Photocatalytic Property of TiO_2 Anchored on Porous Alumina Ceramic Support by the Alkoxide Method

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アルコキシド法によってアルミナ多孔体表面に固定化した TiO_2 の光触媒特性

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TiO_2 fine particles were anchored on a porous alumina ceramic support by the alkoxide method under various hydrolysis conditions. The photocatalytic property of the obtained TiO_2 precipitates, such as the photo-oxidation of ethanol, has been investigated. The amount, the dispersibility and the morphology of TiO_2 precipitates on the ceramic support were closely related to the efficiency of the photo-oxidation of ethanol.

Key-words : TiO_2 photocatalyst, Anchorage of TiO_2 on supports, Alkoxide method, Photo-oxidation of ethanol, Efficiency of photocatalytic reaction

1. Introduction

In recent years there has been remarkable advances in TiO_2 photocatalysis. Many works^{1)–9)} had focused on the photocatalytic reactions proceeding at the surface of the photocatalysts without considering the influencing factors of the materials as the photocatalyst. Photocatalytic reactions can not take place until the following processes go well; the photocatalyst absorbs light to generate electron-hole pairs which are separated by the electric field within the space charge region near the surface of the photocatalyst, and then the photo-generated electrons and holes diffuse to the surface without recombination, followed by the capture with oxidants and reductants. It should be noticed that an understanding of the relationship between the factors of the photocatalyst and the photocatalytic property is essential to improve the properties of photocatalysts.

The author has discussed the effects on the photocatalytic properties of the crystallinity, the specific surface area and the microstructure of TiO_2 fine powders, which were prepared by the hydrolysis of alkoxide.^{10),11)} It was found that TiO_2 powders of anatase phase and a trace of rutile phase, which consist of fine and individual particles of 20–30 nm in diameter without necking, exhibited a good photocatalytic property.

For the application of TiO_2 photocatalyst, the anchorage of TiO_2 on supports^{12)–15)} is necessary for easy recovery of the photocatalyst from the system after photo-reaction.

This paper describes the conditions for the anchorage of TiO_2 on a support as a photocatalyst by the alkoxide method and discusses the photocatalytic properties.

2. Experimental procedure

2.1 Anchorage of TiO_2

Materials as supports should be selected carefully, because they affect both the band structures and the activities of the photocatalysts. It has been confirmed previously^{12),13),15)} that the Al_2O_3 – SiO_2 system is not harmful to the photocatalytic activity of TiO_2 . In this study porous alumina based ceramics were selected as supports of TiO_2 photocatalyst. The porous alumina ceramics were prepared by spraying a slurry containing Al_2O_3 (70 wt%) and SiO_2 (30 wt%) on polyurethane foams and heating at 1000°C for 1 h after calcining up at 400°C for 30 min. Figure 1 shows the photographs of the porous alumina ceramic thus prepared. The ceramic support of coaxial cylinder in shape (ID 45 mm/OD 55 mm $\times$ H 130 mm, as shown in Fig. 1(a)), was adopted in this study so that the inner surface could be effectively illuminated by a high pressure mercury lamp. The alumina ceramic supports have macro-pores about 1–3 mm in diameters (shown in Fig. 1(b)) and micro-pores about several micron meters in diameters (shown in Fig. 1(c)). The macro-pores allow the deep penetration of the light and the micro-pores seem to play an important role in the anchorage of TiO_2 , respectively.

Titanium tetraisopropoxide ($\text{Ti}(\text{O}i\text{-C}_3\text{H}_7)_4$) was dissolved in absolute ethanol. The concentrations of the alkoxide (M) were 0.1, 0.5 or 1.0 mol·dm^{−3}. After stirring, the porous alumina ceramic support was dipped in the alkoxide solution for about 30 min. The hydrolysis was promoted by adding an appropriate amount of deionized water into the alkoxide solution. The molar ratios of the water to the alkoxide (R) were 0, 1, 10, 100, 1000 or ∞ . The solutions were vigorously stirred for 1 h to complete the hydrolysis reaction. Then, pH of the solutions were controlled to be 3, 8 or 11 by using acetic acid or aqueous ammonia. The solutions were settled for 1 h. The porous

Fig. 1. Photographs of porous alumina ceramic support. (a) the appearance, (b) and (c) the surfaces observed by SEM.

alumina ceramics with alkoxy-derived TiO_2 precipitates were taken out from the solutions and heated at 700°C for 1 h after drying at 100°C in air. The heat treatment conditions were determined according to the previous results of the preparation of TiO_2 powders giving excellent photocatalyst.^{10,11)}

