Characterization of TiO₂ Nanopowders Synthesized by Thermal Plasma

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Abstract: Nano-sized TiO₂ powders were synthesized from TiCl₄ and SiCl₄ using thermal plasma. The effect of dopant SiCl₄ on the characteristics of TiO₂ powder was investigated. The result was that anatase phase increased with the feed rate of SiCl₄. Also, phase composition of the powder was influenced by collection position and these powder morphology and phase compositions were analyzed by XRD, SEM, TEM/EDS, FT-IR. At the reaction tube, the powder was mainly obtained as rutile, while at the collection vessel it was mainly obtained as anatase.

The synthesized powders were estimated for the photocatalytic activity by photochemical reaction of acetaldehyde under UV-irradiation. The photodesorption rates of acetaldehyde increased with the content of anatase in the powders. The dopant SiCl₄ increased the content of anatase but Si species in the powder led to decrease the photodesorption rates of acetaldehyde.

Keywords: nanopowder, titanium dioxide, characterization, synthesis, photochemical reaction

Introduction

Nanostructured materials distinguished from conventional polycrystalline materials by their extremely fine crystalline size, are most commonly produced in the form of powders [1,2]. Also, when two or more phase are mixed together to make a composite, these show combination of properties that are not available in any of the individual components, and so nanocomposites offer new properties, and a variety of application, including structural materials, high-performance coatings, catalysts, electronics, photonics, and magnetic and biomedical material [3,4]. Among these nanopowders TiO₂ powder has been used in wide applications such as UV screen, opacifier and catalyst support [5,6]. Nano-sized TiO₂ also has been attracted in environmental applications such as environmental purification, decomposition of carbonic acid gas, and generation of hydrogen gas. In the above applications, particle morphology, average size, size distribution, and phase composition are the key characteristics of powders.

TiO₂ powders are commonly produced by two processes; the sulfate process and chloride process. The chloride process is considered as the more modern process, and initially used by Du Pont for producing of high-purity rutile by burning a fuel or heating the reactant directly [5]. Also, we have been produced nano-sized TiO₂ powders using thermal plasma without additives [7,8]. It has been believed that the high temperature in thermal plasma reactor leads to short processing times which translates into relatively small reactor with high throughput. Furthermore, the attractive feature of this process for synthesis of nano-sized powders includes an environmentally cleaner process with substantially less offgases, and the potential of producing high quality powders in one step [9]. The effect of dopants on the characteristics of the powder has been reported. Introduction of dopant SiCl₄ leads to anatase and the presence of trace amounts of SiCl₄, FeCl₃, AlBr₃, and ZrCl₄ decrease the mean particle size, narrow the particle size distribution [10,11].

In this work, we aimed to investigate the effect of dopant SiCl₄ on the characteristics and photochemical activity of synthesized TiO₂-based nanopowder. TiO₂ and SiO₂-TiO₂ nanopowders were synthesized by oxidation of TiCl₄ and SiCl₄ in a thermal plasma reactor. The powders were collected in the water-cooled reaction tube, collection vessel, and the filter attached to the outlet of the vessel. To comparison with commercial TiO₂ powders for photocatalytic activity, acetaldehyde was destructed under UV-irradiation using synthesized powders.

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Experimental

Synthesis of TiO₂ Nanopowder
The schematic diagram of an experimental apparatus is shown in Figure 1. The system mainly consisted of plasma torch, reaction tube, collection vessel, and evacuation system. A plasma torch is typically run at 8 kW input power with flow rate of 15 L/min of Ar gas. Most of the parts were fabricated with water-cooled stainless steel double wall. Reaction tube set between plasma torch and collection vessel with inner diameter of 35 mm and length of 40 mm. Titanium tetrachloride (99.9%, Aldrich Co.) and silicon tetrachloride (99%, Aldrich Co.) were used as raw materials. These source materials were pre-mixed and injected into plasma flame with flow rate of from 0.2 to 1.0 mL/min using a metering pump. As a reactant, excess oxygen gas injected into top of the reaction tube and collection vessel. Evacuated gases passed through a metal filter and scrubber by vacuum pump. Experiment was performed for approx. 5 min and synthesized powders were collected at reaction tube wall, collection vessel and filter, respectively. Phase compositions of powders were analyzed with X-ray diffractometer (Model PW 1710, Philips Co.) and FT-IR spectrometer (MB104, Bomen Co.). The weight fractions of anatase and rutile phases in the prepared powders were calculated from the relative intensities of the strongest peak corresponding to anatase (101) and rutile(110) as described by Spurr and Myers [8,12]. The particle size and size distribution were determined by transmission electron microscopy/electron dispersive spectrometer (Model CM 200, Philips Co.) and scanning electron microscopy(Model S-4200, Hitach Co.).

