



## CHAPTER III EXPERIMENTAL

### 3.1 Preparation of Photocatalysts

#### 3.1.1 Materials

Hexachloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6(\text{H}_2\text{O})$ ) obtained from Aldrich, silver nitrate ( $\text{AgNO}_3$ ) and tetraethylorthotitanate ( $(\text{C}_2\text{H}_5\text{O})_4\text{Ti}$ ) or TEOT supplied by Fluka, were used as precursors for platinum, silver and titania ( $\text{TiO}_2$ ), respectively. The hydrolysis of TEOT was achieved with 37% hydrochloric acid (HCl), 99.7% ethanol both from BDH, 65% nitric acid ( $\text{HNO}_3$ ) from Lab-Scan and deionized water. The activity of the photocatalysts prepared by the sol-gel method was compared with commercially available titania (P25) obtained from Degussa Corporation.

#### 3.1.2 Preparation Procedures

The pure  $\text{TiO}_2$  catalysts used in this experiment were prepared by two different sol-gel methods.  $\text{TiO}_2$  (sol-gel-1) was prepared by using the same method as described by Jung and Park (1999). TEOT was added into the premixed solution, which contained water, hydrochloric acid and ethanol at room temperature with vigorous stirring. White precipitates of hydrous oxides were produced instantly and the mixture was stirred for 24 hours. The solution was heated up to 75-80 °C for 5 hours by a rotary evaporator to remove alcohol. After the ethanol evaporation, the solution was dried in an oven at 100 °C for 24 hours and then undergone the calcination step at 400 °C for 5 hours to obtain  $\text{TiO}_2$  (sol-gel-1).

$\text{TiO}_2$  (sol-gel-2) was prepared by using the same method as described by Anderson and Bard (1995). TEOT was dissolved in ethanol and then nitric acid was added dropwise to the prepared solution at room temperature. Water was added dropwise to the prepared solution with vigorous stirring. The gelation was allowed to proceed slowly and completed within an hour. The mixture was allowed to age at room temperature in a covered beaker for 10 hours. The gel was dried at 100 °C for

5 hours to become a glassy material and then calcined at 400°C. The mole ratios of alkoxide to water, acid and alcohol of both catalysts are summarized in Table 3.1.

For the Pt/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> preparation, the calculated amount of hexachloroplatinic acid or silver nitrate was dissolved in the premixed solution. Then, Pt/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> were prepared by the same method as TiO<sub>2</sub> (sol-gel-1).

**Table 3.1** Preparation conditions of TiO<sub>2</sub> by two sol-gel methods.

Catalyst	Mole ratio				
	TEOT	Ethanol	Water	HCl	HNO <sub>3</sub>
TiO <sub>2</sub> (sol-gel-1)	1	1	100	0.2	-
TiO <sub>2</sub> (sol-gel-2)	1	52	13	-	0.8

## 3.2 Catalyst Characterizations

### 3.2.1 Crystal Structures

The phase analysis of TiO<sub>2</sub> was carried out by an x-ray diffractometer (Rigaku D/max-2200) at room temperature. X-ray diffraction patterns of all TiO<sub>2</sub> particles were obtained by using a Phillips PW 1830/00 No. SY 1241 diffractometer equipped with a graphite monochromator and a Cu tube for generating a CuK $\alpha$  radiation (wavelength 1.5406 Å). The particles were spread on a glass slide specimen holder and its diffraction angles were examined between 5-90° at a scanning rate of 2 $\theta$  of 1.5° per minute with 0.02° increments. CuK $\alpha$  radiation of the x-ray source at  $\lambda = 0.154$  nm was operated at 40 kV, 30 mA, and 1.20 kW. The digital output of the proportional x-ray detector and the goniometer angle measurements were transmitted to an online microcomputer for storing the data and the data were analyzed using PC-APD version 3.5B. Peak positions were compared with the standard files to identify crystalline phases.

