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The effect of SiO_2 addition in super-hydrophilic property of TiO_2 photocatalyst

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The relation between the effect and the amount of SiO_2 addition on photo-generated hydrophilicity of TiO_2 thin film, was investigated by measuring the X-ray diffraction, the microstructure, the specific surface area and the TG-DTA. It was found that the optimum range existed in the amount of SiO_2 addition to TiO_2, 10–30 mol % SiO_2 addition was most effective for contact angle of water. The SiO_2 addition less than 30 mol % has a suppressive effect on the transformation of anatase to rutile and on the crystal growth of anatase in calcination, and it has large surface area. With the consequence that the photocatalytic activity of TiO_2 and the capability of holding absorbed water which increases during UV irradiation improved. © *1999 Kluwer Academic Publishers*

1. Introduction

The research on the semiconductor photocatalyst represented by TiO_2 started in the Honda-Fujishima effect [1] in the beginning of the 1970s. Until now, various researches have been performed about antibacteria [2], deodorization, NO_x removal [3], and wet solar battery [4], and so on. In recent years, authors have examined the method for fixing photocatalysts, such as TiO_2, on the surface of tiles or sanitary wares in order to give antibacterial effect to them [5]. We discovered that when the TiO_2 thin film was irradiated by ultraviolet-ray (UV), the contact angle of water decreased gradually, and finally, it became almost zero [6]. We call this phenomenon super-hydrophilicity. Then, in the case of the thin film which consists of only TiO_2, the contact angle of water almost becomes zero during UV irradiation. However, it was found that the contact angle goes up and is restored early comparatively in a dark place. It is desirable that the contact angle rises slow in a dark place, and maintains low for a long time, because if actual use is considered, it is not always irradiated by UV light, such as sunlight. Then, in order to improve these characteristics, we tried to add various additives to TiO_2. Consequently, it was found out that by adding SiO_2, the contact angle of water was low from immediately after production, and the maintenance of hydrophilicity in a dark place was also good.

As for TiO_2-SiO_2 system material, many researches were performed in the past on glasses, humidity sensors, and so on. For example, Kamiya and Sakka [7] has measured the amount of water by IR-spectra about TiO_2-SiO_2 glasses which consist of 0–15 wt % TiO_2 and fired at 1173 K. Shikatani and Takechi [8] has reported the microstructure and the humidity-resistivity characteristic of $70 \cdot TiO_2$-$30 \cdot SiO_2$ mol % humidity sensor. Hosaka and Meguro [9] produced the TiO_2-SiO_2 pellet with 0–100 mol % SiO_2 calcined at 773 K from metal alkoxide, and they examined surface hydrophilicity and surface acidity. However, photo-generated hydrophilicity of TiO_2-SiO_2 system has not been reported yet.

In this paper, we report the effect and amount of SiO_2 addition on photo-generated hydrophilicity of TiO_2 thin film, and explain the mechanism by measurement of X-ray diffraction, SEM observation, specific surface area, and TG-DTA.

2. Experimentals

As the starting materials, commercial TiO_2 sol (Ishihara Sangyou Kaisya, Ltd., STS-11, solid content 15 wt %) and SiO_2 sol (Nissan Chemical Industries, Ltd., Snowtex20, solid content 20 wt %) were used. Exterior tile with graze (TOTO Ltd., AB02E11, size about 50×100 mm) was used as substrate.

First, TiO_2 sol or the mixed solution of TiO_2 sol and SiO_2 sol was coated on the surface of substrate tiles using air spray. The amounts of application are 3.0 g/m^2 by wet weight. After drying this sample at room temperature, it was calcined at 800 °C and sorking time 1 hour by muffle fuenace (Yamato Science Co. Ltd., FP-31). Thus, we obtained the samples for examination.

