

## CHAPTER IV

### EXPERIMENT

This work was divided into 3 parts : the preparation of catalysts, the carbon monoxide oxidation reaction, and the determination and characterization of catalysts. In each part, the details of procedures, chemicals and reagents, and instruments used were described.

#### 4.1 Preparation of Catalysts

##### 4.1.1 Chemicals and Reagents

The chemicals used in this experiment were normally analytical grade, only some critical chemicals had to be specified as follows :

-  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was manufactured by E. MERCK Frankfurter strasse 250, D-6100 Darmstadt, Federal Republic of Germany.

-  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  was manufactured by WAKO PURE CHEMICAL INDUSTRIES, LTD.

-  $\gamma\text{-Al}_2\text{O}_3$  Support (type KNH-3) was obtained from SUMITOMO ALUMINUM SMELTING CO., LTD.

- Hydrogen, Nitrogen, and Air were bought from THAI INDUSTRIAL GASES LIMITED.

#### 4.1.2 Instruments and Apparatus

##### 4.1.2.1 Unit for Grinding and Screening Support.

This unit consists of pestle, mortar, and sieve. It is used for reducing and screening the size of support down to 40/60 mesh (See Figure 4.1).



Figure 4.1 Unit for Grinding and Screening Support.

4.1.2.2 Unit for Impregnation. This unit consists of pipet, flask, dropper, and volumetric flask. It is used for preparing aqueous solution and impregnating the solution onto the support (See Figure 4.2).



Figure 4.2 Unit for Impregnation

4.1.2.3 Unit for Calcination. This unit is an electrical furnace which consists of an insulator, a heating coil, an automatic temperature controller and a variable voltage transformer. It is used for calcining catalysts at high temperature (See Figure 4.3).



Figure 4.3 Unit for Calcination

#### 4.1.3 The Preparation of Catalysts

The main catalyst used in this study is copper supported on alumina. The modification made on this catalyst is the inclusion of platinum onto the same support. The preparation procedures will be presented separately.

4.1.3.1 Preparation of the Copper Catalyst In this study the incipient impregnation method is chosen for depositing the metal component on to the support. The important characteristic of this method is the equal volume of the impregnating solution and the support pore volume. The procedure is described, in steps, as follows:

(1) The alumina support was ground to the required mesh size of 40/60 and then washed with distilled water 3-4 times in order to remove the dust particles and the impurities. Finally, it was dried in the oven at 110 °C overnight.

(2) The alumina support was placed in 50 ml. flask and the aqueous solution of research grade cupric nitrate was slowly added (See Appendix A., Methods for calculating the volume of cupric nitrate solution and weight of support used in the preparation). Continuous stirring of the mixture in the flask was required to obtain the homogeneously distributed metal component on support.

(3) The impregnated material was left in ambient temperature for over 6 hours and then dried at 110 °C overnight.

After a step (3) of the preparation procedure, the impregnated material was ready to be calcined at high temperature in electrical furnace under desired conditions (various temperatures, times, and atmospheres); (See Table 4.1).

4.1.3.2 Preparation of the Platinum Promoted Copper Catalysts. The same method is used as above, but in this section there will be two metal components on the same support. The consecutive impregnation method was chosen in this study. The procedure is described as follows:

(1) The method for platinum loading is the same as step (2) and (3) in section 4.1.3.1, but the aqueous solution of cupric nitrate is replaced by an aqueous solution of chloroplatinic acid (See Appendix A., Method for calculating the volume of chloroplatinic acid solution and weight of support used in the preparation).

(2) The impregnated material was then calcined in the flow of air with space velocity of about  $1200 \text{ h}^{-1}$ , heating rate of  $10^\circ\text{C}/\text{min}$ . was used to attain the temperature of  $500^\circ\text{C}$ . The catalyst was held in this condition for 4 hours.

(3) The platinized alumina was re-impregnated with an aqueous solution of cupric nitrate by the same method as step (2) and (3) in section 4.1.3.1. The catalyst was then ready to be calcined under desired conditions (See Table 4.2).

Table 4.1 Preparation Conditions of 8% Cu/Al<sub>2</sub>O<sub>3</sub>

Catalysts Code Assigned	Preparation Conditions		
	Calcination Atmosphere**	Calcination Temperature (°C)	Period of Calcination (h.)
CAT.1	*	*	*
CAT.2	air	500	1
CAT.3	10% H <sub>2</sub> in N <sub>2</sub>	500	3
CAT.4	10% H <sub>2</sub> in N <sub>2</sub>	600	3
CAT.5	10% H <sub>2</sub> in N <sub>2</sub>	700	3
CAT.6	10% H <sub>2</sub> in N <sub>2</sub>	800	3
CAT.7	10% H <sub>2</sub> in N <sub>2</sub>	500	7

\* CAT.1 is 8% copper on alumina which was prepared by using the same condition as reported by Huang et al.[5], calcined the catalyst sample at 500 °C in air for 4 h and subsequently reduced at 300 °C in 10% H<sub>2</sub> in N<sub>2</sub> for 2 h after that recalcined at 800 °C in 10% H<sub>2</sub> in N<sub>2</sub> for 12 h and subsequently oxidized at 300 °C for 1 h.

\*\* Space velocity of air and 10% H<sub>2</sub> in N<sub>2</sub> were 1200 and 2000 h<sup>-1</sup>, respectively.

