CHAPTER IV

EXPERIMENTAL

The synthesis of titania using organic solvent is explained in this chapter. The chemicals and reaction apparatus are shown in sections 4.1 and 4.2, respectively. In sections 4.3 and 4.4, the catalyst preparation and characterization are explained.

4.1 Chemicals

These synthesis mixtures are prepared with the following reagent:

1. Titanium (IV) tert-butoxide (TTB, $Ti[O(CH_2)_3CH_3]_4$) available from Aldrich, 97%
2. 1,4 Butanediol (1,4-BG, $HO(CH_2)_4OH$) available from Aldrich, 99%
3. Toluene ($C_6H_5CH_3$) available from APS Finechem, 100%

Table 4.1 Reagents used for the synthesis of titania

Reagents	Weight/Volume
TTB (various starting material concentrations)	5, 7.5, 10, 15, 25 g
Organic solvents (1,4-BG, toluene)	
In the synthesis mixtures	100 cm^3
In the gap	30 cm^3

For photocatalytic measurements:

Reactant gas	: Air (used as O_2 source)
	: Ethylene
Source of light	: 500 W high-pressure mercury lamp (Philips, HPL-N)
Concentration of ethylene	: 0.1% ethylene in air
Pressure operation	: 1 bar
Reaction temperature	: 40-55 °C
Space velocity of air	: 375 $mL.h^{-1}.g^{-1}$

4.2 Equipment

All equipment using for the catalyst consisted of:

4.2.1 Autoclave reactor

- Made from stainless steel
- Volume of 1000 cm^3
- 10 cm inside diameter
- Maximum temperature of 350°C
- Pressure gauge in the range of 0-140 bar
- Relief valve used to prevent runaway reaction
- Iron jacket was used to reduce the volume of autoclave to be 300 cm^3
- Test tube was used to contain the reagent and glycol

The autoclave reactor is shown in Figure 4.1

4.2.2 Temperature program controller

A temperature program controller CHINO DB1000F was connected to a thermocouple with 0.5 mm diameter attached to the reagent in the autoclave.

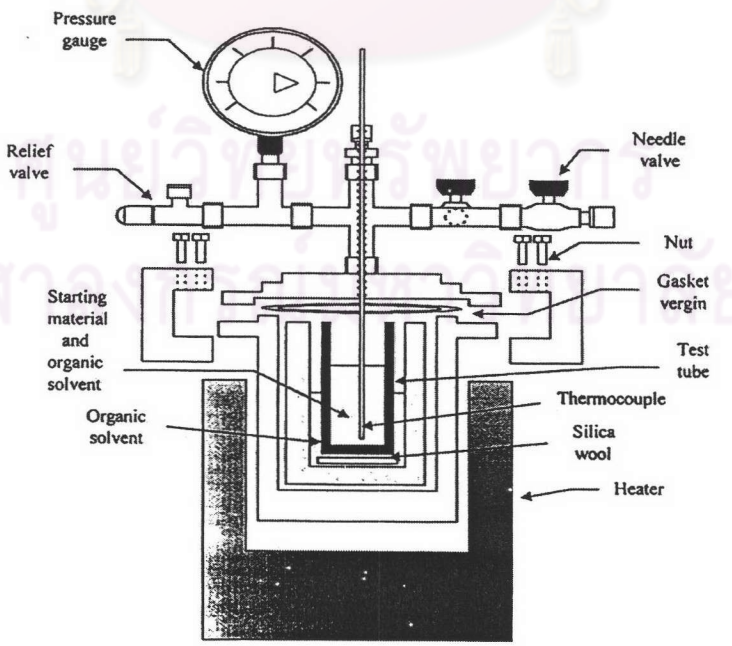


Figure 4.1 Autoclave reactor

4.2.3 Electrical furnace (Heater)

Electrical furnace supplied the required heat to the autoclave for the reaction.

4.2.4 Gas controlling system

Nitrogen was set with a pressure regulator (0-150 bar) and needle valves are used to release gas from autoclave.

