

CHAPTER IV

EXPERIMENTAL

The synthesis of titania by solvothermal method is explained in this chapter, which is divided into four parts including catalyst preparation, catalyst characterization, and reaction study in photocatalytic process and CO hydrogenation. 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 (TNB, $\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$) available from Aldrich, 97%
2. Toluene ($\text{C}_6\text{H}_5\text{CH}_3$) available from APS Finechem, 100%

Table 4.1 Reagents used for the synthesis of titania

Reagents	Weight/Volume
TNB (various starting material concentrations)	15, 25 g
Organic solvents (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	: 313-328 K
Space velocity of air	: 375 $\text{ml}\cdot\text{hr}^{-1}\cdot\text{g}^{-1}$

4.2 Equipment

All equipment using for the catalyst consisted of:

4.2.1 Autoclave reactor

- Made from stainless steel
- Volume of 1000 cm³
- 10 cm inside diameter
- Maximum temperature of 623 K
- 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 cm³
- 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.

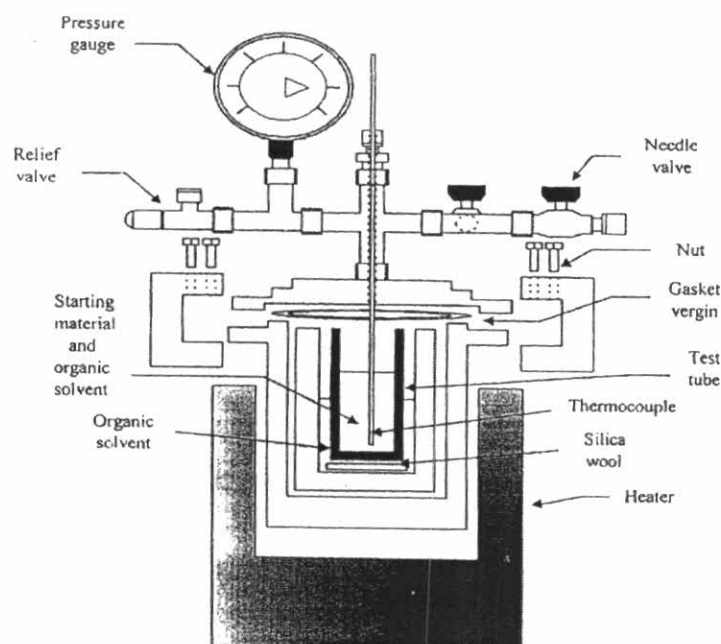


Figure 4.1 Autoclave reactor

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

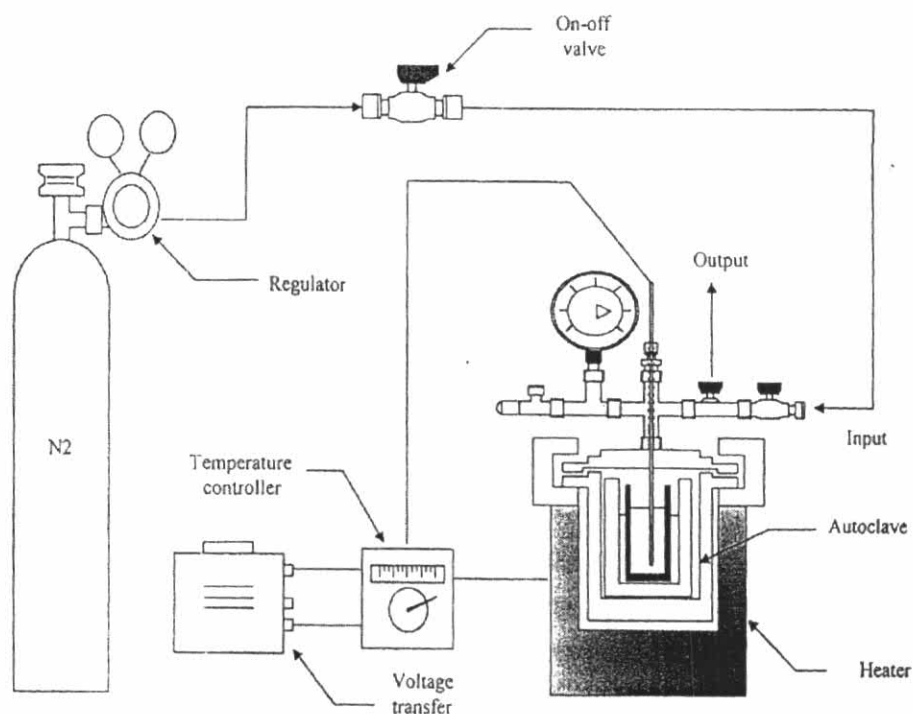


Figure 4.2 Diagram of the reaction equipment for the catalyst preparation.

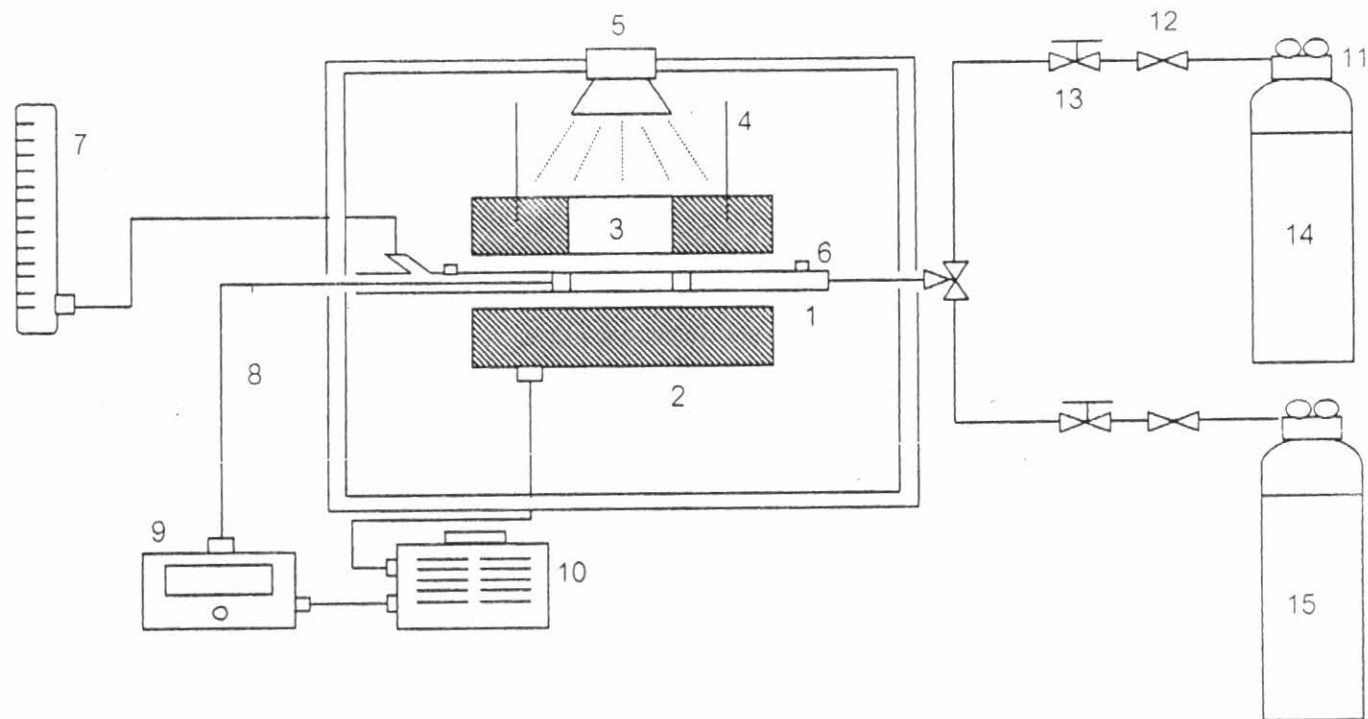
4.2.5 Photocatalytic Reactions

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 cylinder 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 1000 ppm was continuously supplied to the horizontal quartz at a constant flow rate. 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. An air stream was passed through the photoreactor in UV illumination until the gas-solid adsorption equilibrium (60 min, depending upon the nature and the concentration of VOC) 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.