Next, ultraviolet-ray irradiated to the surface of the sample by commercial 20 W black light blue fluorescent light (BLB; Sankyo Denki, FL20SBLB). The UV intensity of 330–390 nm is 0.3 mW/cm^2 (measured by UIT-101+UVD-365PD, Ushio Electric Co. Ltd.). And

the contact angle of water was measured by a contact angle meter (Kyowa Interface Science Co. Ltd., CA-X150 type) every 24 hours. In addition, the surface of the thin film which consists of TiO_2 or TiO_2-SiO_2 obtained on tile substrates was observed by a field-emission type scanning electron microscope (FE-SEM; Hitachi, S-4100).

Powder sample was prepared apart from the above-described tile samples. Titanium dioxide sol or mixed-solution of TiO_2-SiO_2 sol which has the same composition as the tile sample were dried at 110 °C in air bath, it was ground by agate mortar and it was calcined at 800 °C for 1 hour by muffle furnace. X-ray diffraction patterns of these powder sample were measured and evaluated with a diffractometer (Mac Science, MXP-18). Specific surface area was measured by nitrogen absorption on a micromeritics FlowSorb II 2030type. TG and DTA analyses were performed in a Seiko Instruments Inc. TG/DTA320, under air atomosphere, at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Contact angle of water in TiO_2-SiO_2 thin films

Fig. 1 shows the contact angle of water in various amount of SiO_2 to TiO_2, as-sintered, after BLB irradiation for 24 hours and in a dark place for 24 hours.

The contact angle of the sample after calcination which consists of only TiO_2 was about 25°. And up to 30 mol % SiO_2 addition, the contact angle was below 25°. However, more than 42 mol % SiO_2 addition, the contact angle was same level with only TiO_2.

After BLB irradiation for 24 hours, it decreased to 10° with only TiO_2 sample. And the minimum angle was 4° after BLB irradiation for 1 week. On the one hand, in the range of 7–30 mol % SiO_2 addition, contact angle of water became lower than only TiO_2. Especially, in the range of 7–15 mol % SiO_2, the contact angle of water became below the measurement limit. This is described as 0°. Since the initial contact angle was low in this SiO_2 amount, the contact angle became 0° in a very short time of UV irradiation. However, in the range of more than 42 mol % SiO_2, it is rather higher than only TiO_2. And it increases with increasing SiO_2 contents.

After putting samples for 24 hours in a dark place, the contact angle increased in all samples except 100 mol % SiO_2. In the case of only TiO_2, the contact angle went up from 10° to 18°. The sample of 12–30 mol % SiO_2 addition are in the super-hydrophilic state such as 10° or less. Furthermore, the contact angle of 12 and 15 mol % SiO_2 samples after leaving in a dark place for 1 week were 7.2° and 9.6°, respectively. In this range of SiO_2 contents, the contact angle increased very slow and it maintained super-hydrophilic state for a long time.

From the above result, by adding SiO_2 to TiO_2 thin film, initial contact angle and minimum one during UV irradiation can be reduced, and the super-hydrophilic state can be maintained for a long time.

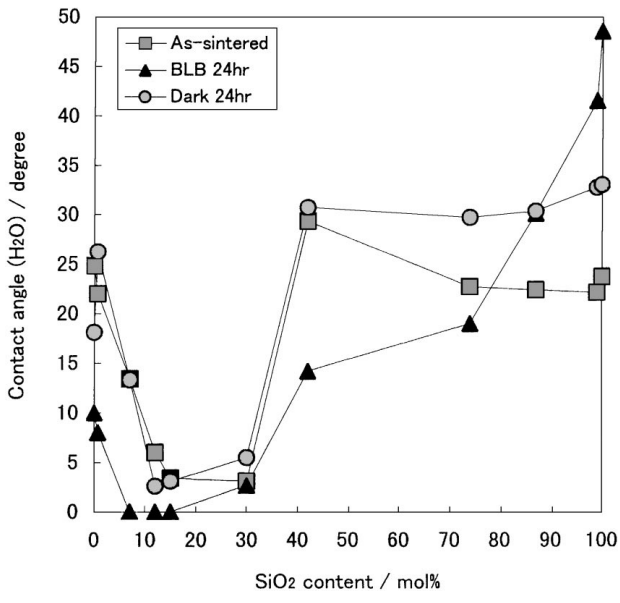

Figure 1 Contact angle of the surface of TiO_2-SiO_2 thin films sintered at 800 °C for 1 hour.