X-ray diffraction is based on the fact that an x-ray diffraction pattern is unique for each crystalline substance. Thus, if an exact match can be found between

the patterns of an unknown and an authentic sample, chemical identity can be assumed. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

X-ray diffraction patterns were used for the crystallite size (d) estimation by line broadening measurements in the Debye-Scherrer equation:

$$d = k\lambda / b\cos\theta \quad (3.1)$$

where

- $\lambda$  = the wave length (nm)
- $k$  = the Debye-Scherrer constant (1.0)
- $b$  = the full width at half maximum (FWHM) of the broadened peak
- $\theta$  = the Bragg angle of the reflection (degree)
- $d$  = the crystallite size (nm)

### 3.2.2 Surface Morphology

The size, shape, and morphology of TiO<sub>2</sub> were observed using a transmission electron microscope or TEM (Joel JEM-200 CX) and a scanning electron microscope or SEM (Joel JSM-5200).

The TiO<sub>2</sub> powder sample was placed on a copper stub and coated with gold at 40 mA for 4 minutes. The TiO<sub>2</sub> sample was then examined using the SEM at a constant accelerating voltage of 25 kV.

For the TEM examination, a small amount of sonicated titanium dioxide particles was dispersed in acetone solution on a 300-mesh Formvar coated copper grid supported on filter paper. The particle size of precipitate titanium dioxide was determined at a constant accelerating voltage of 100 kV.

### 3.2.3 Surface Area Measurement

The surface area, pore volume, and pore size of all prepared TiO<sub>2</sub> samples were determined by measuring the quantity of gas adsorbed onto or desorbed from their solid surfaces at some equilibrium vapor pressures by static volumetric method. The solid sample was maintained at a constant temperature below the critical temperature of the adsorbate. Adsorption or desorption causes the change in pressure of the sample cell until the equilibrium is established. The resulting volume-pressure data are used to calculate the BET surface area.

BET surface areas of all catalyst samples were obtained by using a surface area analyzer (Autosorb I, Quanta Chrom, U.S.A). The titanium dioxide powder was first outgased to remove the humidity and volatile adsorbents adsorbed on its surface under vacuum at 300 °C for three hours before starting the analysis to determine the surface area. Autosorb ANYGAS Version 2.10 was used to analyze the results.

The adsorption data were calculated by using the Brunauer-Emmett-Teller (BET) equation:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m c} + \frac{(c-1) P}{V_m c P_0} \quad (3.2)$$

where

- V = the volume of gas adsorbed or N<sub>2</sub> in this work
- P = the pressure of gas
- P<sub>0</sub> = the saturated vapor pressure of the liquid at the operating temperature
- V<sub>m</sub> = the volume equivalent to an adsorbed monolayer
- c = the constant related to the energy of adsorption in the first adsorbed layer, the magnitude of adsorption in the first adsorbed layer, and the magnitude of adsorbate/adsorbent interaction, which is given by:

$$c = \exp \frac{H_i - H_L}{RT} \quad (3.3)$$

where

$H_1$	=	the fixed heat of adsorption
$H_L$	=	the latent heat of evaporation
$R$	=	the gas constant
$T$	=	the temperature

The surface area can be determined by the following equation:

$$S_g = \frac{V_m}{0.0224} (6.02 \times 10^{23})(A) \quad (3.4)$$

where

$S_g$	=	the specific surface area ( $m^2/g$ )
$A$	=	the area occupied by each adsorbate molecule ( $m^2$ )