Table 4.2 Preparation Conditions of Platinum Promoted Copper Catalysts\*

Catalysts Code Assigned	Preparation Conditions			
	%Pt loading	Calcination Atmosphere	Calcination Temperature(°C)	Period of Calcination(h.)
CAT.8	0.3	10% H <sub>2</sub> in N <sub>2</sub>	500	1
CAT.9	0.3	10% H <sub>2</sub> in N <sub>2</sub>	500	3
CAT.10	0.3	10% H <sub>2</sub> in N <sub>2</sub>	500	5
CAT.11	0.3	10% H <sub>2</sub> in N <sub>2</sub>	500	7
CAT.12	0.3	10% H <sub>2</sub> in N <sub>2</sub>	500	9
CAT.13	0.05	10% H <sub>2</sub> in N <sub>2</sub>	500	7
CAT.14	0.1	10% H <sub>2</sub> in N <sub>2</sub>	500	7
CAT.15	0.5	10% H <sub>2</sub> in N <sub>2</sub>	500	7
CAT.16	0.3	air	500	7
CAT.17 <sup>e</sup>	0.3	10% H <sub>2</sub> in N <sub>2</sub>	500	7

\* Conditions in this table is used after step (3) in section 4.1.3.2 was accomplished.

\*\* Space velocity of air and 10% H<sub>2</sub> in N<sub>2</sub> were 1200 and 2000 h<sup>-1</sup>, respectively.

<sup>e</sup> Non-loading of copper in this catalyst.



## 4.2 Carbon Monoxide Oxidation

### 4.2.1 Chemicals and Reagents

- Carbon monoxide of ultra high purity grade (99.99%) was bought from UNION CARBIDE THAILAND LIMITED.

- Oxygen and Nitrogen were bought from THAI INDUSTRIAL GASES LIMITED.

### 4.2.2 Instruments and Apparatus

4.2.2.1 Reactor The CO oxidation reactor is a conventional microreactor made from Quartz tubing, so it can be operated at high temperature. The reaction was carried out under ordinary gas flow and atmosphere pressure.

4.2.2.2 Automatic Temperature Controller This consists of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller series RE-96 connected to a thermocouple attached to the catalyst bed in reactor. A dial setting establishes a set point at any temperature within the range between 0 °C to 400 °C.

4.2.2.3 Electrical furnace This supplies the required heating to the reactor for CO oxidation reaction. The reactor can be operated from room temperature up to 900 °C at maximum voltage of 200 volt.

#### 4.2.2.4 Gas Controlling System.

The system consists of:

- a carbon monoxide cylinder equipped with a pressure regulator (0 - 800 kPa), an on-off valve and fine-metering valve used to adjust flow rate of carbon monoxide.
- an oxygen and a nitrogen cylinder equipped with a pressure regulator (0 - 120 psig), an on-off valve and a needle valve used to adjust flow rate of oxygen and nitrogen, respectively.

#### 4.2.2.5 Gas Chromatograph

Thermal Conductivity Detector Gas Chromatograph was used to analyze the concentrations of carbon monoxide and oxygen at the inlet and outlet of the reactor. Operating conditions used are as follows:

G.C.	: SHIMADZU GC-8A
Detector	: T.C.D.
Packed column	: MS-5A
Carrier gas	: Helium
Flow rate of carrier gas	: 30 cc/min.
Column temperature	: 90 °C
Detector temperature	: 100 °C
Injector temperature	: 100 °C

The photograph of gas chromatograph and the chromatogram obtained from gas analysis are shown in Figure 4.4 and Appendix B, respectively.



Figure 4.4 Gas Chromatograph System

ศูนย์วิทยทรัพยากร  
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#### 4.2.3 Procedure

