

Photocatalytic Activity of Sol–Gel TiO₂ Thin Films on Various Kinds of Glass Substrates: The Effects of Na⁺ and Primary Particle Size

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To study the effects of ions diffused from the glass substrate on TiO₂ photocatalysis, TiO₂ thin films were prepared on different kinds of glass substrates at different heating temperatures. The TiO₂ films were characterized using X-ray photoemission spectroscopy (XPS), X-ray diffraction (XRD), ellipsometry, and absorption spectroscopy. The photocatalytic activities of the TiO₂ thin films were evaluated using the degradation reaction of trichloroethylene (TCE). Diffused ions such as Na⁺ and Si⁴⁺ raised the anatase formation temperature and increased the particle size of TiO₂ thin films (r_c). The photocatalytic activity of the thin films largely depended on the particle size of TiO₂; the reciprocal number of the half-life of the TCE degradation, $t_{1/2}^{-1}$, was roughly proportional to $r_c^{-1.8}$. The conventional recombination center hypothesis for the Na⁺ ions might not hold for the sol–gel TiO₂ films.

1. Introduction

Recent progress in research on TiO₂ photocatalysts has dramatically raised the practical importance of photocatalysis. Various applications (e.g., self-cleaning glass, anti-fogging mirrors, and sterilization of surfaces) have also proved effective and promising.¹ More specifically, a number of soil and/or underground water-purification plants based on gas-phase photocatalytic reactions are already at work in Japan and other countries to decompose chlorinated hydrocarbons such as trichloroethylene (TCE), one of the main environmental pollutants.^{2–5}

Factors affecting the photocatalytic activity of TiO₂, however, are not yet fully understood. Thus, characterizing and controlling these factors remains of great interest. Numerous factors have been proposed to explain the behavior of the TiO₂ photocatalyst. For particulate TiO₂, crystal phase (e.g., anatase or rutile),^{6–9} lattice defects,⁶ surface area,^{10,11} particle size,^{12–14} and dopants from raw materials¹⁵ were reported to be the factors. For TiO₂ thin films coated onto substrates such as glass, the number of probable factors increases, including film thickness, surface morphology, and ions such as Na⁺ and Si⁴⁺, which are diffused from substrates and reportedly function as recombination centers of photogenerated electrons and holes (recombination center hypothesis).^{16,17} Some of these factors remain, however, speculative for several reasons: (1) the photocatalytic reactions are generally considered difficult due to the fact that the reactions take place at a solid surface exposed to a complicated atmosphere containing air, reactants, and products including reaction intermediates; (2) these factors are sometimes impossible to study separately; and (3) the reaction conditions employed in the former experiments were not various enough to draw convincing conclusions. Thus, it is still necessary to clarify the contributions of these factors to the reactions on the TiO₂ photocatalyst.

Among the factors listed above, the effect of the diffused ions, particularly of Na⁺, from the substrate is a central issue for further understanding the behavior of the TiO₂ thin films, which are indispensable to various future applications. Tada et al. reported that the photocatalytic activity of a TiO₂ film coated on a soda-lime glass substrate was lower than that coated on quartz plate, and it was due to Na⁺ ions acting as the recombination center, or disordering the crystallinity of TiO₂.¹⁸ Several reports have also indicated that the Na⁺ ions are considered to act as recombination centers.^{16–19} However, these hypotheses for the Na⁺ ions were based on the following two findings: (1) the TiO₂ films coated on glass contained Na⁺, and (2) the films showed lower activities than those of films with a lower concentration of Na⁺ ions. No further evidence has been reported. Nonetheless, Na⁺ ions, via this mechanism, are considered as one of the “standard” factors governing the photocatalytic activity of the TiO₂ films.