2.2 Photocatalytic property

The photocatalytic property of TiO_2 anchored on the porous alumina ceramic support was characterized by the photo-sensitized oxidation of ethanol ($\text{C}_2\text{H}_5\text{OH}$). The reaction proceeded as follows: $\text{C}_2\text{H}_5\text{OH}$ was oxidized to acetaldehyde (CH_3CHO) and then acetic acid (CH_3COOH). CH_3COOH then decomposed to carbon dioxide. The mechanisms of the oxidation of ethanol by the photo-generated holes were described in detail elsewhere.¹⁶⁾

The porous alumina ceramic support with TiO_2 precipitates was immersed in an aqueous solution, a mixture of water (300 cm^3) and ethanol (1.5 mmol). The solution was illuminated with a high pressure 100 W mercury lamp while being stirred and being bubbled with oxygen at 25°C . Oxygen was used for consuming photo-generated electrons. The reduction of oxygen to hydroxy groups simultaneously proceeded with the oxidations of organic species by photo-generated holes.¹⁷⁾ The organic species contained in the solution (1 cm^3) were quantitatively analyzed every 30 min by the gas chromatography.

The change of ethanol content in the solution, which was permitted to stand for 30 min in the dark, was monitored in order to determine the amount of ethanol adsorbed on the porous alumina ceramic support with TiO_2 precipitates. Blank test was also performed for the porous alumina ceramic without TiO_2 precipitates.

3. Results and discussion

3.1 Appearance of TiO_2 anchored on the porous alumina ceramics

Figure 2 shows scanning electron microscopy (SEM) photographs of the alkoxy-derived TiO_2 precipitated on the porous alumina ceramics by controlling pH of the solution after hydrolysis reaction. Dispersibility and homogeneity of TiO_2 precipitates were affected by pH. In cases of $\text{pH}=3$ and $\text{pH}=11$, formed TiO_2 particles aggregates on some parts of the surface of porous alumina ceramics and the rest of the surface was not covered with TiO_2 precipitates as shown in Figs. 2(a) and (c). On the contrary, TiO_2 particles, which were precipitated from the solution with $\text{pH}=8$ in the range between the isoelectric points of TiO_2 and Al_2O_3 , were dispersed homogeneously all over the surface of porous alumina ceramic as shown in Fig. 2(b).

Figures 3 and 4 show SEM photographs and EDX profiles of TiO_2 anchored on the porous alumina cer-

Fig. 2. SEM photographs of alkoxy-derived TiO_2 settled on the porous alumina ceramics by controlling pH of the solutions at (a) 3, (b) 8 and (c) 11 after hydrolysis.

Fig. 3. SEM photographs of TiO_2 anchored on the porous alumina ceramics by using the alkoxide solutions of (a) $M=0.1 \text{ mol}\cdot\text{dm}^{-3}$, (b) $M=0.5 \text{ mol}\cdot\text{dm}^{-3}$ and (c) $M=1.0 \text{ mol}\cdot\text{dm}^{-3}$, and heating at 700°C .

Fig. 4. EDX profiles of TiO_2 anchored on the porous alumina ceramics by using the alkoxide solutions of (a) $M=0.1 \text{ mol}\cdot\text{dm}^{-3}$, (b) $M=0.5 \text{ mol}\cdot\text{dm}^{-3}$ and (c) $M=1.0 \text{ mol}\cdot\text{dm}^{-3}$, and heating at 700°C .

amics by using the alkoxide solutions with various concentrations ($M=0.1, 0.5$ or $1.0 \text{ mol}\cdot\text{dm}^{-3}$) and heating at 700°C . The amount of TiO_2 anchored on the ceramic support was found to depend on the concentration of the alkoxide solution. For example, the amount of TiO_2 , which was anchored on the ceramic support by using the solution of $M=0.5 \text{ mol}\cdot\text{dm}^{-3}$ and heating at 700°C , was about $0.3\text{--}0.4 \text{ g}$ by weight. Using the alkoxide solution of $M=1.0 \text{ mol}\cdot\text{dm}^{-3}$, some macro-pores were filled with TiO_2 , leading to too much precipitations.

