CHAPTER IV
EXPERIMENT

This chapter contains detail about the synthesis of titanium (IV) oxide by using glycothermal method, the catalyst characterization, and the photocatalytic activity measurements. In this section, details of experimental procedures including the materials and apparatus used are described.

4.1 Catalyst preparation

4.1.1 Chemicals

The synthesis mixtures are prepared with the following reagents:

1. Titanium (IV) tetra-tert butoxide (TTB, $Ti[O(CH_2)_3CH_3]_4$) available from Aldrich, 97%
2. 1,4 Butanediol ($HO(CH_2)_4OH$) available from Aldrich, 99%
3. 2-Propanol (C_3H_8O) available from Merck, 99.7%

4.1.2 Instruments and apparatus

The schematic diagram of the reaction apparatus for the synthesis of titanium (IV) oxide is shown in figure 4.1

4.1.2.1 Autoclave reactor: The autoclave is made of stainless steel with 1000 ml and 10 cm inside diameter. This consists of a pressure gauge with in the range of 0 to 140 bar and a relief valve, which used to control pressure in the autoclave. This autoclave can be operated at high temperature and pressure. The reaction was carried out under autogenous pressure, which gradually increased as the temperature was raised. (Figure 4.2)

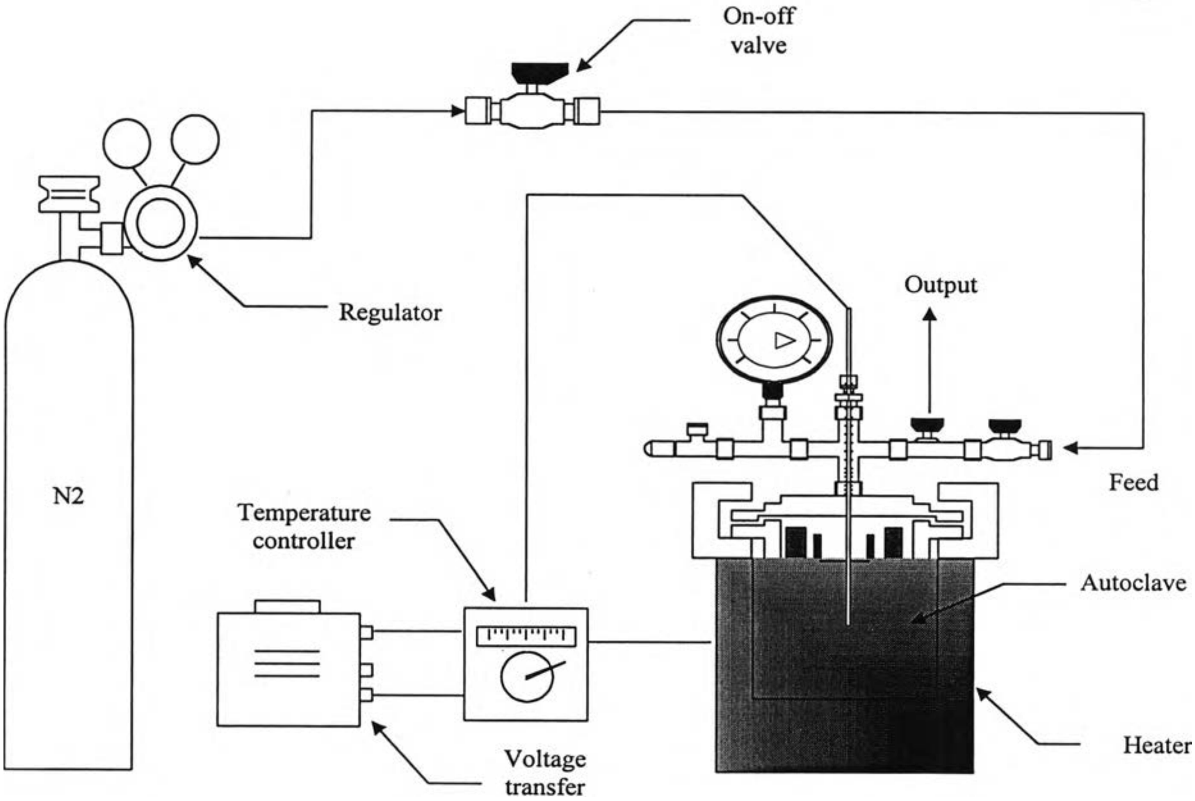


Figure 4.1 Schematic diagram of the reaction apparatus for the titanium (IV) oxide synthesis