We have studied the photocatalytic activity and physical properties of the TiO₂ thin film coated on various glass substrates. The result that the photocatalytic activity of the TiO₂ thin film depended greatly on the particle size of anatase was obtained. The photocatalytic activity of the TiO₂ thin film coated on various glass substrates was explicable with variation of particle size of anatase, even without the discussion of the recombination center hypothesis for the Na⁺ ions. In this paper, the photocatalytic activity and the properties of the TiO₂ thin films coated on various glass substrates, in particular with reference to the influence of the Na⁺ ion, will be described.

2. Experiment

2.1. Substrates. To prepare the TiO₂ thin films containing different concentrations of Na⁺, the following different substrates were used: fused silica, crown glass, crown glass coated with a SiO₂ layer (Crown/SiO₂), and ITO glass. The fused silica has no Na⁺, and crown glass contains 11 wt % of Na₂O as its component. For crown/SiO₂ systems, the SiO₂ layer is known

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TABLE 1: Existence of the Anatase Phase in the TiO₂ Thin Films on Each Glass Substrate and the TiO₂ Powders^a

		heating temp (°C)						
	dry	200	250	300	350	400	450	500
Thin Films								
crown glass		×	×	×	×	A	A	A
ITO glass		×	×	×	×	A	A	A
crown/SiO ₂ glass (20 and 80 nm) ^b		×	×	A	A	A	A	A
fused silica glass		×	×	A	A	A	A	A
Powders								
Na 0 mol/L	×	A	A	A	A	A	R	R
Na 0.1 mol/L	×	A	A	A	A	A	A(85) ^c /R	A(46) ^c /R
Na 1.0 mol/L	×	×	×	×	×	×	A	A

^a Key: A, anatase; ×, amorphous; R, rutile. ^b The thickness of the precoated SiO₂ film. ^c Anatase amount (%).

to hinder Na⁺ diffusion to another layer, such as TiO₂, coated onto the surface.^{19–22} ITO glass is a crystallized substrate, whereas the other glass substrates are amorphous. The size of all glass substrates was 6.1 × 2.6 × 0.1 cm³.

2.2. Preparation of the Thin Films. All films were prepared by the sol–gel method.

2.2.1. SiO₂ Layer. A SiO₂ layer was prepared as a barrier film for interrupter diffusion ions. Crown/SiO₂ substrates with different SiO₂ thicknesses (20 and 80 nm) were prepared with different amounts of tetraethyl silicate (TES). A mixture containing 11 or 23 mL of TES, 200 mL of dehydrated ethanol, and 2.7 mL of HCl was stirred for 30 min, and the crown glass substrates were dipped into and pulled up from the solution at 4.6 cm/min, followed by drying in air. The dip-coating process was repeated three times, and the samples were heated at 500 °C for 30 min.

2.2.2. TiO₂ Thin Films. TiO₂ sol solution was made from 29 mL of Ti isopropoxide, 200 mL of dehydrated ethanol, and 2.7 mL of HCl. After the solution was stirred for 2.5 h to obtain a transparent solution, the TiO₂ films were dip-coated onto each substrate. The dip-coating process was repeated eight times. The films were heated at different temperatures in a range of 200–500 °C with a 50 °C interval for 3.5 h.

2.3. Preparation of Powder TiO₂. NaOH was added to the TiO₂ sol solution like solutions used in the TiO₂ film preparation. The solutions were dried for 50 days at room temperature, and then the samples were heated under the same conditions as those employed in the TiO₂ film preparation.

2.4. Characterization of the Thin Films. The TiO₂ thin films were characterized with an X-ray diffractometer (XRD: Rigaku), a microprobe X-ray photoelectron spectrometer (XPS: Shimadzu-Kratos Analytical XSMA 800), a spectrophotometer (SP: Hitachi 220), and an ellipsometer (EM: JASCO). From the XRD data, crystal phase and particle size were determined. The primary particle size of TiO₂ was calculated using the Scherrer formula and the XRD peak width. Element analyses with XPS gave the atomic concentrations of Na in the 2 nm surface layers of the TiO₂ films. By using SP and EM, film thicknesses, in addition to optical properties such as absorption spectra and refractive indexes, were measured.

