

Preparation of TiO₂ film by the MOCVD method and analysis for decomposition of trichloroethylene using in situ FT-IR spectroscopy

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Abstract

MOCVD (molecular organic chemical vapor deposition) method was demonstrated in this study to prepare TiO₂ thin film of anatase structure with high photo-activity. From the results of characterization of XRD and SEM spectroscopy, it was identified that a TiO₂ thin film exhibited pure anatase structure and it was stably attached on a substrate. To investigate the photo-catalytic performance of the TiO₂ film, the trichloroethylene (TCE) decomposition was done. The conversion of TCE remarkably increased over the TiO₂ film synthesized by CVD method compared with that of TiO₂ film prepared by Degussa P-25 colloidal solution, in particular, the conversion over TiO₂ film synthesized by the CVD method reached above 90% after 120 min, otherwise, it was 85% over Degussa P-25 film. On the other hand, the intermediates produced from TCE decomposition were investigated by in situ method using a FT-IR spectroscopy. As a result, it was confirmed that TCE was transferred into dichloroacetylchloride (DCAC) and trichloromethane (CHCl₃) in transition state, and then, finally, it turned to CO₂, HCl, and H₂O. In addition, the addition of H₂O enhanced TCE decomposition. However, it was not affected to mechanism of TCE photo-catalytic decomposition.

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1. Introduction

The world has to manage a tremendous set of environmental problems, and thus extensive research activities are carried on advanced chemical, biochemical, and physicochemical methods for elimination of

hazardous chemical compounds from air and water [1–4]. In this field, many works have been done on the photo-catalytic treatment of environmental pollutants using semiconductors like TiO₂, Fe/Ti, and Zn/Ti etc. In particular, titanium dioxide (TiO₂) has many applications: as photo-catalysis [5,6], dielectric materials and optical-coating materials. When a semiconductor of TiO₂ absorbs a photon and then is promoted to an excited state, an electron is transferred from valance band to the conduction band where it can function as a reducing moiety, leaving a hole

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in the valence band that is a strong oxidizing entity. This photo-degradation reaction was very useful in environmental technology because of elimination the secondary pollutants.

On the other hand, the powder type was generally used as a type of TiO_2 as the photo-catalyst. However, it has several problems as follows [7,8]: (1) separation of the catalyst from 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) coated catalysts are easily detached from the supports. To avoid these problems, TiO_2 thin films have recently been prepared by many methods. TiO_2 thin film has been prepared by sputtering [9], sol-gel [10–12], and chemical vapor deposition (CVD) [13–16] methods. Among these techniques, the CVD method is most useful because a thin film with a high quality, high uniformity and well-controlled properties can be attained. CVD has several important advantages, which make it the preferred process in many cases. These can be summarized as follows:

1. It is not restricted to a line of sight deposition, which is a general characteristic of sputtering, evaporation and other PVD processes. As such, CVD has high throwing power. Deep recesses, holes, and other difficult three-dimensional configurations can usually be coated with relative ease. For instance, integrated circuit via holes with an aspect ratio of 10:1 can be completely filled with CVD tungsten.
2. The deposition rate is high and thick coatings can be readily obtained (some cases centimeters thick) and the process is generally competitive and, in some cases, more economical than the PVD processes.
3. CVD equipment does not normally require ultrahigh vacuum and generally can be adapted to many process variation. Its flexibility is such that it allows many changes in composition during deposition and the codeposition of elements or compounds is readily achieved.

CVD, however, is not the universal coating panacea. It has some disadvantages, a major one being that it is most versatile at temperature of 600 °C and above; many substrates are not thermally stable at these temperatures. However, metallo-organic CVD partially offsets this problem. Another is the requirement

of high vapor pressure and removal of by-products generated in CVD reaction.

Of great significance are the recent findings of Fujishima et al. [17,18], that some semiconductors also exhibited a photo-induced super hydrophilic effect. They are rendered more wettable by water after exposure to ultra-band gap irradiation and that this process is reversible, in the dark. In particular, as the most recent, nanocrystalline films of titania can be produced by the commercially more established process of CVD [14,15]. In these papers, the TiO_2 coated on silica gel particles by CVD method was used. The product is a readily filtered powder photo-catalyst that can be used in a flow system. However, these properties were regarded in academic literature area. This is the more striking given the recent announcement by the major glass manufacturer, Pilkington Glass,¹ i.e. ActivTM, the active ingredient of which is a 20 nm coat of titania deposited by an atmospheric pressure CVD technique, APCVD.