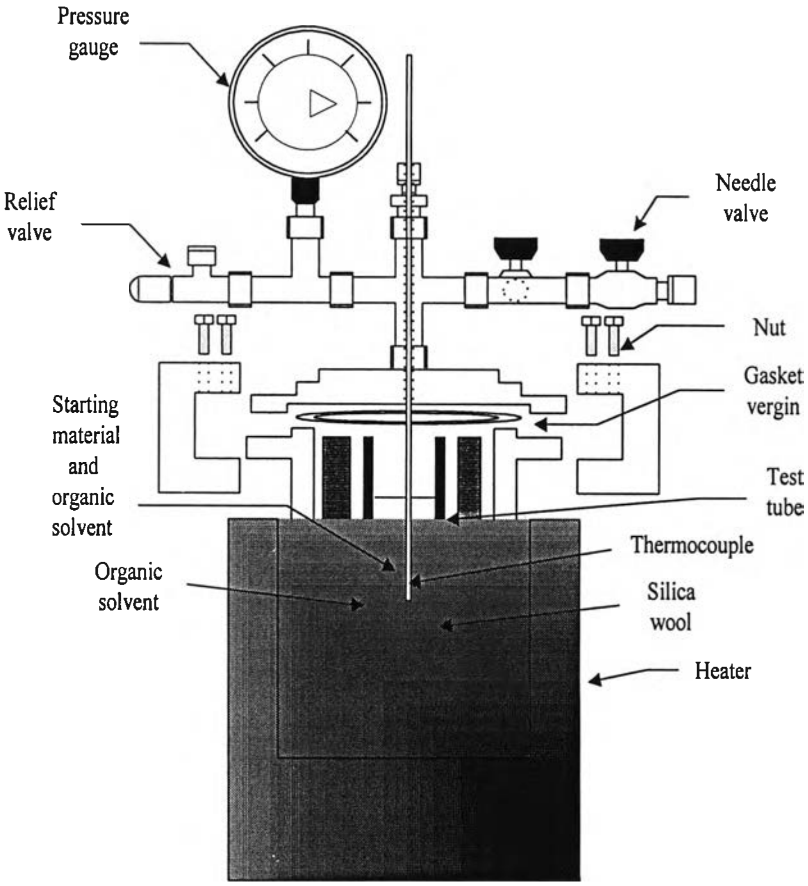


Figure 4.2 Autoclave reactor

4.1.2.2 Automatic Temperature controller: This consists of a magnetic switch connected to a variable voltage transfer and a temperature controller connected to a thermocouple with 0.5 mm diameter attached to the synthesis mixtures in autoclave. A dial setting establishes a set point at any temperature within the range 0 to 400°C

4.1.2.3 Electrical furnace (Heater): This supplied the required heated to the autoclave for the reaction. Autoclave can be operated from room temperature up to 300°C at voltage of 200 volts

4.1.2.4 Gas controlling system: Nitrogen cylinder is equipped with a pressure regulator (0-150 bar), and needle valves were used to release gas from autoclave.

4.1.3 Catalyst preparation

Titanium (IV) tetra-tert butoxide (TTB), 25 g, was dissolved in 100 ml of the different volume ratio of 1,4 Butanediol to 2-Propanol in a test tube, which was then set in the autoclave. In the gap between the test tube and the autoclave wall, 30 ml of the calculated volume ratio of 1,4 Butanediol to 2-Propanol was added. Table 4.1 shows the reactants used for the titanium (IV) synthesis. The autoclave was purged with nitrogen, heated to a desire temperature (300°C) at a rate of 2.7 °C min^{-1}, and held at this temperature for 2 hrs. Autogenous pressure during the reaction gradually increased as temperature was raised and depended on the kind of the organic solvents. After the autoclave was cooled, the resulting powders were washed repeatedly with methanol by centrifugation and dried in air. The calcination of the thus-obtained product carried out in air. The product was heated at a rate of 10°C min^{-1} to 550 °C and held at that temperature for 6 hrs. The instrument parameters of calcination are given in Appendix A.

