

# PHOTOCATALYTIC DEGRADATION OF 2-CHLOROPHENOL USING TiO<sub>2</sub> THIN FILMS PREPARED BY CHEMICAL VAPOR DEPOSITION AND ION BEAM SPUTTERING METHOD

Oh-Jin Jung<sup>†</sup>, Sam-Hyeok Kim, Ji-Eun Jo, and Chul-Ho Hwang

School of Environmental Engineering, Chosun University, Gwang-ju 501-759, Korea

(received August 2002, accepted October, 2002)

---

**Abstract :** Chemical vapor deposition (CVD), ion beam sputtering (IBS) and sol-gel method were used to prepare TiO<sub>2</sub> thin films for degradation of hazardous organic compounds exemplified by 2-chlorophenol (2-CP). The influence of supporting materials and coating methods on the photocatalytic activity of the TiO<sub>2</sub> thin films were also studied. TiO<sub>2</sub> thin films were coated onto various supporting materials including steel cloth (SS), copper cloth, quartz glass tube (QGT), and silica gel (SG). Results indicate that SS (37 μm)-TiO<sub>2</sub> thin film prepared by IBS method improves the photodegradation of 2-CP. Among all supporting materials studied, SS(37 μm) is found to be the best support.

---

**Key Words :** 2-chlorophenol, CVD-IBS, photocatalytic degradation, reaction kinetics, TiO<sub>2</sub> thin film

## INTRODUCTION

In light of the increasing concern over the contamination of environment by hazardous chemicals, there is a great need to develop innovative technologies for safe destruction of toxic pollutants. The processes must be cost-effective, easy to operate, and capable of achieving total or near total mineralization. This has prompted researchers to investigate innovative chemical oxidation technologies. The oxidative destruction of chemicals provides ultimate solutions for the treatment of hazardous wastes.

TiO<sub>2</sub> thin film particulate systems have been employed to photo-decomposition of organic pollutants. In such a system, the thin films are

excited with ultraviolet (UV) or visible light to induce charge separation. The photogenerated holes would then oxidize the organic pollutants. Upon irradiation, the TiO<sub>2</sub> particles generate electron/hole pairs with positive holes (h<sup>+</sup>) in the valance band (vb) and free electron (e<sup>-</sup>) in the conduction band (cb),<sup>1)</sup> the holes migrate to the TiO<sub>2</sub> particle surface and are reacted with the adsorbed water molecules to generated hydroxyl radicals, which can oxidize a host of organic pollutants.

Many researchers have studied the photocatalytic degradation of organic contaminants using thin film particles with large band gap.<sup>2~4)</sup> In a slurry-based photocatalytic reactor system, the rate-determining step in the degradation process is considered to be the reduction of oxygen by trapped electrons on the thin film surface to produce reduced species such as superoxide radical ions. The photogenerated

---

<sup>†</sup>Corresponding author

E-mail: ojjung@mail.chosun.ac.kr

Tel: +82-62-230-6644, Fax: +82-62-234-6754

electron-hole pairs can also recombine. If  $\text{TiO}_2$  is used as an aqueous suspension, the catalyst must be removed following its deployment. Post-treatment removal requires a solid liquid separation, which raises the overall capital and operational costs. Therefore, suppressing the recombination of hole-electron pairs and prolonging the life time of carriers are essential for improving the efficiency of net charge transfer at the thin film/electrolyte interface. Alternatively, the catalyst such as  $\text{TiO}_2$  may be coated onto a suitable solid support matrix, which would eliminate the need for solid-liquid separation as a post-process. These  $\text{TiO}_2$  thin film systems can be prepared by several methods and supports such as quartz glass, glass bead, glass plate, glass fiber, sand, optical fiber, thin oxide, silica-gel, titanium, and stainless steel<sup>5,6)</sup> as a means to enhance of the photodegradation of organic pollutants.

However, in spite of such an intensive effort, it is still unclear which methods and supports are most effective to improve the mechanical stability and photocatalytic activity of the thin film. The chemical vapor deposition (CVD), ion beam sputtering (IBS) and thermal pyrolysis (TP) are but some of the common methods for preparation of various thin films and semiconductors. The molecular precursors on the thin film surface are able to react at high or room temperature in the gas phase or molecular solid. However, only little report has been made on the photodegradation of organic pollutants by  $\text{TiO}_2$  thin films or semiconductors prepared by CVD or IBS method.<sup>7,8)</sup>

The aim of this study is to investigate the catalytic behavior of supported  $\text{TiO}_2$  catalyst prepared by the IBS and CVD method.<sup>9)</sup> The change in the photocatalytic activity of thin film,  $\text{TiO}_2$ , was exemplified by the oxidation of 2-chlorophenol (2-CP) under air saturation and cooling condition. The photocatalytic efficiency of the thin films coated on various supportive surface such as stainless steel cloth (SS), copper cloth, quartz glass tube (QGT), and silica gel (SG) were also investigated.

## MATERIALS AND METHODS

### Materials

$\text{TiO}_2$  (P25) was supplied by Degussa Co., Ridgefield Park, NJ. Type 304 stainless steel or copper cloth (SS; 37  $\mu\text{m}$  and 75  $\mu\text{m}$  or Cu; 75  $\mu\text{m}$ , 40  $\pi\text{ cm}^3$ ) was supplied by MSC industrial supply Co., Plainview, NY, USA. P25 powder has a primary particle size of 40  $\mu\text{m}$ , a specific surface area of  $50 \pm 1.5\text{ m}^2/\text{g}$ , and its crystalline mode is 12% rutile and 88% anatase type. Titanium tetraisopropoxide (TTIP), 2-chlorophenol and silica-gel I (Davisil<sup>TM</sup>, 355~250  $\mu\text{m}$ ) were purchased from the Aldrich Chemical Co. All chemicals were analytical grade and used without further purification. The deionized and double distilled water were used throughout this study. The pH of solutions was adjusted by high concentrated solution of NaOH or  $\text{HClO}_4$ .