On the other hand, in the case of surface reaction, the simply mechanisms of decomposition of pollutant were reported by many researchers [19,20]. However, some of them are still not clear, in addition, the application is limited because the performances observed were very low. Therefore, if the products are detected in photo-destruction reaction, the mechanism could be resolved and extended to other applications. In this study, trichloroethylene (TCE) was exemplified. There has been active interest in the photo-oxidation of TCE using TiO_2 [19,20]. As a widely used solvent in industrial processes, TCE is most common and abundant pollutant in ground water. Since oxidation rates are typically orders of magnitude higher in the gas phase than in aqueous solution, an approach that strips the TCE from water stream is being considered. Thus, the study of the TiO_2 photo-oxidized oxidation of TCE is practically useful. In addition, various mechanisms are currently proposed for TCE photo-oxidation on the TiO_2 surface. As examples, Pruden and Oilis [21] suggested that hydroxyl radicals initiate the reaction, and that dichloroacetaldehyde in an intermediate. And Phillips and Raupp [22] reported that hydroxyl radical or hydro peroxide radical initialized the reaction and involved dichloroacetaldehyde as an intermediate. In addition, Anderson et al. [23] proposed a mechanism

¹ <http://www.pilkington.com>.

involving hydroxyl radicals and monochloroacetate as intermediates.

In this study, MOCVD (molecular organic chemical vapor deposition) method was introduced to prepare TiO₂ thin film. To investigate the photo-catalytic performance of the TiO₂ film, the trichloroethylene decomposition was done. In addition, the intermediates produced from TCE decomposition were investigated by in situ method using a FT-IR spectroscopy in various conditions.

2. Experimental

2.1. Catalyst preparation

The schematic apparatus of CVD chamber are shown in Fig. 1. Reagents used for preparation of TiO₂ thin film were as follows; titanium tetra-isopropoxide (99.95%, TTIP, Junsei Chemical, Japan) was selected as a titanium precursor. As well known, when TiCl₄ was used as a precursor, the CVD equipment was

easily rusted because of volatilized Cl₂ gas. High purity O₂ was used as O₂ sources with a carrier gas of N₂. TTIP was vaporized at 50 °C. The growth conditions of TiO₂ film are as follows: substrate: glass plate or glass beads; TTIP/O₂ ratio: 1/5; annealing temperature: 500 °C; press: 10 Pa; RF power: 50 W.

2.2. Characterizations of synthesized catalyst

The synthesized samples were identified by powder X-ray diffraction analysis (XRD, model PW 1830 from Philips) with nickel filtered Cu K α radiation (30 kV, 30 mA) at an angle of 20°, θ ranges from 5 to 70°. The scan speed was 10°/min and time constant was 1 s. The diffraction angle of 25.0° was selected to discuss the crystallinity of the sample.

The particle size and shape of TiO₂ film catalyst were observed by scanning electron microscope (SEM, model JEOL-JSM35CF).

The chemical compositions were analyzed by ICP (inductively coupled plasma–AES). The analysis was carried out with the conditions of power 1.0 kW, pump

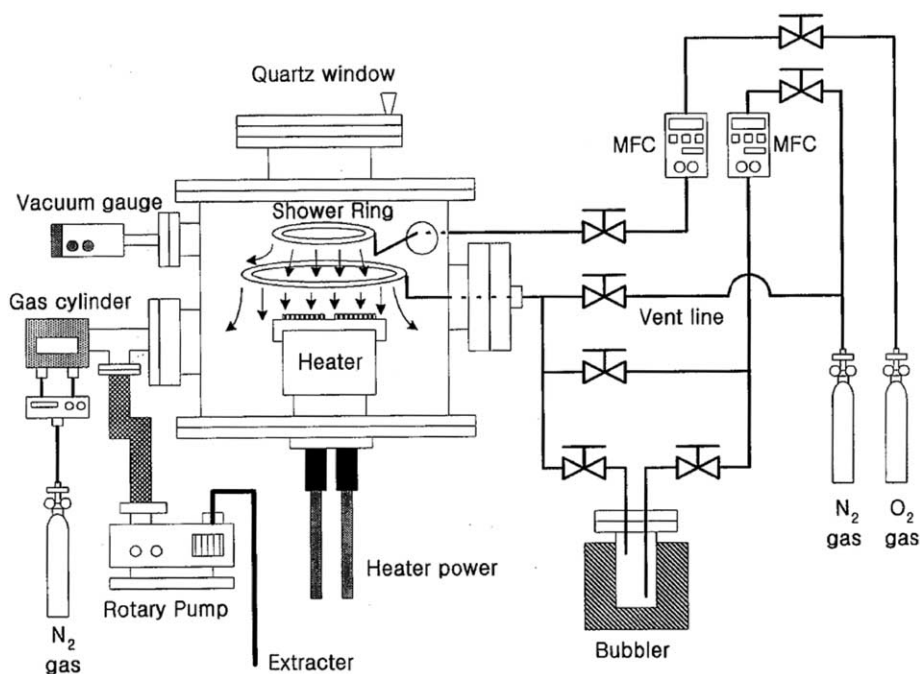


Fig. 1. The schematic apparatus of CVD chamber.