2.5. Photocatalytic Activity. The photocatalytic activities were measured by degradation of TCE in gas-phase. The TiO₂ thin film was placed in a batch-type reactor (volume = 106 mL) made of Pyrex glass and having Si windows. Liquid TCE (0.4 μL) was injected into the reactor and vaporized for 10 min (concentration = 960 ppmv). The degradation reaction of TCE was carried out using eight 20 W black light fluorescent lamps (peak wavelength = 352 nm). The concentration of TCE in the reactor was monitored through the Si windows with a Fourier transform infrared spectrometer (FT-IR: Nicolet 800).

3. Results and Discussion

3.1. Characterization of the TiO₂ Thin Films. 3.1.1.

Thickness of the TiO₂ Thin Films. The thickness of the TiO₂ thin films coated on crown glass varied in the range of ca. 360–420 nm, while those of the films coated on fused silica glass varied in ca. 370–430 nm. Both thicknesses decreased with the increase in heating temperature. This may be due to an increase in density of the TiO₂ thin film by the decrease in porosity.^{23,24} The photocatalytic activity was reported to increase with the increase in the thickness of the TiO₂ film until a certain thickness, because of the increase in the amount of light absorbed by TiO₂.¹⁸ Yoshida et al.²⁵ and Tada et al.¹⁸ obtained the maximum photocatalytic activity in the thickness equal to or greater than ca. 300 nm and ca. 140 nm, respectively. The thickness that gives a maximum photocatalytic activity obtained can be different according to the preparation methods (i.e., sol-solution, heating temperature, and so on) and experimental conditions (i.e., the light source, distance of light source and photocatalyst, and so on). Kim et al. reported that the maximum photocatalytic activity was obtained in the thickness of ca. 390 nm.²⁶ In this study, the preparation method of the TiO₂ thin film and conditions of degradation were referred to experiments by Kim et al. Therefore, the thickness (ca. 360–430 nm) of the prepared TiO₂ thin films may be the optimum thickness for high photocatalytic activity. In addition, the thickness of the TiO₂ thin films heated at the same temperature was nearly the same, independent of the kinds of glass substrates. Therefore, in this study, the influence of the thickness of the TiO₂ film on the photocatalytic activity was neglected.

3.1.2. Element Analysis. From the results of the element analysis for the 2 nm surface layer of the TiO₂ films, Na content was found to vary from 0 to 12 atomic %, depending on the substrate and the heating temperature. As expected, the Na⁺ content was zero for fused silica, and was high for crown glass-based substrates. Na⁺ content decreased in the thicker SiO₂ layer, which was also expected, indicating that the layers act as a diffusion barrier.

It is noteworthy that Si⁴⁺ was observed in TiO₂ films for all the substrates examined here, although the amount was smaller than that of Na⁺; the content of both ions increased as the heating temperature increased.

3.1.3. Crystal Phase. Table 1 shows the crystal phase of the TiO₂ films determined by XRD. In the table, the symbol “A” indicates that the anatase phase was observed, and “×” indicates that the peak of the TiO₂ crystal (anatase, rutile, and brookite) was not observed; that is, the films were amorphous. For fused silica, the anatase phase was observed at 300 °C and above. For the Crown/SiO₂ substrates, the anatase phase was observed also at 300 °C and above, although the substrates had layers of very different SiO₂ thickness. In contrast, the anatase phase was