3.2. X-ray diffraction

X-ray diffraction patterns which obtained from powder of the same composition as the thin film of tile samples are shown in Figs 2 and 3. Fig. 2 is the patterns before calcination, Fig. 3 is the patterns after calcining at 800 °C for 1 hour.

As shown in Fig. 2, TiO_2 sol before calcination has monophase of anatase crystalline, SiO_2 sol is amorphous and TiO_2-SiO_2 system is both mixture of them.

As shown in Fig. 3, the rutile peak (transition from anatase) is slightly seen in the sample of only TiO_2 calcined at 800 °C for 1 hour. Moreover, since anatase peak height is larger as compared with before calcination, sintering of TiO_2 crystals progress and grain growth is expected. It does not form solid solution in TiO_2-SiO_2 system [10] calcined at 800 °C for 1 hour, and they are mixture of TiO_2 and SiO_2. Moreover, the peak of rutile phase which existed the sample of only TiO_2 is not seen at all. Since the anatase peak height has been hardly changed by calcination, even at 800 °C for 1 hour, sintering of TiO_2 particles has seldom progressed. And it is expected that the particle size of TiO_2 is almost the same as before calcination.

In the above-mentioned contact angle measurement, 12 mol % SiO_2 was slightly better than 30 mol % SiO_2 in the maintenance of hydrophilicity in a dark place. But the X-ray diffraction patterns did not show the difference between 10 mol % SiO_2 and 30 mol % SiO_2.

3.3. Microstructures

Fig. 4 shows SEM photographs of the surface of TiO_2-SiO_2 system thin films, (a) SiO_2 0 mol %, (b) SiO_2 10 mol %, (c) SiO_2 30 mol %. It is observed that the shape and the particle size of TiO_2 are considerably different with the existence and the amount of SiO_2.

That is, in the case of the thin film which consists only TiO_2 (Fig. 4a), TiO_2 crystal is the form with roundness, and the particle size is about 50–100 nm. On the other hand, the thin film which added 10 mol % SiO_2 (Fig. 4b) has the particle size of TiO_2 crystal as small as about 30–70 nm, and it has a little angular form as compared with Fig. 4a. As for the thin film which added 30 mol %