### Preparation of $\text{TiO}_2$ Thin Films by CVD and IBS Method

Detail steps for the preparation of  $\text{TiO}_2$  thin films by IBS method was reported elsewhere.<sup>10)</sup>

Thin film deposition was carried out by dc reactive sputtering using a Sputtron II Balzers equipment. In this particular deposition equipment, titanium (metal titanium 99% from Lesker) disk-shaped target (SS) is placed inside a chamber in which a gas pressure of the order of 0.1 Pa is maintained. A plasma discharge is generated by an electron gun, and the Ti target is connected to the negative dc bias source, so as to be bombarded by positively charged ions present in the plasma. Since it is desired to deposit titanium oxides, an  $\text{Ar}/\text{O}_2$  mixture is used in the chamber. Oxygen can then react with the titanium atoms impinging on the support, whence the name of reactive sputtering. The most significant effect of replacing  $\text{O}_2$  by  $\text{H}_2\text{O}$  in the gas mixture is a change in the proportion of O and  $\text{O}_2$  species present in the discharge. No trace of hydrogen could be found in the deposited films.

The hot-wall low-pressure reactor setup for preparation of  $\text{TiO}_2$  thin film by CVD method

was discussed previously.<sup>12)</sup>

### Preparation of TiO<sub>2</sub> Thin Film by Sol-Gel Method

TiO<sub>2</sub> thin film was prepared by photo-reducing TiO<sub>2</sub> onto the supporter using P25 powder or titanium tetraisopropoxide solution following a method similar to the one described by Jung.<sup>12)</sup>

### Thin Film Characterization

Structure characterization of the TiO<sub>2</sub> thin films was done by X-ray diffractometer (XRD). The  $2\theta$  scans on the patterns of thin films were recorded by a Rigaku D-Max B diffractometer equipped with a graphite crystal monochromator and using CuK $\alpha$  radiation. The peak areas and full widths at half maximum with reference to CuK $\alpha$  were calculated by standard profile fitting on patterns collected according to Bragg-Brentano geometry. The element concentration on the surface of the TiO<sub>2</sub>/Supporter, were measured by X-ray photoelectron spectroscopy (XPS Model ESCA 750) using an Al K $\alpha$  exciting radiations. The thin films were loaded onto the holder in order to obtain information on the external surface of the particles. For each sample, a fast scan detected the type of element on the surface, and then slow scan was performed for each element, O (1s), Si (2s), and Ti (2p). The calculated TiO<sub>2</sub> concentrations were used as the TiO<sub>2</sub> external surface concentration. The binding energy scales were referenced by setting the hydrocarbon (CH<sub>2</sub>) peak maxima in the C<sub>1s</sub> spectra to 284.6 eV. The precision of the binding energy determined with respect to this standard value was within  $\pm 0.3$  eV. The observation of surface morphology and average grain size and distribution was performed by means of AMRAY1810 Model scanning electron microscopy (SEM).

### Photoreactor and Light Source

The photoreactor consisted of a cylindrical pyrex-glass cell with the size of 20 cm in

diameter and 30 cm in height inside-coated mirror. The UV light lamp (100 or 200 W Hg lamp purchased from Ace Glass Inc., NJ) was immersed into the solution with the cold air-cooling jacket.<sup>12,20)</sup> The maximum energy emission at the wavelength of 365 nm was achieved after the lamp was turned on. At cooling jacket, an energy density of 5.3 and 7.2 mW/cm<sup>2</sup> was measured at 100 and 200 W Hg lamp, respectively.

An EG&G Gama scientific (San Diego, CA, USA) Model GS 3100 spectroradiometer was used to measure UV light intensity. A miniature cosine receptor was connected to the spectroradiometer by using a fiber optical probe. The light intensities measurement system was calibrated with an EG&G Gamma Scientific Model GS-5150 Deuterium lamp in a wavelength range of 250~400 nm.

### Procedure and Analysis

An aqueous solution of the sample (usually 1.0 L) was placed in a photoreactor cell. The concentration of test solution was 50 mgL<sup>-1</sup>, and 2-CP solution was adjusted by pH 9.0 excepting test solution of Figure 3. Prior to irradiation, TiO<sub>2</sub> thin films were magnetically stirred in dark for ca. 30 min to establish an adsorption and desorption equilibrium between 2-CP and the thin film surface. At given intervals of illumination, a sample was collected in a test-tube or vial. Each sample solution was analyzed by HPLC (Hewlett-Packard series 1100 system) equipped with a UV detector ( $\lambda_{\max} = 210$  nm) and C-18 Vydac<sup>TH</sup> column (2-CP: 50 mm  $\times$  0.5 mm; Vydac Co., Hesperia, CA). The eluent solvents for 2-CP were acetonitrile and buffer solution (H<sub>3</sub>PO<sub>4</sub>/NaH<sub>2</sub>PO<sub>4</sub>, pH = 3.0), and that for organic acids was 0.1% H<sub>3</sub>PO<sub>4</sub>.