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



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

Figure 4.3 Diagram of the photocatalytic reaction equipment

4.2.6 CO hydrogenation

4.2.6.1 Material

CO hydrogenation was carried out at 493 K and 1 atm total pressure in a fixed-bed stainless steel reactor under differential conversion conditions. A flow rate of $\text{H}_2/\text{CO}/\text{Ar} = 20/2/8 \text{ cm}^3 \text{ min}^{-1}$ was used. Typically, 0.2 g of the catalyst samples was reduced in situ in flowing H_2 ($50 \text{ cm}^3 \text{ min}^{-1}$) at 623 K for 10 h prior to reaction. The product samples were taken at 1 h intervals and analyzed by gas chromatography. Steady state was reached after 6 h time-onstream in all cases.

4.2.6.2 Apparatus

Flow diagram of CO hydrogenation system is shown in Figure 4.4. The system consists of a reactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

4.2.6.2.1 Reactor

The reactor was made from a stainless steel tube (O.D. 3/8"). Two sampling points were provided above and below the catalyst bed. Catalyst was placed between two quartz wool layers.

4.2.6.2.2 Automation Temperature Controller

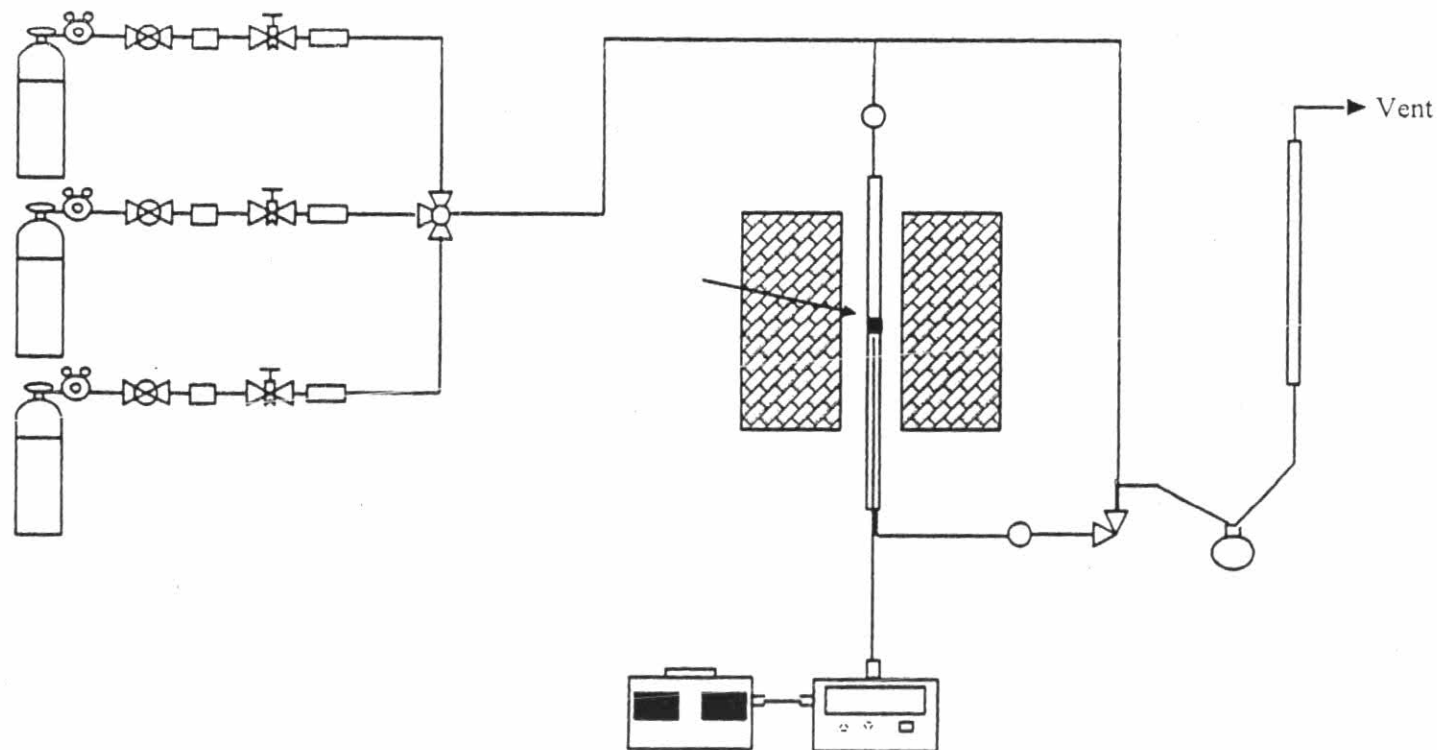
This unit consisted of a magnetic switch connected to a variable voltage transformer and a solid state relay temperature controller model no. SS2425DZ connected to a thermocouple. Reactor temperature was measured at the bottom of the catalyst bed in the reactor. The temperature control set point is adjustable within the range of 273-1073 K at the maximum voltage output of 220 volt.

