Synthesis of TiO$_2$ photocatalyst thin film by solvothermal method with a small amount of water and its photocatalytic performance

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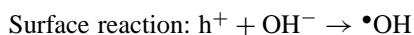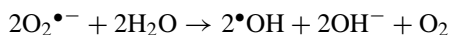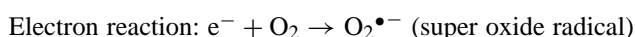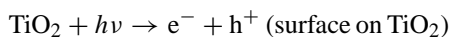
Abstract

Colloidal solutions containing nano-sized TiO$_2$ particles were successfully obtained by adding a small amount of water and employing solvothermal method. A thin film obtained from this colloidal solution (Cat. 2) exhibited much better properties than another film obtained via a sol–gel method (Cat. 1). The former had smaller and more uniform TiO$_2$ particles than the latter; it also had the anatase structure even after drying at 200°C; a much thinner film of Cat. 2 could be obtained and this film could remain stably attached on a silicon wafer or on a pyrex plate after a thermal treatment. Cat. 2 coated on a γ-alumina exhibited excellent performance for photocatalytic decomposition of CHCl$_3$ under UV-light with O$_2$ bubbling (90% conversion in 10 min), when comparing with a result obtained without the catalyst (70% conversion after 1 h). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: TiO$_2$; Thin film; Photocatalyst; Solvothermal method; CHCl$_3$ decomposition; γ-Alumina

1. Introduction

Recently much attention has been paid to nano-sized TiO$_2$ particles for the purpose of cleaning the environment by photocatalytic decomposition of waste materials, pollutants, and harmful bacteria [1–7]. Generally, a photocatalytic reaction is governed by relative rates of various processes such as oxidation reactions by photogenerated holes at the TiO$_2$ surface, reduction reactions by photogenerated electrons at the TiO$_2$ surface, diffusion of the electrons and holes in the TiO$_2$ catalysts, and various electron–hole recombination processes at the surface or in the bulk of TiO$_2$ [8–11]. Generation of the holes and electrons and subsequent oxidation and reduction reactions may be written as follows:

TiO$_2$ + $h\nu$ → e$^-$ + h$^+$ (surface on TiO$_2$)

Electron reaction: e$^-$ + O$_2$ → O$_2$$^{\bullet-}$ (super oxide radical)

2O$_2$$^{\bullet-}$ + 2H$_2$O → 2$^\bullet$OH + 2OH$^-$ + O$_2$

Surface reaction: h$^+$ + OH$^-$ → $^\bullet$OH

Most of photocatalysts have been used as a fine powder form which has strong oxidative power of photogenerated holes on the surface. However, it has several problems as follows [8,9]:

1. Separation of the catalyst from the suspension after the reaction is difficult.
2. The suspended particles tend to aggregate at high concentrations.
3. The amount applied is small and limited.
4. When the catalyst is coated on some supports, detachment from the supports easily occurs in the liquid phase.

To avoid these problems, TiO$_2$ thin films with high photocatalytic activity have recently been prepared by the sol–gel method [9–13] and the MOCVD method [14,15], and applied to various reactions [16–20]. According to some reports [12–16], it was observed that the films exhibit higher photocatalytic activity than the powders.

As a synthesis method of thin-film photocatalysts from colloidal solutions, the sol–gel method has almost exclusively been used until now [12–15]. However, the sol–gel derived precipitates are amorphous in nature, requiring further heat treatment (calcination) at a high temperature to induce crystallization. The calcination process gives rise to particle agglomeration and grain growth and hence may induce undesirable phase transformation [12–20]. Therefore, development of a process

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without the calcination step for crystallization may be more favorable.

In the conventional sol–gel and hydrothermal method, the amount of water added has usually been quite large, i.e., more than 4 mol of water per mole of Ti in the precursor, or excess water has often been employed. In the solvothermal method, generally no water has been added. In this work, however, we introduced a solvothermal method using a smaller amount of water to obtain a colloidal solution for synthesis of a TiO_2 thin film photocatalyst, and compared it with another TiO_2 thin film photocatalyst prepared from the colloidal solution obtained by a sol–gel method. In addition, decomposition of $CHCl_3$ over the TiO_2 photocatalysts coated on a γ-alumina support and glass beads was investigated.

2. Experimental

2.1. Catalyst preparation

The preparation procedures for the TiO_2 thin films are shown in Fig. 1. Reagents used for preparation of the gel mixture were as follows: titanium-tetraisopropoxide (99.99% TTIP, Junsei Chemical, Japan) and ethyl alcohol(Junsei Chemical, Japan) and 1-butyl alcohol (Junsei Chemical, Japan) were used as the TiO_2 source and the solvent, respectively. Distilled water and concentrated hydrochloric acid (35%, Junsei Chemical, Japan) were used to induce the hydrolysis in the mixture.