Morphology of TiO_2 anchored on the porous alumina ceramic also depended on the amount of water used for hydrolysis reaction. Figure 5 shows SEM photographs of TiO_2 anchored on the ceramics by hydrolyzing with various ratios of water to the alkoxide ($R=0, 100$ or ∞) and heating at 700°C . TiO_2 films were formed in the case of hydrolysis with $R=0$ or 1 . In the TiO_2 films after heating, there were many cracks (as shown in Fig. 5) due to a difference in expansion coefficient between the TiO_2 gel films and the alumina ceramics. TiO_2 particles were anchored by hydrolyzing with R higher than 10 . The size of TiO_2 particles depended on the value of R . The larger the value of R , the larger the number of the nuclei and the smaller the size of the particle. As shown in Fig. 5, the size of TiO_2 particles anchored by hydrolyzing with $R=100$ and heating at 700°C was smaller than $0.1 \mu\text{m}$. The size of TiO_2 particles anchored by hydrolyzing with water of $R=\infty$

Fig. 5. SEM photographs of TiO_2 anchored on the porous alumina ceramics by hydrolyzing with (a) $R=0$, (b) $R=100$ and (c) $R=\infty$, and heating at 700°C .

was too small to be observed by SEM.

3.2 Photocatalytic property of TiO_2 anchored on the porous alumina ceramic support

Figure 6 shows the result of the blank test using the porous alumina ceramic support without TiO_2 precipitates. A little decrease in the content of ethanol was observed after the illumination for 4 h, probably due to the adsorption on the porous alumina ceramic.

Figure 7 shows the processes of the photo-oxidation of ethanol on TiO_2 anchored on the porous alumina ceramics by using the solutions of various alkoxide concentrations and $R=100$, and heating at 700°C . Just after illumination, the amount of ethanol began to decrease and then acetaldehyde and acetic acid began to be generated in all the systems. The

Fig. 6. Change of the ethanol content in the solution coexisting with porous alumina ceramics without TiO_2 with illumination time.

Fig. 7. Changes of the contents of ethanol, acetaldehyde and acetic acid in the solutions coexisting with TiO_2 anchored on the porous alumina ceramics with illumination time. The samples were prepared from the alkoxide solutions of (a) $M=0.1 \text{ mol}\cdot\text{dm}^{-3}$, (b) $M=0.5 \text{ mol}\cdot\text{dm}^{-3}$ and (c) $M=1.0 \text{ mol}\cdot\text{dm}^{-3}$, and heated at 700°C .

loss of ethanol on illumination depended on the concentration of the starting alkoxide solutions, in other words, the amount of TiO_2 anchored. The losses of ethanol after 4 h illumination on TiO_2 prepared from the alkoxide solutions of $M=0.1$, 0.5 and $1.0 \text{ mol}\cdot\text{dm}^{-3}$ were 21%, 30% and 53.4%, respectively. On TiO_2 anchored by using the alkoxide solution of $M=1.0 \text{ mol}\cdot\text{dm}^{-3}$, the generations of acetaldehyde and acetic acid did not proceed effectively. Especially, the generation of acetic acid was delayed. This is considered to be due to the adsorption of ethanol on the unilluminated TiO_2 which is shadowed by TiO_2 filling macro-pores of porous alumina ceramic support (as discussed above).

Figure 8 shows the effect of the water content for the hydrolysis of alkoxide on the photo-oxidation of ethanol by TiO_2 anchored on the porous alumina ceramics. In this case the concentration of the alkoxide solution was $M=0.5 \text{ mol}\cdot\text{dm}^{-3}$ and the heating was conducted at 700°C . The generation of acetic acid was observed only for $R=100$. It is considered that the morphology of TiO_2 anchored on the ceramic support affects the progress of the photo-oxidation of ethanol. In TiO_2 films formed by hydrolyzing with $R=0$, viz. under ambient atmosphere, photo-generated electron-hole pairs may have difficulty in separating and diffusing to the surface, where they are captured by chemical species without recombination. Therefore, the photo-oxidation of ethanol does not proceed effectively on TiO_2 films formed on the cer-

Fig. 8. Changes of the contents of ethanol, acetaldehyde and acetic acid in the solutions coexisting with TiO_2 anchored on the porous alumina ceramics with illumination time. The samples were prepared from the alkoxide solutions hydrolyzed with (a) $R=0$, (b) $R=100$ and (c) $R=\infty$, and heat-treated at 700°C .

Table 1. Loss of ethanol in the solutions coexisting with TiO₂ anchored on the porous alumina ceramics. This system was allowed to stand for 30 min before illumination.