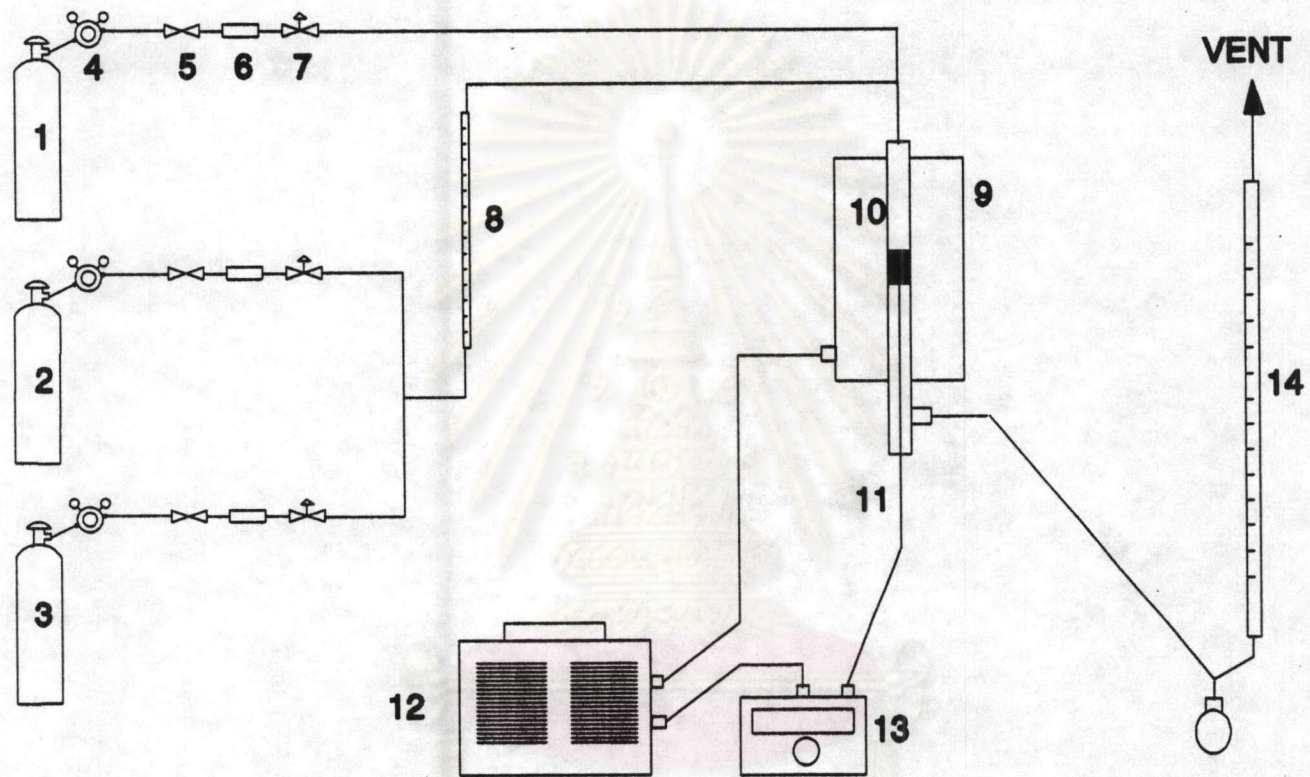
The carbon monoxide activity of the catalyst was measured in a conventional microreactor made from Quartz tubing. Reactions were carried out using an ordinary flow reactor under atmospheric pressure. A 700 cc/min. of gas mixture (consisting of 1.2% by volume of CO, 1.2% by volume of O<sub>2</sub> balanced with N<sub>2</sub>) was passed over 150 mg. of catalyst and the hourly space velocity of the gas was approximately 140,000 h<sup>-1</sup>. The catalytic activity was evaluated at the temperature range that the conversion of CO was changed from 0 to 100%. The temperature of the reactor was started up at 120 °C and held at this temperature for half an hour before increasing to 140 °C. The reactor was heated up every 20 min. (10 °C per time interval). At each of the reactor temperatures, the concentration of CO and O<sub>2</sub> at the inlet and outlet stream was analyzed and the conversion of carbon monoxide was evaluated. The flow diagram of the carbon monoxide oxidation system was shown in Figure 4.5.

### 4.3 Determination and Characterization of Catalysts

#### 4.3.1 Temperature-Programmed Desorption of Carbon Dioxide

##### 4.3.1.1 Introduction

In this study, it was intended to measure the adsorbable strength and the amount of carbon dioxide adsorbed on catalysts. Based on the mechanisms of contact catalysis, desorption of the reaction product from the catalyst particle is an important step of this mechanism. When the reaction products can be strongly



- |                        |                       |                    |                                  |                            |
|------------------------|-----------------------|--------------------|----------------------------------|----------------------------|
| 1. N <sub>2</sub> tank | 4. Pressure regulator | 7. Needle valve    | 10. Reactor                      | 13. Temperature controller |
| 2. CO tank             | 5. On-off valve       | 8. Flow meter      | 11. Thermocouple                 | 14. Bubble flow meter      |
| 3. O <sub>2</sub> tank | 6. Gas filter         | 9. Reactor furnace | 12. Variable voltage transformer |                            |

