EFFECT OF PLATINUM ON THE PHOTOCATALYTIC DECOMPOSITION OF 2-CHLOROPHENOL IN AQUEOUS SOLUTION BY UV/TiO₂

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ABSTRACT

Photocatalytic decomposition of 2-chlorophenol in aqueous solutions with platinum-coated TiO₂ slurry under UV irradiation was examined, utilizing various solution pH levels, dissolved oxygen levels and UV light intensities. The atomic percentage of platinum deposited on the TiO₂ surfaces were identified by X-ray photoelectron spectroscopy (XPS) to be in the range of 0.12 and 0.99%. The decomposition of 2-chlorophenol in acidic aqueous solutions by UV/TiO₂ was enhanced to certain extents for experiments conducted with platinum-coated TiO₂ containing up to 0.82% platinum because of the formation of Schottky barrier between platinum and TiO₂ to prevent the recombination of electric holes and electrons. However, for experiments conducted with TiO₂ coated with higher platinum contents, the decomposition rate of 2-chlorophenol was reduced markedly, possibly because of the depression of the light absorption of TiO₂ by the shielding of coated platinum. The photocatalytic decomposition of 2-chlorophenol in aqueous solution was inhibited for experiments conducted in neutral and alkaline solutions because the presence of platinum increases the repulsion between 2-chlorophenol species and TiO₂ to hinder the adsorption of 2-chlorophenol species on TiO₂. The decomposition rate of 2-chlorophenol in aqueous solution by UV/TiO₂ was found to be improved significantly with increasing UV light intensity.

Key Words: 2-chlorophenol, titanium dioxide, platinum, photocatalytic decomposition.

I. INTRODUCTION

Photocatalysis is considered to be an advanced oxidation process at present for a wide range of environmental applications. Among the photocatalysts studied, titanium dioxide (TiO₂) has been widely studied in connection with ultraviolet (UV)-induced

photocatalytic reactions because it is considered to be relatively inexpensive and chemically stable. The highly oxidative electrical holes generated on the UV-irradiated TiO₂ surface can decompose various organic compounds present in aqueous solutions, given ambient conditions. The efficiency of the UV/TiO₂ process is hindered mainly by the limited active sites and the recombination of electrons and electrical holes on the photocatalyst. Various methods have been developed to modify the structural and morphological properties of TiO₂ catalyst by doping several metals, such as Pt (He *et al.*, 2004; Li and Li, 2002; Sano *et al.*, 2004; Sun *et al.*, 2003), Ag (Moonsiri *et al.*, 2004) and Au and Pd (Sakthivel *et al.*, 2004) to enhance the photocatalytic activity of TiO₂. However, the addition of Pt was found to play a controversial role in the photocatalytic efficiency of TiO₂, depending mainly on experimental conditions. Electrons were more rapidly accumulated on the surface of TiO₂ with

deposited platinum, therefore, the separation of electrons and holes was more effective (Klare *et al.*, 2000). However, the presence of excessive amounts of platinum hinders the photocatalytic decomposition of organic compounds. In this study, the influence of content of platinum; pH values and strength of UV light have been investigated.

II. EXPERIMENTAL

Degussa P-25 TiO₂ powder was used in this study. The Ti plate (a width of 60 mm, and a length of 100 mm) was etched by 18M hydrochloric acid at 80°C for two hours to remove impurities and enhance the adhesion of TiO₂ powders and was then washed in large amount of de-ionized water. The pretreated Ti plate was immersed in the H₂PtCl₆/TiO₂ suspension (0, 0.05, 0.10, 0.30 wt% of Pt) and was then dried under mild conditions. This coating procedure was repeated several times in order to control the weight of TiO₂ coated on the surface of the Ti plate. The TiO₂ coated titanium plate was then put into a muffle furnace at 450°C for 2 hours before it was analyzed by BET (Micromeritics ASA2000) and X-ray photoelectron spectroscopy (XPS) in a Thermo VG Scientific Sigma Probe spectrometer. Photocatalytic decomposition of 2-chlorophenol was carried out in a batch reactor made of Pyrex glass. The UV lamp was vertically inserted in a quartz tube, which was located in the center of the reactor. The light source was a blacklight blue (Model F15T8/BLB, 15 W) lamp with wavelength from 360~370 nm. The intensity of light was determined by digital radiometer (SRC-1000X, Spectroline) and radiation sensor (DIX-365, Spectroline). The concentrations of 2-chlorophenol, total organic carbon, and number of chloride ions in the solution were analyzed by HPLC (P1000, Spectra System), TOC (Model 700, O-I-Analytical) and ion chromatograph (DX-100, Dionex), respectively.

