Synthesis and characterization of TiO₂-coated SiO₂ particles by hydrolysis of titanium alkoxide in alcohol solvents

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TiO₂-coated SiO₂ particles were prepared using industrially-wasted amorphous SiO₂ particles by an alkoxide method. The amorphous SiO₂ particles were used as support for TiO₂ photocatalyst. The mean size of the amorphous SiO₂ particle was approximately 100 nm. The major synthesis parameters were a kind of alcohol solvent (methanol, ethanol, and 1-propanol) and calcination temperature. The SiO₂ particles and titanium tetraisopropoxide were mixed in an alcohol solvent and an appropriate amount of distilled water was added to the suspension for hydrolysis of the alkoxide. The precipitate was calcined in the temperature range from 600 to 1300°C to crystallize the deposited TiO₂. The samples were characterized using XRD, BET and TEM-EDS analyzer. It was found that the use of SiO₂ support, methanol solvent in hydrolysis of Ti alkoxide and freeze-drying of product were effective to keep the anatase phase at high calcination temperature even though the crystallite size of anatase increased and the specific surface area decreased. As a result, the maximum decomposition ratio of methylene blue was obtained on the TiO₂-coated SiO₂ particles synthesized in methanol solution and calcined at 1000°C.

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1. Introduction

The good performance of the photocatalytic activity of TiO₂ is widely known. The photocatalytic purification doesn't use the medicine and the load to the environment is small. Its photocatalytic activity has been widely investigated to be applied to the house space and medical facility in recent years.^{1),2)} The TiO₂ photocatalyst is commercially applied for gas purification, antibacterial use, and decomposition of organic stain on a wall. The photocatalytic activity of TiO₂ depends on the particle size and the crystalline phase of TiO₂, and has been reported to be high on the anatase phase or the mixture of anatase and rutile phases.³⁾ Furthermore, the specific surface area of TiO₂ decreases with transformation from anatase to rutile by heat treatment. This leads to deterioration of the photocatalytic activity.

Several attempts have been made by TiO₂ coating of SiO₂ particles or porous materials.⁴⁾⁻⁶⁾ Kogure et al. reported that anatase was stable in SiO₂-TiO₂ gels produced from a silicon tetraethoxide mixed with titanium tetra-n-butoxide, when SiO₂ content was large.⁵⁾ The dispersion of TiO₂ on the large surface support increases the photocatalytic activity. The authors focus on the use of industrially-wasted SiO₂ particles with TiO₂ coating for photocatalytic application. The wasted SiO₂ particle is very fine and has high purity. Much amount of the wasted SiO₂ particles has been exhausted from photonic glass company etc., and expected to recycle as economical material. The SiO₂ support is effective to improve the hydrophilicity of catalyst, which is important for the application in water. Furthermore, the SiO₂ is effective for an increase in the photocatalyst activity with high optical penetration.

TiO₂ is generally synthesized by hydrothermal methods, sol-

gel methods and other kinds of solution processes. The hydrolysis reaction of titanium alkoxide method has been investigated to prepare raw materials in spherical shape for the sintered product of TiO₂.⁷⁾ However, the surface area of the hydrate product of TiO₂ drastically decreases due to the crystallization.⁸⁾⁻¹⁰⁾ TiO₂ is also prepared from titanium (IV) chloride or titanyl (IV) sulfate by a precipitation method. It is known that the counter anion of the starting titanium salt remains in the product and affects the activity of the catalyst.¹¹⁾ Hydrothermal method has reported that the crystal growth of TiO₂ occurs greatly in the aqueous-solvent system.^{12),13)} The nanocrystalline TiO₂ is prepared by a glycothermal method with glycol as an organic solvent.¹⁴⁾ Kominami et al. reported the hydrolysis of titanium alkoxide in organic solvent and the crystallite size of anatase can be controlled in the range from several nanometers to about 15 nm by reaction conditions.¹⁵⁾

