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Decomposition of gas-phase octamethyltrisiloxane on TiO_2 thin film photocatalysts—catalytic activity, deactivation, and regeneration

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Abstract

The photocatalyzed decomposition reaction of gas-phase octamethyltrisiloxane (OMTS) on TiO_2 thin films was investigated in a batch-type photocatalytic reactor. The effectiveness of TiO_2 photocatalyst for decomposing OMTS was demonstrated by the decrease of OMTS concentration and increase of carbon dioxide concentration with illumination time as monitored using a gas chromatography. However, the photocatalytic activity was found to decrease with increasing reaction time, and catalyst deactivation was finally observed on the TiO_2 film that suffered from a long-time reaction. Formation and accumulation of hydroxylated SiO_x ($x = 3 \sim 4$) on the irradiated TiO_2 surface were detected by X-ray photoelectron spectroscopic (XPS) measurements. An equivalent amount of ∼7 monolayers of OMTS was estimated to be decomposed on the fully deactivated TiO_2 photocatalyst as calculated from the saturated adsorption value and the total decomposed amount of OMTS. It was found that thus formed SiO_x can be easily removed by treatment in an alkaline solution for a short period of time without influencing the underlying TiO_2 film. Regeneration of the photocatalytic activity of the SiO_x-removed TiO_2 thin film was confirmed by the re-decomposition of OMTS under the same experimental conditions.

Keywords: Photocatalysis; Photooxidation; Siloxane; Photocatalyst deactivation; Photocatalyst regeneration

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1. Introduction

TiO_2-based photocatalysis has attracted extensive research interests in the past decades due to its potential applications in air clean-up and water purification (e.g. anti-bacteria, decontamination, de-odorization) [1–3]. As a typical oxide semiconductor, illumination of TiO_2 with photon energy higher than its band gap produces electrons and holes in the conduction band and valence band, respectively. These photo-generated holes and electrons combine with surface adsorbed species such as water and oxygen to form highly reactive radical species (e.g. $^{\bullet}OH$ and $O_2^{\bullet -}$) [4–6], which can oxidize most organic compounds and some inorganic compounds (e.g. NO_x), yielding mostly carbon dioxide and dilute mineral acids (e.g. HNO_3) as the final products. The strong oxidizing power of the photo-generated holes, the chemical stability, and the non-toxicity of TiO_2 have made it superior to other oxide semiconductors (e.g. ZnO, CdS) as a photocatalyst.

On the other hand, silicone products (e.g. grease, oil) are known to be widely used in the electronics, mechanics, chemical engineering, architecture, and many other fields [7]. These high molecular-weight polymers themselves are stable at ambient conditions, however, some low molecular-weight oligomers (i.e. siloxane) being contained in the polymers are relatively volatile and tend to outgas into the indoor atmosphere though their concentrations may be very low [8]. Particularly, in semiconductor industry, it was reported that trace organic contaminants (including both hydrocarbons and volatile siloxanes) adsorbing on silicon wafer surfaces give rise to detrimental impact on the performance and yield of semiconductor devices [8–10]. Conventional wet washing method using a H_2SO_4/H_2O_2 solution cannot remove these contaminants completely [9]. Although improved removal can be achieved by employment of a dilute HF/O_3 solution, exposure of the washed wafer in the clean-room atmosphere gives rise to contamination again [9]. Therefore, it is necessary to search for alternative methods to reduce the organic contaminants in the clean-room space.

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Taking into account of its effectiveness particularly for decomposing low concentration organic contaminations, TiO_2 photocatalysis appears to be one promising approach to meet the above demand. Since research work concerning degradation and decomposition of silicon-containing organic compounds on TiO_2 photocatalyst has been few so far [11,12], in the present work, the photocatalyzed decomposition behavior of gas-phase octamethyltrisiloxane (OMTS, used as a model substance) on the TiO_2 thin film was studied with the purpose to understand whether TiO_2 photocatalysis is effective for decomposing the trace silicon-containing organic contaminations in the clean room, which is the biggest motivation for us to do the present work. The photocatalytic activity, deactivation and regeneration of the TiO_2 thin film-based photocatalyst were reported and discussed. Emphases were particularly put on the latter two issues.