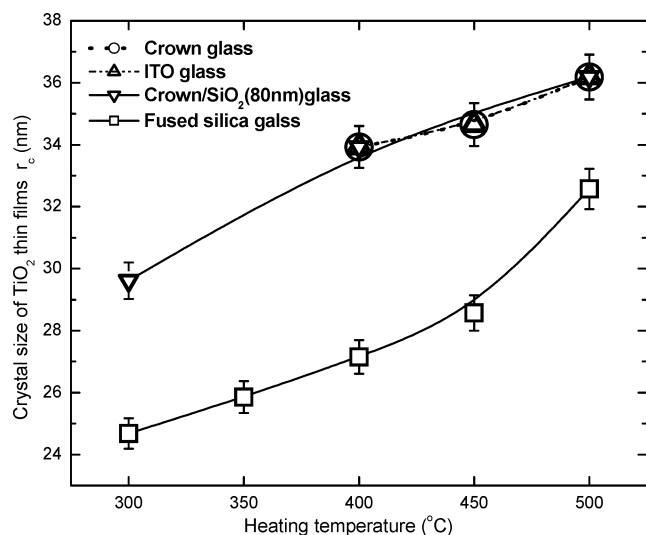


Figure 1. Particle sizes of anatase in the TiO₂ thin films coated on four different substrates heated at different temperatures.

not observed until the heating temperature reached 400 °C for crown glass and ITO glass. We reported recently that the temperature of anatase formation in the TiO₂ thin film varied between two conditions: whether coated on a glass substrate containing Na⁺ or on that without Na⁺.²⁷ Just as the results of a previous paper,²⁷ for thin films containing much Na⁺, anatase was formed at high heating temperature.

Table 1 also shows crystal phases of TiO₂ powders that were prepared in order to confirm the effect of Na⁺ on the formation of anatase. The TiO₂ powder showed anatase formation at the lowest temperature (200 °C) except for the powder containing a high amount of Na⁺ (1.0 mol/L). The TiO₂ powder containing 1.0 mol/L of Na showed anatase formation at 450 °C and 500 °C. This result supports the concept that Na⁺ may suppress the formation of anatase at low heating temperature.

For thin films on fused silica glass, even though fused silica contains no Na⁺, the anatase formation temperature was higher than that for TiO₂ powder without Na⁺. Si⁴⁺ may suppress formation of anatase, because only Si was found with the exception of the Ti and O in the surface of TiO₂ thin films on fused silica glass. Otherwise, it may be due to an interface effect; the interface between the glass substrate and the TiO₂ thin film would affect the phase transition. We have studied anatase formation using a monocrystal wafer of Si, and found that the anatase phase was formed at 200 °C in the case for TiO₂ powder. Therefore, the effect of Si⁴⁺ appears more important than that of the interface for the above result that the anatase in the TiO₂ thin film was formed at higher heating temperature than that in the TiO₂ powder. However, to determine which mechanism is occurring, the substrate giving no Si⁴⁺ diffusion into the TiO₂ thin film should be employed.

3.1.4. Particle Size of TiO₂. Figure 1 shows the particle size of anatase as a function of heating temperature for different samples. The particle size of anatase increased with an increase in the temperature for all the substrates. The particle size for fused silica was about 20% smaller than that for the other substrates.

Figure 2 shows the relationship between particle size and the Na⁺ concentration for different substrates and two different heating temperatures. The figure clearly shows that particle size increases with an increase in Na⁺ concentration, although the rate of the increase becomes small at high Na⁺ concentration. The effect of Na⁺ on crystal size was larger at 300 °C than at 500 °C.

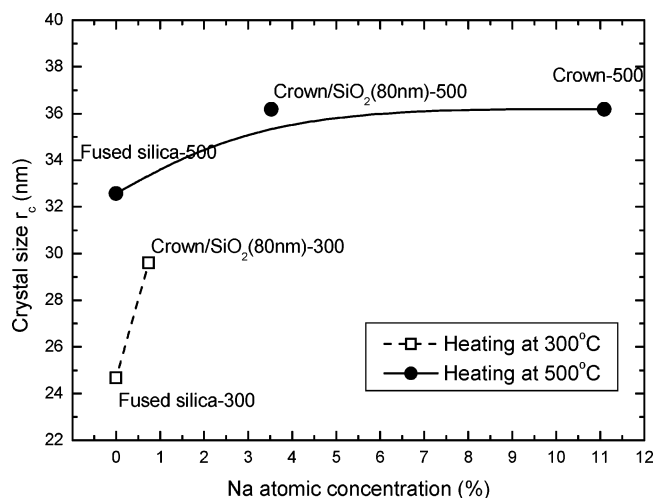


Figure 2. The relationships between the atomic concentrations of Na and the particle sizes of the TiO₂ thin films on different glass substrates.