We have found that the anatase phase remained at high temperatures in the TiO₂-coated SiO₂ particles.¹⁶⁾ It is known that the inclusion of SiO₂ is effective to retard the transformation of anatase to rutile during the calcination.¹⁹⁾ In order to enhance the photocatalytic activity, the increase in specific surface area and the control of crystalline phase to be anatase are needed even under the heat treatment to increase the crystallinity of TiO₂. In the present work, TiO₂-coating of the wasted SiO₂ particles by hydrolysis of Ti alkoxide was investigated with emphasis on the effects of alcohol solvent, heat treatment for the crystallization of TiO₂, and the photocatalytic activity for decomposition of methylene blue. The authors focus on the use of the organic solvent for the preparation of TiO₂-coated SiO₂ particles by hydrolysis of titanium alkoxide, because the hydrolysis rate of titanium alkoxide is expected to change with various alcohols, leading to the change in structure and photocatalytic activity of TiO₂ deposit.

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Fig. 1. SEM image of SiO₂ waste particles.

2. Experimental procedure

2.1 Starting materials and characterization

The wasted SiO₂ particles were used as supplied. The SiO₂ had 99.3% purity and included Fe, Ni, Co as metallic impurities. The X-ray diffraction (XRD) indicated that the SiO₂ was amorphous. The amorphous SiO₂ particles were spherical as shown in the scanning electron microscope (SEM) image (Fig. 1). The particle diameter ranged from 10 to 200 nm. The median diameter was 100 nm, which was determined from the particle size distribution measured by X-ray transmission method (Micromeritics Sedigraph 5100). The specific surface area was 46 m²/g in the BET measurement by N₂ adsorption. Titanium tetraisopropoxide (Kanto Chemical Co., Inc.) and various alcohols (methanol, ethanol, 1-propanol) (Wako Pure Chemical Industries, Ltd.) were used as commercially supplied.

2.2 Preparation of TiO₂-coated SiO₂ particles

TiO₂-coated SiO₂ particles were prepared as follows. The amorphous SiO₂ particles were added to various alcohols (methanol, ethanol, 1-propanol), and dispersed by ultrasonic agitation. Titanium tetraisopropoxide and then distilled water were added to this suspension. The hydrolysis of the Ti alkoxide was carried out in air atmosphere at room temperature for 30 min in 300 ml of conical glass flask under stirring with a magnetic stirrer. The amount of SiO₂ was fixed at 3 g and the amounts of various alcohols at 100 ml. In the previous work, the amounts of Ti alkoxide and water had no essential effect on the properties of TiO₂-coated SiO₂ particles.¹⁶⁾ In the present work, the amounts of Ti alkoxide and water were fixed at 11.7 ml and 100 ml, respectively. The product was separated by centrifugation, and freeze-dried for 48 h at -50°C. In some experiments, the product was oven-dried for 24 h at 105°C. The dried particles were calcined at a temperature from 600 to 1300°C in air to crystallize TiO₂.

2.3 Evaluation

The crystalline phase of the calcined particles was identified by XRD using Cu K α radiation at 40 kV and 30 mA (PANalytical PW1825). The crystallite size of anatase was determined from (101) plane by using the Scherrer's equation. The particle morphology was observed by SEM at 5 kV (Hitachi S-5200) after Pt plating by sputtering. In order to confirm the deposit, the surface of particles was analyzed by TEM-EDS (TOPCON EM-002B). To confirm the conversion from titanium tetraisopropoxide to TiO₂, the content of TiO₂ was determined by X-ray fluorescence analysis (PANalytical MagiX PRO). The specific surface area of TiO₂-coated SiO₂ particles was analyzed by the BET measurement with N₂ adsorption analyzer (Quantachrome AUTOSORB-1).

Fig. 2. SEM images of TiO₂-coated SiO₂ particles synthesized in alcohol solvent and calcined at 1000°C (The precipitate was freeze-dried) (a) Methanol, (b) Ethanol, (c) 1-propanol.

2.4 Evaluation of photocatalytic activity

The photocatalytic activity was evaluated for decomposition of methylene blue. The calcined particles were weighed at 20 mg and mixed with 100 ml of water solution including 50 μ M methylene blue in 300 ml quartz glass beaker. The mixture was first stirred with a magnetic stirrer for 4 h under dark condition to evaluate the adsorption of methylene blue, and then irradiated for 4 h with two black light tubes (λ 365 nm: 6 W $\times$ 2). After centrifugal separation of the particles, methylene blue in the supernatant solution was analyzed with an UV/Vis spectrophotometer at 550–750 nm. The absorbance of methylene blue in water was measured at the maximum peak shift of 664 nm. The decomposition ratio of methylene blue was determined from the difference in concentration of methylene blue between stirring under dark condition and subsequent UV irradiation. The comparison was carried out using the same weight of samples.