The procedure for the sol–gel method employed in this work was similar to a conventional one, but the amount of water added was quite smaller (0.15 ml) than that in other works. A homogeneous sol, or colloidal solution, could be obtained after a few hours of vigorous stirring. A thin film was prepared by subsequent coating, drying, and calcination process. The sample obtained by this method was designated as Cat. 1.

In the solvothermal method, 14.2 ml of TTIP was dissolved in 100 ml of 1-butyl alcohol and then 0.15 ml of water and a few drops about 1.0 ml of the concentrated hydrochloric acid were added. In fact, in order to synthesize the TiO_2 powder, the stoichiometric amount of water needed is 3.5 ml for 14.2 ml TTIP. The total added amount of water was around 0.85 ml, and this corresponds to one-fourth of
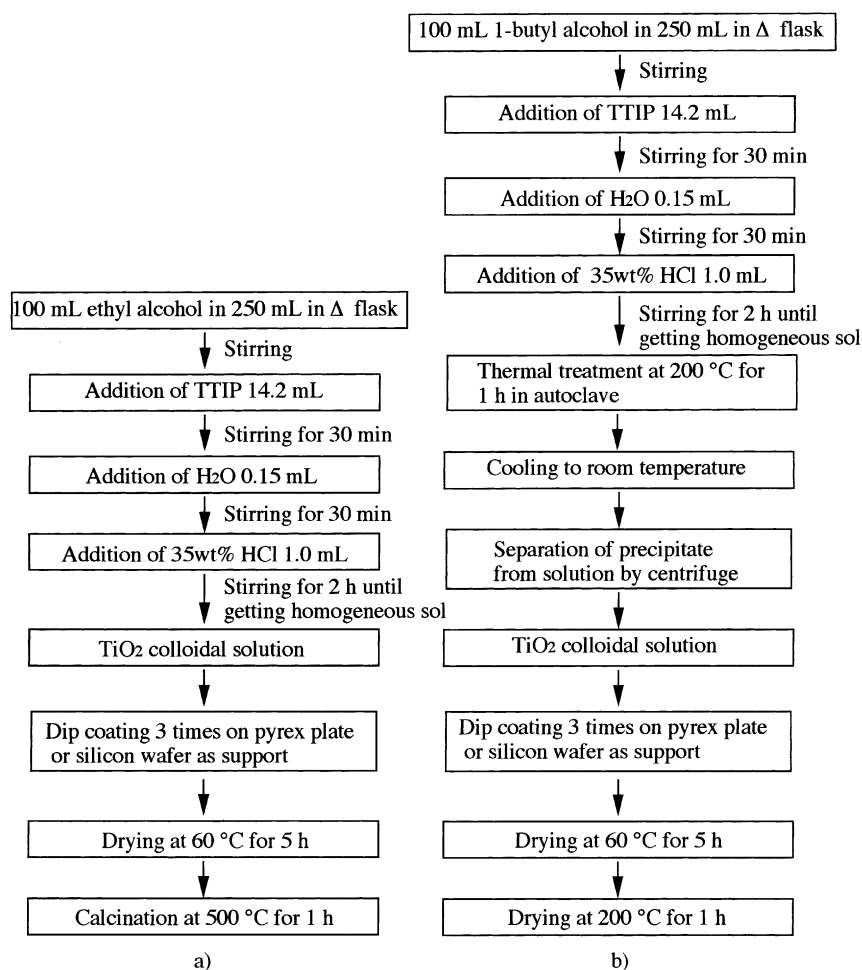

Fig. 1. Preparation of TiO_2 photocatalyst thin films: (a) sol–gel method (Cat. 1) and (b) solvothermal method (Cat. 2).

the stoichiometric amount. The mixture was placed in an autoclave and heated to 200°C with a rate of 5°C/min, and then the temperature was kept constant for 50 min. During the thermal treatment, the autogeneous pressure was 20 atm and TTIP was believed to be hydrolyzed by OH groups in water and 1-butyl alcohol. A very small amount of precipitate was formed during the process, and then it was removed by centrifuge, but the precipitate was almost invisible by naked eyes. The synthesized colloidal solutions were used as the coating solution. The sample obtained by this method was designated as Cat. 2.

For the characterization, thin films were prepared on a pyrex plate and a silicon wafer by dip-coating of three times. To prepare the catalysts for the CHCl$_3$ decomposition, each solution (30 ml colloidal solution, about 5% particle) was coated on 10.0 g of glass beads (diameter: 2 mm, granule type, Junsei Chemical, Japan) or 10 g of γ-alumina (diameter: 2 mm, granule type, Junsei Chemical, Japan) by mixing and then the same subsequent treatment as shown in Fig. 1.