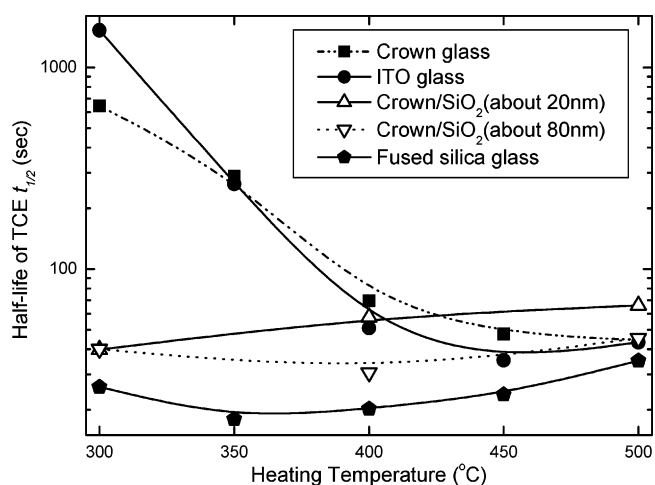


Figure 3. The half-life of TCE for TiO₂ thin films on different glass substrates heated at different temperatures.

From the above result, we conclude that the Na⁺ content in the TiO₂ films affects the primary particle size. The Na⁺ ions appear to act as a flux material for crystal growth. This effect was more remarkable at low heating temperature (Figure 2).

3.2. Photocatalytic Activity of the TiO₂ Thin Films. **3.2.1. Dependence of the Photocatalytic Activity on Preparation Temperature.** The respective photocatalytic activities of the various films were compared in terms of half-life (*t*_{1/2}) of the TCE degradation. The reason for using *t*_{1/2} is that the TCE degradation reaction contains radical chain reactions and the concentration change does not follow simple formulas.

The value of *t*_{1/2} ranged from 20 to 2000 s, depending on the substrates, as shown in Figure 3. For crown glass and ITO glass at lower preparation temperatures (<400 °C), *t*_{1/2} was very large, indicating that photocatalytic activity was very low. This is consistent with the observation that anatase formation was incomplete for these substrates at <400 °C (Table 1). As the heating temperature increased, *t*_{1/2} decreased and the photocatalytic activity was highest at 450–500 °C.

On the other hand, for fused silica and crown/SiO₂ substrates, the photocatalytic activity was very high—even for the low heating temperatures, reached a maximum at 350–400 °C, and then gradually decreased with the increase in temperature. It has been thought that the optimum heating temperature for sol-gel TiO₂ films to have maximum photocatalytic activity is around 500 °C.^{9,23} This is because it is usually considered that

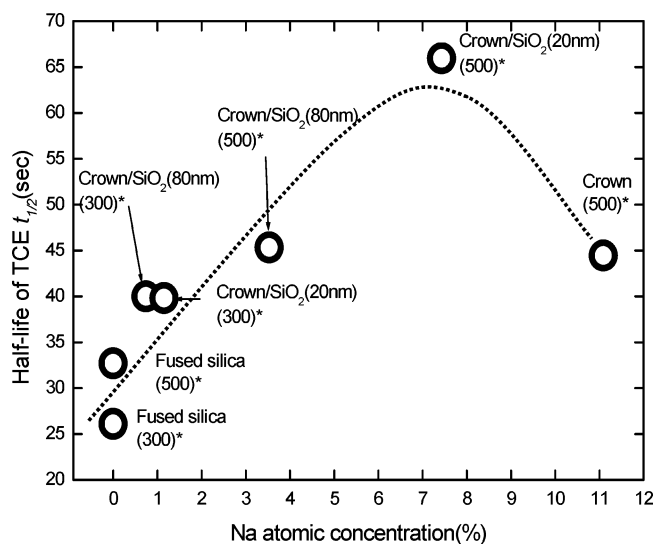


Figure 4. The relationships between the Na atomic concentrations and the half-life of TCE with the TiO₂ thin films on different glass substrates (*: heating temperature).