3. Results and discussion

3.1 Particle morphology of TiO₂-coated SiO₂

Figure 2 shows SEM images of TiO₂-coated SiO₂ particles synthesized in alcohol solvents and calcined at 1000°C. Although the theoretical content of TiO₂ was 80 mass%, the

Fig. 3. TEM-EDS result of TiO_2 -coated SiO_2 particles synthesized in ethanol solution and calcined at 1000°C (a) TEM image, (b) EDX spectra in the center of particle, (c) EDX spectra of flocky deposit on the particle.

Fig. 4. XRD patterns of TiO_2 -coated SiO_2 particles synthesized in methanol solution and calcined at different temperatures (The precipitate was oven-dried).

measured content was about 60 mass %. Compared to the starting SiO_2 particles (Fig. 1), there were some aggregated SiO_2 particles and fine-grained deposit was observed on the SiO_2 particle surface. TiO_2 -coated SiO_2 particles synthesized in methanol was more aggregated, and the apparent grain size of deposited TiO_2 was about 30–70 nm. The TiO_2 deposit looked large as synthesized in methanol. **Figure 3** shows a TEM image of TiO_2 -coated SiO_2 particles synthesized in ethanol solution and calcined at 1000°C . Only Si was detected in the center of particle, whereas only Ti was detected in the flocky deposit on the particle. Thus, the deposition of TiO_2 on the particle surface was confirmed by TEM-EDS.

3.2 Crystalline phase of TiO_2 -coated SiO_2

Figure 4 shows the XRD patterns of TiO_2 -coated SiO_2 particles synthesized in methanol solution after calcination at 600, 1000 and 1300°C , in which the precipitate was oven-dried. The TiO_2 phase was anatase only at 600°C . Although anatase was transformed to rutile with elevation of calcination temperature, the anatase still remained after calcination at 1300°C . There was no crystalline phase of SiO_2 , showing a broad peak around 20° even at 1300°C .

Figure 5 shows the XRD patterns of TiO_2 -coated SiO_2 particles synthesized in various alcohols and calcined at 1000°C , in which the precipitate was freeze-dried. TiO_2 -coated SiO_2 particles synthesized in methanol solution crystallized to a single anatase phase. On the other hand, TiO_2 -coated SiO_2 particles synthesized in ethanol and 1-propanol solutions crystallized to the multiphase of anatase and rutile. From half-bandwidth of anatase (101) plane peak of TiO_2 -coated SiO_2 particles synthesized in methanol, ethanol and 1-propanol solutions, the crystallite size was calculated to be 43.1, 31.2 and 36.2 nm, respectively, by the Scherrer's equation. The maximum

Fig. 5. XRD patterns of TiO_2 -coated SiO_2 particles synthesized in alcohol solvents and calcined at 1000°C (The precipitate was freeze-dried) (a) Methanol, (b) Ethanol, (c) 1-propanol.

crystallite size for anatase was obtained on the TiO_2 -coated SiO_2 particles synthesized in methanol solution. The hydrolyzed product of Ti alkoxide is hydrous TiO_2 , then dehydrated and crystallized by heating. It is confirmed in the other paper that the hydrous TiO_2 crystallizes to anatase at the temperature around 400°C .¹⁷⁾ The anatase-to-rutile transformation occurs significantly at 1000°C in the powdery form.¹⁸⁾ On the other hand, anatase was stable at higher temperatures in the TiO_2 -coated SiO_2 particles in the present work. Thus, after crystallization of anatase, the transformation to rutile was retarded on the SiO_2 support. Ishikawa reported that anatase was stable in $\text{SiO}_2/\text{TiO}_2$ fibers produced from a polycarbosilane doped with Ti butoxide, in which TiO_2 formed on SiO_2 core.¹⁹⁾ The stability of anatase at high temperature is noteworthy to achieve the high crystallinity of anatase phase without transformation to rutile. As described above, the SiO_2 support was effective to make the anatase stable at high temperatures. There is a reason proposed for formation of quasi-stable anatase particles by thermal plasma process from metallorganic precursor.²⁰⁾ The nucleation of anatase easily proceeds compared to rutile because of the low surface energy of anatase although rutile is more stable thermodynamically. Ishikawa describes that the tetrahedral structure of SiO_4 stabilizes the anatase structure.¹⁹⁾