Table 4.1 Reagents used for the synthesis of titanium (IV) oxide

Reagents	Weight/Volume	
Titanium (IV) tetra-tert butoxide, TTB	25 g	
Organic solvents (1,4 Butanediol : 2-Propanol) in the synthesis mixture (100 ml)	1,4 Butanediol (ml)	2-Propanol (ml)
1,4 BTD[a]/2 P[b] = 5:0	100	0
1,4 BTD/2 P = 4:1	80	20
1,4 BTD/2 P = 3:2	60	40
1,4 BTD/2 P = 2:3	40	60
1,4 BTD/2 P = 1:4	20	80
1,4 BTD/2 P = 0:5	0	100
Organic solvents (1,4 Butanediol : 2-Propanol) in the gap (30 ml)	1,4 Butanediol (ml)	2-Propanol (ml)
1,4 BTD/2 P = 5:0	30	0
1,4 BTD/2 P = 4:1	24	6
1,4 BTD/2 P = 3:2	18	12
1,4 BTD/2 P = 2:3	12	18
1,4 BTD/2 P = 1:4	6	24
1,4 BTD/2 P = 0:5	0	30

[a] 1,4 BTD represents 1,4 Butanediol

[b] 2 P represents 2-Propanol

4.2 Catalyst characterization

4.2.1 X-Ray Diffraction, XRD Patterns

X-Ray Diffraction, XRD patterns of the catalyst samples were determinded by using Ni-filtered Cu Kα radiation in the 2θ range of 10 to 80° (SIEMENS XRD

D5000, Petrochemical Engineering Research Laboratory, Chulalongkorn University). Crystallite size was calculated from the half-height width of the (101) diffraction peak of anatase using Sherrer equation. The value of the shape factor, K was taken to be 0.9 and KCl was used to be internal standard.

4.2.2 Morphology

Morphology of the catalyst samples was observed by a JEOL TEM-200CX Transmission Electron Microscope (TEM), which operated at 100 kV at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

4.2.3 Fourier Transform Infrared Spectroscopy (FTIR)

The functional group on the catalyst surface was determined by FTIR using Nicolet model Impact 400 at Petrochemical Engineering Laboratory, Chulalongkorn University. Each sample was mixed with KBr with a ratio of sample to KBr equal to 1:100 before being formed into a thin wafer. Infrared spectra were recorded between 400 to 4000 cm^{-1} on a microcomputer.

4.2.4 Specific Surface Area Measurement

The BET surface area was determined by nitrogen absorption in an automatic apparatus ASAP-2000 constructed by Micromeritics USA. The data obtained were recorded by a microcomputer.

4.2.5 2-Propanol Adsorbability Measurement

The 2-Propanol adsorbability of each catalyst was determined by Temperature Programmed Desorption technique. In this experiment, 0.02 g of catalyst sample was placed in a stainless steel tube. This tube was then placed inside a gas chromatograph. The 2-propanol vapor was injected at 85°C. The injection was repeated until the sample did not adsorb anymore. The system was the heated to desorb the 2-propanol adsorbed on the surface of titanium (IV) oxide. The amount of 2-propanol adsorbed on the surface sample was measured by flame ionization detector gas chromatograph Shimadzu 14A. The operating conditions are described below.

GC Model : Shimadzu 14A
Detector : Flame Ionization Detector, FID
Column initial temperature : 85°C
Column initial time : 0 min
Column program rate : 5° min^{-1}
Column final temperature : 140°C
Column final time : 120 min
Injection temperature : 150°C
Detector temperature : 150°C
Nitrogen gas flow rate : 25 ml min^{-1}

4.3 Photocatalytic activity measurement

The reaction conditions for the photocatalytic oxidation are chosen as follows:

Photocatalyst : Titanium (IV) oxide catalysts synthesized by glycothermal method
Reactant gas : Air (used as O_2 source)
Reactant liquid : 2-propanol ($(CH_3)_2CHOH$)
Source of light : 500 W Mercury lamp
Concentration of 2-propanol : ca. 12400 ppm
Pressure operation : 1 bar
Reaction temperature : 35°C
Volumetric flow rate of air : 20 ml min^{-1}
Weight of TiO_2 catalyst : 0.4 g

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.

A cylinder of air, equipped with a pressure regulator (1 bar), an on-off valve and fine-metering valve used for adjusting the required values before bubbling through a glass saturator containing liquid 2-propanol. The air containing 2-propanol in a concentration range of 12400 ppm was continuously supplied to the horizontal quartz at a constant flow rate.

In a typical test, an air stream contaminating 2-propanol under study was passed through the photoreactor in the absence of UV illumination until the gas-solid adsorption equilibrium under the flow was established. After the adsorption process reached equilibrium (typically 120-180 min, depending upon the nature and the concentration of the VOC), as indicated by identical inlet/outlet VOC concentrations. Then the 500 W mercury lamp (source of UV light), located outside the horizontal quartz (distance between the lamp and catalyst; 25 cm), were switched on to illuminate UV light onto surface of the catalyst particles and the outlet gas was sampled at regular intervals.