The total organic carbon (TOC) of a sample solution was measured at constant irradiation time intervals using TOC analyzer (Tekmar-Dohrmann, DC-190). The Cl<sup>-</sup> ion was analyzed by ion chromatograph (Dionex Bio LC Chromatography) equipped with an electrochemical detector and a Dionex PAX-100 metal-free

anion column (25 cm long, 4.6 mm i.d.). The eluent solution was a mixture of 80% H<sub>2</sub>O, 10% of acetonitrile and 10% 191 mM NaOH. The flow rate was 1 mL/min or the injection loop was 50  $\mu$ L in volume.

The photocatalytic decomposition of 2-CP was again estimated from the yield of carbon dioxide, determined gravimetrically as BaCO<sub>3</sub> and from the yield of carbon dioxide as decreasing results of electric conductivity for Ba(OH)<sub>2</sub> solution and HCO<sub>3</sub><sup>-</sup> in sample solution was measured by ion chromatography.

## RESULTS AND DISCUSSION

Figure 1 is an XRD pattern for TiO<sub>2</sub> thin film coated on the surface of SS by IBS method. The locations of (101), (004), (200), (105), and (211) diffraction peaks show that the film is polycrystalline structure TiO<sub>2</sub> stoichiometry with an anatase type, which is of tetragonal Bravais lattice. Its tetragonal Bravais lattice type was also verified by lattice constant calculated from these peaks. Based on the full width at half maxima of the XRD peaks, the average particle diameter was calculated to be about 27  $\pm$  3 nm by using Scherrers's formula. Because TiO<sub>2</sub> in anatase form is believed to be the most efficient photocatalyst during the chemical reaction,<sup>13,14</sup> anatase structure is quite necessary for all of our samples in this study. In addition, according to the diffraction peaks for the anatase, there are no extra detectable peaks for TiO<sub>2</sub> rutile structure.

The parenthesis figure of Figure 1 shows representatively the XPS pattern for TiO<sub>2</sub> thin film coated on the surface of SS. Besides the oxygen peak, there exist two Ti peaks at 458.4 eV and 464.1 eV for Ti (2P<sub>3/2</sub>) and Ti (2P<sub>1/2</sub>), respectively. This was resulted from different atomic binding environment of Ti in the film, and the 5.7 eV binding energy shift between them indicates the formation of TiO<sub>2</sub>.<sup>14</sup> The surface morphology of the thin film was examined by SEM. Figure 2 show a  $\times 10^5$  magnified scanning electron microscopy image of TiO<sub>2</sub>

nanoparticles coated on the surface of SS by IBS method. The TiO<sub>2</sub> particles are aggregated together and the rough measurements from this image indicate that the size of particles is in the nanoscale range.

Figure 3 shows the effect of pH on 2-CP photodegradation using TiO<sub>2</sub> thin films coated on the surface of QGT by CVD method. The results show that oxidation is favored under acidic or basic conditions.<sup>12,13,20</sup> This implies that different reaction mechanisms may be operative and that photocatalytic oxidation is affected by both H<sup>+</sup> and OH<sup>-</sup> ions. At high pH, the number of hydroxyl ions on the TiO<sub>2</sub> surface should increase due to abundance of OH<sup>-</sup> ions, thereby increasing the population of OH radicals. Hickling and Hill<sup>15</sup> have sug-

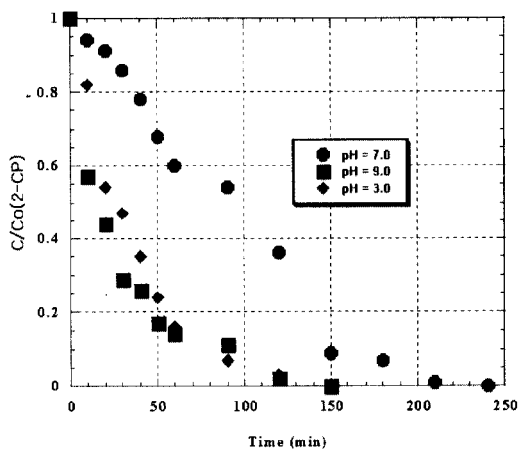


Figure 3. Effect of pH on 2-CP photodegradation TiO<sub>2</sub>-QGT (40.08  $\pi$  cm<sup>3</sup>) thin film prepared by CVD.

gested that at high pH, the adsorbed OH<sup>-</sup> group can be readily converted to an  $\cdot$ OH radical upon irradiation ( $\text{OH}^- \leftrightarrow \cdot\text{OH} + e^-$ ;  $E_0 = +2.0$  Volt vs. NHE). At low pH, the hydroxyl radicals are formed by oxidation of surface water molecules in the process of irradiation ( $\text{H}_2\text{O} + h\nu \leftrightarrow \cdot\text{OH}$ ;  $E_0 = +2.8$  Volt vs. NHE). Both  $E_0$  values are lower than the anodic valance band energy of TiO<sub>2</sub> ( $E_0 = +3.2$  Volt vs. NHE) upon irradiation, therefore the generation of OH radicals may be thermodynamically possible under both high and low pH conditions. Moreover, the relatively low  $E_0$  value at high pH for the formation of  $\cdot$ OH radicals suggests that the oxidation reaction will be more favorable under the high pH condition. Result also exhibits that 2-chlorophenolate ions generated at the range of  $\text{pH} > \text{pKa}$  (at high pH) increases. We have therefore selected pH 9.5 as the default pH value in this study.