Conditions for Anchorage		Loss of Ethanol (mmol)
Conc. of Alkoxide Soln. <i>M</i> (mol dm ⁻³)	Ratio of Water to Alkoxide <i>R</i> =H ₂ O/Ti(Oi-Pr) ₄	
-	-	0.01 *
0.1	100	0.03
0.5	100	0.08
1	100	0.07
0.5	0	0.05
0.5	100	0.08
0.5		0.1

*) the porous alumina ceramic without TiO₂ precipitates.

amic support. TiO₂ particles anchored by hydrolyzing with $R=\infty$ are considered to be too small for creating the photo-generated holes and electrons to be effectively separated. However, the loss of ethanol was significant. This may be due to the adsorption of ethanol on the TiO₂ particles with a large specific surface area. Contrarily, the photo-oxidation of ethanol proceeded effectively on TiO₂ particles anchored by hydrolyzing with $R=100$ and heating at 700°C. This result agrees with the previous one for TiO₂ powders, which were prepared by hydrolysis of the alkoxide under the same conditions and consisted of fine particles of 28 nm in diameter without necking.¹¹⁾ The particle size is considered to correspond to the distance through which the photo-generated electrons and holes can diffuse to the surface of the powder without recombination. It therefore appeared that such a microstructure is suitable for the capture of the electrons and the holes by the chemical species and the desorption of the products from the surface. These results mean that the morphology of TiO₂ anchored on porous alumina ceramic support dominantly influences the photo-oxidation of ethanol.

Table 1 indicates the loss of ethanol in the solution which was allowed to stand for 30 min before illumination. The loss means the amount of ethanol adsorbed on the porous ceramic support. The amount of adsorption of ethanol increased with the concentration of the starting alkoxide solution (*M*) and the value of *R*. It was confirmed that the amount and the morphology of TiO₂ precipitates affect the adsorption of ethanol to a considerable extent.

4. Conclusion

TiO₂ fine particles were anchored homogeneously on porous alumina ceramic support by the hydrolysis of titanium tetraisopropoxide by controlling the concentration of the alkoxide solution, the ratio of water to the alkoxide for hydrolysis and pH of the solution after hydrolysis. The dispersibility and homogeneity of TiO₂ anchored on the ceramic support depended especially on pH of the solution. The efficiency of the photo-sensitized oxidation of ethanol by TiO₂

precipitates on the ceramic support was affected by the amount and the morphology of TiO₂, which was controlled by the concentration of the alkoxide solution and the amount of water used in the hydrolysis reaction. Fine TiO₂ particles (less than 0.1 μm in diameter) proceeded effectively the photo-oxidation of ethanol. This ceramic material may be possibly applied to the purification of a system containing chemical species, which are harmful to environment, by controlling several process factors such as the circulation of reactants.

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References

- 1) W. W. Dunn, Y. Aikawa and A. Bard, *J. Am. Chem. Soc.*, **103**, 3456-59 (1981).
- 2) D. Duonghong, E. Borgarello and M. Gratzel, *J. Am. Chem. Soc.*, **103**, 4685-90 (1981).
- 3) T. Sakata, T. Kawai and K. Hashimoto, *Chem. Phys. Lett.*, **88**, 50-54 (1982).
- 4) S. Nishimoto, B. Ohtani, A. Sakamoto and T. Kagiya, *J. Chem. Soc. Jpn.*, **57**, 246-52 (1984).
- 5) Y. Aikawa, A. Takahashi and M. Sukigara, *J. Chem. Soc. Jpn.*, **57**, 292-98 (1984).
- 6) H. Harada and T. Ueda, *Chem. Phys. Lett.*, **106**, 229-31 (1984).
- 7) M. Anpo, T. Shima, S. Kodama and Y. Kubokawa, *J. Phys. Chem.*, **91**, 4305-10 (1987).
- 8) K. Harada, T. Hisanaga and K. Tanaka, *New J. Chem.*, **11**, 597-600 (1987).
- 9) T. Hisanaga, K. Harada and K. Tanaka, *J. Photochem. Photobiol. A: Chem.*, **54**, 113-18 (1990).
- 10) K. Kato, *Ceramic Transactions*, **22**, 63-68 (1991).
- 11) K. Kato, *Bull. Chem. Soc. Jpn.*, **65**, 34-38 (1992).
- 12) M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis and E. Giamello, *J. Phys. Chem.*, **89**, 5017-21 (1985).
- 13) K. Domen, Y. Sakata, A. Kudo, K. Maruya and T. Onishi, *Bull. Chem. Soc. Jpn.*, **61**, 359-62 (1988).
- 14) M. Takahashi, K. Mita, H. Toyuki and M. Kume, *J. Mater. Sci.*, **24**, 243-46 (1989).
- 15) T. Hisanaga and K. Tanaka, *Denki Kagaku*, **60**, 107-11 (1992).
- 16) K. Iseda, *Bull. Chem. Soc. Jpn.*, **64**, 1160-66 (1991).
- 17) M. A. Fox, *Account Chem. Res.*, **16**, 314-21 (1983).