

CHAPTER IV

EXPERIMENTAL

This chapter describes about materials and methods used in this study. The chapter is divided into three parts including catalyst preparation, catalyst characterization and photocatalytic activity measurement.

4.1 Catalyst preparation

4.1.1 Chemical

1. Titanium isopropoxide ($C_{12}H_{28}O_4Ti$), 97%, available from Sigma-Aldrich.
2. Absolute ethanol 99.9%, available from Merck.
3. Methanol (CH_3OH), available from Merck.
4. Nitric acid, available from J.T. Baker.

4.1.2 Preparation of TiO_2

TiO_2 was prepared by the acid-catalyzed sol-gel method [Dagan and Tomkiewicz 1994]. Titanium isopropoxide was employed as a precursor. For every 1 ml of the precursor, 20 ml of solvents (ethanol or methanol), 0.08 ml of HNO_3 , and 3 ml of water were needed. The sol was prepared by mixing water and HNO_3 in the solvent at room temperature. The precursor was added dropwise into the solution to produce a firm, clear gel at gelation time. Before drying, the gel was washed at least two times with alcohol. TiO_2 aerogel was obtained by supercritical drying using CO_2 . The system was brought to conditions above the critical point of CO_2 ($T > 35^\circ C$ and $P > 7.4 MPa$), followed by slow release of CO_2 to the atmosphere. The wet gel also underwent drying in air to form xerogel. In both cases, TiO_2 powders were fired at a temperature ranging from $350^\circ C$ to $600^\circ C$ under a flow of either air or nitrogen.

4.1.3 System for supercritical CO₂ drying

The schematic diagram of the system used to supercritical CO₂ drying is shown in Figure 4.1. The system consisted of a high-pressure reactor vessel, which had a volume of 50 cm³; a K-type thermocouple; a high-pressure pump, which delivered up to 50 MPa; and a plate heater.

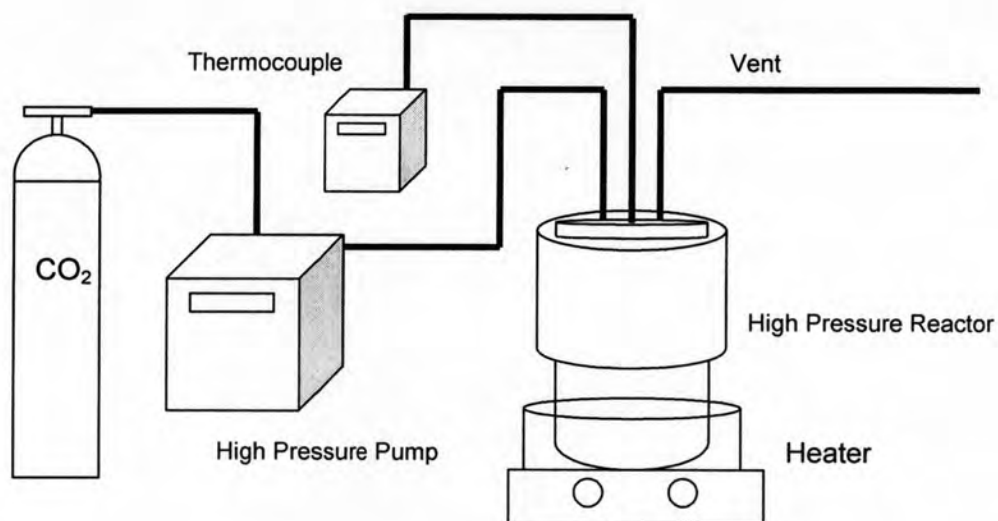


Figure 4.1 Schematic diagram of a system used for supercritical CO₂ drying

4.2 Catalytic characterization

4.2.1 X-ray diffractometer (XRD)

X-ray diffraction (XRD) analysis of TiO₂ powders was performed to determine crystallite phase and crystal size using a SIEMENS D5000 X-ray diffractometer. The measurement was carried out using CuK α radiation with Ni filter. The scan range is between 2 θ values of 10° to 80° with a resolution of 0.04°.

4.2.2 Nitrogen physisorption

Nitrogen physisorption was performed at 77K in a Micromeritics ASAP 2010 to determine specific surface area, pore volume, and pore size distribution.

4.2.3 Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy was performed to determine the functional groups on the TiO₂ surface using a NICOLET 6700 FT-IR. Infrared spectra were recorded from an accumulation of 32 scans in 4000-400 cm⁻¹ range with a resolution of 4 cm⁻¹.

4.2.4 Electron spin resonance (ESR)

Electron spin resonance was carried out using a JEOL JES-RE2X electron spin resonance spectrometer to determine the amount of Ti³⁺ surface defect in TiO₂. Recorded spectra were scanned and converted to a g-value scale referring to a Mn²⁺ marker.

4.2.5 Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to determine amount of organic compounds remained at the surface using a SDT Analyzer Model Q600 from TA Instruments, USA. The measurements were carried out from room temperature to 1000 °C at a heating rate of 100°C/min under a flow oxygen or nitrogen.

