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Effect of SiO₂ nanoparticles on the phase transformation of TiO₂ in micron-sized porous TiO₂–SiO₂ mixed particles

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ABSTRACT

Spherical and nanoporous TiO₂ and TiO₂–SiO₂ mixed micro-particles with four different compositions (20/80, 50/50, 80/20, 90/10 in weight ratio of TiO₂/SiO₂) were prepared by spray drying method from colloidal mixtures of amorphous silica and anatase titania nanoparticles. The as-prepared particles were heat-treated at 900 °C for 0.5–5 h. The TiO₂ and TiO₂–SiO₂ particles were spherical in shape and the average particle diameter was about 1 μm. The anatase mass fraction and the specific surface area of TiO₂–SiO₂ (50 wt.% SiO₂) mixed particles were kept to 61.5% and 30.6%, respectively, of their initial values after 5 h heat-treatment whereas these values of TiO₂ particles were rapidly decreased to 13.0% and 1.2% of their initial values, respectively, within 30 min after heat-treatment. And the anatase mass fraction and specific surface area increased as SiO₂ content in the TiO₂–SiO₂ mixed particles increased.

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1. Introduction

Titania (TiO₂) has three crystal phases, i.e., brookite, anatase and rutile, and the commercial applications of titania depend on its crystal phase. Anatase titania is widely used in the field of catalysis [1], gas sensor [2], and photocatalysis [3–5] whereas rutile titania is preferred in the pigments industry [6]. Further, the anatase titania irreversibly transforms to rutile titania which is the most thermodynamically stable form. For the high temperature application of titania as catalyst, gas sensor, and photocatalyst, stable anatase phase and high surface area are essential and these have been usually achieved by doping metal ion [7] or by mixing other metal oxide such as SiO₂ [8–10] Y₂O₃ [11], V₂O₅ [12], SnO₂ [6] and ZrO₂ [13] to TiO₂ nanoparticles.

Numerous reports have described the superior properties of TiO₂ nanoparticles and their wide applications. Additionally, it has raised issues of toxicity, workplace safety and environmental impact of nanoparticles [14]. Recently, spherical and porous micro-particles composed of TiO₂ nanoparticles have been proposed as an alternative material for TiO₂ nanoparticles, of which surface area is comparable with the nanoparticles [15–18]. Furthermore, it is well known that the addition of SiO₂ improves the activity of TiO₂ nanoparticles [8,9].

To the best of our knowledge, the effect of SiO₂ addition on the anatase–rutile phase transformation in spherical and porous TiO₂–SiO₂ mixed micro-particles as an alternative material has never been studied. It is essential to understand how anatase fraction and specific surface area are reduced by heat-treatment, especially for the

spherical and porous TiO₂–SiO₂ mixed particles. Therefore, in this study, we prepared spherical and porous TiO₂–SiO₂ mixed micro-particles by spray drying method from colloidal mixtures of amorphous SiO₂ and anatase titania nanoparticles and investigated the effect of SiO₂ nanoparticles on the anatase fraction in TiO₂ and specific surface area of the TiO₂–SiO₂ particles.

2. Experimental

Commercial colloidal suspensions of amorphous silica nanoparticles (SS-SOL 30, Shin Heung Silicate Co., Korea) and anatase phase titania nanoparticles (SG-TO7SW, Sukgyung AT Co., Korea; anatase phase) were used as silica and titania sources for the preparation of spherical and porous TiO₂–SiO₂ mixed micro-particles. The specific surface areas (corresponding average diameters, d_{BET}) of silica and titania nanoparticles were 156.4 m²/g ($d_{\text{BET}} = 17.4$ nm) and 151.7 m²/g ($d_{\text{BET}} = 9.9$ nm), respectively. The aqueous colloidal mixtures as starting materials were prepared by adding 0 wt.%, 10 wt.%, 20 wt.%, 50 wt.%, and 80 wt.% of SiO₂ while keeping the total solid concentration to 5 wt.%.

The experimental apparatus consisted of an ultrasonic atomizer (UN-511, Alfesa Pharm Co., Japan), an electric tubular furnace (540 mm in length, 25 mm in inner diameter of heating zone), and a filter (PTFE, pore size: 1.2 μm) sampler. Micron-sized droplets of the precursor suspension generated by the ultrasonic atomizer were carried by 1.0 l/min of air into the electric furnace (temperature set to 300 °C), in which spherical and porous TiO₂–SiO₂ mixed particles were prepared by co-assembly of TiO₂ and SiO₂ nanoparticles during the evaporation of the droplets.

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In order to investigate the effect of SiO₂ content in the TiO₂–SiO₂ micro-particles, an alumina boat filled with the as-prepared particles was inserted into another electric furnace of which temperature was set to 900 °C. The heat-treatment was achieved by flowing air with a flow rate of 1.0 l/min for 0.5–5 h.