2. Experimental

TiO_2 thin films with thicknesses of ~0.4 μm were prepared on one side of silica-coated soda lime glass (5.0 cm × 7.5 cm) by a dip-coating process using a commercial titanium isopropoxide solution (NDH-510C, Nippon Soda Co. Ltd.). The withdrawal rate was controlled to produce a 0.1 μm-thick film for each dip-coating process. The coating procedures were repeated four times. After each procedure, the coated sample was dried at 120 °C for 40 min, and then heated at 500 °C for 30 min. Finally, the sample was calcined at 500 °C for 1 h. X-ray diffraction measurements showed that thus obtained TiO_2 films are mainly composed of anatase structure.

Photocatalytic decomposition reaction of OMTS (Wako Pure Chemical Ltd., Tokyo, Japan) was carried out in a 500 ml pyrex glass vessel under synthetic air condition. The TiO_2-coated glass substrate of 5.0 cm × 5.0 cm in size, obtained by cutting the original 5.0 cm × 7.5 cm substrate, was utilized as the photocatalyst and placed on the bottom of the reactor. Gas-phase OMTS-containing synthetic air was obtained by passing the synthetic air through an OMTS liquid reservoir at room temperature. Samples containing various concentrations of OMTS were prepared by injecting measured quantities of OMTS-synthetic air mixture gas into the reaction vessel using a syringe. Black light bulbs were used as UV light sources and the light intensities were measured using a UV power meter (TOPCON UV-1). Illumination was conducted at room temperature after adsorption equilibrium of OMTS on the TiO_2 film was reached. The OMTS concentration was measured using a Gas Chromatography (GC-8A, Shimazu) equipped with a 2-m OV-1 column (GL Science Co. Ltd.), and a flame ionization detector, using N_2 as the carrier gas. The CO_2 concentration was measured using the same type GC, equipped with a 2-m Porapak-Q column (GL Science Co. Ltd.), with a methanizer and a flame ionization detector, also using N_2 as the carrier gas.

The amount of OMTS adsorbed on the TiO_2 sample was estimated by measuring the decrease of the gas-phase OMTS concentration in the glass vessel containing TiO_2 film sample versus that in a separate empty glass vessel. The concentrations were measured 2 h after a given concentration of gas mixture was introduced into the glass vessel. X-ray photoelectron spectroscopic (XPS) measurements were performed on a Perkin-Elmer Model 5600 spectrometer. Aluminium Kα radiation (photon energy, 1486.6 eV) was used, and photoelectrons were collected at a takeoff angle of 45° with respect to the film surface normal.

3. Results and discussion

Since a photocatalytic reaction takes place on an irradiated TiO_2 surface, adsorption of the reactant on the TiO_2 surface is generally considered to be necessary for accomplishing the reaction. Therefore, it is important to know the adsorption behavior of the reactant on the TiO_2 surface. Fig. 1 shows the experimental data for the adsorption isotherm in the form of an inverse plot of the adsorbed amount of OMTS (mg) on the TiO_2 thin film surface versus the equilibrium OMTS concentration (mg/l) in the gas phase. The linearity of the plot implied that the adsorption behavior of OMTS on the TiO_2 thin film surface can be characterized by Langmuir-type adsorption (Eq. (1)):

$$\frac{1}{C_{\mathrm{ad}}} = \frac{1}{C_{\mathrm{sat}}} + \frac{1}{C_{\mathrm{sat}}KC} \tag{1}$$

where C_{ad} represents the reactant concentration adsorbed on the substrate at a certain equilibrium concentration (C), and C_{sat} is the maximum concentration (i.e. the saturated concentration) that can be adsorbed on the substrate. In Langmuir-type adsorption, C_{sat} usually refers to the value of a monolayer coverage, and K represents the adsorption equilibrium constant. From the data as shown in Fig. 1, the values of K and C_{sat} for the adsorption of OMTS on the TiO_2 thin film surface were estimated to be ~0.00067 m^3/mg and

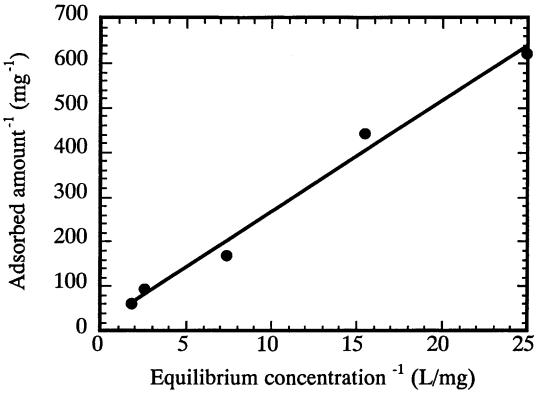

Fig. 1. An inverse plot of the OMTS amount (mg) adsorbed on a 5.0 cm × 5.0 cm TiO_2 thin film surface vs. the gas-phase equilibrium concentration (mg/l).