films with higher crystallization will result in higher photocatalytic activity, and that the activity will decrease when the rutile phase appears in the films at a much higher temperature. This notion regarding the optimum heating temperature seems to hold for the substrates of crown glass and ITO glass, but not for fused silica and crown/SiO₂ substrates. Thus, high heating temperatures are not necessary to obtain high photocatalytic activity when appropriate substrates (i.e., those with a low concentration of Na⁺) are employed.

3.2.2. Factors Affecting the Photocatalytic Activity of the TiO₂ Films. As described above, the photocatalytic activity of the sol–gel TiO₂ films depends on the substrate and the heating temperature. We further examined the determining factors governing photocatalytic activity.

First, we attended to atomic concentration of Na. Na⁺ ions have been proposed to act as recombination centers for photogenerated electrons and holes.^{16–19} However, there is not enough evidence to support this proposition, and the study of Na⁺ on photocatalytic activity is insufficient. Therefore, the dependence of atomic concentration of Na in the film surface on the photocatalytic activity was examined as shown in Figure 4. The value of $t_{1/2}$ increased with an increase in atomic concentration of Na up to around 7.43%. However, it decreased at higher atomic concentrations of Na (11.09%). Thus, high atomic concentration of Na is not necessarily a cause of low photocatalytic activity. As mentioned in the Introduction, Na⁺ ions have been suggested to act as the recombination center.^{16–19} The impurity level of Na⁺ in the TiO₂ can be one form of evidence to confirm whether the Na⁺ ion acts as a recombination center or not. However, to the best of our knowledge, such a study of the behavior of Na⁺ including impurity level in the TiO₂ has not been reported. Zwingel et al. reported that an impurity center of Na⁺ is similar to that of Li⁺ in ZnO, and it occupies a cation-site and then becomes an acceptor center.²⁸ The state of Li⁺ in TiO₂ is expected to differ from that in ZnO. Kinsbery et al. reported that the Li impurity makes a shallow donor in TiO₂.²⁹ If Na⁺ is similar to Li⁺ in TiO₂, Na⁺ will also make a shallow donor. The shallow donor level alone is hard to become the recombination center without a deep impurity level. Therefore, the recombination hypothesis may not hold.

Second, we examined relations between $t_{1/2}$ and the amount of photons (Np) absorbed by the films; Np depends on the

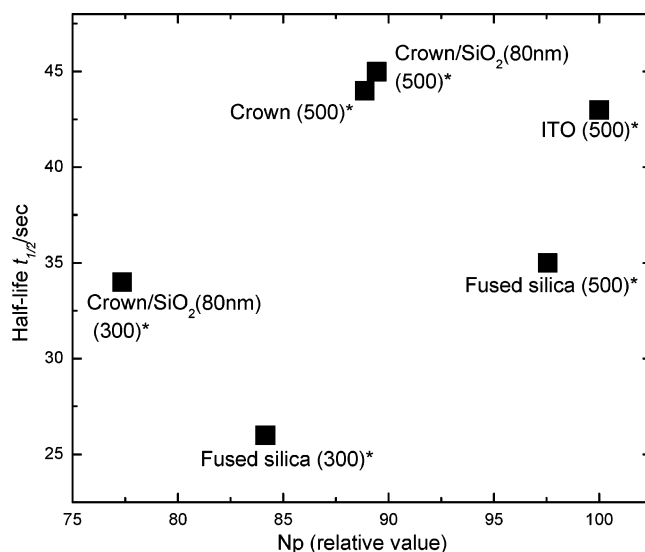


Figure 5. The relationships between the Np (relative value) and the half-life of TCE with the TiO₂ thin films on different glass substrates (*: heating temperature).