Figure 4 show the results of the photocatalytic degradation of 2-CP by TiO<sub>2</sub> thin film coated on stainless steel cloth (SS) and copper (Cu) supports by the IBS method. It is seen that generally the 2-CP concentration decreases with irradiation time. These results also indicate that stainless steel support is slightly advantageous compared to copper support. Moreover, finer stainless steel (37  $\mu\text{m}$ ) size

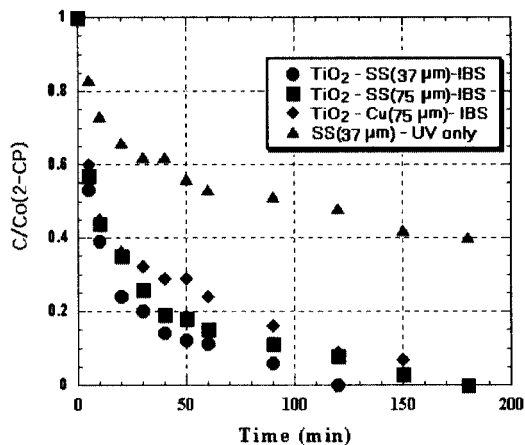


Figure 4. Comparison of 2-CP photodegradation by TiO<sub>2</sub> thin film coated on the surface of three different support by ion beam sputtering method.

yields better 2-CP degradation than coarse mesh (75  $\mu\text{m}$ ). The photocatalytic activities in terms of 2-CP degradation follows the decreasing order: SS (37  $\mu\text{m}$ ) > SS (75  $\mu\text{m}$ ) > Cu (75  $\mu\text{m}$ ). These results also have shown that thin films used in this study are superior to TiO<sub>2</sub> suspension method discussed under identical experimental conditions.

The presence of Cu, detected by XPS in the surface layer of TiO<sub>2</sub> thin film coated on the copper cloth substrate, was in the forms of Cu(OH)<sub>2</sub> and Cu<sub>2</sub>O, which ratio changed with heating temperature. Thus, the substrate of copper can not be used for the preparation of TiO<sub>2</sub> thin film by CVD or sol-gel method because the Cu oxides, particularly Cu<sub>2</sub>O, decreased the photoefficiency of TiO<sub>2</sub> to some extent.<sup>7)</sup> However, these phenomena have not been observed in the substrate of SS. Moreover, increase in specific surface area is brought by the crystallite in the thin films: the nano-size grains can provide large surface area that is key to the improvement in the photocatalytic activity. The uniformity of the distribution and size of TiO<sub>2</sub> nano-crystallite in the thin films provides large surface area and enhances the activity of photocatalysts. Therefore, nearly stoichiometric and conducting TiO<sub>2</sub> thin film prepared with H<sub>2</sub>O are better catalysis

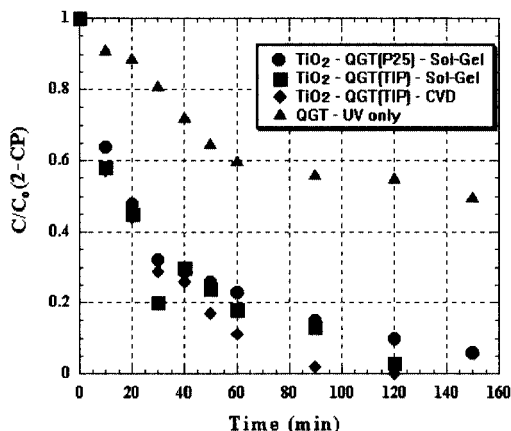


Figure 5. Comparison of 2-CP photodegradation by  $TiO_2$ -QGT ( $40.08 \pi \text{ cm}^3$ ) in film prepared by three different method.

than semi-insulating thin films. And the catalytic performances show some dependence on the nature of the supports used for  $TiO_2$  immobilization.

Figure 5 shows the results of 2-CP degradation by thin film  $TiO_2$  prepared on the surface of QGT by different coating method, namely, sol-gel method by  $TiO_2$  (P25) and TTIP, or CVD method by TTIP. There is no significant difference between sol-gel and CVD method and between P25 and TTIP as far as the photocatalytic activity of  $TiO_2$  thin film is concerned.

Figure 6 show the results of 2-CP degradation by  $TiO_2$  thin film prepared by IBS or CVD method. These results show that IBS thin film brings a little faster rate in 2-CP degradation than CVD. Results also show that thin film  $TiO_2$  is much efficient than P25 suspension in degrading 2-CP.

Results in Figure 7 show that silica-gel (SG) thin film prepared by CVD method is less photoactive than  $TiO_2$  thin film supported on SS by IBS and CVD. Results show that the 2-CP degradation follows the order:  $TiO_2$ -SS ( $37 \mu\text{m}$ )-IBS >  $TiO_2$ -QGT-CVD >  $TiO_2$ -SG-CVD  $\gg$  0.1% P25 (suspension). Specially, 99% of 2-CP were destructed within 60 min by  $TiO_2$ -SS-IBS thin film.

The surface of semiconductor plays an im-

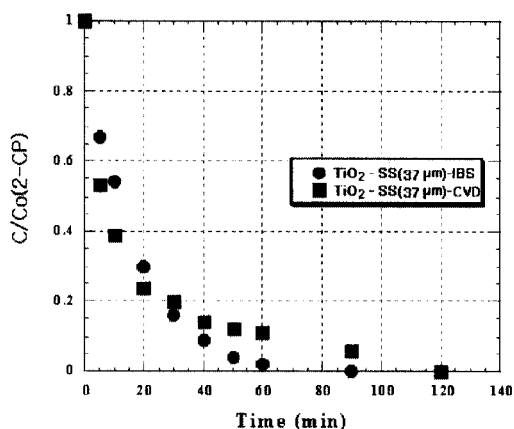


Figure 6. Comparison of 2-CP photodegradation by  $TiO_2$ -SS ( $37 \mu\text{m}$ ,  $40 \pi \text{ cm}^3$ ) thin film prepared by different methods.