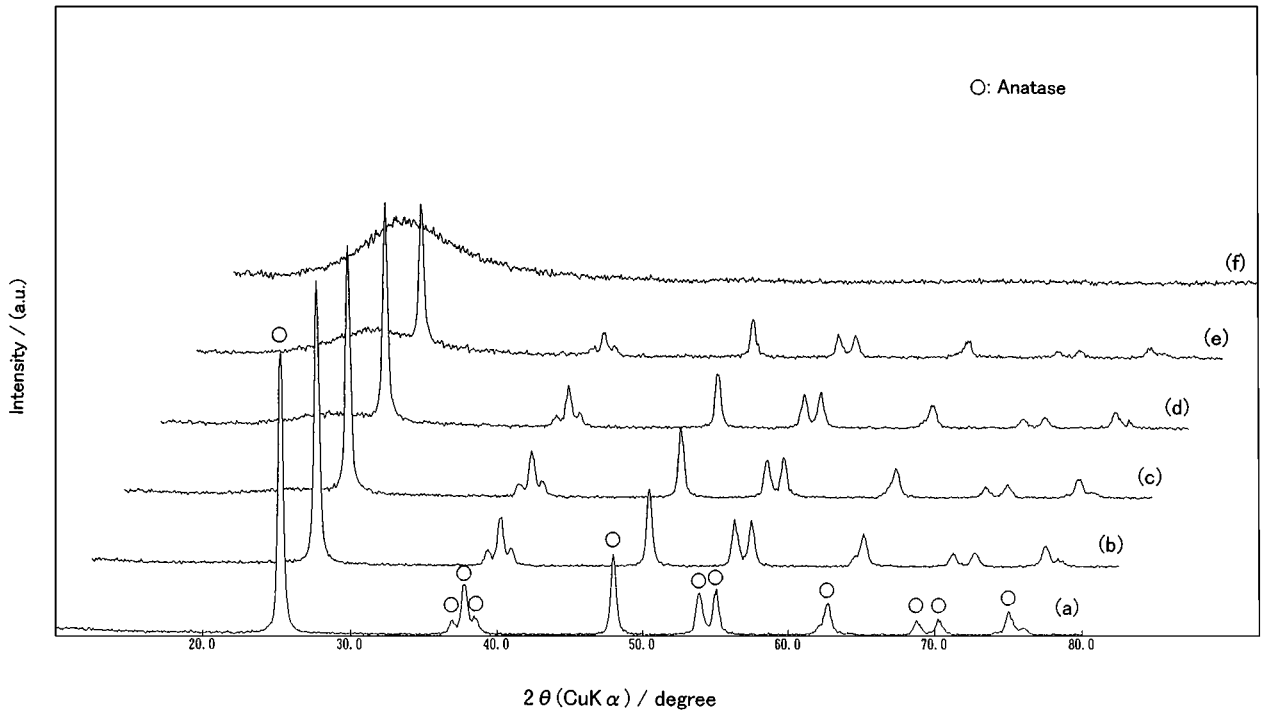

Figure 2 X-ray diffraction patterns of TiO_2-SiO_2 powder before calcination. SiO_2 content: (a) 0 mol %, (b) 10 mol %, (c) 30 mol %, (d) 50 mol %, (e) 75 mol %, (f) 100 mol %.