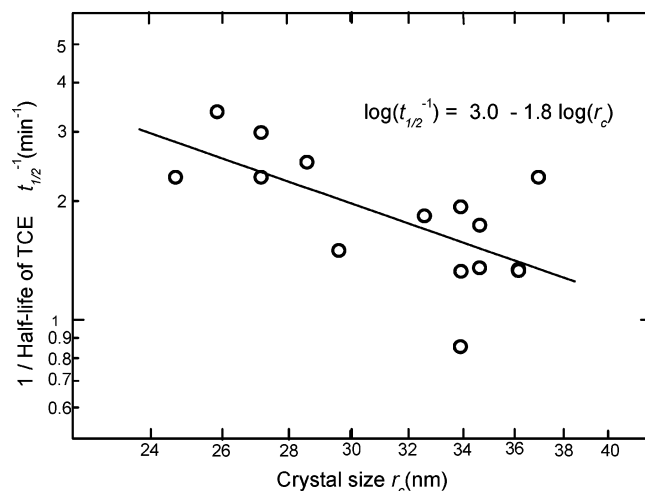


Figure 6. The relationships between the particle sizes of anatase in the TiO₂ thin films and the half-life of TCE.

absorption spectra and the film thickness that are changed according to the substrate and the heating temperature. In fact, the absorption spectra showed blue shifts for the films having small crystal sizes, which is consistent with findings reported earlier.⁶ In Figure 5, the values of $t_{1/2}$ were plotted against relative Np values estimated from the absorption spectra of the films and the distribution of the emission from the light source.³⁰ The relative Np was calculated as follows:

$$\text{Relative Np} = \sum_{\lambda} A_{\lambda} \cdot I_{\lambda}$$

where A_{λ} represents absorbance of the TiO₂ thin film at wavelength λ , and I_{λ} is the intensity of the emission of a black-light lamp at wavelength λ .

The $t_{1/2}$ value tends to decrease with increasing Np, although the plot is rather scattered. This tendency conflicts with the conventional idea that larger Np should give a higher reaction rate. This apparently strange result can be explained by considering the effect of the particle size as discussed below.

Figure 6 shows the relation between $t_{1/2}^{-1}$ and the primary particle size (r_c); only the results for the films showing distinct anatase peaks were employed here. A rather good linear relation

can be seen in the figure; from a log–log plot, the next relation was derived: $t_{1/2}^{-1}$ is proportional to $r_c^{-1.8}$. Thus, photocatalytic activity of the sol–gel TiO₂ films appeared to be largely governed by the size of the primary particles composing the films. Oh et al. studied the photocatalytic activity of Fe-doped TiO₂ powder. They obtained results that the size of TiO₂ was slightly decreased with the addition of Fe-species, and the photocatalytic activity increased with the addition of Fe-species.³¹ Their result is a case that particle size varied by added ions in TiO₂ affected the photocatalytic activity, like our results in this paper.

On the basis of this finding, the relation in Figure 5 is explained as follows. The particle size increases with the preparation temperature to result in a red shift in the absorption spectrum, which gives a larger Np, the number of photons absorbed by the TiO₂ films. At the same time, however, the larger particle size causes an increase in $t_{1/2}$ as shown in Figure 6. According to the results shown in Figures 5 and 6, the latter effect is much larger than the former. Therefore, the slope of the plot in Figure 6 should become smaller if the $t_{1/2}$ values are corrected by Np.