The diagram of the reaction equipment is shown in Figure 4.2

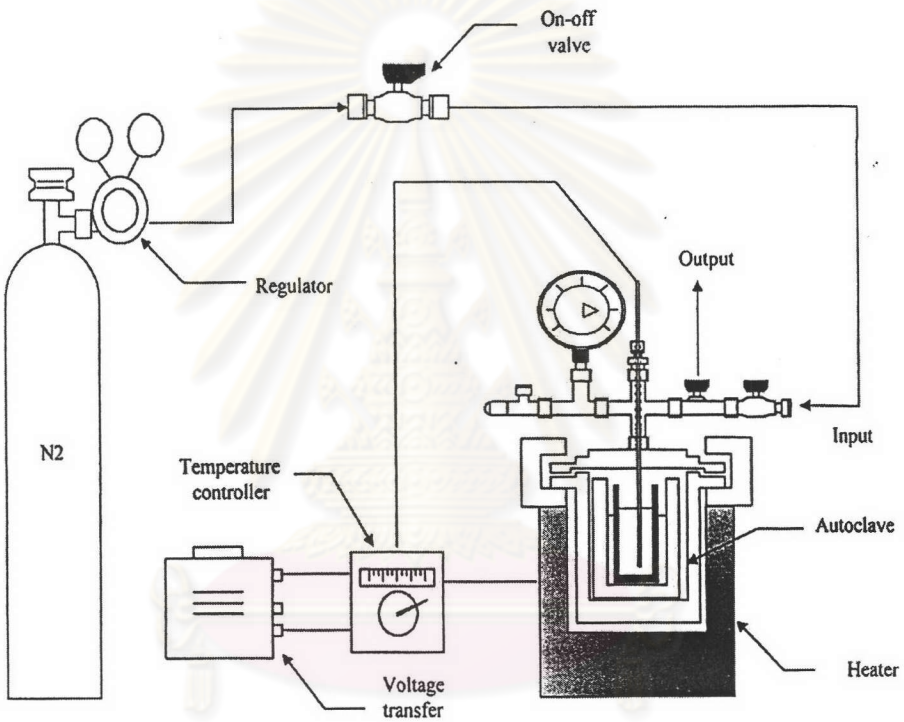


Figure 4.2 Diagram of the reaction equipment for the catalyst preparation.

4.3 Preparation of titania

Titania was prepared by using TTB for various starting material. The starting material were suspended in 100 ml of solvent and in the test tube, and then set up in an autoclave. In the gap between the test tube and autoclave wall, 30 ml of solvent was added. After the autoclave was completely purged with nitrogen, the autoclave was heated to desired temperature (300°C-320°C) at the rate of 2.5°C min^{-1} and held at that temperature for 0.5-6 hours. In this study, for desired crystallite sizes (10, 13, 17 nm in both synrthesized solvent) the reaction time and reaction temperature were

also varied by following Wachiraphan (2002). Autogeneous pressure during the reaction gradually increased as the temperature was raised. After the reaction, the autoclave was cooled to room temperature. The resulting powders were collected after repeated washing with methanol by centrifugation. They were then air-dried.

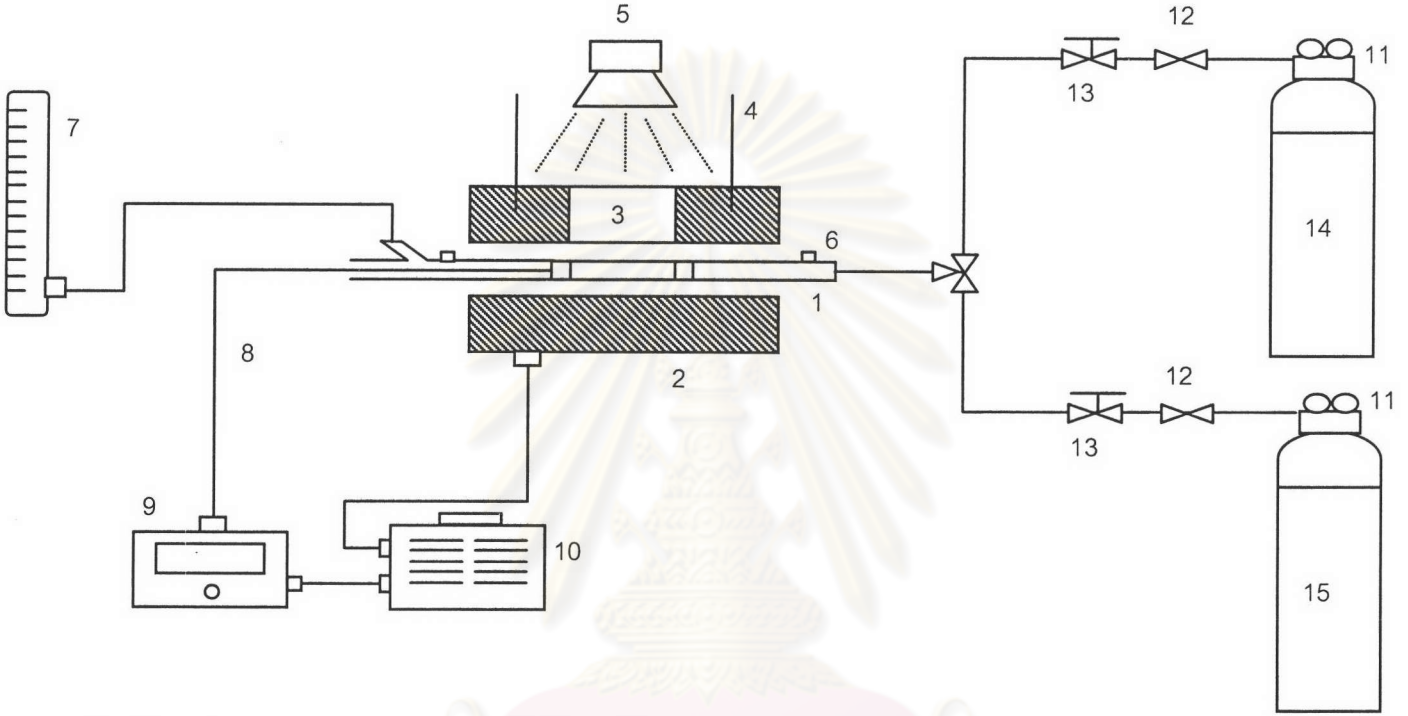
The heating of the thus-obtained product was carried out in a box furnace. The product was heated at a rate of $10^{o}C\ min^{-1}$ to a desired temperature and held at that temperature for 0-2 hour.