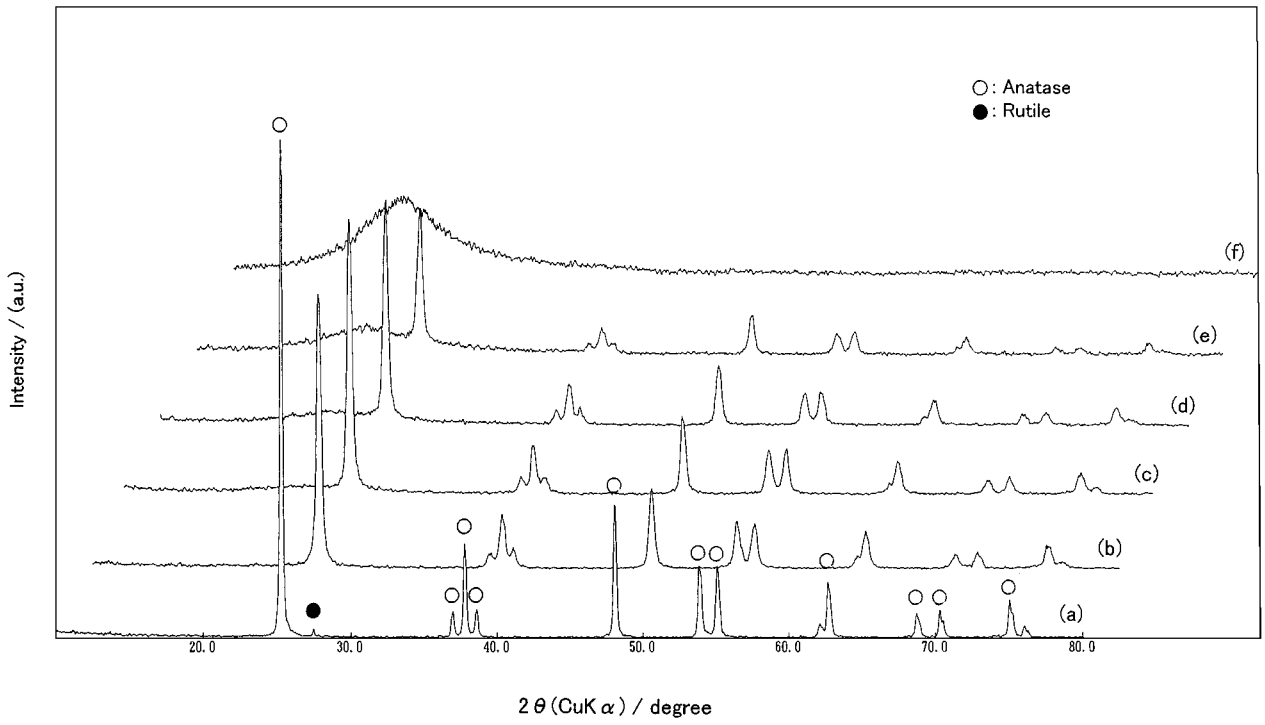

Figure 3 X-ray diffraction patterns of TiO_2-SiO_2 powder calcined at 800 °C for 1 hour. SiO_2 content: (a) 0 mol %, (b) 10 mol %, (c) 30 mol %, (d) 50 mol %, (e) 75 mol %, (f) 100 mol %.

SiO_2 (Fig. 4c), particle size became as smaller as about 20–50 nm.

If the film consists of only TiO_2, because of sintering and grain growth progress, many comparatively large particles with roundness are observed. As for the sample with SiO_2 addition, contact between TiO_2 particles is barred by SiO_2. In spite of the temperature to which sintering happens, originally, grain growth of TiO_2 crystal is suppressed and particle size is maintained as before calcination. Therefore, it is considered that small particles are observed as compared with SiO_2-free sample. Although it was not recognized in X-ray diffraction, in the range of 10–30 mol % SiO_2, it was found that the suppressive effect of grain growth is higher as much SiO_2 contents.

3.4. Specific surface area

Fig. 5 shows the result of measured specific surface area by BET method using the powder of the same composition as the thin film on tile samples.