The morphology of heat-treated particles was observed with a field emission scanning electron microscope (FE-SEM; Sirion, FEI). The specific surface area of the particles was measured with a nitrogen adsorption analyzer (Quadrasorb SI, Quantachrome) employing the BET equation. The crystal phases of TiO₂–SiO₂ particles were studied by X-ray diffractometry (XRD; RTP 300 RC, Rigaku Co.) with CuK α target operated at 30 kV and 40 mA. The scans were conducted with a scan speed of 8°/min in 0.05° increments. The anatase mass fraction in an anatase–rutile mixture was determined from the ratio (I_R/I_A) of the intensity of the strongest rutile reflection (110) to the intensity of the strongest anatase reflection (101) using following equation [19]:

$$f_A = 1/(1 + 1/K(I_R/I_A)) \times 100$$

where K is a constant and is taken as 0.79 ($f_A > 20\%$) or 0.68 ($f_A \leq 20\%$).

3. Result and discussion

TiO₂–SiO₂ mixed particles were prepared with four different compositions (20/80, 50/50, 80/20, 90/10 in weight ratio of TiO₂/SiO₂, hereafter TS80, TS50, TS20, and TS10, respectively). The pore sizes of all the samples ranged from 2 to 6 nm in diameter. And the FE-SEM images of (a)–(b) TS50 and (c)–(d) TiO₂ (hereafter T100) particles heat-treated at 900 °C for 5 h were shown in Fig. 1. FE-SEM images exhibit the morphology of particles was spherical and the average particle diameter was about 1 μ m. Fig. 1(b) and (d), the magnified images of Fig. 1(a) and (c), show that the particles were composed of nanoparticles even though the particles were heat-treated at 900 °C for 5 h. Furthermore, the primary particle size of TS50 is smaller than that of T100. It is worth noting that the SiO₂ addition definitely restricts the primary nanoparticles growth in the mixed micro-particles.

XRD spectra of TS50 and T100 particles before and after heat-treatment were compared at Fig. 2. Samples of TS50 and T100 before the heat-treatment were identified as TiO₂ (anatase phase) and amorphous

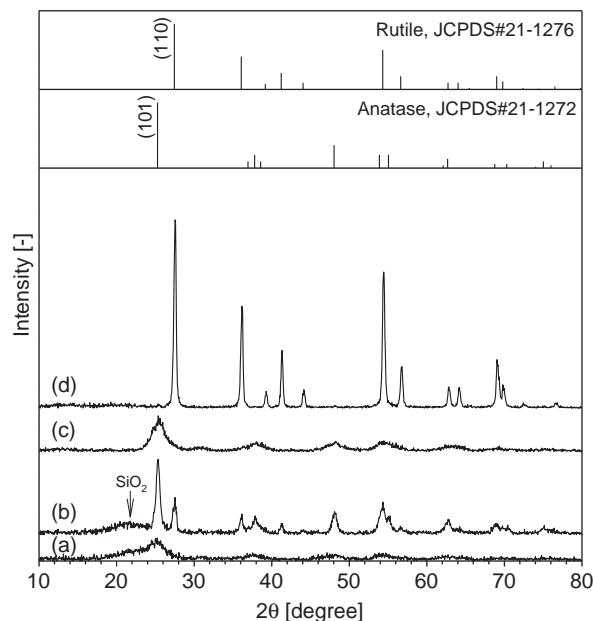


Fig. 2. XRD spectra of TS50 and T100 micro-particles with the standard JCPDS data: (a)–(b) TS50, (c)–(d) T100; (b) and (d) are XRD spectra of samples (a) and (c) heat-treated at 900 °C for 5 h, respectively.

silica by a good agreement in the XRD pattern with a JCPDS data for TiO₂ (JCPDS No. 21–1272) as shown in Fig. 2(a) and (c), respectively.

After heat-treatment at 900 °C for 5 h, the TS50 was partially transformed from anatase to rutile (JCPDS No. 21–1276) whereas T100 was fully transformed to rutile. It revealed clearly that the silica addition prevented the anatase–rutile phase transformation. It is resulted from the well-dispersion of SiO₂ around TiO₂ and then the formation of the Ti–O–Si bond between the amorphous SiO₂ and anatase TiO₂ at high temperature [8,9,20]. Further, we increased the SiO₂ content to 80 wt.% (TS80). After heat-treatment at 900 °C for 5 h, XRD result revealed that crystalline SiO₂ (cristobalite, JCPDS No. 39–1425) was observed.

Variations of anatase mass fraction along with heat-treatment time for the samples of T50 and T100 were shown in Fig. 3. And the