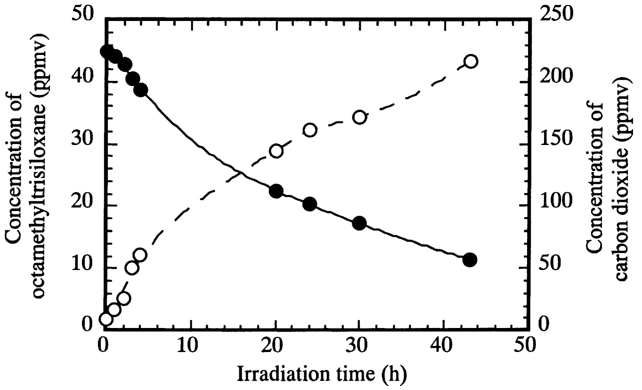

Fig. 2. Concentration changes of gas phase OMTS and CO_2 as a function of the irradiation time during the decomposition of OMTS. Light intensity, 2.0 mW/cm^2; (●) OMTS; (○) CO_2.

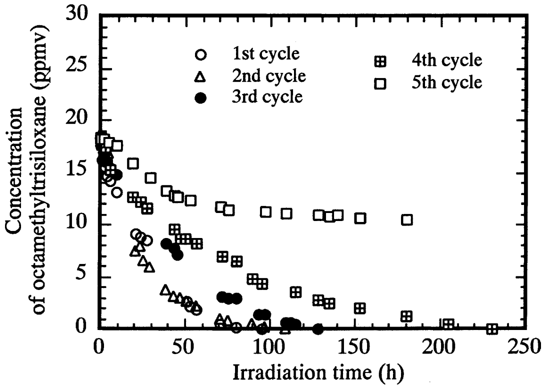

Fig. 3. Cyclic experiments of the photocatalytic decomposition of OMTS on a TiO_2 thin film-coated glass substrate. After the injected OMTS being decomposed completely (one cycle), the next sample was injected and the reaction was repeated. Light intensity, 2.0 mW/cm^2.

0.0024 mg/cm^2, respectively. Adsorption of OMTS on the TiO_2 surface may occur through "hydrogen bonds" between the oxygen atoms of OMTS and the surface OH groups of TiO_2.

In Fig. 2 is presented a typical experimental data set showing the concentration changes of OMTS and CO_2 in the reactor with illumination time. The decrease of OMTS concentration and increase of CO_2 concentration with illumination time demonstrated the effectiveness of TiO_2 photocatalyst for decomposing OMTS. In addition to the main product of CO_2, smaller concentration of CO was also detected from the reactor. No other decomposition products (or intermediates) were detectable within the experimental sensitivity in the present work. It was noticed that decomposition of one OMTS molecule produces ∼6.4 molecules of CO_2 and ∼1.2 molecules of CO under the present experimental conditions. The total molecules of CO_2 and CO (∼7.6 molecules) detected in the products were found to be close to the theoretical values of eight molecules (theoretically, complete decomposition of one molecule OMTS should produce eight molecules CO_2 because eight $-CH_3$ groups exist in one molecule OMTS). This concordance inferred that the photocatalytic decomposition reaction of OMTS on TiO_2 occurs almost stoichiometrically. In addition, existence of lower concentration of CO in the products suggests the possibility that, oxidation of the $-CH_3$ groups produces CO intermediates first, and the final product of CO_2 comes from the further oxidation of CO. The much higher concentration of CO_2 than that of CO in the products implied that most of the carbon monoxide be further oxidized to CO_2 before they desorb from the TiO_2 surface. However, other possibilities still cannot be completely excluded. Worthy noting, generation of carbon monoxide in photocatalytic reaction has also been observed in other reaction systems. For example, Larson and Falconer [13] ever reported the production of CO during the decomposition of trichloroethylene (TCE) on a TiO_2 photocatalyst as confirmed by temperature-programmed desorption (TPD) measurements.