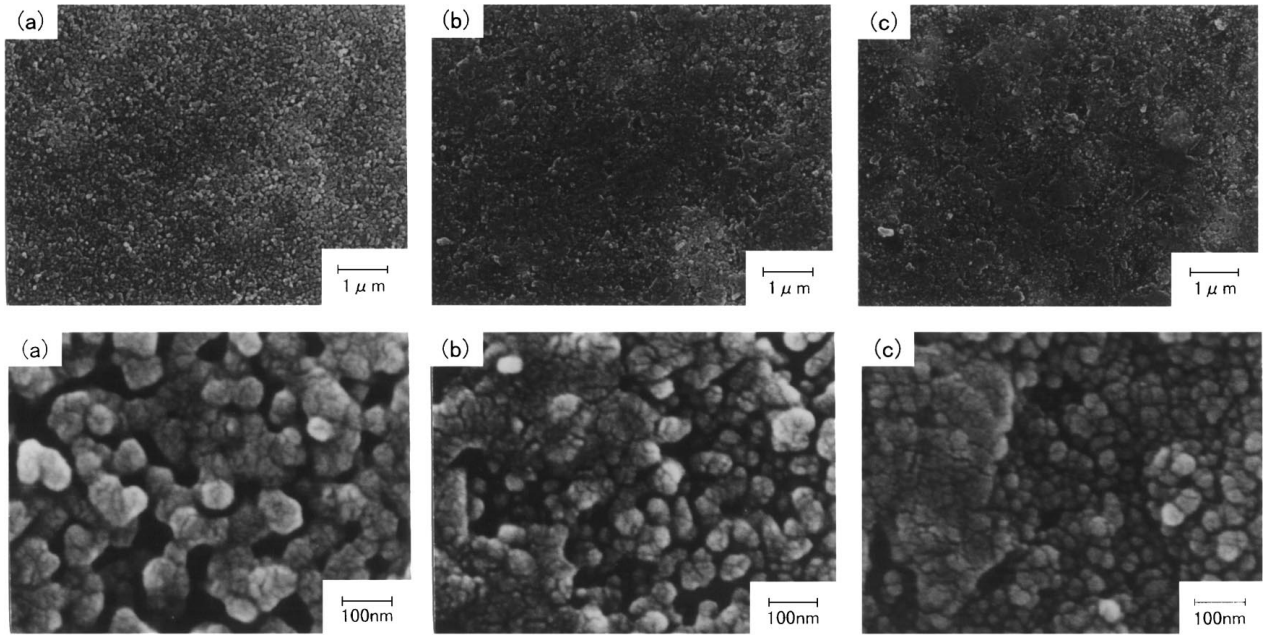

Figure 4 SEM photographs of the surface of TiO_2-SiO_2 thin film on tiles calcined at 800 °C for 1 hour (a) SiO_2 0 mol %, (b) SiO_2 10 mol %, (c) SiO_2 30 mol %.

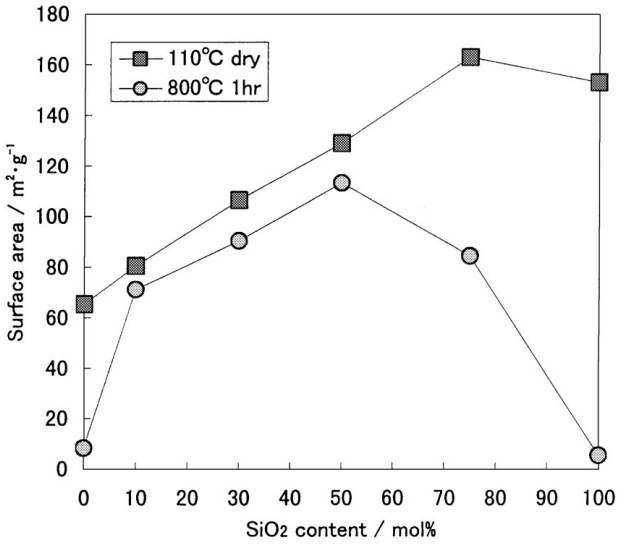

Figure 5 BET surface area of TiO_2-SiO_2 powder.

As for the specific surface area of powder dried at 110 °C which corresponds before calcination, pure TiO_2 powder is the smallest. Surface area of TiO_2-SiO_2 system was increased almost linearly in proportion to SiO_2 contents. On the one hand, the specific surface area of the pure TiO_2 powder which calcined at 800 °C for 1 hour decreased to about 1/8. In the range of 10–50 mol % SiO_2 addition, reduction of specific surface area was slight as compared with before calcination.

However, at 75 mol % SiO_2 addition, it decreased in the half before calcination. In the case of only SiO_2, it became 1/30 and the amount of reduction was the maximum.

The result of specific surface area measurement is considered with the result of X-ray diffraction and SEM observation mentioned above. In the case of only TiO_2, it is suggested that crystal growth was taken place by sintered at 800 °C and the surface area decreased. This suggestion and the measurement results are in agreement. In the range of the 10–50 mol % SiO_2 addition, contact of TiO_2 particles is barred by SiO_2, and grain growth which should take place at 800 °C sintering is suppressed. Consequently, it is considered that the small size particles can be maintained before calcination, then the decrease of surface area is controlled. If the amount of SiO_2 addition increases, since contact of SiO_2 particles will increase and sintering will become easy to take place, it is considered that decrease of surface area by sintering of SiO_2 is brought.

It is considered that the change of surface area calcined at 800 °C for 1 hour in TiO_2-SiO_2 system, in less than 50 mol % SiO_2, it increases by suppressing on the sintering of TiO_2 and SiO_2, in SiO_2 more than 50 mol %, it decreases by the sintering of SiO_2.

3.5. Thermogravimetric analysis

Figs 6 and 7 show the result of thermogravimetric analysis which was obtained from powder of the same composition as film samples. Fig. 6 shows the curves before calcination, and Fig. 7 shows the curves after calcining at 800 °C for 1 hour. TG was measured from room temperature to 200 °C. Within this temperature range, desorption gas may be consider as absorbed water which existed on the sample surface [11].

As shown in Fig. 6, with powder before calcination, weight loss of only TiO_2 was the smallest, it became large with SiO_2 addition, and weight loss of pure SiO_2 was the largest. These results are appropriate, because it is expected from the result of surface area measurement.