III. RESULTS AND DISCUSSION

The chemical compositions of the photocatalyst thin film (Pt/TiO₂) and the atomic percent (at.%) of Pt on the TiO₂ surface were evaluated from the Ti 2p, O 1s, and Pt 4f peak areas corrected by appropriate sensitivity factors of $S_{Ti} = 1.798$, $S_O = 0.711$ and $S_{Pt} = 4.674$, respectively. Table 1 indicates the atomic percent (at.%) of Pt present on surface of TiO₂ thin film. Since no platinum salts were found on TiO₂ surface, Pt^(IV) species was reduced completely to Pt⁰ on the surface of TiO₂ by high temperature calcinations. Sakthivel *et al.* (2004) also prepared the Pt/TiO₂ photocatalyst by calcinating the suspension containing the salt of Pt and TiO₂ (P-25) at 400°C. The specific surface area of Pt/TiO₂ under

Table 1 XPS analytic results of Pt contents on the surface of TiO₂ thin film

Pt contents in the TiO ₂ suspension (wt%)	Atomic percentage of Pt on TiO ₂ thin film after calcinations (at.%)
0	0
0.05	0.12
0.10	0.82
0.30	0.99

Table 2 Specific surface area of Pt/TiO₂ with various dosages of Pt deposited on TiO₂

Pt added (at.%)	Specific surface area (m ² /g)
0 at.%	46
0.12 at.%	51
0.82 at.%	56
0.99 at.%	57

various dosages of Pt deposition is listed in Table 2. The surface area decreasing without addition of Pt was due to the step of calcination. However, the surface area slightly increased with loading Pt on TiO₂. It possibly occurred without a decrease in the porous radii and formed additional vacancy sites as the Pt loading increased. Chen *et al.* (1999) prepared the Pt/TiO₂ photocatalyst by the reduction of H₂PtCl₆/TiO₂ suspension. They also found a similar trend of surface area variation with loading Pt dosage.

There was only about 3% decomposition of 2-chlorophenol after 5 hours by photolysis with 365 nm UV or adsorption with platinum doped titanium dioxide, respectively. There was about 7% decomposition of 2-chlorophenol after 5 hours by photocatalysis with 365 nm UV plus platinum-deposited titanium dioxide, with nitrogen bubbling through the reaction solution. This means that the photolysis by UV-A and adsorption by catalyst in this system could be neglected. Figs. 1 to 4 show the decomposition of 2-chlorophenol versus reaction time with various dosages of Pt at pH 3, 7, 9 and 11, respectively. There were 4 levels of deposition of Pt: at.% 0%, 0.12%, 0.82% and 0.99%. 0.82% appears to best encourage decomposition. Levels of 0.12% and 0.99% both produced worse results than 0.82%. The values of the reaction rate constant can be obtained by the regression of the experimental data using a pseudo-first-order Langmuir-Hinshelwood rate equation. The reaction rate constants are listed in Table 3 with differences of pH values and mss percentages of deposited Pt. Further, we discuss the effect of Pt dosage on decomposition of 2-chlorophenol from low pH to high pH value. At low pH value (pH 3), there is a maximum efficiency of decomposition of 2-chlorophenol

Fig. 1 Decomposition of 2-chlorophenol by the UV/TiO₂ with various dosages of Pt added on TiO₂ in aqueous solution of pH 3

Fig. 3 Decomposition of 2-chlorophenol by the UV/TiO₂ with various dosages of Pt added on TiO₂ in aqueous solution of pH 9