The feed and product stream was analyzed by flame ionization detector gas chromatograph Shimadzu 14A. The amount of CO_2 formed in the reaction was measured using a gas chromatograph Shimadzu GC-8A equipped with thermal conductivity detector. The operating conditions of GC are described in appendix B.

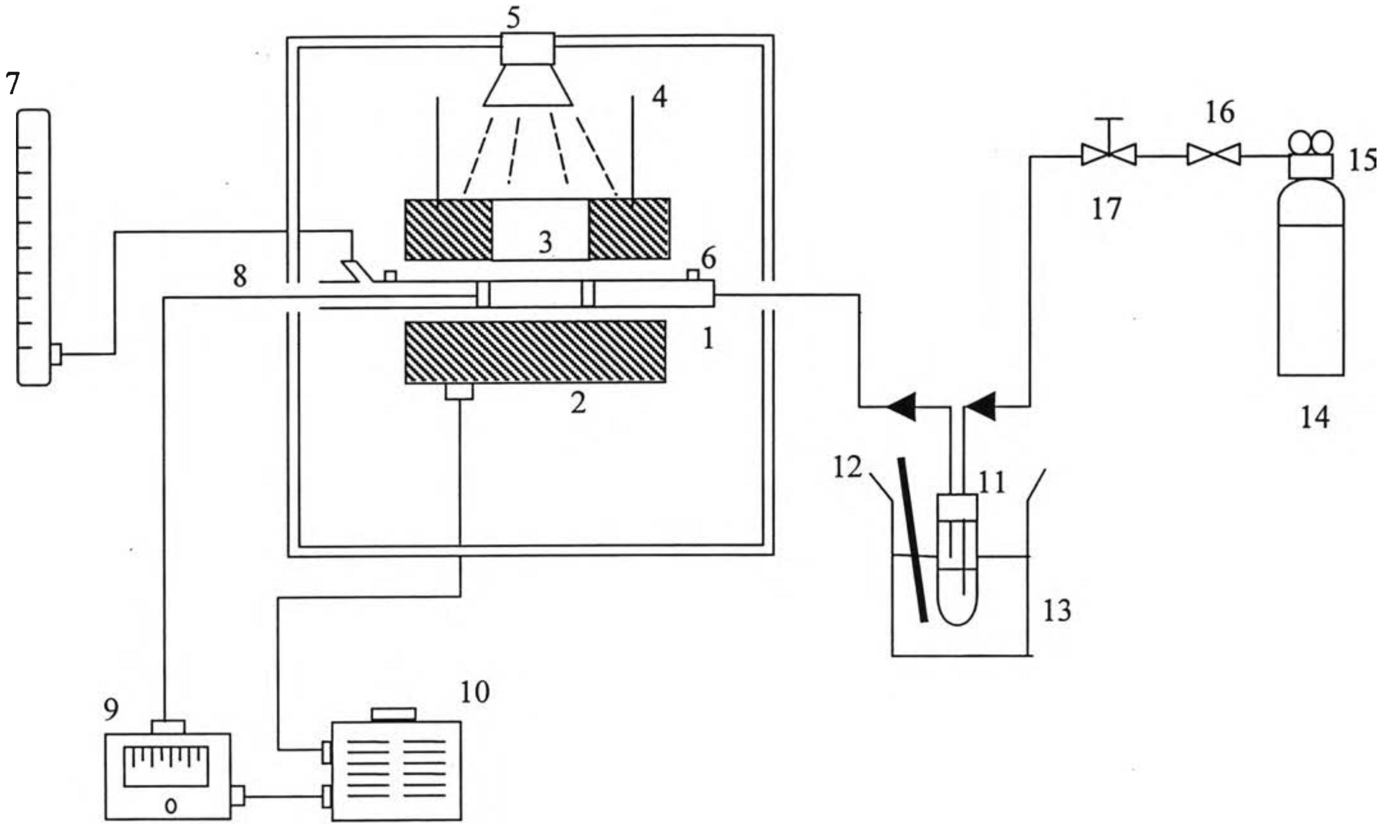
The result of photocatalytic test was calculated in the term of:

$$\%\ \text{A converted} = \frac{\text{mole of A reacted}}{\text{mole of A in feed}} \times 100\ \%$$

$$\% \text{ selectivity to B} = \frac{\text{mole of A converted to B}}{\text{mole of A reacted}} \times \frac{\text{no. C atom of B}}{\text{no. C atom of A}} \times 100\%$$

(A is reactant)

(B is product reaction)



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. Saturator
12. Thermometer
13. Water bath
14. Air cylinder
15. Pressure regulator
16. On-off valve
17. Metering valve

Fugure 4.3 Flow diagram of the photocatalytic reaction system