4.2.6.2.3 Electrical Furnace

The furnace supplied heat to the reactor for CO hydrogenation. The reactor could be operated from temperature up to 1073 K at the maximum voltage of 220 volt.

4.2.6.2.4 Gas Controlling System

Reactant for the system was each equipped with a pressure regulator and an on-off valve and the gas flow rates were adjusted by using metering valves.



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|-----------------------|-----------------------|----------------------------------|----------------------------|
| 1. Pressure Regulator | 2. On-Off Valve | 3. Gas Filter | 4. Metering Valve |
| 5. Back Pressure | 6. 3-way Valve | 7. Catalyst Bed | 8. Sampling point |
| 9. Furnace | 10. Thermocouple | 11. Variable Voltage Transformer | 12. Temperature Controller |
| 13. Heating Line | 14. Bubble Flow Meter | | |

Figure 4.4 Flow diagram of CO hydrogenation system

4.2.6.2.5 Gas Chromatograph

The composition of hydrocarbons in the product stream was analyzed by a Shimadzu GC-14B (VZ-10) gas chromatograph equipped with a flame ionization detector. A Shimadzu GC-8A (molecular sieve 5A) gas chromatograph equipped with a thermal conductivity detector was used to analyze CO and H₂ in the feed and product streams. The operating conditions for each instrument are shown in the Table 4.2.

Table 4.2 Operating condition for gas chromatograph

Gas Chromatograph	SHIMADZU GC-8A	SHIMADZU GC-14B
Detector	TCD	FID
Column	Molecular sieve 5A	VZ10
– Column material	SUS	-
– Length	2 m	-
– Outer diameter	4 mm	-
– Inner diameter	3 mm	-
– Mesh range	60/80	60/80
– Maximum temperature	663 K	353 K
Carrier gas	He (99.999%)	N ₂ (99.999%)
Carrier gas flow (ml/min)	30 ml./min	30 ml./min
Column temperature		
- initial (K)	333	343
- final (K)	333	343
Injector temperature (K)	373	373
Detector temperature (K)	310	423
Current (mA)	353	-
Analysed gas	Ar, CO, H ₂	Hydrocarbon C ₁ -C ₄

4.2.6.3 Procedures

CO hydrogenation was performed using 0.2 g of catalyst was packed in the middle of the stainless steel microreactor, which located in the electrical furnace. The total flow rate was 30 ml/min with the H₂/CO ratio of 10/1. The catalyst sample was re-reduced *in situ* in flowing H₂ at 623 K for 10 h prior to CO hydrogenation. CO hydrogenation was carried out at 493 K and 1 atm total pressure. The product streams were analyzed by gas chromatography (GC). In all cases, steady-state was reached within 5 h.