Evaluation of Photocatalytic Activity of Synthesized Powder
Photocatalytic activity of synthesized powder was evaluated from decomposition efficiency of acetaldehyde. Photochemical reaction system mainly consisted of UV reactor, recycle pump, mixing pump and oxygen cylinder as shown in Figure 2. The light source was used two fluorescent lamp of 8 W(main wavelength-254 nm, Sankyo Denki Co), and was placed at a 10 cm distance from a glass plate. The synthesized powder and commercial TiO₂ powder(Degussa P25) were coated on the glass plates as followings. The glass plates were deepened in the alcohol solution, which dispersed with TiO₂ powder. Drawing out, the glass plate was dried and heated at 100 ℃. Above procedure was repeated and gained the glass plate thin coating layer. Acetaldehyde was recycled in the reactor system by recycling pump with flow rate of 3 L/min until entirely mixed with dilution gas of oxygen. After the concentration was maintained at 500 ppm, decomposition of acetaldehyde was experimented under UV irradiation. The entire reactor system was enclosed by a glove box and maintained at 313 K. According to various reaction times, the concentration of acetaldehyde was determined by gas chromatography (GC-8A/FID, Shimadzu).

Results and Discussion

The Effect of Dopant SiCl₄ and Collecting Position on the Phase Composition
Figure 3 showed X-ray diffraction patterns of the powders collected at the reaction tube. As dopant SiCl₄ increased, rutile content in the powder decreased from 75% to 25%. However, phase composition did not
Figure 3. X-ray diffraction patterns of the powders synthesized at the reaction tube using various ratio of SiCl$_4$/TiCl$_4$ (a) pure TiCl$_4$ (b) SiCl$_4$/TiCl$_4$ = 0.02 (c) SiCl$_4$/TiCl$_4$ = 0.1 (d) SiCl$_4$/TiCl$_4$ = 0.2.

significantly changed at over SiCl$_4$/TiCl$_4$ = 0.1. These results suggested that dopant SiCl$_4$ inhibits the transformation of anatase to rutile due to the formation of interstitial solid solution of SiO$_2$ and TiO$_2$. Because the ionic radius of Ti$^{4+}$ is 0.061 nm, while that of Si$^{4+}$ is 0.040 nm[13], Si$^{4+}$ could be easily entered into the TiO$_2$ lattice interstitially and inhibit the transformation of anatase to rutile. The formation of interstitial solution was also cleared by FT-IR spectra in Figure 4. As an increase of the ratios of TiCl$_4$/SiCl$_4$ from 0.02 to 0.1 led to a slow rise in Ti-O-Si connectivity, which is corresponded to the peak at 950 cm$^{-1}$. However, it did not significantly changed at over TiCl$_4$/SiCl$_4$ = 0.1.

Figure 5 showed phase compositions of pure TiO$_2$ (T-powder) and SiO$_2$ doped TiO$_2$ powders(ST-powder) synthesized in the condition of SiCl$_4$/TiCl$_4$ = 0.02. Higher rutile content of the powders was observed at the reaction tube rather than at collection vessel in both cases of T-powder and ST-powder. The effect of collecting position was derived from the facts that synthesized powder at the collection vessel was rapidly quenched by water-cooled vessel wall, while the powder at reaction tube was transformed to rutile as well as partly sintered by radiation heat from plasma flame. It was observed that anatase content increased up over 90% at collection vessel by introduction of dopant SiCl$_4$.