Fig. 3 illustrates the decreasing reactivity of the TiO_2 photocatalyst with increased reaction time. In this experiment, UV irradiation was performed continuously until the injected OMTS was decomposed completely (which process being referred to as one cycle). Before the next OMTS sample was injected and a new cycle of experiment was conducted at the same condition, the air in the reactor was replaced sufficiently using fresh synthetic air. It can be seen that, in contrast to the first two cycles, in which no obvious loss of the photocatalytic activity was observable, apparent decrease of the reactivity was observed in the third and fourth cycles, because longer time was taken before complete decomposition of the injected OMTS. Particularly, complete deactivation of the catalyst was observed in the fifth cycle, and no decomposition reaction took place further more after that cycle. It was found that replacement of the reactor with fresh air could not recover the catalyst at all. The total amount of OMTS decomposed on the deactivated TiO_2 thin film was calculated to be ∼0.0165 mg/cm^2 TiO_2.[1] If dividing this value by the saturated adsorption value (C_{sat}, a value obtained from Fig. 1) of OMTS on the TiO_2 thin film, and also if taking C_{sat} as the concentration needed to cover the TiO_2 surface with a monolayer, then an equivalent amount of ∼7 monolayers' OMTS was estimated to be decomposed before the TiO_2 photocatalyst became fully deactivated.

Fig. 4 demonstrates the change of the XPS spectra of the TiO_2 thin film in the (a) O 1s and (b) Si 2p regions before and after UV illumination for various times. Before UV illumination, a very weak peak near the binding energy of

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[1] The total amount of OMTS (A) decomposed on the deactivated TiO_2 was calculated according to the following formula: $A = ((N_{OMTS} V_r \times 10^{-6})/V_m)(M_{OMTS}/S_{TiO_2})$, where N_{OMTS} represents the total concentration of OMTS (ppmv) being decomposed before deactivation of the TiO_2 (obtained from the data as shown in Fig. 3). V_r is the volume of the reactor (l), and V_m the volume of 1 mol ideal gas at 1 atm (in convenience, the gas-phase OMTS was approximately treated as an ideal gas), M_{OMTS} and S_{TiO_2} represent the molecular weight of OMTS and the area of the TiO_2-coated substrate, respectively.

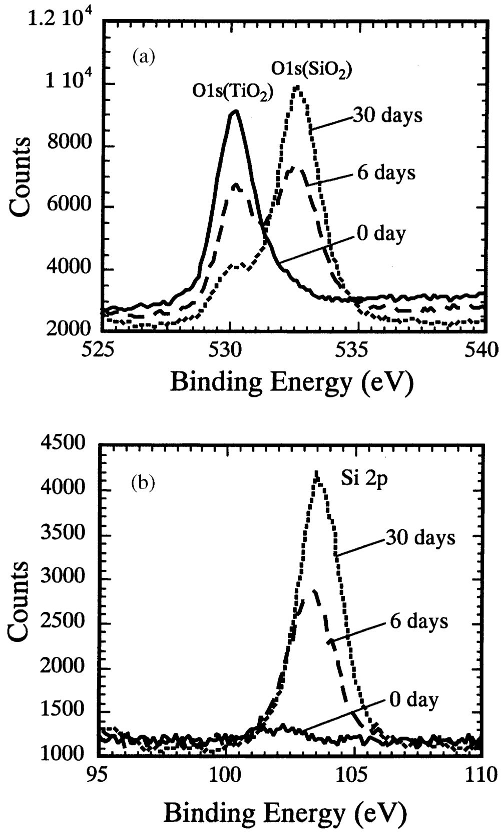

Fig. 4. Changes of the XPS spectra of the TiO_2 thin film in the (a) O 1s and (b) Si 2p regions before and after UV illumination for various times. After 30 days' reaction, the catalyst became inactive.

