reported previously, the monoclinic phase is the stable phase at low temperatures, but the tetragonal phase is formed first on heat treatment [24]. The presence of the tetragonal phase at low temperatures can be attributed to several factors, such as chemical effects (the presence of anionic impurities), phase of structural similarities, as well as particle size effects (based on the lower surface energy in the tetragonal phase compared with the monoclinic phase) [25]. Improved stability of the tetragonal phase over a large temperature range has been observed in zirconia doped with small amounts of CaO, MgO and Y_2O_3 [26–28] including mineralisers such as CeO_2 [29]. The stabilisation of t-ZrO_2 is attributed to the structural similarity of the dopant oxides

Table 1. Percentage of monoclinic zirconia phase in the calcined powders.

Calcination temperature (°C)	Monoclinic phase (%)	
	Calcined for 2 h	Calcined for 6 h
600	18	20
800	11	8
1000	0	0
1200	56	79

Table 2. Particle size of the calcined powders calculated using Debye Scherer formula.

Calcination temperature (°C)	Particle size (nm) calcined for 2 h		Particle size (nm) calcined for 6 h	
	Tetragonal	Monoclinic	Tetragonal	Monoclinic
600	17	14	18	17
800	17	8	16	17
1000	9	–	14	–
1200	28	14	18	19

and ZrO_2, and to the larger dopant cation radius compared with the Zr^{4+} radius [30]. However, in the SiO_2–ZrO_2 binary oxide, these arguments are not applicable, since the Si^{4+} radius is smaller than the Zr^{4+} radius and silica remains in its amorphous state during the thermal treatments. In addition, silica crystal structure would not be cubic, tetragonal or monoclinic [16]. Another explanation for the stability of the tetragonal phase of zirconia in CaO-, MgO- or Y_2O_3-doped zirconia systems is based on the formation of oxygen vacancies resulting from the presence of divalent and/or trivalent cations. The increase in oxygen vacancies improves the stability of the tetragonal phase in Y_2O_3–ZrO_2 system [31], because of the increase in lattice strains and/or crystal defects on the tetragonal structure. Xu [32] and Hasse et al. [33] have reported the increase of monoclinic phase in the zirconia powder synthesised by co-precipitation on increasing the calcination temperature. The coarsening of the particles at higher temperatures has been cited as the reason for the transformation of tetragonal phase to the monoclinic phase. This explanation is not very reasonable, since the tetragonal phase in zirconia powder (3 mol% Y_2O_3) can be retained at room temperature even when the grain size is 300 nm or more [34–36]. As reported elsewhere [36], the monoclinic phase content in the powder prepared by homogeneous precipitation was much less than by co-precipitation, which suggests that the increase of the monoclinic phase at a higher calcination temperature was more likely due to the inhomogeneous distribution of Y_2O_3 in the ZrO_2 powder. This inhomogeneous distribution caused by the Y_2O_3 content in some ZrO_2 particles is less than 3 mol% and so, the tetragonal phase could not be retained at room temperature when the particles are coarsened. Based on the homogenous distribution of Y_2O_3 in SiO_2 as reported elsewhere [37], the phenomena in this study could be explained by the homogeneous distribution of SiO_2 in ZrO_2 powder. The process could be described as follows: at first a homogenous precursor solution is formed. After the addition of NH_4OH, $Zr(OH)_4$ is formed and precipitated. When the silica sol is added, $Si(OH)_4$ layer is formed homogeneously on the $Zr(OH)_4$ precipitates. This layer prevents the coarsening of ZrO_2 particles during calcination. The particle size reduction is due to the dehydoxylation of hydroxides. Finally, during calcining, SiO_2 infiltrated into ZrO_2 particles and so the monoclinic phase transforms to tetragonal phase. The hydrothermal treatment of the gel [33] could greatly decrease the content of the monoclinic phase. In this synthesis, no other treatment is needed and the transformation to monoclinic phase could be effectively avoided during the calcination due to the presence of SiO_2 layer. This is a unique advantage of this process.