Particle Morphology According to Different Ratios of SiCl$_4$ to TiCl$_4$

Particle morphology was observed with scanning electron microscope and transmission electron microscope as shown in Figure 6, which corresponded to the powders in Figure 5, respectively. In (a), the T-powder showed partly sintered due to radiation heat of plasma flame at the reaction tube. Also, it was resulted in the transformation of anatase to rutile as shown in Figure 5(a) and (b). The T-powder in (b) was evenly distributed.
and smaller size than the powder in (a) due to rapid quenching by high temperature gradient from plasma region to water-cooled vessel wall. Introduction of SiCl₄ decreased the size of the powder and kept spherical shape as shown in (c). However, there was not significant change in both T-powder and ST-powder collected at the collection vessel as shown in (b) and (d). These results indicated that synthesized powders were grown and acted on phase transformation by heat from plasma flame at the reaction tube. The transformation of anatase to rutile was inhibited by introduction of dopant SiCl₄, also the presence of SiO₂ slowed down the effective sintering rate of the ST-powders, resulting in decreasing particle size and a degree of agglomeration. At the collection vessel, synthesized powders were not influenced by radiation heat from plasma flame, whereas the powder was smaller and evenly distributed.

Figure 7 showed TEM photographs of the ST-powders synthesized in the ratio of SiCl₄/TiCl₄ = 0.1. The powders in (a) collected at the reaction tube was more grown due to heat from plasma flame. The size of the powder collected at collection vessel was below 50 nm as shown in (b).

**Photocatalytic Activity of Synthesized Powder**

Figure 8 showed the photochemical reduction of acetaldehyde using various powders under UV-irradiation (main wavelength = 254 nm). Using T-powder collected at the reaction tube, the concentration ratio of acetaldehyde was widely decreased according to the irradiation time in (a), due to the higher rutile content of 75% and bigger size of ave. 200 nm. Using the powder of (c) and (d), acetaldehyde was rapidly destructed due to higher anatase content of 90% and smaller size of ave. 50 nm, which resulted in the higher destruction rate over 90% for 30 min.

The effect of dopant SiCl₄ on photochemical activity was shown as in Figure 9, which the powders were collected at the reaction tube. Although anatase contents increased with increasing the ratio of dopant SiCl₄, destruction efficiency decreased due to increasing Si species, which covered the active site on the surface of TiO₂ powder. Figure 9(c) and (d) showed that acetaldehyde destructed more effectively by the powder synthesized at lower ratio of SiCl₄/TiCl₄ = 0.02 than by pure TiO₂ powder. It indicated that higher anatase content was more effective for destruction efficiency, whereas Si species on the surface of TiO₂ inhibited destruction of acetaldehyde.

From these results, it was considered that photocatalytic activity of synthesized powder was mainly influenced by average size and it was also depended on the phase
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Figure 7. TEM photographs of ST-powders collected at different position in the condition of the ratios of SiCl₄/TiCl₄ = 0.1 (a) ST-powder at the reaction tube (b) ST-powder at the collection vessel.

Figure 8. Decomposition efficiency of acetaldehyde as a function of irradiation time using pure TiO₂ powder (a) TiO₂, collected on reaction tube (b) Degussa P25 (c) TiO₂, collected on collection vessel (d) TiO₂, collected on filter.

composition as well as the existence of dopant species on the surface of TiO₂.

Conclusions

We synthesized pure TiO₂ powder(T-powder) and SiO₂-doped TiO₂ powder(ST-powder) using TiCl₄ and SiCl₄ in thermal plasma reactor. Characteristics of synthesized powders were estimated for destruction of acetaldehyde under UV-light.

(1) Phase composition of the powder depended on collecting position and dopant SiCl₄. Rutile content was higher at reaction tube due to radiation heat from plasma flame, while the powder at collection vessel was quenched by water-cooled collection vessel wall. Dopant SiCl₄ inhibited the transformation of anatase to rutile, thus increased the content of anatase up to 90%.

(2) Synthesized powder at the reaction tube was more
aggregated and partly sintered, while the powder at the water-cooled collection vessel was evenly distributed and its size was estimated below 50 nm.

(3) Photochemical activity of the powder collected at the collection vessel was higher than other collected at the reaction tube, due to smaller particle size as well as higher anatase content. By introduction of dopant SiCl₄, photochemical activity decreased due to existence of Si species on active surface of TiO₂.

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References