Moreover, the dependence of the $t_{1/2}$ on the preparation temperature shown in Figure 3 can be considered as the result of the anatase formation and particle size change; as the preparation temperature increases, the photocatalytic activity increases until a sufficient amount of the anatase phase appears in the films, then the photocatalytic activity decreases in association with the increase in the particle size resulting from crystal growth. All the present results are reasonably explained by considering the particle size change. Therefore, we conclude that Na⁺ in the TiO₂ films may affect the photocatalytic activity through changing the particle size, and not through acting as a recombination center.

3.2.3. Relation between the Film System and the Dispersed Particle System. The relation between the particle size and the photocatalytic activity for the TiO₂ films, shown in Figure 6, is close to that for particulate TiO₂ in solution. Harada et al. tested the effect of particle size on the photocatalytic activity for powdered rutile TiO₂ in methanol–water solution, and reported that the slope of the log–log plot for the activity vs the particle size was -1.6 .³² They argued that the decrease of the particle size caused an increase in charge separation rather than an increase of surface area, based on the fact that the slope of activity was less than -1 . Considering that the sol–gel films are possibly very porous,²² a similar mechanism could be operative in the sol–gel TiO₂ films employed in the present study. In fact, based on the ellipsometry measurements for the fused silica substrate, which gives no Na⁺ and little Si⁴⁺ to the TiO₂ film, the refractive index of the TiO₂ films (2.0–2.1) was considerably smaller than that for bulk TiO₂, suggesting highly porous conditions of the films. Employing the values of the refractive index to be 2.0 for the films and 2.5 for bulk crystals, porosity is roughly given as 0.4; this value is consistent with that for the close packing of spheres, i.e., it is a model for the porous film. The fact that the TCE molecules are small enough to penetrate into the porous TiO₂ films probably makes the behavior of the photocatalytic activity of the films similar to that for the particulate TiO₂ in solution. In our result, therefore, the value of -1.8 as the slope (of the log–log plot for the particle size vs the reciprocal number of the half-life of TCE degradation shown in Figure 6) suggests that the activity of the TiO₂ thin film does not depend solely on the surface area.

3.2.4. Predicted Photocatalytic Activity for Extended Conditions. Anpo et al. reported that in the range of less than 10 nm

in particle size, a drastic increase in the quantum yields of photocatalytic hydrogenation was observed for TiO₂ powders.¹³ If this holds for the sol–gel TiO₂ films, the $t_{1/2}^{-1}$ shown in Figure 6 can become over 17 min^{-1} ($t_{1/2} < 3.5 \text{ s}$) together with reduction in particle size. On the other hand, the film preparation processes that give a larger particle size will give lower photocatalytic activity, irrespective of their Na⁺ concentration. In addition, other dopant ions should be reexamined as well in terms of the particle size so that the intrinsic effect of these various ions can be evaluated.

4. Conclusions

We have demonstrated that conventional ideas on the photocatalytic activity of the sol–gel TiO₂ films should be reconsidered as follows. First, the optimum preparation conditions of the TiO₂ films, particularly, the preparation temperature of the TiO₂ films, were largely different from the conventional ones; i.e., conventionally, the optimum temperature is around 500 °C. Rather low temperatures (e.g., 350 °C) gave the optimum photocatalytic activity for substrates containing little or no Na⁺. The rather high optimum temperature reported in the literature is probably due to the fact that Na⁺ in the TiO₂ sol–gel film increases the amorphous–anatase phase transition temperature. Second, the recombination center hypothesis for the Na⁺ ions thermally diffused from the substrates containing Na⁺ does not hold for the sol–gel TiO₂ films. Instead, Na⁺ in the film affects the photocatalytic activity of the TiO₂ films through changing the particle size of anatase, in terms of the carrier separation process in the primary particles. As a result of the porous structure of the sol–gel films, the carrier separation efficiency appears to increase with decreasing particle size in a manner similar to that for dispersed TiO₂ systems.

The photocatalytic activity obtained in the present study for TCE degradation is close to the theoretically attainable maximum condition, although it may be increased by further reduction of the primary particle size.

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