### 3.3 Photocatalysis Experiment

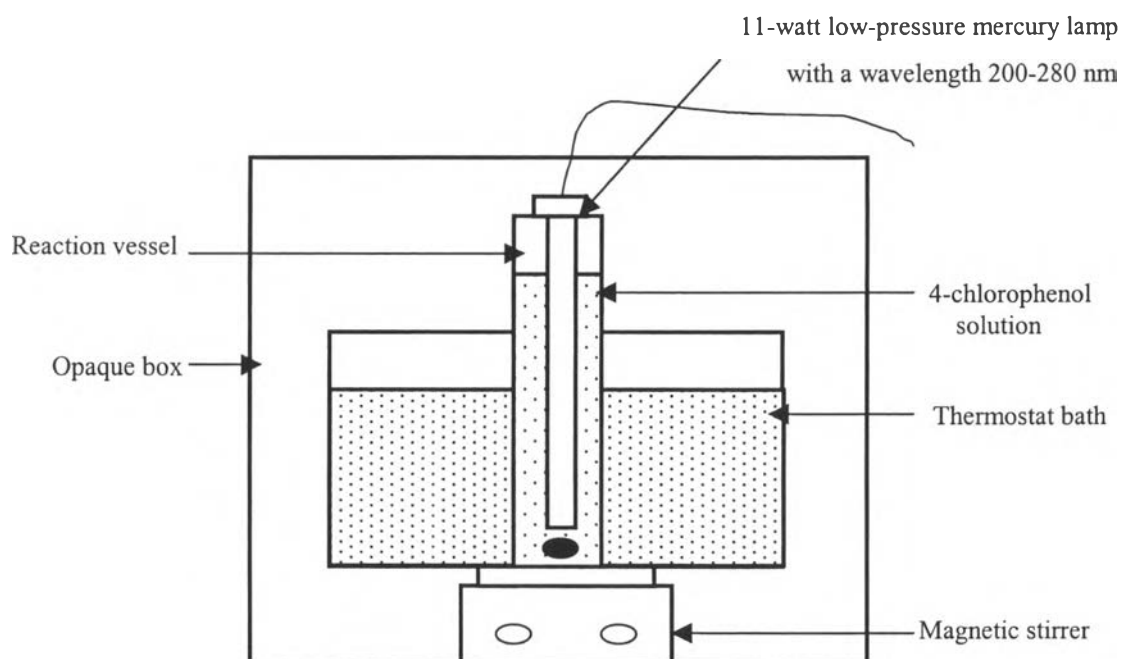
#### 3.3.1 Materials

98% purity of 4-chlorophenol ( $C_6H_5OCl$ ) or 4-CP obtained from BDH was used as a model pollutant in this study. Benzoquinone obtained from Fluka, hydroquinone from Ajax and hydroxybenzoquinone from Aldrich were used for the analysis of intermediate products. HPLC grade of acetonitrile ( $CH_3CN$ ) purchased from Lab-Scan were used as a mobile phase for a High Performance Liquid Chromatograph (HPLC). 99.8% high purity of oxygen and nitrogen were obtained from Thai Industrial Gases Public, Co. Ltd.

#### 3.3.2 Experimental Set-up

A 1000 ml reagent bottle was used as a batch reactor in the study. The UV light source was an 11-watt low-pressure mercury lamp (Philips) with a wavelength in the range of 200-280 nm. This wavelength range gives high energy enough to activate molecules of the photocatalysts. The UV lamp was dipped into

the bottle in order to illuminate throughout the solution. A thermostat bath and magnetic stirrer were used to control the temperature and continuous mixing during the experiment. The reactor was covered by an opaque PVC box to prevent the outer effects and for UV protection. The set-up of the photocatalytic reactor is shown in Figure 3.1.



**Figure 3.1** A schematic diagram of the experimental set-up.

### 3.2.3 Experimental Procedure

For the irradiation experiment, a 450 ml solution containing 0.5 mM 4-CP and 0.5 g/l catalyst was added into the reactor. Before the irradiation, the solution was stirred well for 1 hour to allow for the equilibrium adsorption of the system. Temperature was maintained at room temperature (about 25°C) by the thermostat bath in conjunction with a cooling/heating unit. The experiment started when the UV lamp was turned on. A 25 ml sample was taken every 30 minutes for 360 minutes during the irradiation.

### 3.3.4 Analytical Methods

Before analysis, the solution sample was centrifuged and filtered with a nylon filter membrane (0.2- $\mu\text{m}$  pore size, 25-mm diameter) to remove all solid particles. The concentrations of 4-CP and intermediate products in the filtered sample were determined by a Hewlett Packard HPLC equipped with an UV detector adjusted to 270 nm for the detection of 4-CP and the ODS-2 spherisorb column (125-mm length, 4-mm internal diameter, and 5  $\mu\text{m}$  particle diameter). The mobile phase was a mixture of 40:60 volume ratio of acetonitrile to deionized water with the flow rate of 1.0 ml/min. Total organic carbon of the solution was also determined by a Shimadzu TOC analyzer (TOC-5000A).