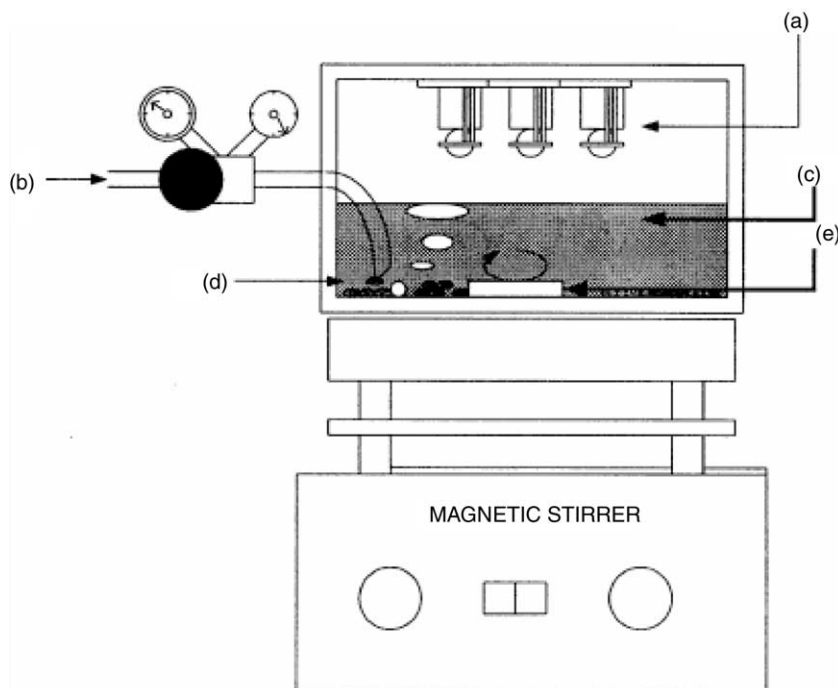


Fig. 2. A closed reactor apparatus for the decomposition of TCE. (a) UV lamp, (b) Air bubbling, (c) TCE solution, (d) Catalyst, and (e) Stirrer.

rate 1.0 ml/min, and coolant 13 l/min. The analyzed wavelength of Ti was 334.94 nm.

2.3. Reaction method and analysis of product for decomposition of TCE

The decomposition of TCE was carried out using a closed apparatus as shown in Fig. 2. 1.0 g of the catalysts (with substrates: glass beads or γ -alumina) was added into a stainless steel square reactor with the dimensions of 21 cm \times 15 cm \times 7 cm, and the reaction mixture was 1000 ppm TCE in 1000 ml of distilled water. The UV lamps (model BBL, 254 nm, 8 W \times 3, 20 cm length \times 1.5 cm diameter, Shinan Co., Korea) were used and the air bubbling was 500 ml/min. The reaction was done in the dark condition. The reaction solution was analyzed by a FID-type gas chromatograph (GC). A HP-624 column was used for the analysis of TCE remaining in the reaction solution. The GC operating conditions were as follows; injection temperature: 150 °C; initial temperature: 70 °C;

final temperature: 150 °C; detector temperature: 250 °C.

2.4. In situ method using a FT-IR spectroscopy

Fig. 3 shows an IR chamber apparatus used for the in situ FT-IR spectroscopy, which was manufactured in our laboratory. The FT-IR spectra were recorded as a Mattson 1000 spectrometer with room temperature by diffuse reflectance method. The TiO₂ film coated on γ -alumina by CVD method was pressed into a pellet form, and then it was set to IR quartz chamber with cylinder type as shown Fig. 3. Used UV-irradiation is a 15 W (254 nm) high-pressure mercury arc lamp (Shinan Co., Korea) and 1000 ppm TCE was flowed into the reactor. Used CHCl₃ (TCE) was purchased from Aldrich with a quoted minimum purity of 99.9%. The compound was transferred under nitrogen balance. Both of the added O₂ concentration and H₂O were 10% for the total gas amount. Before reaction, the pellet was kept at a temperature of 300 °C for 2 h

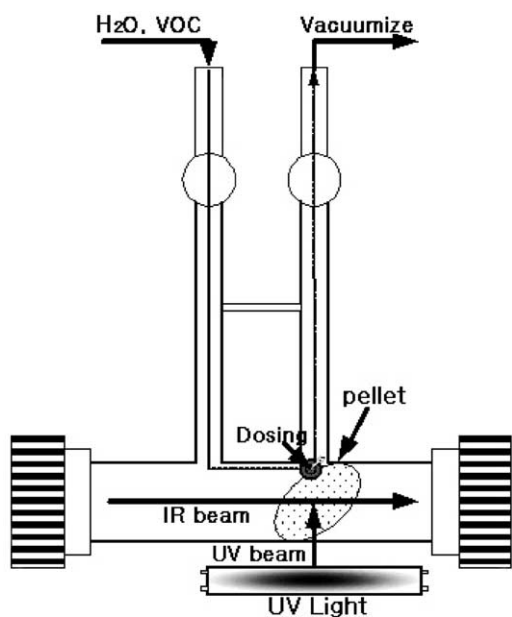


Fig. 3. An infrared chamber apparatus for the in situ FT-IR spectroscopy.

to diminish the influence of H_2O and then N_2 gas of balance gas was flowed to eliminate the effect of O_2 . The system was pumped at 1×10^{-8} Torr. The analysis of the TCE decomposition was done after 60 min to stabilize the reaction. A FT-IR spectrometer (RS-1, Mattson) was used for analysis of TCE decomposition. The scan range was from 400 to 3600 cm^{-1} , and 50 scans were accumulated so as to get 4.0 cm^{-1} resolution.