TEM observations on ZrO_2–SiO_2 binary oxide show spherical morphology (Figures 4 and 5). The particle size of the powder calcined for 2 h initially decreases from 26 nm (600°C) to 8 nm (1000°C) and then increases to 29 nm (1200°C). Upon increasing the calcination duration to 6 h, the average particle size decreases from 31 nm (600°C) to 9 nm (1000°C) and then increases to 50 nm (1200°C). As reported elsewhere [17], the TEM pictures of the ZrO_2–SiO_2 (Figure 6) show the presence of crystalline zirconia particles surrounded by a layer of amorphous SiO_2. The capability of a thin layer to constrain the growth of crystalline particles must be explained by taking into account the chemical interactions at the ZrO_2–SiO_2 interface. These chemical interactions, considered as chemical impurities, must be responsible for the mentioned lattice deformations and further stabilisation of the tetragonal phase [17]. Figure 6 shows the energy-dispersive X-ray spectroscopy (EDX) analysis of zirconia
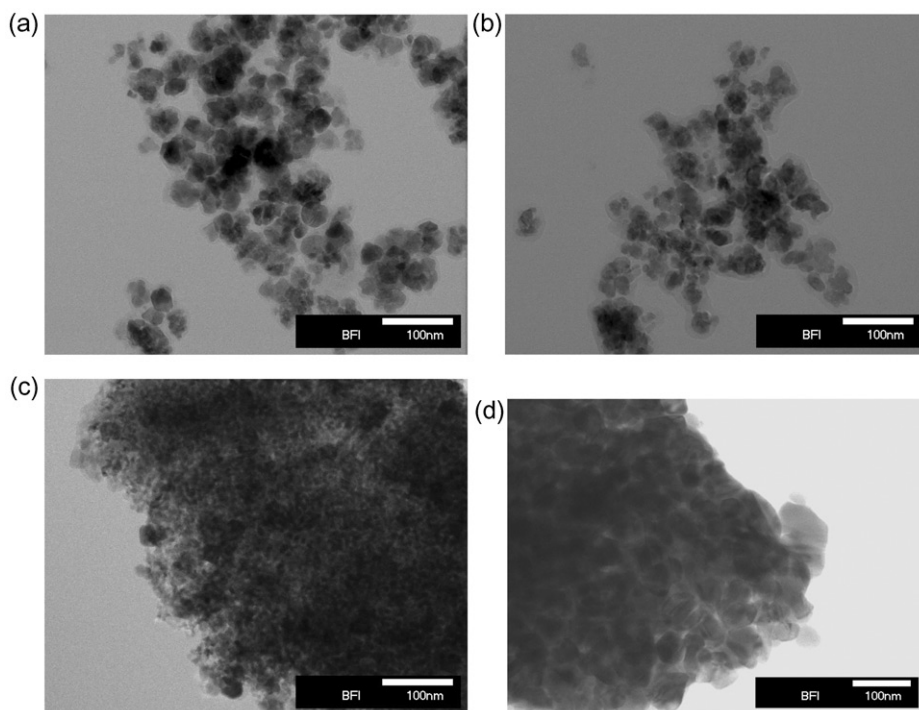
Figure 5. TEM micrographs of the zirconia powder with 10 wt% silica calcined for 6 h at (a) 600°C; (b) 800°C; (c) 1000°C and (d) 1200°C.

powder with 10 wt% silica calcined at 800°C for 6 h. It indicates the presence of both silica and zirconia.