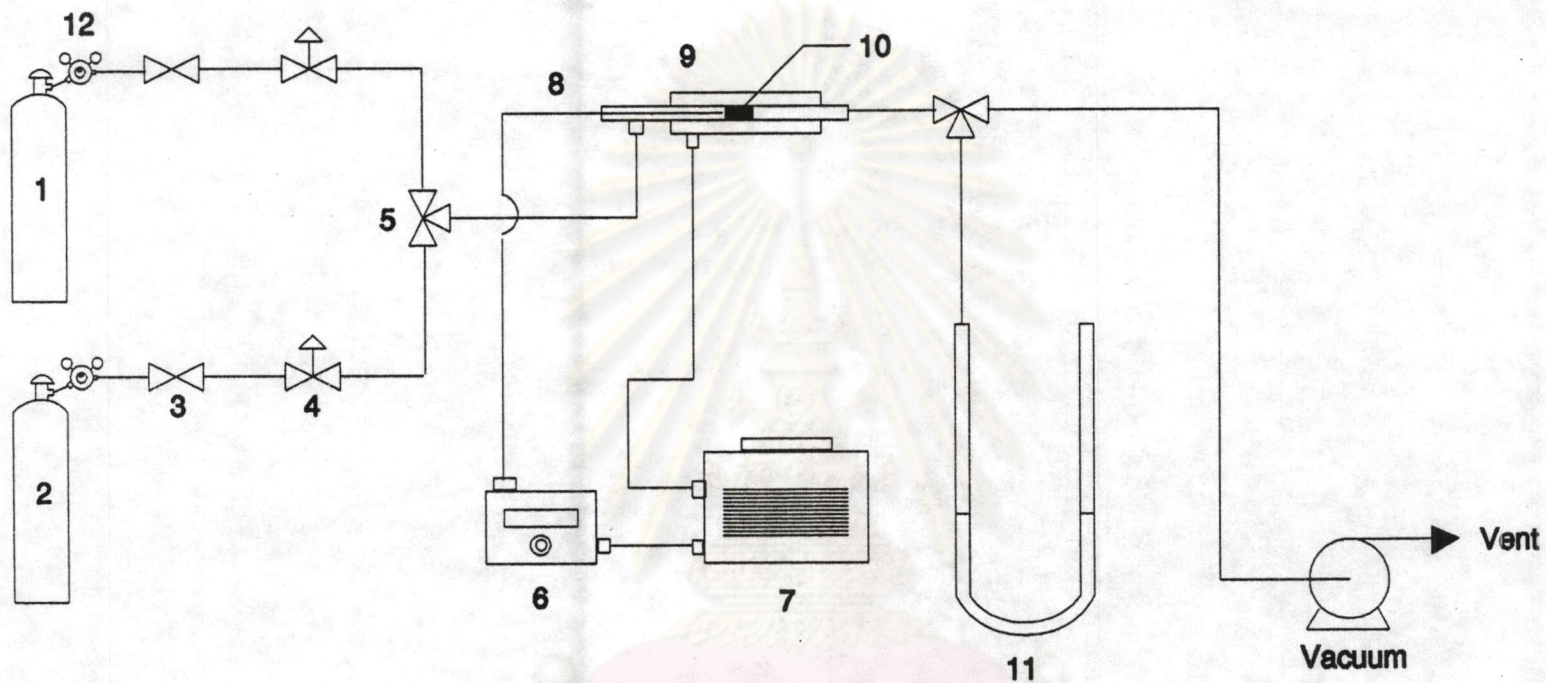
Figure 4.5 Flow diagram of the carbon monoxide oxidation system

adsorbed on the catalyst surface, it will prevent the reactants from reaching the catalyst surface [48]. Therefore, the activity of catalyst depends on the ability to desorb the reaction products from its surface. Because the desorption of the adsorbed gas is stimulated by elevating temperature. Thus, the proportion of the desorbed gas at various temperatures establishes a good measurement of the adsorbable strength of the catalyst.

#### 4.3.1.2 Procedure

The temperature-programmed desorption (TPD) of carbon dioxide on a catalyst was done in a quartz tube reactor packed with 300 mg of catalyst sample and connected to an ordinary vacuum line or adsorption unit (See Figure 4.6). The catalyst was treated in air stream under atmospheric pressure with a flow rate of 30 cc/min. for 1 hour at 300 °C and then evacuated at the same temperature under pressure of  $6.13 \times 10^4 \text{ N.m}^{-2}$  (-30 mm.Hg) for 30 minutes. Carbon dioxide was introduced into the reactor under a pressure of  $2.01 \times 10^5 \text{ N.m}^{-2}$  (100 kPa), while simultaneously cooling the reactor to room temperature (30 °C). The tube containing catalyst was evacuated for 10 minutes and repeatedly introduced with carbon dioxide at pressure of  $2.01 \times 10^5 \text{ N.m}^{-2}$  for 30 min. in order to completely absorb carbon dioxide on the site of catalyst surface.

The reactor was removed from Adsorption Unit and connected to Desorption Unit (See Figure 4.7). Helium was introduced into the reactor at a flow rate of 20 cc/min. The temperature of catalyst was increased at a rate of 30 °C/min. The amount of desorbed carbon dioxide was measured by thermal conductivity detector.



- |                               |                                 |                        |
|-------------------------------|---------------------------------|------------------------|
| 1. CO or CO <sub>2</sub> tank | 5. Three way valve              | 9. Heater              |
| 2. Air or H <sub>2</sub> tank | 6. Temperature controller       | 10. Catalyst bed       |
| 3. On-off valve               | 7. Variable voltage transformer | 11. Manometer          |
| 4. Needle valve               | 8. Thermocouple                 | 12. Pressure regulator |