3. Results and discussion

3.1. Characterization

Fig. 4 shows the XRD pattern of synthesized TiO_2 film. In general, the TiO_2 photo-catalyst with anatase structure exhibited more high performance for VOC decomposition than that of other types, like rutile, brookite, and amorphous. Thus, the TiO_2 film in this study was annealed at 500°C to produce anatase structure. In general, the structure was changed with

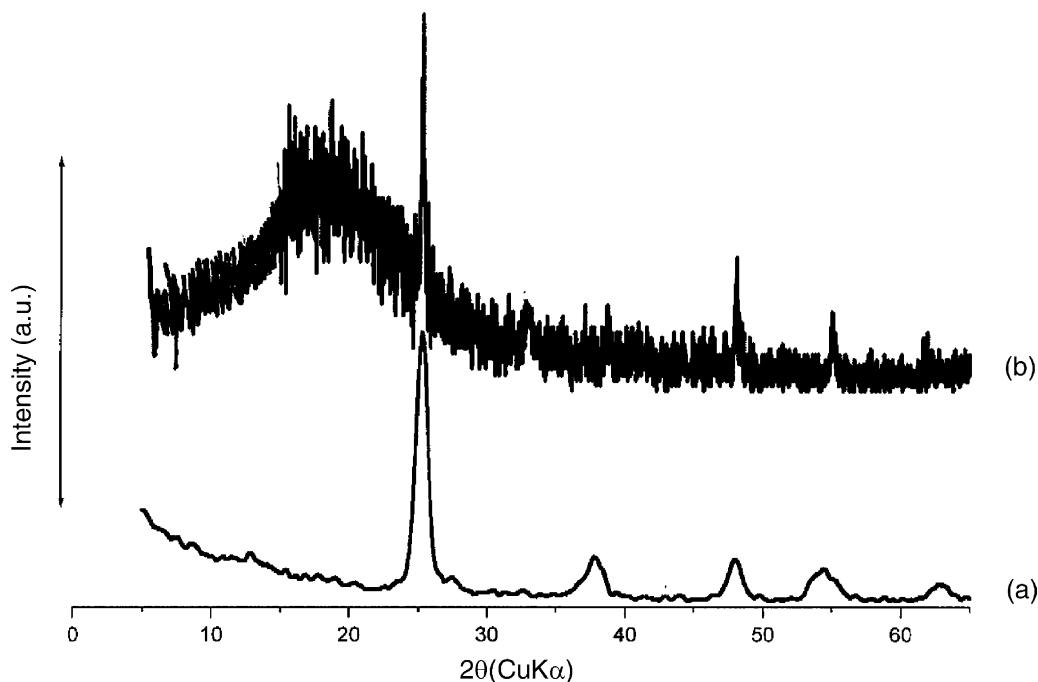


Fig. 4. XRD patterns of synthesized TiO_2 film. (a) Anatase structure of TiO_2 and (b) synthesized TiO_2 film.