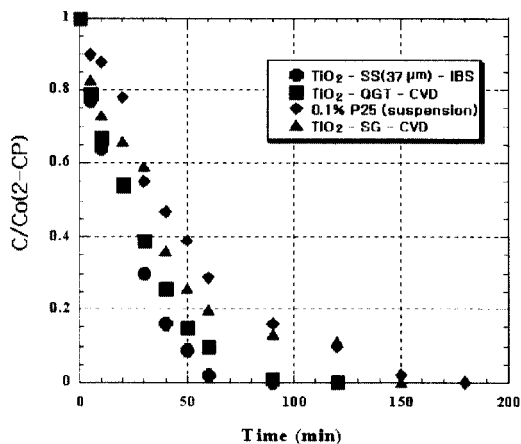


Figure 7. Comparison of 2-CP photodegradation by  $TiO_2$ -SS ( $37 \mu\text{m}$ ,  $40 \pi \text{ cm}^3$ ) thin film prepared by IBS and CVD methods.

portant role on the photocatalytic efficiency.<sup>16)</sup> It was expected that the crystal structure of  $TiO_2$  nanoparticles coated on the supports such as silica-gel, quartz glass tube and stainless steel cloth would act as electron scavengers, increasing consequently the photodegradation efficiency due to the decrease in the electrons and positive hole recombination rate. Stainless steel cloth were proven to have potential as a supporting material for  $TiO_2$  thin film.  $TiO_2$  catalyst supported on SS is excepted

to have photocatalytic activities comparable to those supported on the surface of SS and QGT reveals some unique properties, which has not been observed with silica-gel supported catalyst.

The adhesion of TiO<sub>2</sub> on its support was of good quality with the exception of silica gel since no detachment of TiO<sub>2</sub> could be observed during several photocatalytic tests. This adhesion was induced by heating the sample at the range of 550~650°C in vacuum state. As a consequence, there is a migration of some cations (e.g., Na<sup>+</sup>, Si<sup>4+</sup>) from the support such as silica gel to the TiO<sub>2</sub> layer.<sup>17)</sup> Since these ions dissolved in the lattice of TiO<sub>2</sub> thin films, it constitute the recombination of hole-electron centers and inhibitors. Hence, this could explain why silica-gel decrease the photocatalytic activity of TiO<sub>2</sub> thin films. However, the SS and QGT, which by contrast is much more inert and stable under heating, allowing the preparation of more stable thin films. It has been also found that the thin films coated on the surface of SS or QGT retained a constant photocatalytic activity when after mere rinsing of the thin films in deionized water and reused. This indicates that deposited TiO<sub>2</sub> thin films is not deactivated during the photoreaction either by inhibition or loosening or poisoning of the photocatalyst and can be re-utilized in subsequent runs.

The structural characterization of TiO<sub>2</sub> thin films prepared by IBS, CVD, and sol-gel method and its effect on the photochemical properties were studied with an attempt to understand the photocatalytic degradation of 2-CP. The photocatalytic efficiencies have been dramatically enhanced in the order of decrease of heating temperature when TiO<sub>2</sub> thin films were prepared by IBS (25°C), CVD (450~550°C), and sol-gel (600~650°C) method. A relation between the photochemical behavior of TiO<sub>2</sub> coating and its structure can be established with respect to the effect of heat-treatment temperature.<sup>7,12,13,20)</sup> The great enhancement of the photocatalytic properties above 400°C was a result of crystallization of TiO<sub>2</sub>, while the poor photo-effect bellow this temperature was

attributed to its amorphous structure in the case of thin film preparation by the sol-gel method. Moreover, it is well known that there is shrinkage of the gel under heat-treatment. Intuitively, the thickness of TiO<sub>2</sub> coating decreased with increasing heating temperature. Though, no attempt was made to observe the TiO<sub>2</sub> thin films coated by IBS and CVD method have been greatly enhanced than one coated by the sol-gel method.

The sputtering technique provides good prospects for the preparation of immobilized, TiO<sub>2</sub>-based photocatalyst. A highly efficiency is obtained in the mineralization of 2-CP for the catalysts prepared in mixed Ar-H<sub>2</sub>O atmosphere. At room temperature and in similar irradiation condition, the efficiency of the understoichiometry in TiO<sub>2-x</sub> with weight percentage of about 0.1 is slightly lower than for that of more stoichiometric TiO<sub>2</sub> photocatalysts prepared with H<sub>2</sub>O as the reactive gas. The adsorption of O<sub>2</sub> could compete with the adsorption of organic pollutants such as 2-CP or organic intermediates produced in the process of photodegradation to enhance the degradation rate.

Figure 8 shows the effect of incident radiation intensity on 2-CP photodegradation. As expected, an increase in the intensity of incident radiation leads to an enhancement of the efficiencies of photodegradation on organic pollutants such as 2-chlorophenol. Especially, 99%-2-CP has been removed within 50 min when TiO<sub>2</sub> thin films coated on the surface of QGT illuminated by 200 W UV lamp ( $\lambda_{\max} = 365 \text{ nm}$ ,  $7.2 \text{ mW/cm}^2$ ) under air cooling and saturation condition. Whereas, it has been taken 90 minutes in case of the illumination of 100 WUV lamp at the same experimental conditions. The kinetic results on the photodegradation of 2-CP aquatic solution using TiO<sub>2</sub>-SS thin films prepared by CVD method were  $2.62 \times 10^{-3}$  and  $3.18 \times 10^{-3} \text{ mM} \cdot \text{min}^{-1}$  at 100 and 200 WHg lamp, respectively.