It should be also noted that, even when methanol was used as solvent, a small amount of rutile formed in the oven-dried sample, whereas only anatase remained in the freeze-dried sample after calcination at 1000°C . This result implies that methanol solvent and freeze-drying are important factors to retain anatase phase. As seen in Fig. 2, the particle morphology of TiO_2 deposit was different among the used alcohol solvents. When ethanol and 1-propanol were used, fine TiO_2 particles accumu-

Fig. 6. Crystallite size of anatase of TiO₂-coated SiO₂ particles synthesized in alcohol solvents and calcined at various temperatures (The precipitate was freeze-dried).

lated on SiO₂. In such a case, the outer surface of TiO₂ deposit is little affected by SiO₂ to stabilize anatase during calcination. On the other hand, coarse TiO₂ particles deposited directly on SiO₂, which is effective for stabilization of anatase on SiO₂. The change in particle morphology of TiO₂ may be attributed to hydrolysis rate of titanium alkoxide in various alcohols. The high hydrolysis rate of titanium tetraisopropoxide was observed in methanol compared to ethanol and 1-propanol. The freeze-drying is effective to retard particle agglomeration. If the agglomeration is inhibited, it may lead to retardation of crystal growth of rutile from anatase.

3.3 Effect of calcination temperature and solvent on crystallinity of TiO₂

Figure 6 shows the variation of crystallite size of anatase with calcination temperature of TiO₂-coated SiO₂ particles synthesized in alcohol solvents. The anatase crystallite size was larger as synthesized in methanol than as synthesized in ethanol. The crystallite size of anatase on the TiO₂-coated SiO₂ particles synthesized in methanol solution increased over 50 nm at 1200°C. This means the crystal growth of anatase. The crystallite size of anatase at 1300°C is obscure because rutile formed at this temperature and the XRD peak of anatase became small. The crystallite size of anatase on the TiO₂-coated SiO₂ particles synthesized in ethanol solution increased gradually with a rise of temperature, significantly at above 1200°C, and reached over 30 nm at 1300°C.

Figure 7 shows the variation of the specific surface area with calcination temperature of TiO₂-coated SiO₂ particles synthesized in alcohol solvents. The high temperature led to decrease of the specific surface area. The specific surface area was higher as synthesized in ethanol solution than as synthesized in methanol solution up to 1200°C in agreement with the difference in crystallite size. The specific surface area significantly decreased at 1300°C to almost the same in both samples. This is due to the sintering of TiO₂-coated SiO₂ particles themselves.

3.4 Photocatalytic activity of TiO₂-coated SiO₂ particles

The anatase phase was maintained even after calcination at high temperatures, and expected to exhibit high photocatalytic activity. The effects of alcohol solvent and calcination temperature in the formation of TiO₂-coated SiO₂ particles were

Fig. 7. Specific surface area of TiO₂-coated SiO₂ particles synthesized in alcohol solvents and calcined at various temperatures (The precipitate was freeze-dried).

Fig. 8. Variation of decomposition ratio of methylene blue in water and specific surface area with calcination temperature of TiO₂-coated SiO₂ particles synthesized in ethanol solvent (The precipitate was oven-dried).

examined on the photocatalytic decomposition of methylene blue in water.

3.4.1 Effect of calcination temperature

Figure 8 shows the temperature dependence of decomposition ratio of methylene blue in water and specific surface area of TiO₂-coated SiO₂ particles synthesized in ethanol solution, in which the precipitate was oven dried. The decomposition ratio increased with elevation of calcination temperature up to 1000°C. This may be due to the improvement of crystallinity of TiO₂ by the heat treatment because the lattice defects work as electron trap site. However, rutile formed by calcination and the specific surface area of TiO₂-coated SiO₂ particles decreased with a rise of temperature. These are negative effects for the photocatalytic activity. Actually, the decomposition ratio decreased at temperatures above 1000°C. According to SEM observation in **Fig. 9**, the SiO₂ particles themselves started to be sintered above the higher temperatures. Thus, the calcination temperature should be appropriately controlled to improve the crystallinity of TiO₂, maintain the anatase phase and inhibit the particle coarsening.