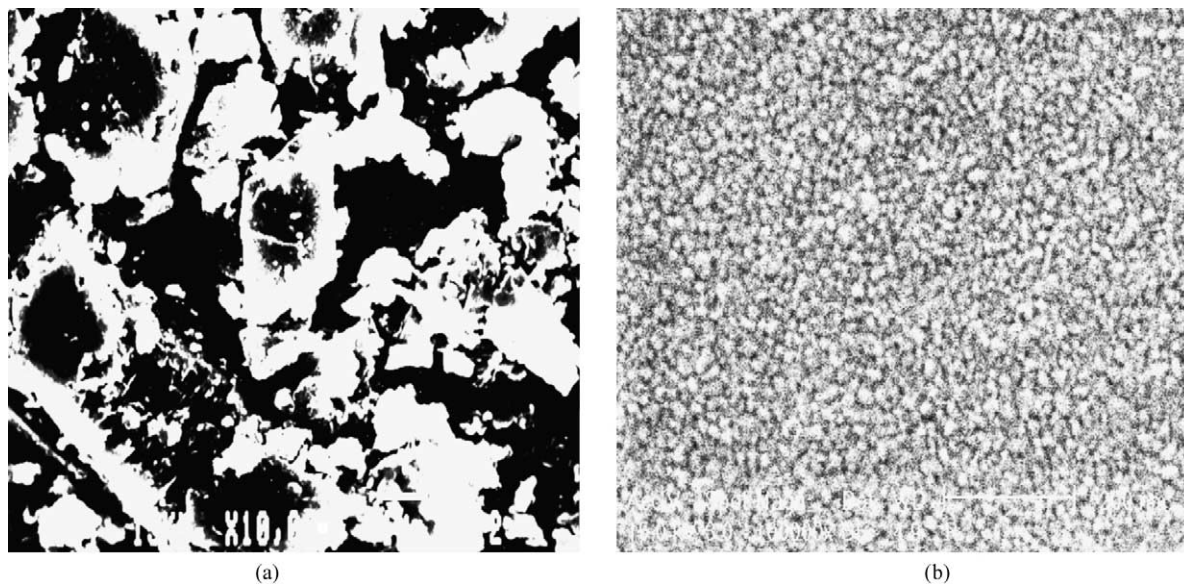


Fig. 5. SEM photographs of synthesized TiO_2 particle. (a) TiO_2 particle over γ -alumina and (b) TiO_2 particle over glass plate.

precursor species. The anatase structure generated near 350°C when TTIP was used as a precursor. Of course, the temperature may be low. However, the structure was also pure anatase without rutile part at 500°C . The structure was transferred to rutile form around 600°C in our experimental. Otherwise, when TiCl_4 was used as a precursor, the anatase structure was started at 300°C , and the intensity was the strongest at 450°C , and then the structure was transferred to rutile above 500°C . As shown, a sharp 25.0° peak, one of special peak for anatase structure, was displayed. And the XRD patterns of TiO_2 film coated on Pyrex slides include unstable base line with broad 20.0° band. On the other hand, it was identified that the amount of TiO_2 fixed on slide glass was about 1 wt.%, from the result of ICP and EDAX analysis.

The SEM photographs of synthesized TiO_2 film is shown in Fig. 5a). The TiO_2 was more stable when it was coated on γ -alumina than glass bead. The TiO_2 particles (white colored) existed in γ -alumina particles. However, the particle size could not calculated, because it was very irregular. And the atomic ratio of Al:Ti was 99.0:1.0 from the EDS analysis. To analyze TiO_2 particle size, the TiO_2 particle was coated on glass plate by CVD method with the same condition. As the result, it was identified that the particle size dis-

tributed around 20–50 nm. The SEM image was added in Fig. 5b).

3.2. FT-IR spectrums for decomposition of TCE in photo-catalytic system

Fig. 6a and b shows the IR-spectrum of TCE (CHClCCl_2) before reaction and the TCE decomposition in O_2 flowing/UV-radiation system. The assignments of observed bands are summarized in Table 1. As shown, bands of five types were observed: C–H band around 3100 cm^{-1} , C=C band around 1500 cm^{-1} , CH–Cl band around 1250 cm^{-1} ,

Table 1
The assignments of observed bands in Figs. 6 and 7

TCE	Infrared frequency (cm^{-1})	Compound	Infrared frequency (cm^{-1})
C–H	3166	CO_2	2358
	3097		
C=C	1585	DCAC	
	1555		
CH–Cl	1253	$\nu(\text{C}=\text{O})$	1711
C–Cl	979	COCl_2	1555
	943		
C–H	848	$\nu(\text{C}-\text{Cl}_2)$	