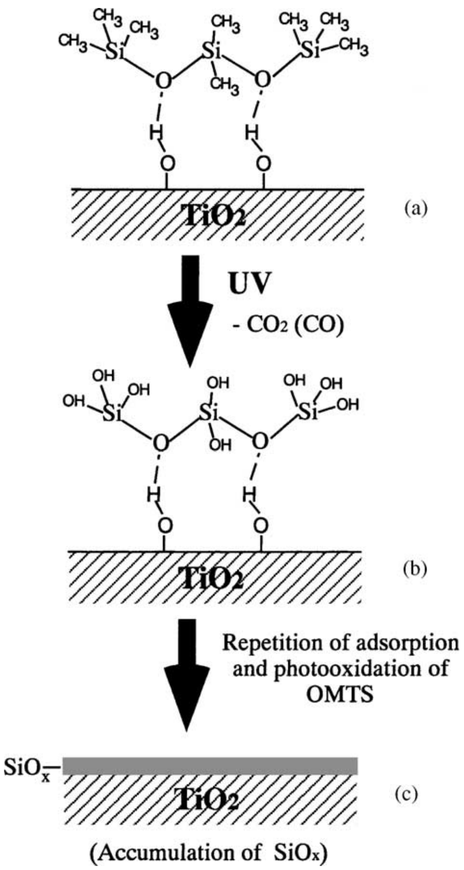

Fig. 5. A schematic model for (a) adsorption, (b) decomposition of OMTS, and (c) accumulation of SiO_x on the TiO_2 photocatalyst thin film surface.

102.0 eV was detected in the Si 2p region (Fig. 4 (b)), which was ascribed to the adsorbed OMTS. In the corresponding O 1s region, a sharp peak coming from TiO_2 (O 1s (TiO_2)) was observed (Fig. 4 (a)). Upon UV illumination, however, the Si 2p peak increased remarkably with increasing illumination time (Fig. 4 (b)), accompanied with a slight shift of the peak position to the higher binding energy side (from 102.0 to 103.6 eV) until the TiO_2 catalyst lost the reactivity completely (after 30 days' reaction). Meanwhile, a new O 1s peak was observed at the higher binding energy side in the corresponding O 1s region, and the intensity of this peak also increased with increasing illumination time. These XPS measurements combining with the decomposition results obtained above make it possible for us to deduce a reasonable mechanism for the catalyst deactivation, as schematically shown in Fig. 5. Photooxidation of the Si–CH_3 groups of OMTS produces Si–OH groups accompanied with the generation of CO_2 through the following reactions:

$$\mathrm{TiO_2} + h\nu \rightarrow \mathrm{TiO_2} + \mathrm{e^-} + \mathrm{h^+} \tag{2}$$

$$\mathrm{OH^-(surface)} + \mathrm{h^+} \rightarrow {}^{\bullet}\mathrm{OH} \tag{3}$$

$$\mathrm{O_2(ads)} + \mathrm{e^-} \rightarrow \mathrm{O_2{}^-(ads)} \tag{4}$$

$$\mathrm{O_2{}^-} + \mathrm{H^+} \rightarrow \mathrm{HO_2{}^{\bullet}} \tag{5}$$

$$\text{–Si–CH}_3 + {}^{\bullet}\mathrm{OH} \rightarrow \text{–Si–CH}_2{}^{\bullet} + \mathrm{H_2O} \tag{6}$$

$$\text{–Si–CH}_2{}^{\bullet} + \mathrm{O_2} \rightarrow \text{–Si–CH}_2\mathrm{OO}^{\bullet} \tag{7}$$

$$\text{–Si–CH}_2\mathrm{OO}^{\bullet} + \mathrm{e^-} \rightarrow \text{–Si–CHO} + \mathrm{OH^-} \tag{8}$$

$$\text{–Si–CHO} + {}^{\bullet}\mathrm{OH} \rightarrow \text{–Si–CO}^{\bullet} + \mathrm{H_2O} \tag{9}$$

$$\text{–Si–CO}^{\bullet} + \mathrm{O_2} \rightarrow \text{–Si–(CO)OO}^{\bullet} \tag{10}$$

$$\text{–Si–(CO)OO}^{\bullet} + \mathrm{HO_2{}^{\bullet}} \rightarrow \text{–Si–(CO)OOOOH} \tag{11}$$

The tetraoxide formed by Eq. (11) decomposes to form radical products (–Si–(CO)$O^{\bullet}$ and ${}^{\bullet}OH$) [14]. Further decomposition of –Si–(CO)$O^{\bullet}$ produces –$Si^{\bullet}$ and CO_2 (Eq. (13)).