The UV absorption by TiO<sub>2</sub> thin films can be described by the Lambert-Beer equation with respect to rates of reaction of the positive

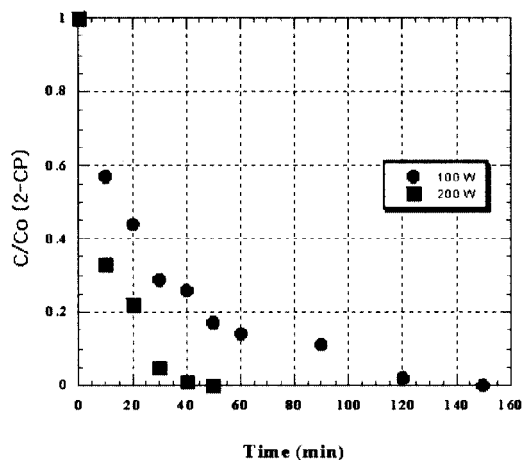


Figure 8. Effect of light intensity on 2-CP photodegradation by  $\text{TiO}_2$ -QGT ( $40.08 \pi \text{ cm}^3$ ) thin film prepared by CVD method.

holes and electrons. An increase in the intensity of incident radiation leads to an increase in the amount of light absorbed. However, the rate of recombination of  $e^-h^+$  pairs is also enhanced at higher light intensity. Therefore, even though the quantum yield nearly is not increased with increasing intensity of illumination,<sup>18,19)</sup> the relative number of  $h^+$  ions is increased with increasing intensity of incident radiation because the recombination of  $e^-h^+$  pairs is suppressed by dissolved oxygen as an electron acceptor.

Figure 9 shows concentration for the 2-CP degradation, chloride ion (Cl<sup>-</sup>) and total carbon dioxide ( $[\text{CO}_2]_g + [\text{HCO}_3^-]$ ) products as a function of illumination time by  $\text{TiO}_2$ -SS thin film.

Although the appearance of chloride ion emergence lags behind the 2-CP, all of the chlorinated intermediates were destroyed within about 160 minutes in the batch mode. The formation of chloride ions is slower than the degradation of 2-CP. About 82% of 2-CP have been degraded, but only 70% of chloride ions are observed after 60 minutes. It is also noted that Cl<sup>-</sup> remains detectable 150 minutes after the complete degradation of 2-CP. The difference in the 2-CP degradation and dechlorination suggests the formation of some chlorinated

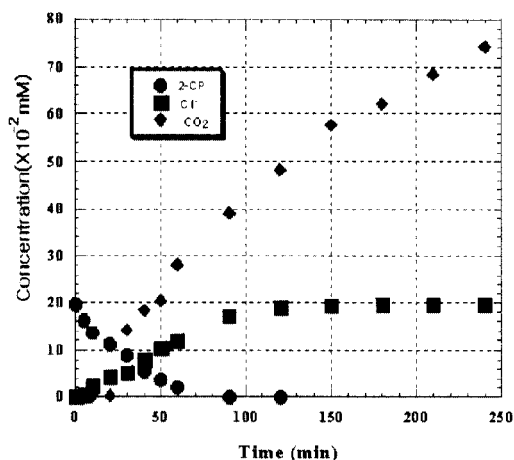


Figure 9. Changes of [2-CP],  $[\Sigma\text{CO}_2]$ , and [Cl<sup>-</sup>] during 2-CP photodegradation by  $\text{TiO}_2$ -SS ( $40 \pi \text{ cm}^3$ ,  $37 \mu\text{m}$ ) thin films prepared by IBS method.

intermediate. This agrees with the above analysis of reaction products where chlorinated intermediates have been determined as the major reaction products.

These results also indicate that the total carbon dioxide appears after complete disappearance of 2-CP and chlorinated intermediates. The rate of the evolution of total carbon dioxide is much slower than that of the formation of chloride ions, which suggests the formation of non-chlorinated products. For example, although 100% of chlorinated intermediates have been degraded, the products of total carbon dioxide is only about 42% at 150 minutes of photooxidation. However after 240 minutes, about 63% of total carbon dioxide have been released. It has been suggested that some major organic acids such as tartaric, glyoxalic, succinic, maleic, oxalic, acetic and formic acid as part of reaction products.<sup>12,20)</sup> This clearly indicates that the photocatalytic oxidation process with  $\text{TiO}_2$ -SS thin films prepared by CVD and IBS methods is effective in completely mineralizing 2-CP to carbon dioxide and chloride ions within 300 min under the present experimental conditions. However, it is interesting to note that UV photolysis alone only yields about 2% carbon dioxide, and



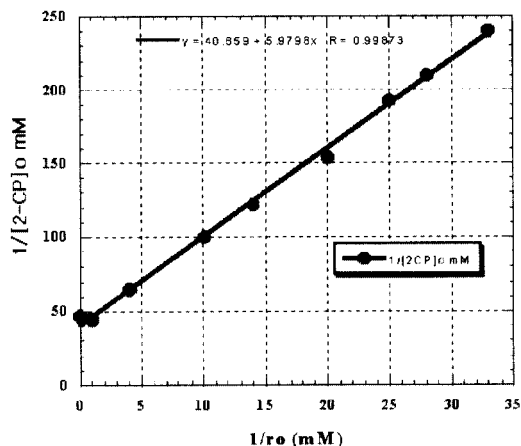


Figure 10. The linearised Langmuir-Hinshelwood plots.

the photolysis by TiO<sub>2</sub>-SS thin films/UV system yield about 95% carbon dioxide under similar experimental conditions.