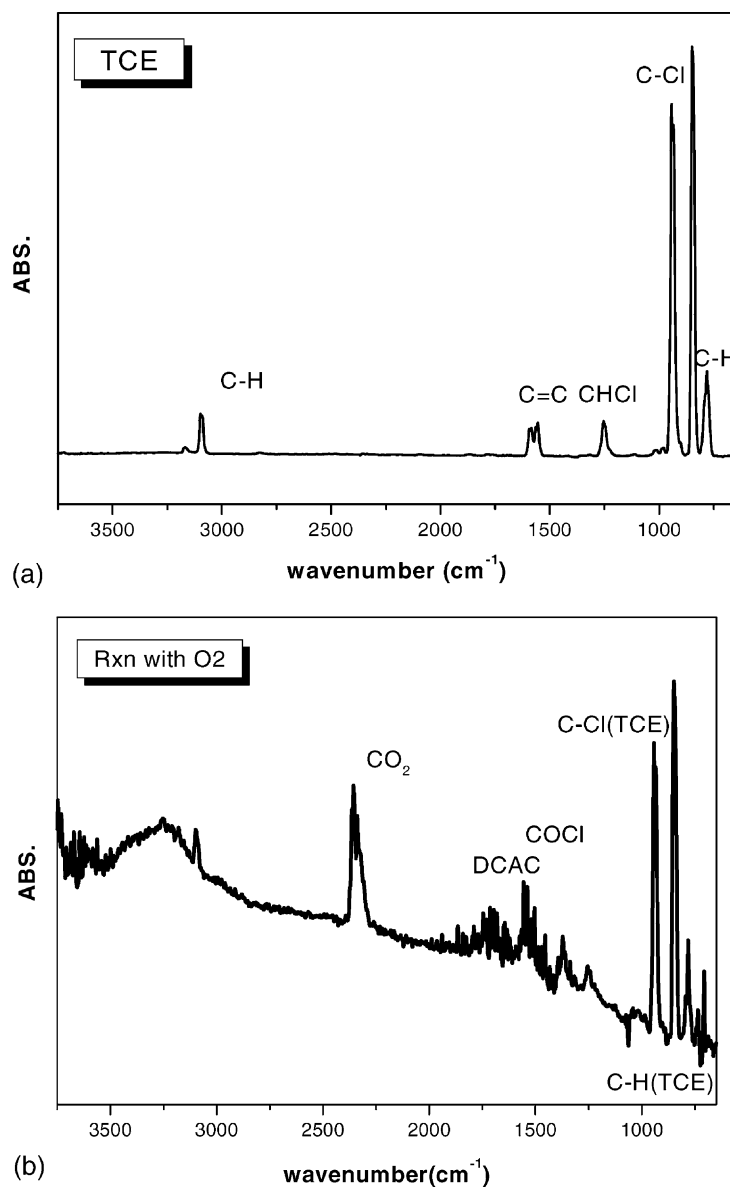


Fig. 6. IR-spectrum of TCE (CHCl_3) and TCE decomposition under O_2 flowing/UV-radiation system. (a) IR-spectrum of TCE (CHCl_3) before reaction and (b) TCE decomposition under O_2 flowing/UV-radiation system.

C–Cl band around 970 and 940 cm^{-1} , and finally C–H band around 840 cm^{-1} . The C–Cl bands of two types from TCE were very stronger than other bands. Though not mentioned in this figure, the TCE was not decomposed only in UV-radiation. However, under O_2 flowing/UV-radiation system, differently to a), new bands were observed as intermediates: C=O

band in CO_2 around 2300 cm^{-1} , the other C=O band in dichloroacetylchloride (DCAC), and C–Cl band in COCl_2 around 1550 cm^{-1} . These bands were resulted from TCE decomposition. This was ascribed that O_2 was broken by UV-radiation and it transferred into O radical, and then it oxidizes TCE without catalysts. On the other hand, with reaction time, the intensity of

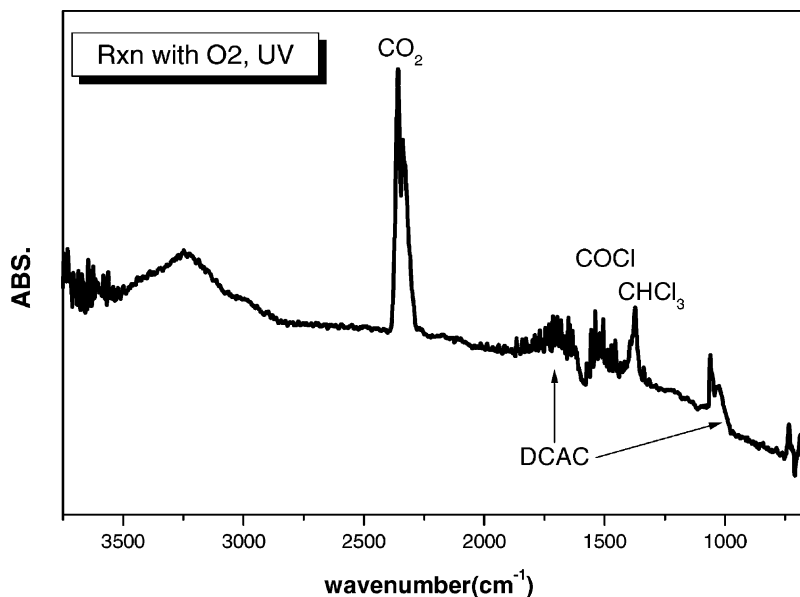


Fig. 7. TCE decomposition under UV-radiation/O₂ flowing/TiO₂ system.

these new bands increased, otherwise, the intensity of bands of CH–Cl around 1250 cm⁻¹ and C–Cl around 970 and 940 cm⁻¹ decreased. From these results, it was confirmed that the dichloroacetylchloride and carbon dioxide were produced as intermediates by TCE decomposition under O₂ flowing/UV-radiation.

Fig. 7 shows the TCE decomposition under UV-radiation/O₂ flowing/TiO₂ system. As shown, the CO₂ band was very strong; otherwise, the bands assigned to special bands from TCE as above mentioned were very weak. This result was ascribed to rapid decomposition of TCE. From this result, it was reconfirmed that the TCE decomposition with TiO₂ system more enhanced than that without TiO₂ catalyst. On the other hand, the appearance of CHCl₃ was expected from the increase of the intensity in CH–Cl band around 1250 cm⁻¹. If this band was only CH–Cl from pure TCE, the band must be decreased with reaction time. However, the band rather increased with reaction time. Thus, we confirmed that the CH–Cl band was attained from dichloroacetyl chloride as an intermediate by TCE decomposition.