$$\text{–Si–(CO)OOOOH} \rightarrow \text{–Si–(CO)O}^{\bullet} + \mathrm{O_2} + {}^{\bullet}\mathrm{OH} \tag{12}$$

$$\text{–Si–(CO)O}^{\bullet} \rightarrow \text{–Si}^{\bullet} + \mathrm{CO_2} \tag{13}$$

$$\text{–Si}^{\bullet} + {}^{\bullet}\mathrm{OH} \rightarrow \text{–Si–OH} \tag{14}$$

Taking account of the fact that low concentration of CO was detected in the experiment, occurrence of the following reaction (Eq. (15)) may be also possible.

$$\text{–Si–CO}^{\bullet} \rightarrow \text{–Si}^{\bullet} + \mathrm{CO} \tag{15}$$

The generated CO_2 (or CO) desorbs while the Si–OH groups remain on the TiO_2 surface (Fig. 5 (b)). As the consequence, the TiO_2 surface is covered with hydroxylated SiO_x ($x = 3 \sim 4$). Because the binding energy of the O 1s (SiO_x) is higher than that of the O 1s (TiO_2) [15], with the decomposition reaction going on, a new peak appeared at the higher binding energy side in the O 1s region because of the formation of SiO_x.

On such a Si–OH terminated surface, further OMTS molecules may be adsorbed and oxidized, leading to accumulation of SiO_x on the surface (Fig. 5 (c)). This was confirmed by the increased intensities in the Si 2p (SiO_x) and O 1s (SiO_x) peaks with increasing reaction time as shown in Fig. 4. The slight shift of Si 2p peak position to higher binding energy side may be ascribed to the increased formation of Si–O–Si network with increasing reaction time [12]. It was supposed that this adsorption–oxidation–adsorption–oxidation process can be repeated until the SiO_x accumulates enough so that the photogenerate active species (e.g. $^{\bullet}OH$ and $O_2{}^{\bullet -}$) become impossible to reach the surface to participate in the reaction further more (i.e. causing catalyst deactivation). As demonstrated above, for the TiO_2 thin film used in the present work, accumulation of ∼7 monolayers' SiO_x caused complete deactivation of the catalyst.

A similar deactivation phenomenon was also observed by Tada [12] during his study on the photo-induced oxidation reaction of chemisorbed 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) on the TiO_2 photocatalyst. He reported that sequential cycles of chemisorption of TMCTS followed by photo-irradiation results in layer-by-layer growth of hydroxylated SiO_x. As a result, the decomposition rate decreases exponentially with the increase of the SiO_x thickness. On the other hand, Pelizzetti and coworkers ever studied the photodegradation reactions of octaphenylcyclotetrasiloxane (OPCTS) and poly(methylphenylsiloxane) (PMPS) adsorbed on the TiO_2 in aqueous suspensions [11]. They reported that no significant change in the TiO_2 photoactivity during and after silicone degradation was observed, because the degradation products of soluble silicates do not coat the photocatalytic surface. This indicates that the reaction atmosphere (i.e. gas-phase or aqueous solution) is very important for the decomposition of silicon-containing organic compounds on TiO_2 photocatalysts.

Photocatalyst deactivation is an important issue that has to be considered if taking practical applications of photocatalyst into account. In the recent years, increasing attentions are being paid on such problems and several related issues have been reported [16–21]. For example, Sauer and Ollis [16] surveyed the literatures on photocatalytic air treatment and purification, and accentuated the emerging photocatalyst deactivation issues in 1996. They made a comparative study on the results reported in the literatures and showed that photocatalyst deactivation is generally found in single-pass fixed-bed photocatalytic reactors. Photocatalyst deactivation has been observed in decomposition reactions of trichloroethylene (TCE) [13], toluene [21], benzene [20], toluene/trichoropropene (TCP) [17], toluene/perchloroethylene (PCE) [17], pyrrole [18], indole [18], 1-butanol [19], decamethyltetrasiloxane (DMTS) [18], and 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) [12], etc. Two possibilities may explain the photocatalyst deactivation behavior. One is the accumulation on the TiO_2 surface of reaction intermediates or by-products that are hard to be decomposed under photocatalytic conditions. Deactivation caused during decomposition of pyrrole, indole, DMTS, TMCTS and OMTS in the present work may belong to this type. The other is the formation of surface species (intermediates or by-products) that have higher adsorption ability than the reactant on the TiO_2 surface. As the consequence, adsorption of the reactant on TiO_2 surface is inhibited and corresponding deactivation occurs. Deactivation in the cases of benzene, toluene, toluene/TCE, toluene/PCE, and 1-butanol belongs to this type. In these cases, benzoic acid (or butanoic acid in the case of 1-butanol), which has much higher adsorption ability than the corresponding reactant was detected on the deactivated TiO_2 surfaces.