Fig. 2 Decomposition of 2-chlorophenol by the UV/TiO₂ with various dosages of Pt added on TiO₂ in aqueous solution of pH 7

Fig. 4 Decomposition of 2-chlorophenol by the UV/TiO₂ with various dosages of Pt on TiO₂ in aqueous solution of pH 11

as mass percentage of deposited Pt on TiO₂ is 0.82 at.%. There are two reasons to be described. First, the surface area of TiO₂ increased as Pt dosage from 0.12 to 0.82 at.% deposited on TiO₂ P-25. The effect of Pt dosage on the surface area was similar to the conclusion of photocatalytic mineralization of methanol and ethanol on platinum-coated titanium dioxide reported by Chen *et al.* (1999). They suggested that some of the platinum deposited in pores, meaning the

efficiency of reductive sites on the total surface increased.

The formation of a Schottky Barrier between TiO₂ and Pt hindered electrons on Pt/TiO₂ from transferring. Therefore, electrons were stored in the Schottky Barrier and the recombination of electron-hole pairs was decreased (Sze, 2002). The schematic diagram for the description of energy level variation on n-type semiconductor-metal interfaces is shown in Fig. 5. For an n-type semiconductor in contact

Table 3 Reaction rate constant (10^{-4} min^{-1}) of decomposition of 2-chlorophenol with various pH values and Pt dosages

pH	Pt Dosage			
	0 at. %	0.12 at. %	0.82 at. %	0.99 at. %
3	11.3	15.3	19.6	8.39
7	6.78	5.39	4.47	3.33
9	5.57	4.80	3.91	2.93
11	4.65	3.83	3.23	2.93

with a metal, the work function (ϕ_m , the energy level of free electrons in the metal) of metal (platinum) is bigger than that of n-type semiconductor (titanium dioxide) alone. When platinum and titanium dioxide get into contact, the electrons near the interface in titanium dioxide will flow into the metal until the Fermi levels are equal. The process will reach steady state. Because of loss of electrons at the interface in titanium dioxide, the layer will accumulate positive charge and result in the band turning upward. As the major charge carrier depletes into platinum, a depletion layer is formed. Because the band at the interface turns upward, any electrons flowing from TiO_2 to Pt or from Pt to TiO_2 must have energy levels higher than the energy barrier (Schottky Barrier). Therefore, electrons were stored in the Schottky Barrier near Pt and the recombination of electron-hole pairs was decreased. The phenomenon was the same as the conclusion of decomposition of methylene blue by a UV/ TiO_2 process with deposition of Au by Wang *et al.* (1998). It means that, under this condition, the rate of degradable 2-chlorophenol will be increased.

The efficiency of decomposition of 2-chlorophenol was decreased as excess of Pt deposited on TiO_2 . When there is excess Pt in the TiO_2 solution, a dense solution can be observed and TiO_2 particles congregate more easily than in the original solution. Excess of Pt deposited on TiO_2 caused the decrease of reaction surface of TiO_2 . This phenomenon leads to adverse on the reaction rate. Al-Sayyed *et al.* (1991) added platinum salt to treat pollutant and deduced that the addition of platinum salt will cause the coagulation of TiO_2 particles that result in the pollutants diffusion rate to the TiO_2 surface decreasing. In addition, the surface of TiO_2 would be metallized which would lead to photons being unable to across the metal layer, which might result in the depression of photon absorption efficiency and entirely inhibit the photocatalytic reaction. The same results can be found at the conclusion of the decomposition of methylene blue by a UV/ TiO_2 process with deposition of Au by Wang *et al.* (1998). It indicates that the addition of excess Au may cover the surface of the TiO_2 and cause a decrease of the photocatalysis rate.