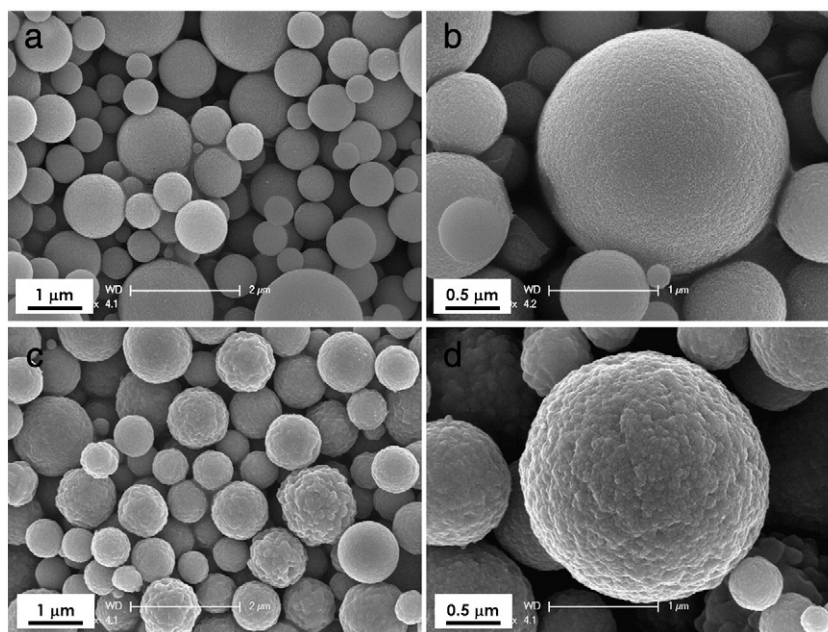


Fig. 1. FE-SEM images of spherical and porous (a)–(b) TS50 and (c)–(d) T100 micro-particles heat-treated at 900 °C for 5 h. (b) and (d) are the magnified images of (a) and (c), respectively.

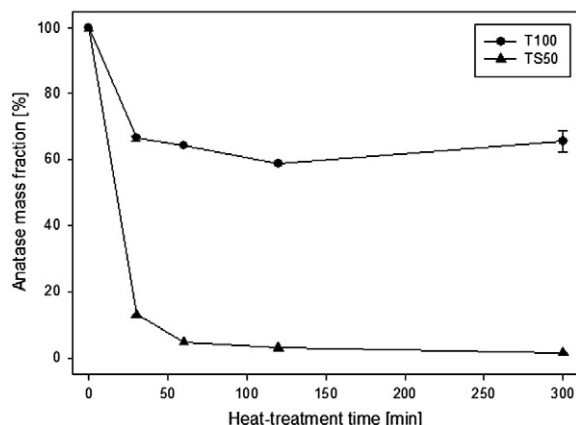


Fig. 3. Variation of anatase mass fraction along with heat-treatment time for samples of TS50 and T100 micro-particles. Error bar indicates a standard deviation.

anatase mass fraction and specific surface areas of all the samples with respect to heat-treatment time and SiO₂ content were summarized in Table 1.

In the case of spherical and porous TiO₂ particles, the anatase mass fraction and specific surface area were rapidly decreased to 13.0% and 1.2% of their initial values, respectively, within 30 min after heat-treatment. When the heat-treatment time reached to 5 h, the anatase mass fraction of T100 particles was down to 1.5%. These results revealed that the TiO₂ micro-particles after 5 h heat-treatment were almost useless as a catalyst. However, in the case of TiO₂-SiO₂ mixed micro-particles, the anatase mass fraction and specific surface area of TS50 were 65.6% and 32.2% of their initial values, respectively, at 30 min after heat-treatment. Furthermore, these values of TS50 were kept to 61.5% and 30.6%, respectively, of their initial values after 5 h heat-treatment. And the anatase fraction and specific surface area increased as SiO₂ content in the TiO₂-SiO₂ mixed particles increased. Therefore, it can be presumed that the spherical and porous TiO₂-SiO₂ mixed micro-particles prepared in this study can be a candidate material as alternatives of anatase TiO₂ nanoparticles for high temperature application, e.g., a CO sensor to monitor automobile engine performance [21].

4. Conclusions

Spherical and nanoporous TiO₂-SiO₂ mixed micro-particles with different composition were successfully prepared by spray drying method from colloidal mixtures of amorphous SiO₂ and anatase TiO₂ nanoparticles. Also, the effect of SiO₂ nanoparticles on the anatase-rutile phase transformation in the TiO₂-SiO₂ mixed micro-particles was systematically investigated. Amorphous SiO₂ nanoparticles dispersed in the TiO₂-SiO₂ particles prevented the phase transformation of TiO₂

Table 1

Anatase mass fraction in anatase-rutile mixtures and specific surface areas of spherical and porous TiO₂-SiO₂ mixed micro-particles.

Heat-treatment time [h]	Anatase mass fraction [%]				Specific surface area [m ² /g]			
	TS50	TS20	TS10	T100	TS50	TS20	TS10	T100
0	100	100	100	100	198.2	204.6	197.5	179.6
0.5	66.4 ± 0.8	34.1	17.1	13.0	63.8	48.4	26.6	2.1
1	64.3	-	-	4.8	-	-	-	-
2	58.8	-	-	3.0	-	-	-	-
5	65.0 ± 3.3	32.3	8.2	1.5	60.7	40.5	21.2	-

definitely and inhibited the growth of primary particles effectively. Furthermore, the decrease in the surface area of porous TiO₂-SiO₂ particles was relatively less than porous TiO₂ particles when the particles were heat-treated at 900 °C for 0.5–5 h. These results revealed that the spherical and porous TiO₂-SiO₂ mixed micro-particles can be a promising material as alternatives of anatase TiO₂ nanoparticles for high temperature application.

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