Establishment of regeneration methods for the deactivated photocatalyst is certainly important from the viewpoint of process economics. However, very few efforts have been done so far on this subject. In the present work, we found that the deactivated TiO_2 photocatalyst occurred during decomposition of OMTS can be regenerated easily by removing the accumulated SiO_x from the TiO_2 surface using dilute alkaline solutions without influencing the underlying TiO_2 film. Fig. 6 shows the XPS spectra (survey scan from 0 to 1100 eV) of the deactivated TiO_2 catalyst treated in distilled water and NaOH solutions with various pH values. It was found that treatment in water or NaOH solutions with pH <11 cannot remove the SiO_x completely even at extended treating times under agitation conditions (curves 2 and 3). Nevertheless, complete removal was achieved on the samples treated in NaOH solutions with pH higher than

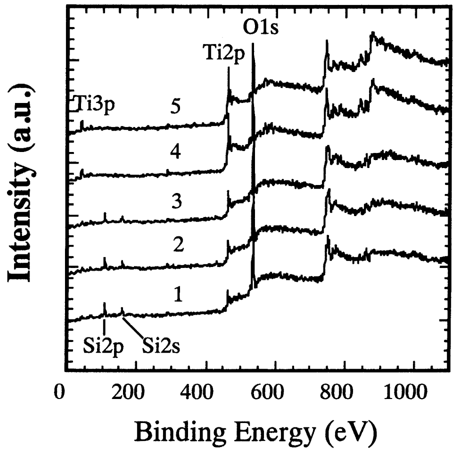

Fig. 6. XPS spectra (survey scan from 0 to 1100 eV) of the deactivated TiO_2 catalyst treated in pure water and NaOH solutions with various pH values for 30 min. Curve 1, deactivated TiO_2; curve 2, water; curve 3, pH 11; curve 4, pH 12; curve 5, pH 13.

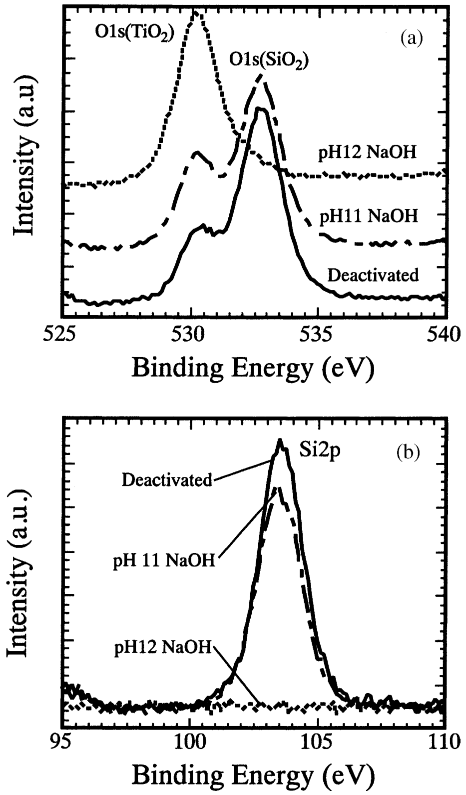

Fig. 7. XPS spectra (multi-scan) of the deactivated TiO_2 catalyst in the (a) O 1s and (b) Si 2p regions treated in pH 11 and 12 NaOH solutions for 30 min.

12 (curves 4 and 5), as confirmed by the disappearance of the Si 2p and 2s peaks.