2.2. Film characterization

The prepared thin films, both before and after calcination, were characterized by powder X-ray diffraction (XRD) analysis (Model PW1830 from Philip) with nickel-filtered Cu Kα radiation (40 kV, 60 mA) and the 2θ range from 5 to 70°. The scan speed was 10°/min and the time constant was

1 s. The diffraction angle of 25.0° was selected to discuss the crystallinity of the samples.

The size, shape, and coated film thickness of the particles were observed by a scanning electron microscope (SEM; Model JSM35CF-JEOL). The power and working distance were 15 kV and 39 cm, respectively.

The particle size distribution of the samples in collidal solution was observed by dynamic light scattering (DLS) spectrophotometer (Photal Otsuka Electronics) right after ultrasonic wave treatment with 140 W for 2 min.

UV–visible spectra were recorded by a Shimadze MPS-2000 spectrometer and the scan range was from 200 to 700 nm.

2.3. Chloroform decomposition

The decomposition of CHCl$_3$ was carried out by using a stationary closed system shown in Fig. 2. The TiO$_2$ photocatalysts of 3.0 g coated on the glass beads or γ-alumina was charged into the stainless steel square reactor with the dimension of 21 cm × 15 cm × 7 cm, which contained 1000 ppm of CHCl$_3$ in 600 ml of distilled water. In addition, the catalysts were compared with Degussa P-25 well known as a commercial photocatalyst with high activity. Degussa P-25 of 5 wt.% was dispersed in ethyl alcohol of 100 ml, and then this solution was coated on γ-alumina.
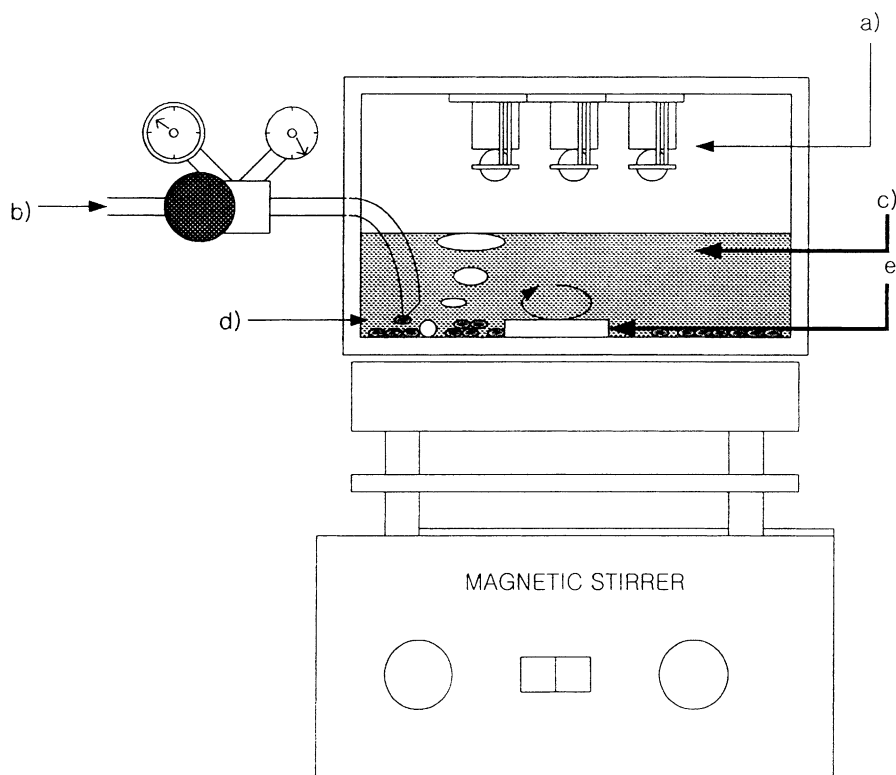

Fig. 2. Stationary reactor apparatus for CHCl$_3$ decomposition: (a) UV-lamp (8 W × 3350–400 nm); (b) air bubbling (500 ml/min); (c) CHCl$_3$ solution (1000 ppm, 600 ml); (d) Cat. (3 g with support/l); and (e) stirrer.

Three UV-lamps (Model BBL, 254 nm, 8 W, length 20 cm × diameter 1.5 cm, Shinan, Korea) and air bubbling of 500 ml/min were employed in a dark condition.

The reaction product was analyzed by an FID-type gas chromatography. An HP-624 column was used for analysis of $CHCl_3$ remaining in the reaction solution. The GC analysis conditions were as follows; injection temperature 120°C, initial oven temperature 70°C, final oven temperature 150°C, detector temperature 250°C, and split ratio 10:1.