3.4.2 Effect of alcohol solvent

The photocatalytic activity was compared among TiO₂-coated SiO₂ particles synthesized in various alcohols (methanol, ethanol, 1-propanol) and calcined at 1000°C, in which the precipitate was freeze-dried. The UV/Vis spectra of methylene blue solution are shown in **Fig. 10**. The shape of spectrum was the same before and after UV irradiation, and the absorbance totally decreased in

Fig. 9. SEM images of TiO_2 -coated SiO_2 particles synthesized in ethanol solution and calcined in the temperature range from 1100 to 1300°C (The precipitate was oven-dried) (a) 1100°C, (b) 1200°C, (c) 1300°C.

Fig. 10. Absorbance measurement before and after decomposition of methylene blue in water by TiO_2 -coated SiO_2 particles synthesized in alcohol solvents (The precipitate was freeze-dried) (a) 1-propanol, (b) Ethanol, (c) Methanol.

the presence of TiO_2 . The measured content of TiO_2 was almost the same as about 60 mass % for all samples. The kinetic constant of the photocatalytic degradation was calculated on the assumption of pseudo-first-order kinetics. The results are listed in **Table 1**. The kinetic constant of methylene blue decomposition was higher for TiO_2 -coated SiO_2 particle prepared in methanol

Table 1. Properties of TiO_2 -coated SiO_2 particles synthesized in various alcohols and calcined at 1000°C (The precipitate was freeze-dried)

Alcohol	Specific surface area / $\text{m}^2\cdot\text{g}^{-1}$	Crystallite size /nm	Kinetic constant of methylene blue decomposition/ h^{-1}
1-propanol	30	36	0.031
Ethanol	30	31	0.070
Methanol	22	43	0.084

solution than in the other alcohol solutions. TiO_2 -coated SiO_2 particle prepared in methanol solution contained anatase only even after calcination at 1000°C although the specific surface area was smaller. The high photocatalytic activity may be attributed to high crystallinity of anatase calcined at high temperatures.

When the photocatalytic activity of TiO_2 -coated SiO_2 particles prepared in ethanol solvent by oven-drying was compared to that of TiO_2 -coated SiO_2 particles prepared in ethanol solvent by freeze-drying, the decomposition ratio of methylene blue was higher as 34.4% in freeze-dried sample than as 29.9% in oven-dried one. The freeze-drying was effective to keep the anatase phase as explained in Fig. 5 and the high surface area as seen in Figs. 7 and 8. As understood above, the drying process is also important as well as use of methanol solvent.

4. Conclusions

TiO_2 -coated SiO_2 particles were successfully prepared by a hydrolysis of titanium tetraisopropoxide in SiO_2 -alcohol suspension. After calcination at 1000°C, anatase and rutile phases crystallized on TiO_2 -coated SiO_2 particles synthesized in ethanol and 1-propanol, whereas only anatase phase crystallized on TiO_2 -coated SiO_2 particle synthesized in methanol. Thus, the anatase phase was stable at high temperatures in the TiO_2 -coated SiO_2 particles. The calcination temperature was important to enhance the photocatalytic activity. This may be due to the improvement of crystallinity of TiO_2 with the retardation of anatase-to-rutile transformation although the crystallite size increased and the specific surface area decreased. As well as use of methanol solvent, the freeze-drying seemed to be better to retain the high specific surface area and the anatase phase.

The maximum photocatalytic activity for decomposition of methylene blue was obtained on TiO_2 -coated SiO_2 particles synthesized in methanol solution by freeze-drying and calcined at 1000°C. The present results indicate that the methanol solution is an excellent medium in hydrolysis of Ti alkoxide to form TiO_2 -coated SiO_2 photocatalyst, although the effect of methanol for hydrolysis process should be clarified, additionally with freeze-drying effect.

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