The FTIR spectra of zirconia precursor with 10 wt% silica calcined at different temperatures are shown in Figure 7. The absorption band observed at $3425\,cm^{-1}$ and $1635\,cm^{-1}$ attributed to OH stretching vibration indicating the presence of molecular water. The presence of molecular water in the calcined sample may be due to the absorption of moisture during testing. The band around $2380\,cm^{-1}$ can be attributed to the absorption of CO_2. The absorption band of CO_2 decreases in intensity as the calcination temperature increases. The asymmetric Si–O–Si network reported at $1100\,cm^{-1}$ for pure silica [38] shifted to approximately $1080\,cm^{-1}$ suggests that Si–O–Si is perturbed by the presence of Zr in its environment. The characteristic bands ascribed to the monoclinic phase of zirconia are 574 and $732\,cm^{-1}$ [39] and tetragonal zirconia is $480\,cm^{-1}$ [40]. In this study, these bands are observed at 587 and $745\,cm^{-1}$ for monoclinic zirconia and $490\,cm^{-1}$ for tetragonal zirconia. At 1000°C, the characteristic band corresponding to tetragonal phase alone is present. For zirconia, shifts in wavenumber for the tetragonal and monoclinic phase have been reported in binary oxides prepared by the addition of divalent or trivalent oxides [40]. The incorporation of these oxides causes lattice
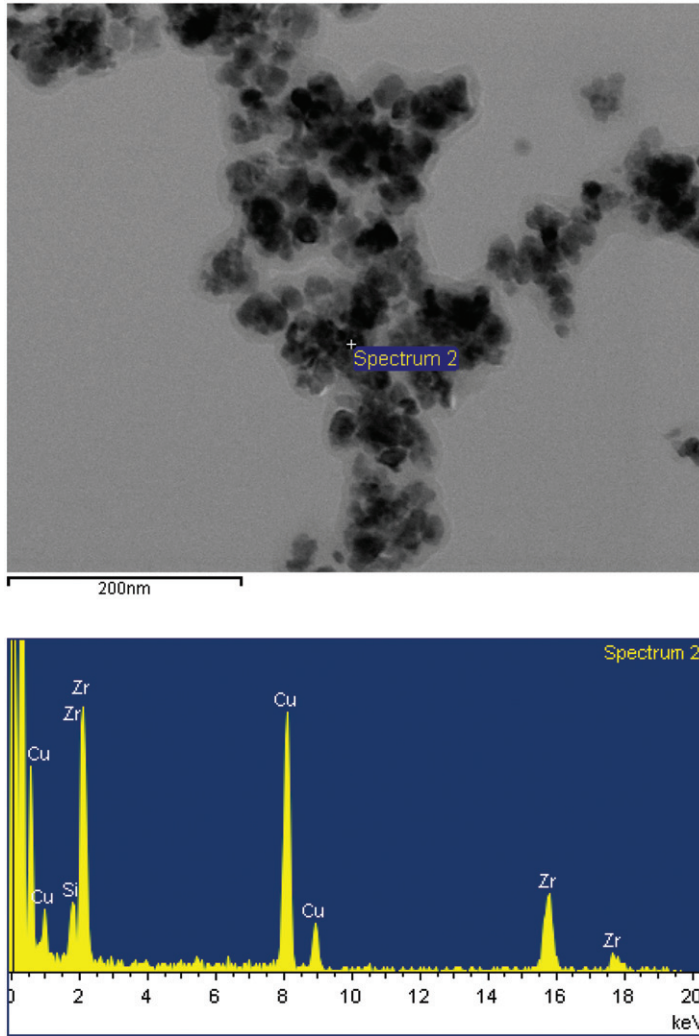
Figure 6. EDAX analysis of the powder calcined at 800°C for 6 h.

deformation on the crystalline structure, with subsequent modification on the force constants of Zr–O and related bonds.

4. Conclusions

Ultrafine zirconia nanoparticles can be synthesised by a simple solution based process with SiO_2 as a stabilising agent. The bulk tetragonal phase formed at 780°C is retained up to 1000°C. The mean particle size of the t-ZrO_2 nanoparticles was found
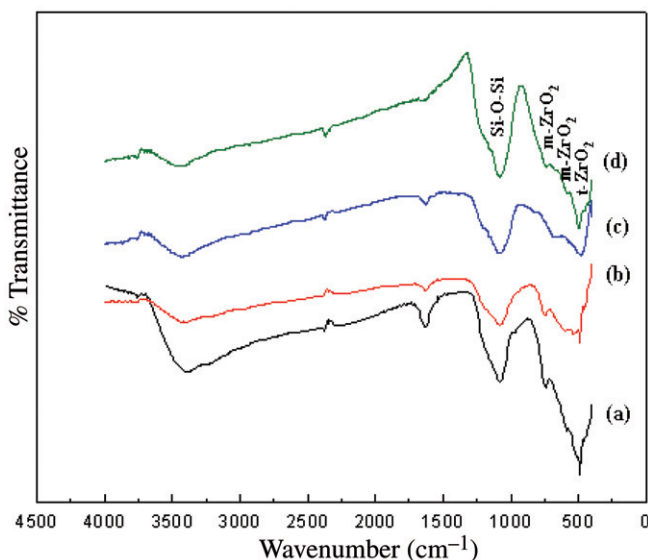
Figure 7. FTIR spectra of zirconia powder with 10 wt% silica calcined for 6 h (a) 600°C; (b) 800°C; (c) 1000°C and (d) 1200°C.

to be around 8–10 nm after calcination at 1000°C. The presence of silica layer prevents the growth of zirconia particles and so the particles are retained in the tetragonal form.