3. Results and discussion

3.1. Properties of catalysts

XRD patterns of TiO_2 thin films coated on a pyrex plate are shown in Fig. 3. As shown, Cat. 1 before calcination appeared to be almost amorphous with a very broad small peak around 21.08. Therefore, to obtain the anatase structure, Cat. 1 had to be treated at 500°C for 1 h. On the contrary, Cat. 2 prepared from the hydrothermal method was observed to have the anatase structure, showing the presence of a peak at 25.0° which is the major peak for the anatase structure. In general, it was well known the anatase type could be formed above 300°C. However, the crystallization temperature is different with the synthesis conditions. In this study, the crystallization rate might be enhanced by the thermal
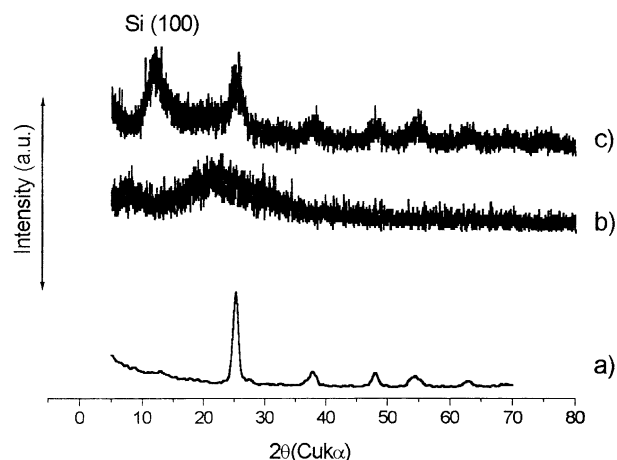

Fig. 3. XRD patterns of TiO_2 thin films coated on a pyrex plate: (a) TiO_2 powder with anatase structure; (b) Cat. 1 before calcination; and (c) Cat. 2.

treatment (pressure of 20 atm). As this result, the TiO_2 film with anatase structure was formed at 200°C.

The SEM photographs are shown in (a) and (b) of Fig. 4. To investigate the effect of thermal treatment, both Cat. 1 and Cat. 2 were heat treated at 500°C for 1 h. The film thickness of Cat. 2 was 200 nm and this was much thinner than the thickness of 5 μm of Cat. 1. In addition, the film of Cat. 2 was very uniform, and was almost unchanged after the
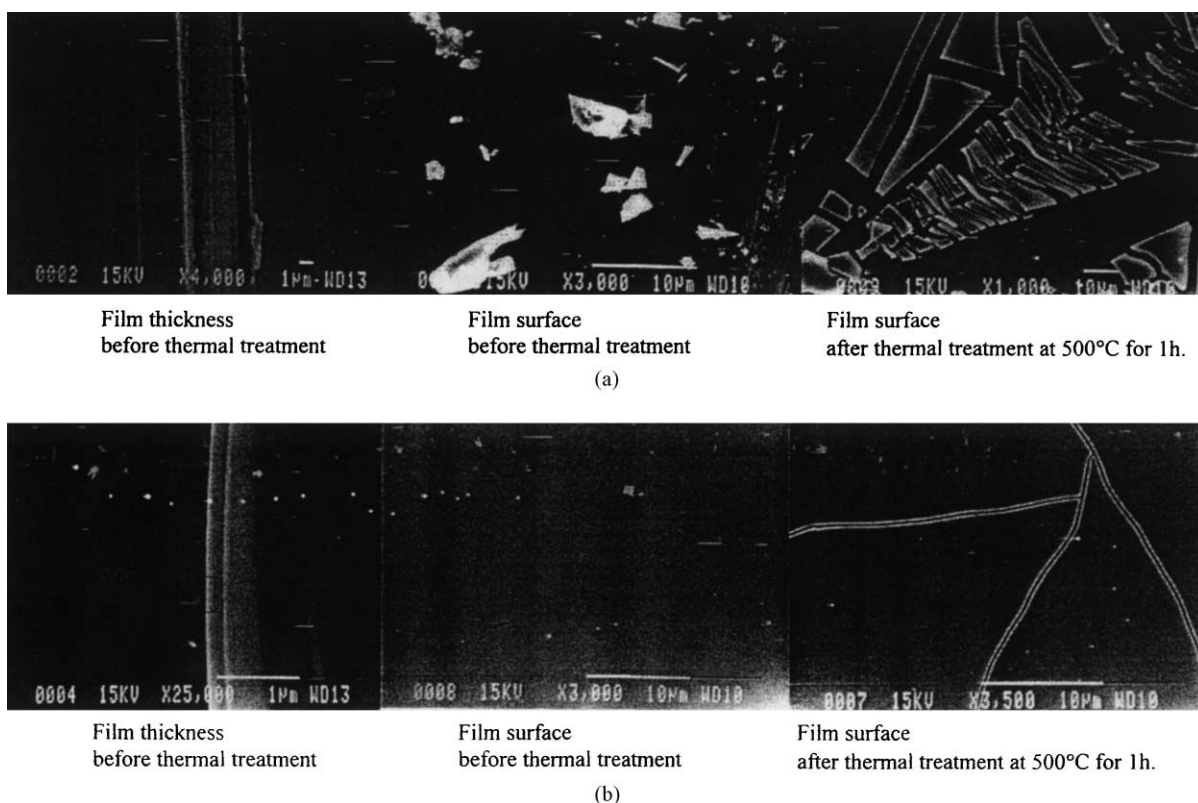

Film thickness before thermal treatment

Film surface before thermal treatment

Film surface after thermal treatment at 500°C for 1h.

