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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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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-T075W, 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_{BET} = 17.4 nm) and 151.7 m²/g (d_{BET} = 9.9 nm), respectively. The aqueous colloidal mixtures as starting materials were prepared by adding 0 wt.%, 10 wt.%, 20 wt.%, 30 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, Alfaesa 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.
In order to investigate the effect of SiO<sub>2</sub> content in the TiO<sub>2</sub>–SiO<sub>2</sub> 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 TiO<sub>2</sub>–SiO<sub>2</sub> particles were studied by X-ray diffractometry (XRD; RTP 300 RC, Rigaku Co.) with CuKα 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]:

\[
f_A = \frac{1}{1 + \frac{1}{K}(I_R/I_A)} \times 100
\]

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

TiO<sub>2</sub>–SiO<sub>2</sub> mixed particles were prepared with four different compositions (20/80, 50/50, 80/20, 90/10 in weight ratio of TiO<sub>2</sub>/SiO<sub>2</sub>, 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) TiO<sub>2</sub> (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 μm. 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 SiO<sub>2</sub> 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 TiO<sub>2</sub> (anatase phase) and amorphous silica by a good agreement in the XRD pattern with a JCPDS data for TiO<sub>2</sub> (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 SiO<sub>2</sub> around TiO<sub>2</sub> and then the formation of the Ti–O–Si bond between the amorphous SiO<sub>2</sub> and anatase TiO<sub>2</sub> at high temperature [8,9,20]. Further, we increased the SiO<sub>2</sub> content to 80 wt.% (TS80). After heat-treatment at 900 °C for 5 h, XRD result revealed that crystalline SiO<sub>2</sub> (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.
different composition were successfully prepared by spray drying.

Therefore, it can be presumed that the spherical and porous TiO₂ particles prevented the phase transformation of TiO₂–SiO₂ rutile mixtures and specific surface areas of spherical and porous TiO₂–SiO₂ mixed micro-particles.

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

<table>
<thead>
<tr>
<th>Heat-treatment time [h]</th>
<th>Anatase mass fraction [%]</th>
<th>Specific surface area [m²/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TS50</td>
<td>TS20</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>0.5</td>
<td>66.4 ± 0.8</td>
<td>34.1</td>
</tr>
<tr>
<td>1</td>
<td>64.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>58.8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>65.0 ± 3.3</td>
<td>32.3</td>
</tr>
</tbody>
</table>

3.0

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

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
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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