Figure 4.6 Flow diagram of adsorption unit of temperature-programmed desorption

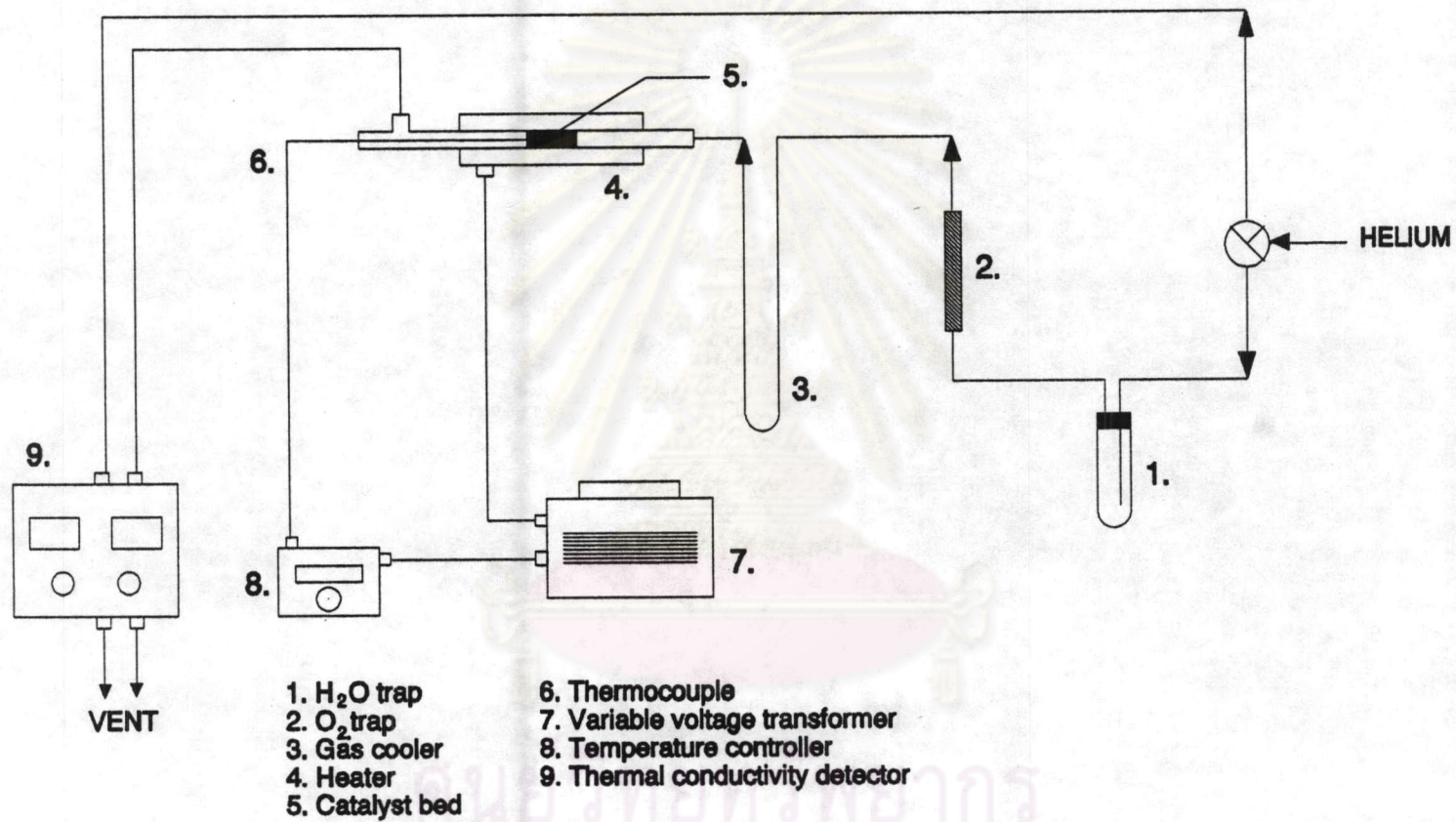


Figure 4.7 Flow diagram of desorption unit of temperature-programmed desorption



#### 4.3.2 Carbon Monoxide Adsorption Capacity Measurements

##### 4.3.2.1 Introduction

In recent years, it was found that the enhancement of catalyst activity of copper catalyst for carbon monoxide oxidation might be caused by a strong metal-support interaction effect [5]. Therefore, in this section of the experiment, the carbon monoxide adsorption capacity measurement of a series of the prepared catalysts (used in part 4.2) was done in order to compare with its activities.

##### 4.3.2.2 Procedure

Carbon monoxide adsorption capacity measurements were carried out in the same apparatus as TPD of carbon dioxide. 300 mg. of catalyst sample was packed in the reactor. The catalyst was degassed for 30 min. at 300 °C under pressure of  $6.13 \times 10^4 \text{ N.m}^{-2}$  (-30 mm.Hg). Subsequently, the catalyst was reduced with 30 cc./min. of hydrogen at 300 °C for 1 h. and then degassed again at the same temperature for 30 min. under pressure of  $6.13 \times 10^4 \text{ N.m}^{-2}$ . The catalyst sample was then cooled down to room temperature under the same pressure. Carbon monoxide was introduced into the reactor under a pressure of  $2.01 \times 10^5 \text{ N.m}^{-2}$  (100 kPa) for 30 min. in order to adsorb carbon monoxide completely on the metal site of catalyst surface.

The reactor was removed from Adsorption Unit and connected with Desorption Unit. Helium was introduced into the reactor at a flow rate of 20 cc./min. The temperature of catalyst

was increased at a rate of  $30^{\circ}\text{C}/\text{min}$ . The amount of desorbed carbon monoxide was measured by thermal conductivity detector.

#### 4.3.3 BET Surface Area Measurement

##### 4.3.3.1 Introduction

Specific surface area of the catalyst was measured by a BET Surface Area Analyzer. This method uses a physical adsorption of  $\text{N}_2$  on the surface of catalyst to find the specific surface area. Results from this measurement could be used to confirm whether the adsorption of  $\text{CO}$  or  $\text{CO}_2$  on the catalyst is a physical adsorption.

##### 4.3.3.2 Procedure

BET surface area was measured by a surface area analyzer as shown in Fig. 4.8. The gas mixture of He and  $\text{N}_2$  flowed through the system at  $\text{N}_2$  partial pressure of 0.3. The gas detector used was of thermal conductivity type (T.C.D.) and operated at detector temperature of  $80^{\circ}\text{C}$  and filament current of 80 mA.