(a)

Film thickness before thermal treatment

Film surface before thermal treatment

Film surface after thermal treatment at 500°C for 1h.

(b)

Fig. 4. SEM photographs of TiO_2 thin films coated on a silicon wafer before and after thermal treatment 500°C for 3 h: (a) Cat. 1 and (b) Cat. 2.
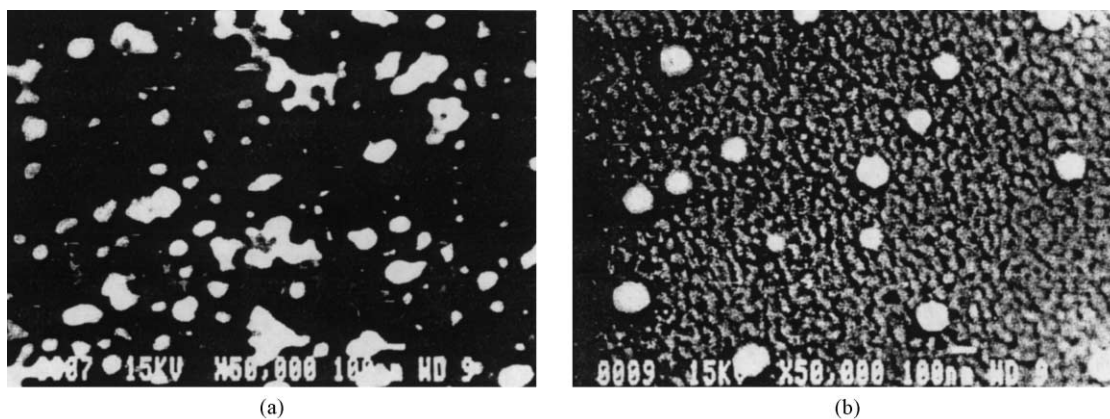
Fig. 5. The shape and size of TiO$_2$ photocatalysts coated on a pyrex plate observed by SEM photographs: (a) Cat. 1 (after calcination) and (b) Cat. 2 (after drying).

thermal treatment, except that some cracks were formed. On the other hand, the film of Cat. 1 was not uniform, and after the thermal treatment, it was so unstable that the film was shattered into small pieces and readily detached or peeled off the wafer. In general, when the TiO$_2$ film was prepared by sol–gel method, some binders were added to colloidal solution for stable fixation on a substrate. Added binders are easily lumped with the TiO$_2$ colloidal particle. In addition, the remained binders after calcination forms byproduct in VOC decomposition. From this result, the photocatalytic performance of the TiO$_2$ film decreases. To avoid this problem, some binders was not used in this study. The result was that the TiO$_2$ film was easily taken off on substrate. This result shows that the hydrothermal method for the preparation of thin films was a very reliable method compared with the sol–gel method.

In fact, we had prepared a thin film by the solvothermal method without adding the water at all. However, the film thus obtained had poorer properties, i.e., more cracks were formed after the thermal treatment and the film was easily detached and pealed off from the plate; in addition, the film surface appeared to be hydrophobic so that water droplets were formed on the surface. Therefore, the investigation for this films was not carried out further.

In Fig. 5, morphologies of the TiO$_2$ particles coated by dipping one-time on the pyrex plates are shown. To get the anatase structure, Cat. 1 was thermally treated at 500°C for 1 h. As shown in this figure, the particles of Cat. 2 were fairly uniform and spherical with 50–100 nm size, but the particles of Cat. 1 after calcination were irregular and the size distribution was wide, ranging from 30 to 200 nm.