As shown in Fig. 7, with powder calcined at 800 °C for 1 hour, weight loss of pure SiO_2 was smaller than pure TiO_2. This result is also in agreement with the result of specific surface area measurement. When the powder calcined at 800 °C for 1 hour, it turns out that sintering of SiO_2 particles progresses considerably. As

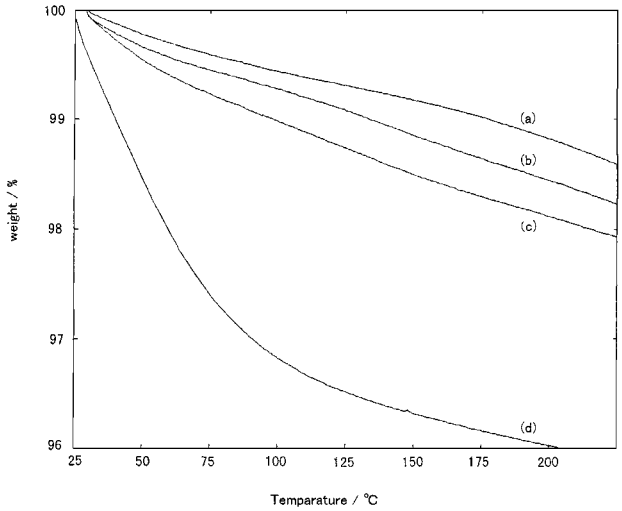

Figure 6 Thermogravimetric analyses of TiO_2-SiO_2 powder before calcination. SiO_2 content: (a) 0 mol %, (b) 10 mol %, (c) 30 mol %, (d) 100 mol %.

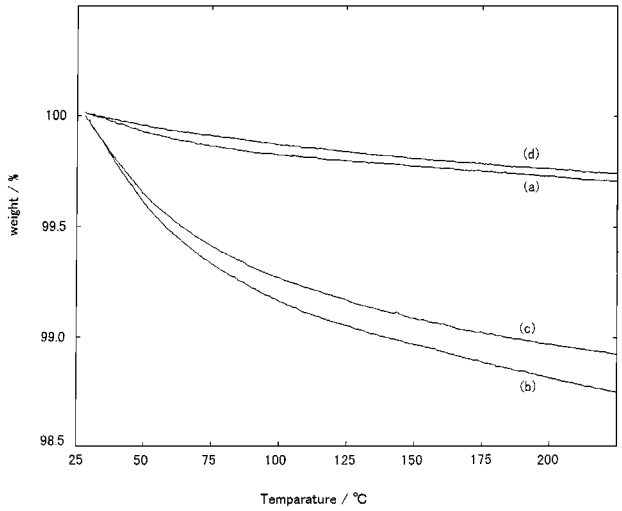

Figure 7 Thermogravimetric analyses of TiO_2-SiO_2 powder calcined at 800 °C for 1 hour. SiO_2 content: (a) 0 mol %, (b) 10 mol %, (c) 30 mol %, (d) 100 mol %.

compared with pure TiO_2, the weight loss is about 4 times in 10 mol % SiO_2 addition and it is about 3.5 times in 30 mol % SiO_2 addition. According to Fig. 1, since SiO_2 10 mol % was better than SiO_2 30 mol % in the maintenance of hydrophilicity in a dark place, this difference of weight loss is considered to influence the contact angle in a dark place.

However, when there is much SiO_2 addition, in specific surface area measurement, it becomes large and it is opposite to the result of weight loss. Although the whole surface area of 30 mol % SiO_2 sample is larger than 10 mol % SiO_2, it is guessed pore size distribution of TiO_2 or SiO_2 does not differ. And it is considered as a future subject for details.

From the above result, the relationship between SiO_2 addition and the change of contact angle is considered. Pure TiO_2 is transformed from anatase into rutile slightly by calcining at 800 °C for 1 hour. The photocatalytic activity of anatase is usually larger than that of rutile. Moreover, since the surface area decreases when sintering progresses and grain growth takes place, the capability of holding absorbed water becomes small.