4.4 Photocatalytic Reaction

The basic experimental set up used in the present work is shown in Figure 4.3. The catalyst particles were spread along horizontal quartz tube with an internal diameter of 1.0 cm (the length of the catalyst spread; 9 cm) between quartz glass wool layer.

The cylinders of air and 0.1% ethylene in air, equipped with a pressure regulator (1 bar), an on-off valve and fine metering valve used for adjusting the required values. The air containing ethylene in a concentration of 1000 ppm was continuously supplied to the horizontal quartz at a constant flow rate about 10 mL/min. A 500 W high-pressure mercury lamp (Philips, HPL-N) was used as the light source.

In a typical test, the 500 W mercury lamp, located outside the horizontal quartz (distance between the lamp and catalyst; 20 cm), were switched on to illuminate UV light onto surface of the catalyst particles and the outlet gas was sampled at regular intervals of every 30 minute. An air stream was passed through the photoreactor in UV illumination for clean titania surface about 60 minute under the flow was established. After the adsorption process reached equilibrium, then an air stream contaminating ethylene under study was substituted until the gas-solid adsorption equilibrium.



1. Reactor
2. Furnace
3. Window for irradiation
4. Aluminium plate
5. Source of light
6. Sampling port
7. Bubble flow meter
8. Thermocouple
9. Temperature controller
10. Variable voltage transformer
11. Pressure regulator
12. On-off valve
13. Metering valve
14. Air cylinder
15. Ethylene cylinder

Figure 4.3 Diagram of the photocatalytic reaction equipment

The feed and product stream was analyzed by flame ionization detector gas chromatograph Shimadzu 14B. The operating conditions of GC are described in appendix B.

4.5 Characterization

4.4.1 X-ray diffraction spectroscopy (XRD)

The X-ray diffraction (XRD) patterns of powder were performed by Siemens D5000 X-ray diffractometer at Center of Excellences on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University. The experiments were carried out by using Ni-filtered CuKα radiation. The crystallite size was estimated from line broadening according to the Scherrer equation (see Appendix A) and α-Al_2O_3 was used as standard.

4.4.2 Scanning electron microscopy (SEM)

The morphology and size of secondary particle of the samples were observed by Scanning electron microscopy (SEM). Model of SEM for experiments: JSM-5410LV at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC).

4.4.3 Transmission electron microscope (TEM)

The morphology and size of primary particles of samples were observed by a JEOL TEM-200cx transmission electron microscope, operated at 100 kV at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC).

4.4.4 Surface area measurement

The multipoint BET surface area of the samples were measured by a micromeritics model ASAP 2000 using nitrogen as the adsorbate at the Analysis

Center of the Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. The operating conditions are as follows:

Sample weight	~ 0.3 g
Degas temperature	200°C for as-synthesized sample
	300°C for calcined sample
Vacuum pressure	< 10 μmHg

4.4.5 CO_2 Temperature Programmed Desorption (CO_2 TPD)

Temperature Programmed Desorption using CO_2 as a probe molecule (CO_2 TPD) was carried out. At first, a 0.35 g of catalyst was purged with 3 mL/min of CO_2 at -150°C for 1 hour. Then 30 mL/min of He stream was introduced to be the carrier gas from -150°C to 0°C. The heating rate used in this study is 10°C/min. The amount of CO_2 desorbed from the catalyst surface was recored by a thermal conductivity detector, TCD. The operating condition for CO_2 TPD was fixed as follows:

Carrier gas and flow	He, 30 mL/min
Detector temperature	80°C
Detector current	80 mA