Distributions of the TiO$_2$ particle size in the film determined from DLS are shown in Fig. 6. In case of Cat. 2, the particles were distributed sharply at around 220 and 620 nm, which those of Cat. 1 were distributed from 1000 to 1400 nm. This is consistent with the results in Fig. 5.
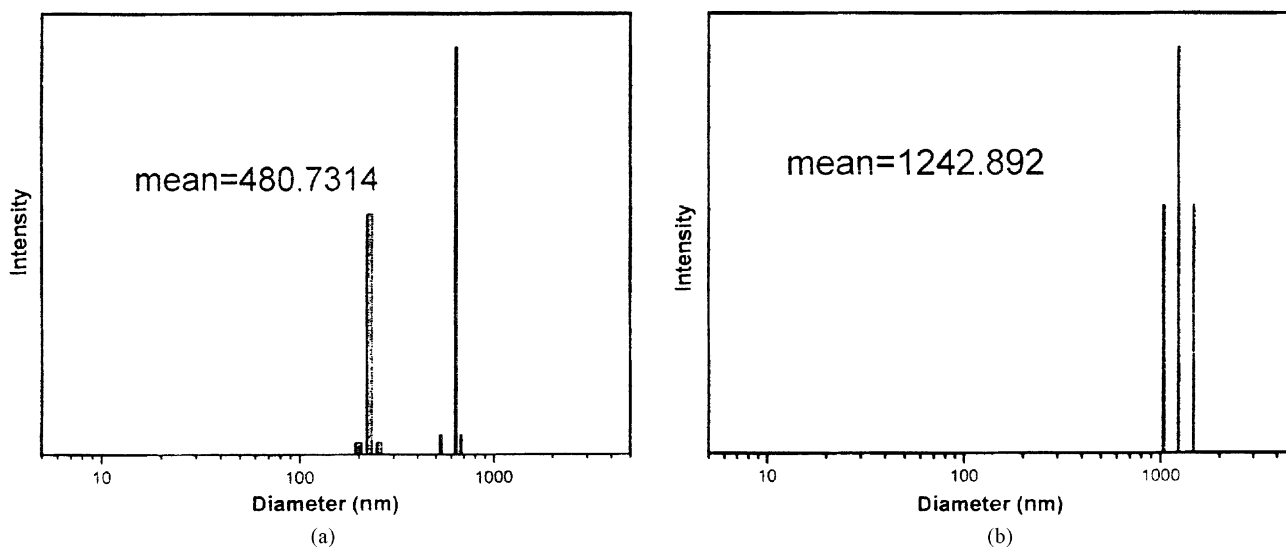

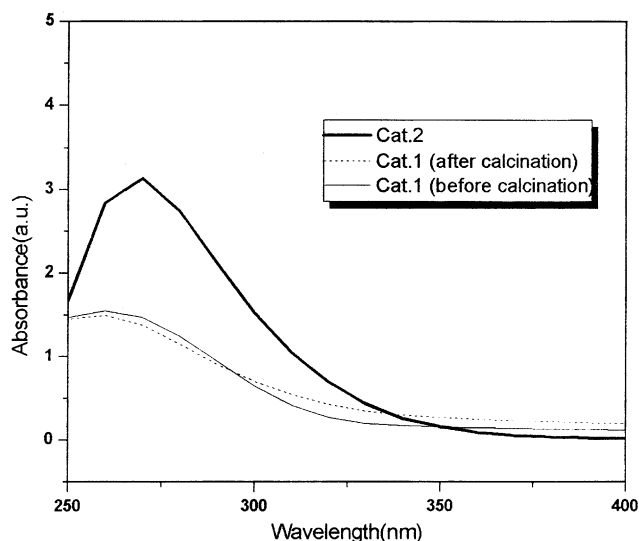Fig. 6. Distribution of particle size in TiO$_2$ thin films determined by DLS: (a) Cat. 2 and (b) Cat. 1.

Fig. 7. UV–visible spectra for TiO_2 thin films coated on a pyrex plate.

Fig. 8. Decomposition of $CHCl_3$ in O_2 bubbling or UV-light: reaction conditions: initial reaction mixture composition: 1000 ppm $CHCl_3$ in 600 ml distilled water; UV-light intensity: 254 nm, 8 W × 3; and air bubbling: 500 ml/min.

In Fig. 7, UV–visible spectra of the samples coated on the pyrex plates are presented. In general, the absorption by Ti^{4+} ions occurs below 370 nm with the maximum at 260–270 nm [21]. As shown, the absorption intensity of TiO_2 in Cat. 2 was stronger and the band shifted to longer wavelength than those of Cat. 1. This result illustrates that the hydrothermal method is more useful than the sol–gel method to obtain TiO_2 with the anatase structure.

3.2. Catalytic performance for chloroform decomposition

Photocatalytic oxidation of organic compounds is of considerable interest for environmental applications, particularly for some specific compounds containing chlorine such as 4-chlorophenol, pentachlorophenol, trichloroethylene (TCE), perchloroethylene (PCE), CCl_4, $CHCl_3$, CH_2Cl_2, vinyl chloride, p-chlorobenzene, and so on. These are widespread in soil and ground water. In this study, $CHCl_3$ was selected as a test compound.