The results can be seen more clearly from the multi-scan spectra in the O 1s and Si 2p regions as shown in Fig. 7, in which the spectra of the deactivated TiO_2 photocatalyst treated in NaOH solutions with pHs 11 and 12 were representatively presented. Apparently, treatment in a pH 11 NaOH solution is not able to eliminate the Si 2p and O 1s (SiO_x) peaks completely. However, treatment in a pH 12 NaOH solution leads to complete disappearance of these two peaks, indicating the removal of the SiO_x from the TiO_2 surface. It was found that treatment for ~20 min in a NaOH solution with a pH higher than 12 is enough for complete removal of the accumulated SiO_x. The non-crystallinity of the SiO_x may dedicate to the solubility in alkaline solutions in the present work. It is known that crystalline silica (e.g. quartz) is scarcely attacked by alkalies, while amorphous silica is soluble in certain alkaline solutions [22]. Atomic force microscopic (AFM) measurements demonstrated that the surface morphology of the TiO_2 thin film surface did not change before and after treatment in a pH 12 NaOH solution within 1 h.

Regeneration of the photocatalytic activity of the SiO_x-removed TiO_2 film was confirmed by the re-occurrence of the decomposition reaction of OMTS (Fig. 8 (a)) and also by the decomposition reaction of methylene blue adsorbed on the TiO_2 surface (Fig. 8 (b)). It can be seen that the reactivity is comparable to that of a freshly prepared TiO_2 film.

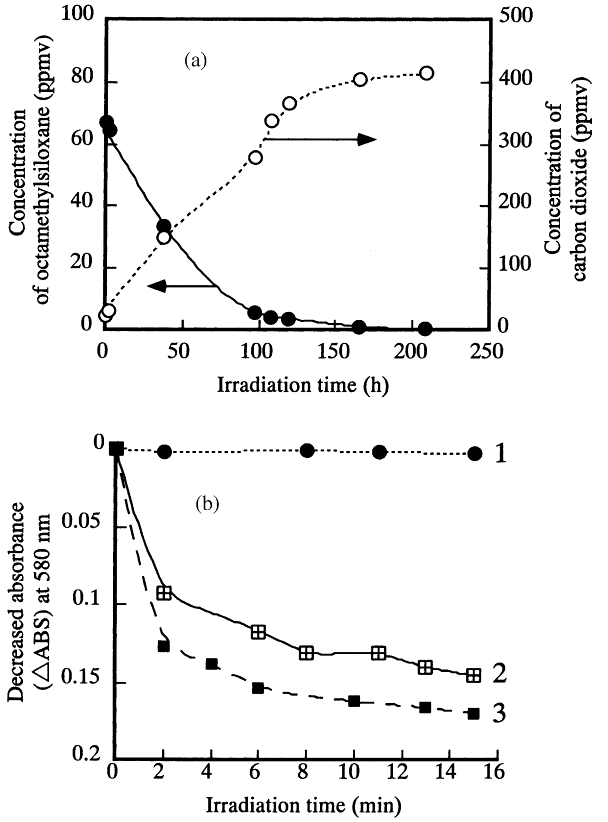

Fig. 8. Regeneration of the photocatalytic activity of the SiO_x-removed TiO_2 catalyst confirmed by (a) the re-occurrence of the decomposition reaction of OMTS and (b) the decomposition of methylene blue adsorbed on the catalyst surface. Curve 1 in (b), deactivated TiO_2; curve 2, deactivated TiO_2 treated in a pH 12 NaOH solution for 30 min; curve 3, freshly prepared TiO_2. The reaction was monitored by the absorbance decrease at 580 nm. Light intensity, 2.0 mW/cm^2.

4. Conclusion

Using OMTS as a model substance, we have shown that TiO_2 photocatalyst is capable of decomposing silicon-containing organic compounds. However, the photocatalytic activity decreased with increasing reaction time, and catalyst deactivation was finally observed on a long-time irradiated TiO_2 film. XPS measurements revealed that, accumulation of hydroxylated SiO_x on the TiO_2 surface is the main reason for the catalyst deactivation. A simple regeneration method was established through removing the SiO_x covered on the deactivated catalyst surface by treatment in a dilute alkaline solution for a short period of time.

When TiO_2 photocatalysis is utilized for the purpose to create a clean and comfortable indoor environment, decomposition of trace siloxane outgas (coming from silicone products used in the room space, e.g. sealant, etc.) may be involved and thus similar catalyst deactivation phenomenon may occur after a long-term usage. Therefore, this simple regeneration method may be of general importance from the viewpoint of process economics and maintenance.

Acknowledgements

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