References

[1] T. Yamaguchi, *Application of ZrO₂ as a catalyst and a catalyst support*, Catal. Today 20 (1994), pp. 199–217.
[2] Y. Nakano, T. Iizuka, H. Hattori, K. Tanabe, H. Hideshi, and T. Kozo, *Surface properties of zirconium oxide and its catalytic activity for isomerization of 1-butene*, J. Catal. 157 (1979), pp. 1–10.
[3] K. Arata, K. Kato, and K. Tanabe, *Epoxide rearrangement: IV. Isomerization of cyclohexene and 1-methyl-cyclohexene oxides over solid acids and bases in gas phase*, Bull. Chem. Soc. Jpn 49 (1976), pp. 563–564.
[4] M.S. Scurrell, *Conversion of methane–ethylene mixtures over sulphate-treated zirconia catalysts*, Appl. Catal. 34 (1987), pp. 109–117.
[5] G.K. Chuah and S. Jaenicke, *The preparation of high surface area zirconia-influence of precipitating agent and digestion*, Appl. Catal. A Gen. 163 (1997), pp. 261–273.
[6] Y. Sun and P.A. Sermon, *Surface reactivity and bulk properties of ZrO₂. Part 1 – Thermochemistry of ZrO₂, Y₂O₃–ZrO₂ and K–ZrO₂ aerogels in O₂ and H₂*, J. Mater. Chem. 6 (1996), pp. 1019–1024.
[7] P. Turliee, J.A. Dalmon, G.A. Martin, and P. Vernon, *Non-porous stabilized ZrO₂ particles as support for catalysts*, Appl. Catal. 29 (1987), pp. 305–310.

[8] P.D.L. Mercera, J.G. Van Ommen, E.B.M. Doesburg, A.J. Burggraat, and J.R.H. Ross, *Stabilized tetragonal zirconium oxide as a support for catalysts: Evolution of the texture and structure on calcination in static air*, Appl. Catal. 78 (1991), pp. 79–96.

[9] C.-K. Loong, J.W. Richardson, and M. Ozawa, *Defects, and dynamics of adsorbed hydroxyl groups and water in pure and Lanthanide modified zirconia: A neutron-scattering study*, J. Catal. 157 (1995), pp. 636–644.

[10] R.G. Silver, C.J. Hou, and J.G. Ekerdt, *The role of lattice anion vacancies in the activation of CO and as the catalytic site for methanol synthesis over zirconium dioxide and yttria-doped zirconium dioxide*, J. Catal. 118 (1989), pp. 400–416.

[11] M. Ozawa and M. Kimura, *Preparation and characterization of zirconium dioxide catalyst support modified with rare earth elements*, J. Less-Common Met. 171 (1991), pp. 195–212.

[12] B. Fegly Jr, P. White, and H.K. Bowe, *Processing and characterization of ZrO_2 and Y-doped ZrO_2 powders*, Am. Ceram. Soc. Bull. 64 (1985), pp. 1115–1120.

[13] M. Inoue, K. Sato, T. Nakamura, and T. Inui, *Glycothermal synthesis of zirconia-rare earth oxide solutions*, Catal. Lett. 65 (2000), pp. 79–83.

[14] S. Soled and G.B. Mc Viker, *Acidity of silica-substituted zirconia*, Catal. Today 14 (1992), pp. 189–194.

[15] J.B. Miller, S.E. Rankin, and E.I. Ko, *Strategies in controlling the homogeneity of zirconia-silica aerogels: Effect of preparation on textural and catalytic properties*, J. Catal. 148 (1994), pp. 673–683.

[16] F. Del Monte, W. Larsen, and J.D. Mackenzie, *Stabilization of tetragonal ZrO_2 in ZrO_2–SiO_2 binary oxides*, J. Am. Ceram. Soc. 83 (2000), pp. 628–634.

[17] F. Del Monte, W. Larsen, and J.D. Mackenzie, *Chemical interactions promoting the ZrO_2 tetragonal stabilization in ZrO_2–SiO_2 binary oxides*, J. Am. Ceram. Soc. 83 (2000), pp. 1506–1512.

[18] J. Chandradass, K.-S. Han, and D.-S. Bae, *Synthesis and characterization of zirconia and silica doped zirconia nanopowders by oxalate processing*, J. Mater. Process. Technol. 206 (2008), pp. 315–321.

[19] S. Zhao, Z. Ji, C. Wang, and J. Du, *Synthesis of mesoporous silica glass by a novel chemical method*, Mater. Lett. 61 (2007), pp. 897–899.

[20] H. Klug and L. Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, John Wiley and Sons, New York, 1974.

[21] R. Gomez, T. Lopez, X. Bokhimi, E. Munoz, J.L. Boldu, and O. Novaro, *Dehydroxylation and the crystalline phases in sol–gel zirconia*, J. Sol–Gel Sci.Tech. 11 (1998), pp. 309–311.

[22] D.H. Aguilar, L.C. Torres-Gonzalez, L.M. Torres-Martinez, T. Lopez, and P. Quintana, *A study of the crystallization of ZrO_2 in the sol–gel system: ZrO_2–SiO_2*, J. Solid State Chem. 158 (2000), pp. 349–357.