Fig. 8 shows the conversion of $CHCl_3$ decomposition in conditions of only UV-light and O_2 bubbling. Surprisingly, decomposition of $CHCl_3$ could occur only under the presence of UV-light and air bubbling without the catalyst. As shown, $CHCl_3$ was decomposed in only UV-light and O_2 bubbling, and the conversions were 20 and 45% after 120 min, respectively. In particular, in O_2 bubbling/UV-light condition, the conversion more increased compared with those in only UV-light and O_2 bubbling. The conversion was up to 70% after 120 min.

In Fig. 9, the catalytic performance test data for $CHCl_3$ decomposition are presented. Over Cat. 2 coated on the γ-alumina, $CHCl_3$ was decomposed so rapidly that the conversion of 90% was achieved in just 10 min and almost complete decomposition could be obtained in 1 h. The performance of coated Cat. 1 was inferior to that of Cat. 2.
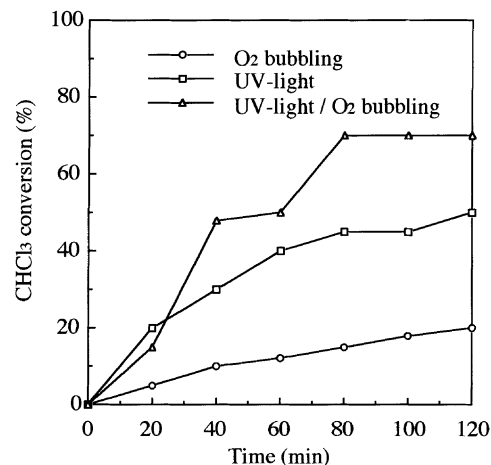
This may be attributable to the presence of more appropriated phase of TiO_2 for the photocatalytic activity in Cat. 2. On the other hand, the performance of the catalysts coated on the glass beads, was poorer compared with the catalysts coated on the γ-alumina. The reason for this is considered due to a larger surface area of TiO_2 coated on the γ-alumina than that on the glass beads since γ-alumina has a much larger surface area [16].

On the other hand, the solution of Degussa P-25 of 5 wt.% was coated on γ-alumina, and then $CHCl_3$ decomposition reaction was done over this catalyst. Fig. 10 compares performances between Cat. 2 and Degussa P-25 in same conditions. As shown, the decomposition of $CHCl_3$ was higher over Cat. 2 than Degussa P-25, and the conversions
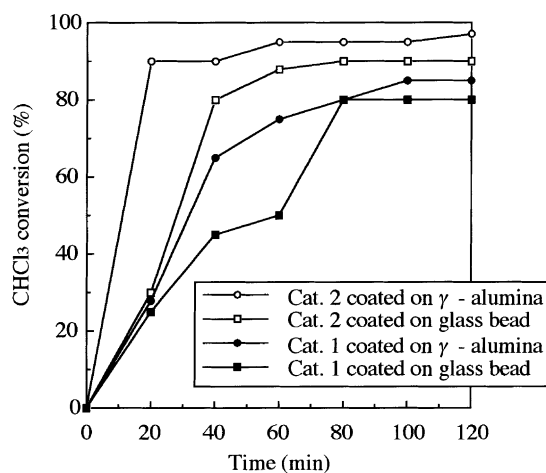

Fig. 9. Performance of TiO_2 photocatalyst thin films coated on γ-alumina and glass beads for $CHCl_3$ decomposition: reaction conditions: Cat. weight: 3.0 g including the support; initial reaction mixture composition: 1000 ppm $CHCl_3$ in 600 ml distilled water; UV-light intensity: 254 nm, 8 W × 3; and air bubbling: 500 ml/min.
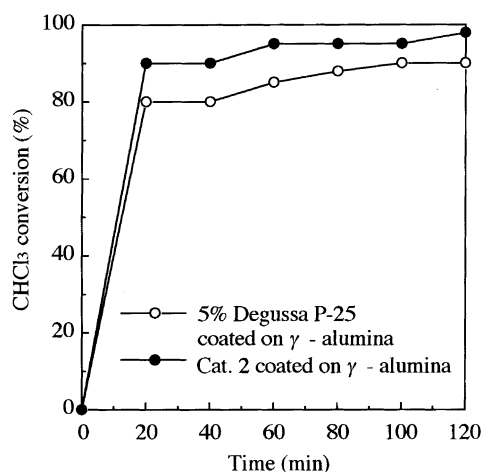
Fig. 10. Comparison of $CHCl_3$ decompositions over Cat. 2 and Degussa P-25: reaction conditions: Cat. weight: 3.0 g including the support; initial reaction mixture composition: 1000 ppm $CHCl_3$ in 600 ml distilled water; UV-light intensity: 254 nm, 8 W × 3; and air bubbling: 500 ml/min.
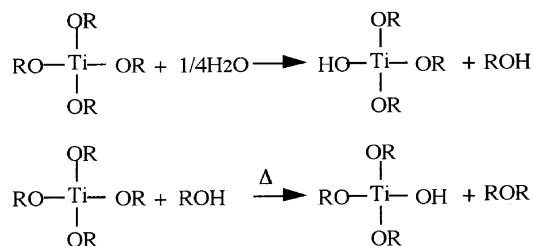
were 95 and 90% after 120 min over Cat. 2 and Degussa P-25, respectively. From these results, it was confirmed that the TiO_2 photocatalyst film prepared by the hydrothermal method was very useful for photodegradation of $CHCl_3$ pollutant.