Fig. 5 Energy level variation at the n-type semiconductor-metal interface: (a) before contact, (b) after contact

At high pH values, the decomposition of 2-chlorophenol decreased as the Pt dosage increased. The surface of TiO_2 presented a negative charge at pH values above 6 because the point of zero charge of TiO_2 is 6. The disassociated ions of 2-chlorophenol in solution also presented negative charge at pH values above 6. Therefore, there is repulsion between TiO_2 and 2-chlorophenol. Increasing of pH value accompanied increasing of repulsion. As the data shows in Table 3, the reaction rate at pH 3.0 was much higher than that at other pH values. This is because a repulsion force between TiO_2 and 2-chlorophenol exists at solution pHs higher than 6. The decreased trend of reaction rate constant can be observed with the enhancement of Pt doping. This phenomenon may result in electron accumulation on the deposited Pt and an ionic charge in the solution. Accumulated electrons result in increasing the negative charge on the photocatalyst surface. The increase of negative charge on the photocatalyst surface and the variation of ionic charge in the solution varied the adsorption ability of 2-chlorophenol on the photocatalyst surface and decreased the reaction rate constant in direct proportion with loading Pt.

Fig. 6 Formation of chlorine ions and degradation of TOC for 2-chlorophenol decomposition by the UV/TiO₂ with various Pt dosages on TiO₂ in aqueous solution of pH 3

Figure 6 illustrates formation of chlorine ions and degradation of TOC by the UV/TiO₂ process at pH 3 with Pt deposited on TiO₂. There was the same trend for the formation of chlorine ions, the degradation of TOC and the decomposition of the 2-chlorophenol at various deposition amounts of Pt on TiO₂. Fig. 7 illustrates the decomposition of 2-chlorophenol by UV/TiO₂ with various light intensities at pH 3 with and without 0.82 at.% of Pt deposited on TiO₂. At maximum light intensity and with 0.82 at.% of Pt deposited on TiO₂, the decomposition percentage of 2-chlorophenol was about 50%. As the light intensity decreased, the 2-chlorophenol decomposition efficiency decreased. The reaction rate constants are listed in Table 4 with differences of light intensity and with/without deposited 0.82 at.% Pt. It shows that 0.82 at.% of Pt deposited on the surface of TiO₂ will improve the 2-chlorophenol decomposition efficiency.

IV. CONCLUSIONS

At low pH values, deposition of appropriate amounts of Pt can improve the efficiency of decomposition of 2-chlorophenol. The reason may be increase of surface area and the formation of a Schottky Barrier between Pt and TiO₂ that electrons are stored in. However, deposition of excessive Pt resulted in the obstruction of light and caused decrease of efficiency of 2-chlorophenol decomposition. The efficiency of 2-chlorophenol decomposition decreased with deposition of Pt on TiO₂ surface when pH value was high. The efficiency of adsorption of 2-chlorophenol

**Table 4 Reaction rate constant (10^{-4} min^{-1}) of de-
ous light intensities and with/without Pt
dosages**

Light intensity(W/m ²)	0 at.% Pt	0.82 at.% Pt
4.2	11.2	19.6
3.2	4.84	7.38
2.2	1.84	4.81

Fig. 7 Effect of light intensity on the decomposition of 2-chlorophenol in aqueous solution by the UV/TiO₂ with 0.82 at.% Pt on TiO₂

by TiO₂ decreased because of the repulsion between TiO₂ and 2-chlorophenol at high solution pH. Furthermore, when excessive Pt was deposited on the TiO₂ surface, it caused the obstruction of light and electron-hole pairs recombination around Pt as the accumulation of electrons on Pt that weren't captured validly by oxygen absorbed on the TiO₂ surface increased.

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NOMENCLATURE

- [2-CP]⁰ the initial concentration of 2-Chlorophenol (mg/L)
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 [TOC]⁰ the total organic carbon containing in original aqueous solution
 [TOC] the total organic carbon containing in the

	aqueous solution
D.O	the concentration of dissolved oxygen in the aqueous solution (mg/l)
E_C	the conduction band of the semiconductor (eV)
E_F	the fermi level of the material (eV)
E_V	the valence band of the semiconductor (eV)
S_{Ti}	the sensitivity factor of Ti for XPS analysis (-)
S_O	the sensitivity factor of O for XPS analysis (-)
S_{Pt}	the sensitivity factor of Pt for XPS analysis (-)

Greek Letters

ϕ_D	the Schottky barrier (eV)
ϕ_m	the work function in the metal (eV)
ϕ_s	the work function in the semiconductor (eV)

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