[23] H.K. Schmid, *Quantitative analysis of polymorphic mixes of zirconia by X-ray diffraction*, J. Am. Ceram. Soc. 70 (1987), pp. 367–376.

[24] R. Srinivasan, R.J. De Angelis, G. Ice, and B.H. Davis, *Critical particle size and phase transformation in zirconia: Transmission electron microscopy and X-ray diffraction studies*, J. Am. Ceram. Soc. 73(11) (1990), pp. 3528–3530.

[25] E. Tani, M. Yoshimura, and S. Somiya, *Formation of ultrafine tetragonal ZrO_2 powder under hydrothermal conditions*, J. Am. Ceram. Soc. 66 (1983), pp. 11–14.

[26] J.S. Lee, T. Matsubara, T. Sei, and T. Tsuchiya, *Preparation and properties of Y_2O_3-doped ZrO_2 thin films by the sol–gel process*, J. Mater. Sci. Lett. 32 (1997), pp. 5249–5256.

[27] A.H. Heuer, N. Claussen, W.M. Kriven, and M. Ruhle, *Stability of tetragonal ZrO_2 particles in ceramics matrices*, J. Am. Ceram. Soc. 65 (1982), pp. 642–650.

[28] D.L. Porter and A.H. Heuer, *Mechanism of toughening partially stabilized zirconia (PSZ)*, J. Am. Ceram. Soc. 60 (1977), pp. 183–184.

[29] V.C. Pandolfelli, M. Rainforth, and R. Stevens, *Sintering and microstuctural studies in the system ZrO_2–TiO_2–CeO_2*, J. Mater. Sci. 25 (1990), pp. 2233–2244.

[30] V.C. Pandolfelli, J.A. Rodrigues, and R. Stevens, *Effects of TiO_2 addition on the sintering of ZrO_2–TiO_2 compositions and on the retention of the tetragonal phase of zirconia at room temperature*, J. Mater. Sci. 26 (1991), pp. 5327–5334.

[31] W.Z. Zhu and M. Yan, *Stability of tetragonal phase in ZrO_2 (2 mol % Y_2O_3) ceramics sintered in reducing atmosphere*, J. Mater. Sci. Lett. 16 (1997), pp. 1540–1543.

[32] Y.P. Xu, *Preparation, sintering kinetics and microstructure of Y-TZP superfine powders*, Ph.D. Thesis, Shanghai Institute of Ceramics, C.A.S., 1990, pp. 71–89.

[33] I. Hasse, Y. Li, E.M. Nicht, X.X. Huang, and J.K. Guo, *Preparation and characterization of ultrafine zirconia powders*, Ceram. Int. 18 (1992), pp. 343–351.

[34] C.D. Sagel-Ransijn, A.J.A. Winnubst, A.J. Burggraaf, and H. Verweij, *Grain growth in ultrafine-grained Y-TZP ceramics*, J. Eur. Ceram. Soc. 17 (1997), pp. 1133–1141.

[35] F.F. Lange, *Transformation toughening: Experimental observation in the ZrO_2–Y_2O_3 system*, J. Mater. Sci. 17 (1982), pp. 240–246.

[36] E. Kato, M. Hirano, Y. Kobaashi, K. Asooh, M. Mori, and M. Nakata, *Preparation of monodisperse zirconia particles by thermal hydrolysis in highly concentrated solutions*, J. Am. Ceram. Soc. 79 (1996), pp. 972–976.

[37] W. Li, L. Gao, and J.K. Guo, *Synthesis of yttria stabilized zirconia nanoparticles by heating of alcohol-aqueous salt solutions*, Nanostruct. Mater. 10 (1998), pp. 1043–1049.

[38] J.D. Lin and J.G. Duh, *Coprecipitation and hydrothermal synthesis of ultrafine 5.5 mol%–2 mol% $YO_{1.5}$–ZrO_2 powders prepared by coprecipitation*, J. Am. Ceram. Soc. 80 (1997), pp. 92–98.

[39] S.K. Saha and P. Pramanik, *Aqueous sol–gel synthesis of powders in the ZrO_2–SiO_2 system using zirconium formate and tetraethoxysilane*, J. Non-cryst. Solids 159 (1993), pp. 31–37.

[40] S.W. Lee and R.A. Condrate Sr, *The infrared and Raman spectra of SiO_2–ZrO_2 glasses prepared by a sol–gel process*, J. Mater. Sci. 23 (1988), pp. 2951–2959.