Figure 10 gives plots of the reciprocal initial rates,  $r_0$  vs. the reciprocal initial 2-CP concentration,  $[2-CP]_0$ . The rate of 2-CP degradation can be described by the Langmuir-Hinshelwood equation.<sup>12,20</sup> Figure 10 shows the linear plot of the Langmuir-Hinshelwood equation with

$$1/r_0 = 1/k + 1/kK[2-CP]_0$$

Results from regression analysis for the TiO<sub>2</sub>-SS (IBS), yields a rate constant ( $k$ ) of  $2.90 \times 10^{-2}$  mM min<sup>-1</sup> and the adsorption coefficient ( $K$ ) is  $6.43$  mM<sup>-1</sup>. The good fit with the Langmuir-Hinshelwood relationship ( $r = 0.99$ ) indicates that the degradation of 2-CP is likely to occur at the surface of TiO<sub>2</sub>-SS thin films. Table 1 gives the pseudo first order rate constants ( $k$ , mole min<sup>-1</sup>) and half period ( $t_{1/2}$ ,

min) for 2-CP photodegradation ( $k_{2-CP}$ ), chloride production ( $k_{Cl}$ ) and total carbon dioxide-generation ( $k_{\Sigma CO_2}$ ) in the presence of 100 WUV alone and TiO<sub>2</sub> plus 100 WUV using various TiO<sub>2</sub> thin films, i.e., TiO<sub>2</sub>-SS (IBS), TiO<sub>2</sub>-SS (CVD), TiO<sub>2</sub>-QGT thin film (CVD) and P25 suspension, respectively.

It is noted that, in the presence of UV alone, the 2-CP photodegradation rate is almost the same as the rates of formation of chloride ions; this implies that the initial step of the direct photolysis reaction may mainly be the dechlorination.<sup>20</sup> However, when the TiO<sub>2</sub> thin films or pure TiO<sub>2</sub> are added to the same system, the dechlorination rates constants are about half that of the 2-CP degradation, which indicates that reaction other than dechlorination occurs.

Apparently, the non-dechlorination reactions occur during the photocatalytic oxidation of 2-CP yielding chlorinated intermediates. The decrease in the reaction rate with increase in reaction time can be attributed to the increase in concentration of bicarbonate ion. Bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) is known ·OH radical scavenger. In this experiment, bicarbonate ion was found to be the primary inhibitor for 2-CP degradation.

## CONCLUSION

From the structural analysis of TiO<sub>2</sub> thin films prepared by sol-gel CVD and IBS method, it is confirmed that the film is polycrystalline structure TiO<sub>2</sub> of the anatase type which is believed to be the most efficient photocatalyst. The average grain size of the

Table 1. Summary of kinetic results of photodegradation of 2-chlorophenol

	UV alone		TiO <sub>2</sub> -SS(IBS)		TiO <sub>2</sub> -SS(CVD)		TiO <sub>2</sub> -QGT(CVD)		P25	
	k	T <sub>1/2</sub>	k	T <sub>1/2</sub>	k	T <sub>1/2</sub>	k	T <sub>1/2</sub>	k	T <sub>1/2</sub>
2-CP	$1.35 \times 10^{-4}$	456	$2.90 \times 10^{-3}$	23	$2.62 \times 10^{-3}$	25	$2.28 \times 10^{-3}$	38	$2.04 \times 10^{-3}$	42
Cl <sup>-</sup>	$1.26 \times 10^{-4}$	500	$1.47 \times 10^{-3}$	42	$1.35 \times 10^{-3}$	47	$1.16 \times 10^{-3}$	61	$1.05 \times 10^{-3}$	61
ΣCO <sub>2</sub>	<10 <sup>-6</sup>		$6.31 \times 10^{-4}$	152	$6.08 \times 10^{-4}$	158	$5.18 \times 10^{-4}$	163	$4.86 \times 10^{-4}$	175

note) TiO<sub>2</sub>-SS:40 π cm<sup>3</sup>(37 μm), TiO<sub>2</sub>-QGT; 84 π cm<sup>3</sup>, P25: 1.0 gL<sup>-1</sup>. k in mM min<sup>-1</sup>, T<sub>1/2</sub> in min.

thin film is approximately 100 nm.

The photocatalytic efficiency of TiO<sub>2</sub> is dramatically enhanced by thin films supported on various matrixes and prepared by various methods including IBS (25°C), CVD (450~550°C), and Sol-Gel (600~650°C). A relation between the photochemical activity above 400 °C was a resulted from the formation of crystalline TiO<sub>2</sub>, nanoparticles. Sol-gel method, however for amorphous TiO<sub>2</sub>. The photocatalytic efficiency of the TiO<sub>2</sub> thin films coated by IBS or CVD method have exhibited better photocatalytic activity than the sol-gel method. Compared SS and QGT, Cu-cloth is not a good support for TiO<sub>2</sub> thin film, because the copper oxides particularly Cu<sub>2</sub>O, decrease the photoefficiency of TiO<sub>2</sub>.

As expected pH plays an important part on the degradation of organic compounds. Oxidation is favored under acidic or acidic conditions. The high pH, the number of hydroxyl ion on the TiO<sub>2</sub> surface should increase due to the abundance of OH<sup>-</sup> ions, thereby increasing the population of ·OH radicals. At low pH, hydroxyl radicals are formed by an oxidation of surface water molecules in the presence of irradiation. The generation of ·OH radicals is thermodynamically possible under both high and low pH conditions.