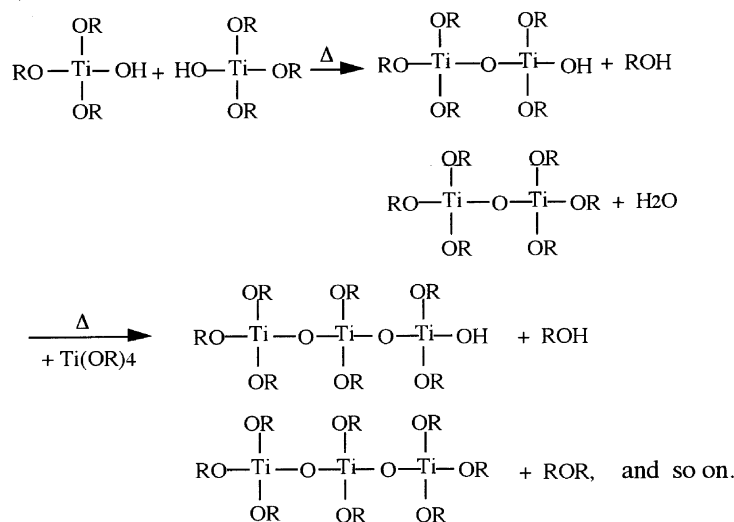### 3.3. Expectation for TiO_2 fine particles in organic solution

The hydrothermal processing provides for excellent chemical homogeneity and the possibility of driving unique super stable structures at medium reaction temperatures. It may suggested that the thermal treatment involves the formation of metal-oxo-polymer network from the metal alkoxide with addition of water.

At the first step, the metal alkoxides may be partially hydrolyzed since the amount of added water was small. Generally, the water amount of 4 mol per Ti precursor of 1 mol needs for hydrolysis in hydrothermal method or sol–gel method. The colloidal solution is progressed to the $Ti(OH)_4$ phase, and then it is transferred to TiO_2 amorphous powder by drying. However, to synthesize the film solution, only the partial OR-terminal groups of Ti precursor, one or two OR-terminal groups, must be hydrolyzed. And then it is transferred to $(Ti(OH)_2(OR))_n-$ by the partial condensation. Subsequently, dimers may be formed by the condensation under a mild thermal treatment. At this point, if the water is not present, the solution is unstable against air or moisture. Otherwise, if the much water is added, the solution is immediately transferred to a precipitate of $Ti(OH)_4$. The condensation may proceed further as shown in Scheme 1, and Ti-oligomers can be gener-

Scheme 1. Expected scheme for TiO_2 fine particles in organic solution: (1) partially hydroxylation and (2) condensation — dimer, oligomer.

ated in the colloidal solution. It may be postulated that liner oligomers are dominant but two- or three-dimensional networks are difficult to form. The condensation does not seem to proceed to a great extent so that the precipitation occurs. The final oligomer solution is stably attached to substrate, and then the TiO_2 anatase film is attained by calcination (drying) at 200°C. Such oligomers are considered to play a favorable role on the formation of the stable thin film.

4. Conclusion

Colloidal solutions of TiO_2 could be obtained by adding a minimal amount of water and employing either the sol–gel method or the solvothermal method. A thin film obtained from the colloidal solution prepared by the solvothermal method (Cat. 2) was identified to have the anatase structure, even though it was dried just at 200°C for 1 h. On the contrary, another film obtained via the sol–gel method was amorphous, and a heat treatment at 500°C for 1 h was needed to get the anatase structure. The particles in the film of Cat. 2 was smaller ($\sim$100 nm) and more uniform than those of Cat. 1. A much thinner film of Cat. 2 could be obtained compared with Cat. 1. Moreover, the film of Cat. 2 remained stably attached on a silicon wafer or a pyrex plate. After a heat treatment at 500°C for 1 h, the film of Cat. 1 was shattered into pieces and easily detached. Cat. 2 coated on a γ-alumina exhibited excellent performance for $CHCl_3$ decomposition under UV-light with O_2 bubbling. When using this catalyst, a conversion of 90% was obtained in 10 min, while without the catalyst a conversion of 70% was obtained after 1 h. Cat. 2 coated on glass beads and Cat. 1 coated on glass beads and γ-alumina showed poorer performance.

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