4.3 Photocatalytic reaction

4.3.1 Photocatalytic reactor system

The schematic diagram of the photocatalytic reactor system used to test the activity of TiO_2 powder is displayed in Figure 4.2. The system consisted of a photoreactor; two mass flow controllers that controlled the flow rates of ethylene and air entering the reactor; a K-type thermocouple; and a bubble flow meter. The reactor was made from Pyrex glass tube with a diameter of 5 mm and a length of 27 cm. The stainless steel tube is 1.5" in length and 3/8" in diameter connected to the both ends of the reactor. Two sampling points were located on the left and right of catalyst bed. Photocatalyst was packed between two quartz wool layers. Ultraviolet light sources were black light blue fluorescent bulbs (8 Watts). Four light bulbs were located 1.5 cm away from the reactor in square configuration. The photoreactor covered with two layers of aluminum foil to minimize radiation losses from the system.

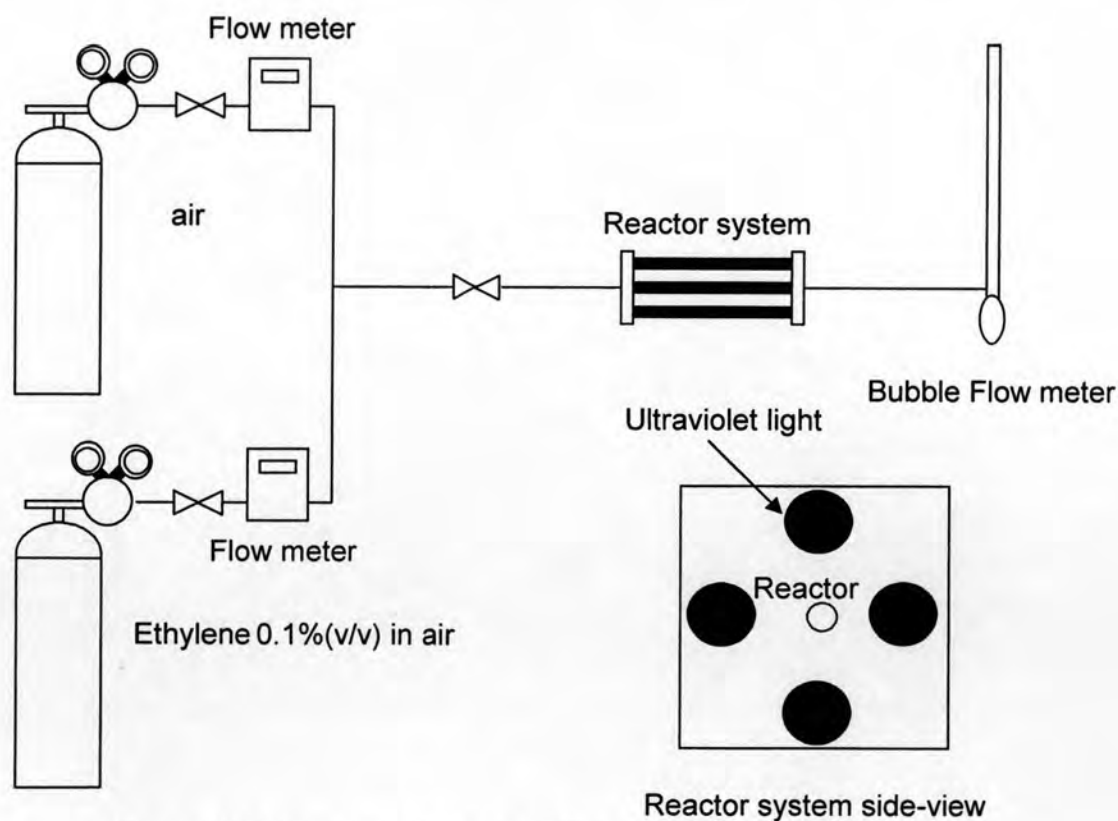


Figure 4.2 Schematic diagram of Photocatalytic system

4.3.2 Measurement of photocatalytic activity

The tubular reactor was packed with 0.02 g of titanium dioxide and was surrounded by four light bulbs. Prior to each experiment, air was fed to the reactor at a flow rate of 15 ml/min and the reactor was illuminated by ultraviolet light bulbs for one hour in order to remove any organic compounds that might remain on the surface of TiO₂. After one hour, the reactant, 0.1%(v/v) ethylene in air, was fed to the reactor at a flow rate of 17 ml/min. The temperature of the reactor under illumination was about 90 °C, as measured using a K-type thermocouple. The flow rate of each gas was measured using a bubble flow meter. The outlet gas sample was analyzed by using a SHIMADZU GC14-B gas chromatograph equipped with a flame ionization detector. The operating conditions for a SHIMADZU GC14-B gas chromatograph were summarized in Table 4.2.

Table 4.2 Operating conditions of gas chromatograph

Gas Chromatograph	SHIMADZU FID GC 14B
Detector	FID
Packed column	VZ10
Carrier gas	H ₂ (99.999%)
Carrier gas flow rate (ml/min)	30
Injector temperature (°C)	100
Detector temperature (°C)	150
Initial column temperature(°C)	70
Final column temperature (°C)	70
Analyzed gas	Hydrocarbon C ₁ -C ₄