When the amount of SiO_2 is 30 mol % or less, since all TiO_2 crystal is anatase type, its photocatalytic activity is large and its hydrophilic activity is also excellent. Grain growth is suppressed and the surface area is kept large. In this case, since the capability of holding absorbed water becomes large, the maintenance of hydrophilicity in a dark place improves. Furthermore, we are expecting about the mechanism that the maintenance of hydrophilicity improves in a dark place, absorbed water of the surface increases by photogeneration of TiO_2, it diffuse on SiO_2 from TiO_2 and SiO_2 holds it.

When SiO_2 addition exceeds 30 mol %, the amount of TiO_2 which generate hydrophilicity decreases and the capability of hydrophilicity becomes small. Sintering of SiO_2 takes place, the reduction of surface area is caused, and then, the maintenance of hydrophilicity in a dark place is also lost.

From the above reasons, in the amount of SiO_2 10–30 mol %, it is considered that the contact angle during UV irradiation falls off and its maintenance in a dark place is excellent.

4. Conclusions

In this research, the thin film in which SiO_2 was added to TiO_2 was produced on the tile, and the relation between the effect and the amount of SiO_2 addition on photogenerated hydrophylicity of TiO_2 thin film was investigated. The following knowledge was obtained as results of X-ray diffraction measurement, SEM observation, specific surface area measurement, and TG-DTA analysis for examining the mechanism.

1. By adding SiO_2 to TiO_2, the initial contact angle and the final contact angle during UV irradiation can be lowered, and the super-hydrophilic state can be maintained for a long time.
2. The optimum range existed in the amount of SiO_2 addition to TiO_2, and it was found that 10–30 mol % SiO_2 addition is most effective for the contact angle of water.
3. SiO_2 addition less than 30 mol % has a suppressive effect on the transformation of anatase to rutile and on the crystal growth of anatase in calcination. Consequently, it is considered that the photocatalytic activity and the capability of holding absorbed water which increases during UV irradiation improves.
4. When SiO_2 addition is more than 30 mol %, TiO_2 amount decreases and surface area decreases by sintering of SiO_2 takes place in calcination. Consequently, it is considered that the photocatalytic activity and the capability of holding absorbed water become small.

References

1. A. FUJISHIMA and K. HONDA, *Bull. Chem. Soc. Jpn.* **44** (1971) 1148; A. FUJISHIMA and K. HONDA, *Nature* **238** (1972) 37.
2. Y. SAEKI, *Kougyou-Zairyou*, **43** (1995) 94–100 (in Japanese).
3. T. IBUSUKI and K. TAKEUCHI, *J. Molec. Catal.* **88** (1994) 93.
4. B. O'REGAN and M. GRÄTZEL, *Nature* **353** (1991) 737–740.

5. M. MACHIDA, E. EOJIMA, K. NORIMOTO, T. KIMURA and T. WATANABE, in FC Annual Report for Overseas Readers (Japan Fine Ceramics Association, 1995) pp. 10–12.
6. R. WANG, K. HASHIMOTO, A. FUJISHIMA, M. CHIKUNI, E. KOJIMA, A. KITAMURA, M. SHIMOHIGOSHI and T. WATANABE, *Nature* **388** (1997) 431–432.
7. K. KAMIYA and S. SAKKA, *J. Chem. Soc. Jpn.* (1981) 1571–1576.
8. N. SHIKATANI and H. TAKECHI, *Res. Bull. Fukuoka Inst. Tech.* **29** (1996) 145–150.
9. H. HOSAKA and K. MEGURO, *Bull. Chem. Soc. Jpn.* **44** (1971) 1252–1256.
10. A. Ueno *et al.*, "Preparation of Catalysts from Metal Alkoxides" (Ai-Pi-Shi, 1993) pp. 292–320 (in Japanese).
11. T. YOKO, K. KAMIYA and S. SAKKA, *Yogyou-Kyokai-Shi* **95** (1987) 150–155.

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