The sample was placed in a sample cell and connected to the surface area analyzer. The sample was then heated up to  $120^{\circ}\text{C}$ , held at this temperature for 1 hour and cool down to room temperature. There were three steps in this surface area measurement: adsorption, desorption, and calibration.

- Adsorption step: The sample cell was dipped into liquid nitrogen. The  $\text{N}_2$  in gas mixture would be adsorbed

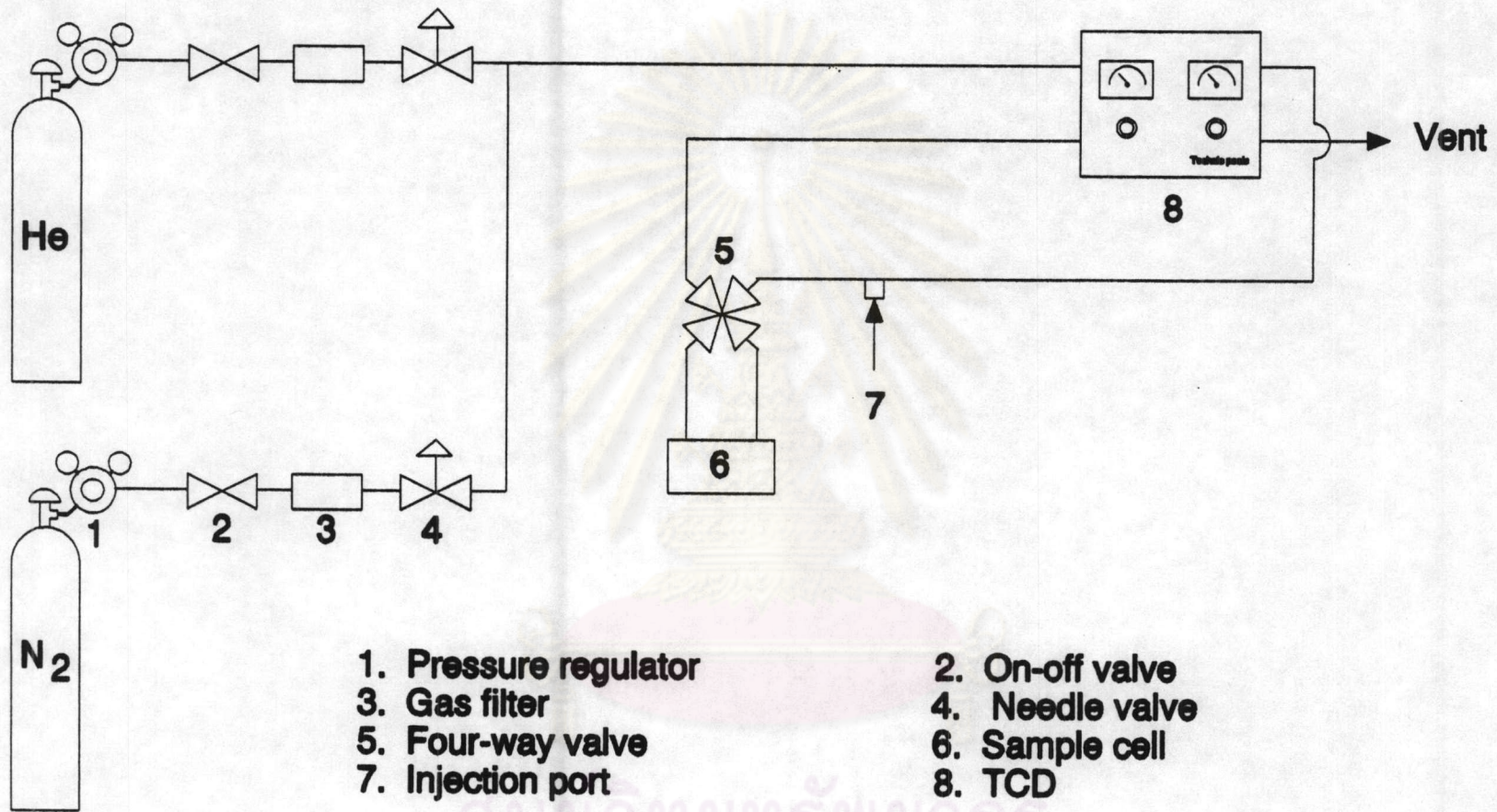


Figure 4.8 Flow diagram of the BET surface area analyzer

onto the surface of the catalyst sample, shown as a peak on the recorder, when the equilibrium was reached, a straight line was shown on the recorder.

- Desorption step: The sample cell was taken out of liquid nitrogen and then dipped into water. The adsorbed  $N_2$  would be desorbed from the surface of the catalyst sample until the equilibrium was reached, shown as a peak in the opposite direction to adsorption.

- Calibration step: Nitrogen gas of 1 cc. at atmosphere pressure was injected at the sampling point. The standard nitrogen peak would appear at the same side of desorption peak.

#### 4.3.4 Electrical Conductivity Measurement

##### 4.3.4.1 Introduction

In this section, it was intended to measure the specific electrical conductivity of the catalyst. Since the metals in strong metal-support interaction (SMSI) state exhibit the high electrical conductivity measurement. The measurement of this value is one of the methods to observe this phenomena.