## REFERENCES

1. Bard, A. J. and Bernhard, K., "Methods of Photocatalytic Decarboxylation of Saturated Carboxylic Acid," *US Patent*, **4**(303), 486 (1981).
2. Suri, R. P. S., Crittenden, J. C., Fellow, P. E., and Hand, D. W., "Removal and destruction of organic compounds in water using adsorption, steam regeneration and photocatalytic oxidation process," *J. Environ. Eng.*, **125**, 897 (1999).
3. Murata, Y., Fukuda, S., Ishikikawa, S., and Yokoyama, S., "Photoelectrochemical properties of TiO<sub>2</sub> rutile microalloyed with 4d and 5d transition elements," *Solar Energy materials and solar cells*, **62**, 157 (2000).
4. Wang, Y., Cheng, H., Hao, Y., Ma, J., Li, W., and Cai S., "Preparation, characterization and photoelectrochemical behavior of Fe(III)-doped TiO<sub>2</sub> nanoparticles," *J. Mater. Sci.* **34**, 3721 (1999).
5. Roberto, J. C., Walter, A. Z., and Anderson, A., "Titanium-Supported Titania Photoelectrodes Made by Sol-Gel Processes," *J. Environ. Eng.*, **125**, 906~912 (1999).
6. Navio, A. J., Testa, J. J., Djedjeian Pablo., Padron, J. R., Rodriguez D., and Litter, M. I., "Ion doped titania powder prepared by sol-gel method: Part II: Photocatalytic Properties," *Applied Catalysis A: General*, **178**, 191~203 (1999).
7. Dumitriu, D., Bally, A. R., Ballif, C., Hones, P., Schmid, P. E., Sanjines, R., Levy, F., and Parvulescu, V. I., "Photocatalytic degradation of phenol using TiO<sub>2</sub> thin films prepared by sputtering," *Applied Catalysis B: Environmental*, **25**, 83~92 (2000).
8. Ding, Z., Hu, X., Lu, G. Q., Yue, P. I., and Greenfield, poul F., "Novel Silica Gel Supported TiO<sub>2</sub> Photocatalyst Synthesized by CVD method," *Langmuir*, **16**, 6216~6222 (2000).
9. Krumdieck, J. S. and Raj, R., "Conversion Efficiency of Alkoxide Precursor to Oxide Film by an Ultrasonic-assisted, Pulsed Liquid Injection, Metalorganic Chemical Vapor Deposition Process," *J. Am. Ceram. Soc.*, **82**, 1605~1616 (1999).
10. Guerin, D. and Saha, S. I., "Reactive Sputtering of Titanium Oxide Thin Films," *J. Vac. Sci. Technol.*, **A 15**, 712~721 (1997).
11. Spurr, A. R. and Myers, M., "Quantitative Analysis of Anatase-Rutile Mixtures ith an X-ray Diffractometer," *Anal. Chem.*, **29**(5), 760~762 (1957).
12. Jung, O. J., "Synergistic effect of the photocatalytic degradation of 2-chlorophenol using TiO<sub>2</sub> thin films doped with some transition metals in aqueous solution," *Bulletin Kor. Chem. Soc.*, **22**(11), 1183~1191 (2001).

13. Jung, O. J., Li, W., Huang, C. P., Ni, C., and Shah, S. I., "Study of Nd<sup>3+</sup>, Pd<sup>2+</sup>, Pt<sup>4+</sup>, and Fe<sup>3+</sup> dopant effect on Photoreactivity of TiO<sub>2</sub> Nanoparticles," *PNAS*, **99**, suppl. 2 (2002).
14. Wanger, C. D. (Ed.), Handbook of X-ray photoelectron spectroscopy, Perkin Elmer, Minnesota, USA (1979).
15. Hickling, A. and Hill, S., "Oxygen Over-voltage. Part III. A Note on the Standard Potentials of the Hydroxyl Radical and Atomic Oxygen," *Disc. Faraday Soc.*, **46**, 557~559 (1950).
16. Takenori, D., Kiyohisa, I., Mitsunobu, I., Hiroaki, T., and Saishiro, I., "Photocatalytically Highly Active Nanocomposite Films Consisting of TiO<sub>2</sub> Particles and ZnO Whisker Formed on Steel Plates," *J. Electrochem. Soc.*, **147**, 2263~2267 (2000).
17. Zhang, Y., John, C. C., David, W. H., and David, L. P., "Fixed-Bed Photocatalysts for Solar Decontamination of Water," *Environ. Sci. Technol.*, **28**, 435~442 (1994).
18. Aguado, M. A., Anderson, M. A., and Hill, C. G. Jr., "Influence of Light Intensity and Membrane Properties on the Photocatalytic Degradation of Formic Acid over TiO<sub>2</sub> Ceramic Membranes," *J. Molecular Cat.*, **89**, 165~178 (1994).
19. Ollis, D. F., Pelizzetti, E., and Serpone, N., "Photocatalyzed Destruction of water contaminants," *Environ. Sci. Technol.*, **25**, 1523~1529 (1991).
20. (a) Jung, O. J., Kim, S. H., and Cheong, K. H., "Photocatalytic Degradation of Pentachlorophenol Using TiO<sub>2</sub> Thin Films Prepared by CVD," *Environ. Eng. Rev.*, **6**(4), 199~210 (2001); (b) Jung, O. J., Choi, H. I., and Cheong, K. H., "Degradation of Some chlorophenols by Coated-TiO<sub>2</sub> Photoreactor," *Environ. Eng. Rev.*, **7**(1), 1~9 (2002).