Fig. 8a and b show the IR-spectrum for TCE (CHClCCl₂) with H₂O addition before and after reaction under UV-radiation/O₂ flowing/H₂O/TiO₂ system. And the assignments of observed bands are

Table 2

The assignments of observed bands in Fig. 8

H ₂ O	Infrared frequency (cm ⁻¹)	Compound	Infrared frequency (cm ⁻¹)
O–H (associated)	3251	CO ₂	
O–H (isolated)	3731	ν(C=O)	2353
		DCAC	
σ O–H (associate)	1100–1400	ν(C=O)	1712
		COCl ₂	
		ν(C–Cl ₂)	1556

summarized in Table 2. As shown, bands of five types were observed: O–H band (associated) around 3250 cm⁻¹, O–H band (isolated) around 3730 cm⁻¹, and O–H band (associated) around 1100–1400 cm⁻¹ were added. In general, the photo-catalytic performance was closely related to the amount of OH group. However, it was not found out whether the good or bad effect. As shown in b, the positions of all bands were the same to Figs. 6 and 7, but, the intensity of CO₂ band was stronger. These results show that the decomposition of TCE was enhanced by the addition of H₂O. This ascribed to the increase of hydroxyl radical produced by H₂O decomposition.

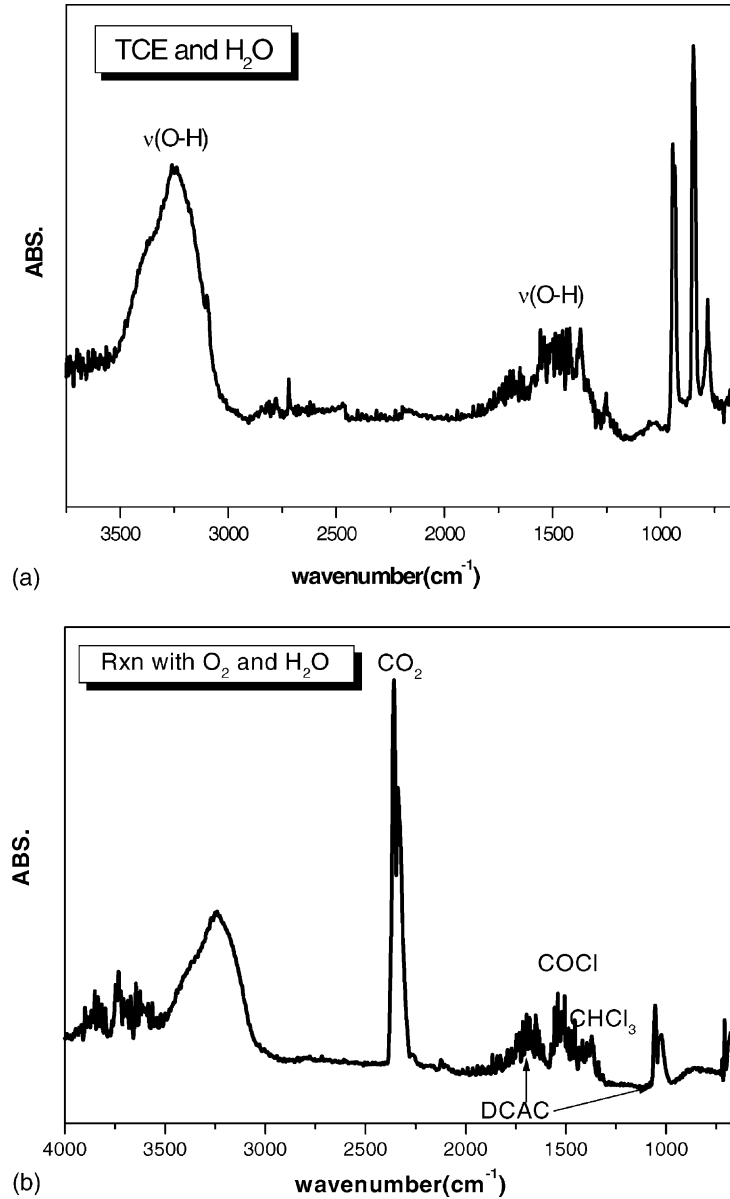


Fig. 8. Effect of H₂O addition on TCE photo-catalytic decomposition. (a) With H₂O addition before reaction and (b) Under UV-radiation/O₂ flowing/H₂O/TiO₂ system.