##### 4.3.4.2 Procedure

The catalyst was ground to finely powder and then reduced with hydrogen stream (30 ml./min.) at  $300^\circ\text{C}$  for 1 hour. At the end of hydrogen period, the finely powder of catalyst was

pressed in a pellet die under 2000 psi for 5 min. The electrical resistance of the pellet was measured by PM 6303 automatic RCL meter (Philips) through the pellet-die assembly. The thickness and the cross section of the pellet were measured so that the specific electrical conductivity could be calculated. These measurements have been used only for qualitative guidance [49].

The photographs of pellet die and PM 6303 automatic RCL meter (Philips) were shown in Fig. 4.9.

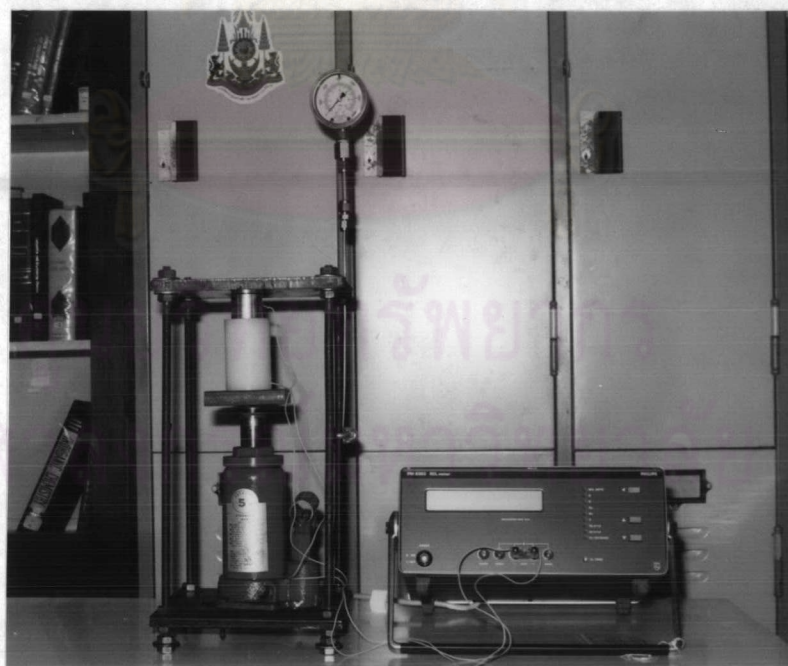
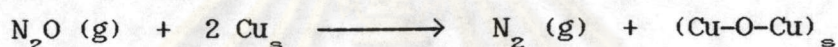


Figure 4.9 Pellet die and PM 6303 automatic RCL meter (Philips)

### 4.3.5 Metal Active Sites Measurement [16]

#### 4.3.5.1 Introduction

Copper active sites of catalyst is measured by the reaction with nitrous oxide ( $N_2O$ ). This method is able to measure metal active sites for both pure and supported copper catalyst. It is based on the decomposition of a nitrous oxide molecule on a copper surface accompanied by the liberation of one nitrogen molecule according to the reaction;



where the subscript 's' signifies surface atom.

Besides the metal active sites measurements, in this study, this method was applied to observe the metal-metal interaction between platinum and copper. Because carbon monoxide chemisorption on copper is weak and reversible [50], therefore it was assumed in the condition of this study that carbon monoxide does not adsorbed on copper catalyst. The applicable method would be mentioned in section 4.3.5.3.

#### 4.3.5.2 Procedure for Metal Active Sites Measurements

Prior to reaction with nitrous oxide, each catalyst was degassed in helium stream (30 cc./min.) at 300 °C for 1 hour. At the end of the reductive period, hydrogen was substituted by argon to pass over the catalyst at the same reduction temperature (300 °C) for 10 min to ensure that all hydrogen was flushed from the

system.

The temperature of the catalyst sample was then decreased from 300 °C to 90 °C and maintained at 90 °C for nitrous oxide reaction. A certain volume of nitrous oxide was injected into the argon stream through injection port of gas chromatograph and passed over the catalyst. The amount of catalyst packed in the reactor ranged from 0.1 and 0.5 gm. depending on their estimated copper active sites and the volume of nitrous oxide was fed in the range between 0.1 and 0.5 cc. The configuration of the thermal conductivity detector (T.C.D.) enables both the nitrous oxide peaks and the nitrogen peak to be determined. The nitrogen and nitrous oxide gases are able to be separated on the Porapak Q column.

The flow diagram of the nitrous oxide reaction system used to measure copper active sites was shown in Figure 4.10.

#### 4.3.5.3 Procedure for the Observation of the Metal-Metal Interaction between Platinum and Copper

Each catalyst was degassed in He stream (30 cc/min) at 150 °C for 30 min and then reduced in hydrogen stream (30 cc/min) at 300 °C for 1 hour. At the end of reductive period, hydrogen was substituted by argon to pass over the catalyst at the same reduction temperature (300 °C) for 10 min to ensure that all hydrogen was flushed from the system.