The effluent gases were sampled to analyse the concentration of hydrocarbon (C1-C4) using GC-14B equipped with a VZ10 column, whereas carbon monoxide concentration was analyzed by GC-8A equipped with a Molecular sieve 5A column. The example of chromatogram of catalyst sample from GC-8A and GC-14B and the calibration curve of reactant (CO) and products (light hydrocarbon such as methane (CH₄), ethane (C₂H₆), propane (C₃H₈), etc.) are shown in Appendix F. Details of the calculation of the catalytic activity to convert carbon monoxide, reaction rate and the selectivity towards hydrocarbon (C1-C4) are given in Appendix G.

4.3 Preparation of catalyst

4.3.1 Preparation of titania

Titania was prepared by using TNB 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 (573-623 K) at the rate of 275.5 K min⁻¹ and held at that temperature for 0.5-8 hours. In this study, for desired crystallite sizes 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 calcination of the thus-obtained product was carried out in a box furnace. The product was heated at a rate of 283 K min^{-1} to 573 K and held at that temperature for 1 hour.

4.3.2 Cobalt loading

The Co/TiO₂ (20 wt. % of Co) catalysts will be prepared by the incipient wetness impregnation of the supports with aqueous solution of cobalt nitrate. The catalyst will be dried at 383 K for 12 hours and calcined in air at 773 K for 4 hours. Details of calculation of preparation are given in Appendix B.

4.4 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 CuK α radiation. The crystallite size was estimated from line broadening according to the Scherrer equation (see Appendix A) and α -Al₂O₃ 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	473 K for as-synthesized sample 573 K for calcined sample
Vacuum pressure	< 10 μ mHg

4.4.5 Temperature programmed reduction (TPR)

TPR was used to determine the reducibility of catalysts. The catalyst sample 50 mg used in the operation and temperature ramping from 308 K to 1073 K at 283 K/min. The carrier gas is 5 %H₂ in Ar. During reduction, a cold trap will be placed to before the detector to remove water produced. A thermal conductivity detector (TCD) was measure the amount of hydrogen consumption. The operating condition of the TCD is shown in Table 4.2. The calibration of hydrogen consumption was used cobalt oxide (Co₃O₄) at the same condition. Details of calculation for reducibility of the catalyst samples are given in Appendix D.

Table 4.3 Operating condition of the thermal conductivity detector for TPR.

Model	GOW-MAC
Detector type	TCD
Carrier gas	5 %H ₂ in Ar
Carrier gas flow rate (ml/min)	30
Detector temperature (K)	353
Detector current (mA)	80

4.4.6 Hydrogen chemisorption

Static H₂ chemisorption at 373 K on the reduced catalysts (re-reduced at 623 K) was used to determine the number of reduce surface cobalt metal atoms and percentage overall cobalt dispersion. H₂ chemisorption was carried out following the procedure described by Reuel and Bartholomew (1984) using a Micromeritics Pulse Chemisorb 2700 instrument at the Analysis Center of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. Prior to chemisorption, the catalysts were reduced at 623 K for 10 hours. Details of calculation of the total hydrogen chemisorption and dispersion are given in Appendix E.

4.4.7 Temperature programmed desorption

Temperature programmed desorption using CO₂ as a probe molecule (CO₂-TPD) was performed to determine the Ti³⁺ site existing on the surface of TiO₂ particle. The CO₂-temperature program desorption was carried out using a homemade equipment composed of a quartz tube in a temperature-controlled bath connecting to a gas chromatograph (GOW-MAC) with thermal conductivity detector. Approximately 0.05 g of a TiO₂ sample was dosed by 1 vol. % CO₂ in helium for 1 h and then desorbed from 143 K to 273 K with the rate of 21.5 K/min.

4.4.8 Electron spin resonance spectroscopy

Electron spin resonance spectroscopy (ESR) was conducted using a JEOL JESRE2X electron spin resonance spectrometer. The intensity of ESR was calculated using a computer software program ES-PRIT ESR DATA SYSTEM (version 1.6). Transmission electron micrographs of the TiO₂ samples were obtained using a JEOL JEM 1220 electron microscope operated at 80 kVa.