3.3. Performance of decomposition of TCE

Fig. 9 compares the performance of TCE decomposition over TiO₂ film (3 wt.% coated on glass beads) synthesized by CVD method and the Degussa P-25 film of 3 wt.%, which was attained from Degussa P-25

powder dispersed into ethyl alcohol of 100 ml and silicon binder of 1 wt.%, and then it was attached on glass beads. And the BET surface area was 60 m²/g with supporters in TiO₂ film by CVD method and it was 72 m²/g in Degussa P-25 film. To prepare Degussa P-25 film, used silica binder was a mixture of

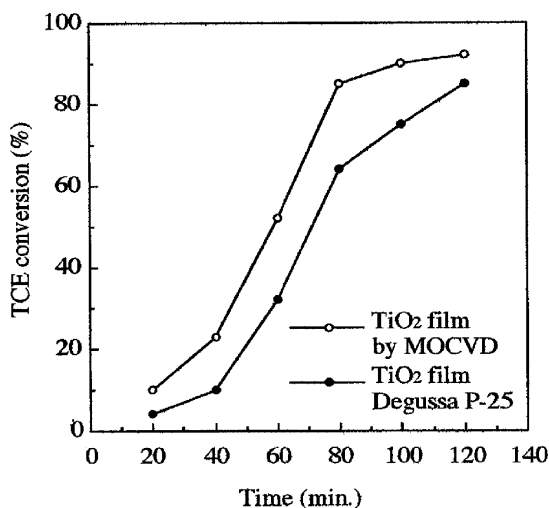


Fig. 9. Comparison of the performance of TCE decomposition over TiO₂ film synthesized by CVD method and the Degussa P-25 film.

TEOS (triethylenorthosilicate) and HCl. After attachment, the Degussa P-25 film was thermally treated at 150 °C for 2 h. The TiO₂ thickness attained from the CVD method was 200 nm per one time coating. In case of Degussa p-25, the thickness was 1 μm per one time coating. As shown, the decomposition of TCE was higher over the TiO₂ film by CVD method than that over Degussa P-25 film. After 120 min, the conversion of TCE was above 90% over TiO₂ film by CVD method, otherwise it was 85% over Degussa P-25 film. From this result, it was confirmed that the CVD method was very useful to prepare the TiO₂ film with high photo-activity. With an increase of the film thickness, the performance of TCE decomposition increased until 10 times coating. But above that, the performance was not changed.

3.4. Expectation of the mechanism for decomposition of TCE

Generally, many papers have been reported about trichloroethylene decomposition [17–19]. However, the mechanism was not cleared. Particularly, the TCE destruction mechanism under the presence of water was not found until now. Thus, our expectation is not absolutely sure. From the results of only Figs. 6–8, we could suggest that TCE was decomposed as shown in Fig. 10. Such that, from our experimental result

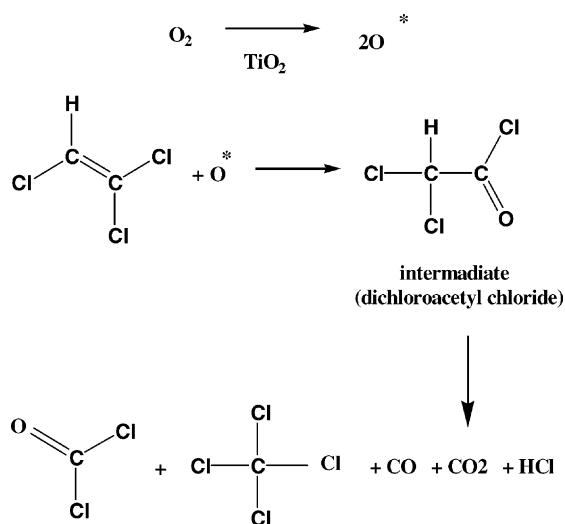


Fig. 10. Suggestion of a mechanism for TCE decomposition.

for in situ FT-IR spectroscopy, it was confirmed that TCE was decomposed into dichloroacetylchloride (DCAC) and trichloromethane (CHCl₃) in transition state, and then these were finally transferred to CO₂, HCl, and H₂O. In addition, the water addition enhanced the TCE decomposition, but it did not affect the mechanism of TCE photo-catalytic decomposition mentioned in Fig. 10.

4. Conclusion

MOCVD method was demonstrated in this study to prepare TiO₂ thin film of anatase structure with high photo-activity. From the results of characterization of XRD and SEM spectroscopy, we have confirmed that a TiO₂ thin film with pure anatase structure and was stably attached on a substrate. The results were as follows:

1. The intermediates produced from TCE decomposition were investigated by in situ methods using a FT-IR spectroscopy, TCE was transferred into dichloroacetylchloride and trichloromethane in the transition state, and then, finally, it turned to CO₂, HCl, and H₂O.
2. The addition of H₂O enhanced TCE decomposition on TiO₂ film. This ascribed the increase of hydroxyl radical produced by H₂O decomposition.

However, it was not affected to mechanism of TCE photo-catalytic decomposition.

3. The conversion of TCE remarkably increased over TiO₂ film synthesized by CVD method compared with that of TiO₂ film prepared by Degussa P-25 colloidal solution: in particular, the conversion over TiO₂ film synthesized by CVD method reached above 90% after 120 min, otherwise, it was 85% over Degussa P-25 film.

Acknowledgements

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