The temperature of the catalyst sample was decreased from 300 °C to room temperature. Prior to reaction with

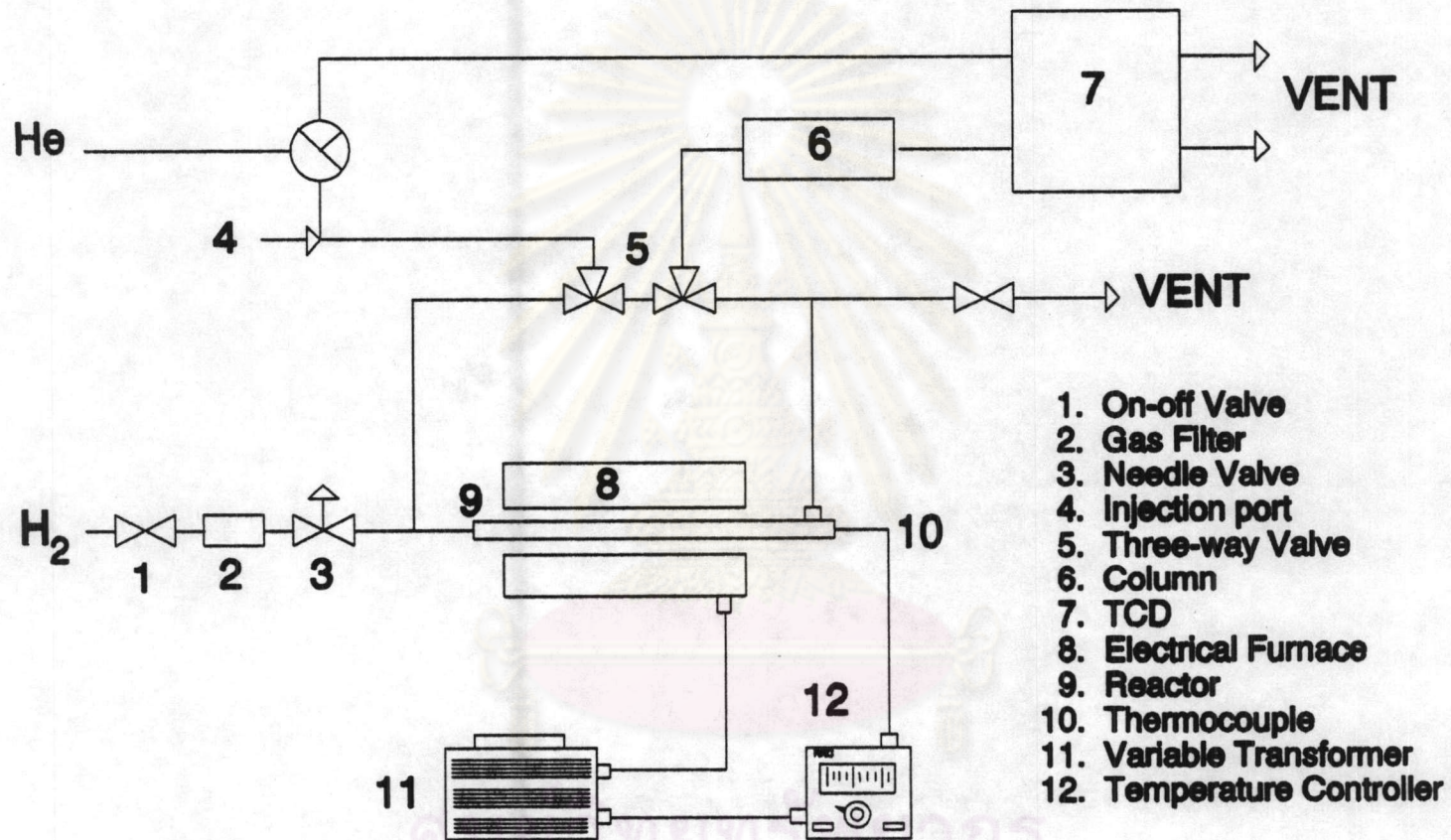


Figure 4.10 Flow diagram of the nitrous oxide reaction for measurement of copper surface area



nitrous oxide, carbon monoxide adsorption of platinum in each catalyst was made. A certain volumes of CO was injected into the argon stream through injection port of gas chromatograph and pass over the catalyst. CO injection was made until its peak area was constant. After CO adsorption, the catalyst was heated up to 150 °C and maintained at this temperature for 10 min in order to remove the adsorbed CO. Then, the temperature of catalyst was decreased to 90 °C and maintained at 90 °C for nitrous oxide reaction. After nitrous oxide reaction, the temperature of the catalyst was again decreased to room temperature and CO adsorption was made. The same apparatus used in section 4.3.5.2 was also used for this applicable method.

#### 4.3.6 Chemical Analysis

Percentage of metals loading was analyzed by Atomic Absorption and Inductively Coupled Plasma Spectrometry method. Catalyst was prepared in solution form by the following procedure:

A certain amount of catalyst (about 100 mg.) was digested by digesting solution; the solution of 20 ml. of conc. HCl, 10 ml. of conc. HNO<sub>3</sub>, and 10 ml. of H<sub>2</sub>O. A mixture was heated up until the color of support was changed into white. During heating step, H<sub>2</sub>O must be added into the mixture to maintain the volume of mixture. Then, 2 drops of HF were added into the mixture in order to digest the support. Go on heating step until the solution was clear. The volume of the solution was made up to 100 ml. using de-ionized water.

The prepared solution was analyzed for copper by Atomic Absorption (AA) and for platinum by Inductively Coupled

Plasma Spectrometry (ICPS). The ICPS measurements were performed by The Scientific and Technological Research Equipment Centre, Chulalongkorn University.



ศูนย์วิทยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย