



## CHAPTER IV

### EXPERIMENT

This experiment was divided into 4 parts : the catalyst preparation, the catalyst and coked catalyst characterization, the catalyst deactivation by propane dehydrogenation and the coked catalyst regeneration. In each part the details of procedure, chemicals and apparatus were described as the following :

#### PREPARATION OF CATALYSTS

##### 1. Materials

The chemicals used in this experiment are normally analytical grade, but only some critical chemical have to specified as follows.

(a). Chloroplatinic Acid (  $\text{H}_2\text{PtCl}_2 \cdot 6\text{H}_2\text{O}$  ) manufactured by Wako Pure Chemical Industries Co., Ltd., Japan.

(b). Stannous Chloride Dihydrate (  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  ) manufactured by Fluka Chemie AG, Switzerland.

(c). Lithium Nitrate (  $\text{LiNO}_3$  ) manufactured by E. Merck , Federal Republic of Germany.

(d). Sodium Nitrate (  $\text{NaNO}_3$  ) manufactured by E. Merck,

Federal Republic of Germany.

(e). Alumina (  $\text{Al}_2\text{O}_3$  ) Support ( type KNH-3 ) was obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan.

## **2. Apparatus**

(a). Unit of grinding and screening support. This unit which consists of pestle, mortar and sieve is used for size reduction of alumina support to 60/80 Mesh.

(b). Unit of dry impregnation. This unit which consists of pipette, flask, beaker, dropper and volumetric flask is used for preparing aqueous solution and impregnating the solution onto the support.

(c). Unit of calcination. This unit which consists of electrical furnace, automatic temperature controller and variable voltage transformer is used for calcining the impregnated catalysts at high temperature.

## **3. Preparation of platinum catalysts**

### **3.1 Preparation of support and stock solution**

#### **3.1.1 Preparation of support**

Alumina support was grounded to the required mesh size of 60/80 and then washed with distilled water 3-4 times to remove the very fine particles and the other imperities, dried at  $110^\circ\text{C}$  overnight, the alumina support

was then calcined in air at 300 °C for 3 hours.

### 3.1.2 Preparation of stock solution

(a). Platinum stock solution. The platinum complex solution was prepared by dissolving 1 gram of chloroplatinic acid in de-ionized water to the total volume of 25 ml.

(b). Lithium stock solution. The lithium nitrate solution was prepared by dissolving 5 grams of lithium nitrate in de-ionized water to the total volume of 25 ml.

(c). Sodium stock solution. The sodium nitrate solution was prepared by dissolving 5 grams of sodium nitrate in de-ionized water to the total volume of 25 ml.

### 3.2 Preparation of platinum catalysts

(a). The impregnating solution for 2 grams of support was prepared by calculating the amount of the stock solution to the required metal loading . Hydrochloric acid , 5 wt % of alumina support, was then added to the solution (70), de-ionized water was finally added until 2 ml. of the solution was obtained.

(b). 2 grams of alumina support was placed in a 100 ml. erlenmeyer flask and then the impregnating solution from platinum stock solution was slowly dripped into the support using a dropper. Continuous stirring of the mixture in the flask while impregnating was required to obtain the homogeneously distributed metal component on the alumina support.

(c). Leave the mixture in the flask for 6 hours to obtain good distribution of metal complex.

(d). The impregnated support was dried at  $110^{\circ}\text{C}$  in air overnight.

(e). For calcination, the dried material was placed in a quartz tube. Nitrogen gas was introduced into the tube at the flow rate of 60 ml./min. The quartz tube was heated at an increasing rate of  $10^{\circ}\text{C}/\text{min}$ . until the temperature reached  $500^{\circ}\text{C}$ . then the nitrogen gas was changed to air at a flow rate of 100 ml./min., the material was held in this condition for 3 hours.

(f). For reduction , after calcination, the material was purged by nitrogen gas then switched to hydrogen gas for another 3 hours at a flow rate of 100 ml./min, finally the material was cooled down to room temperature.

### **3.3 Preparation of platinum-tin catalysts**

The same method was used as above but there were two metal components in the impregnating solution, it called "Co-impregnation method".

### **3.4 Preparation of trimetallic catalysts**

The co - impregnation and re-impregnation were used for trimetallic catalysts, after calcination of co-impregnated platinum - tin catalyst, the calcined material was re-impregnated by lithium impregnation solution (platinum - tin- lithium catalyst) or sodium impregnation solution (platinum-tin-sodium catalyst), the calculation of lithium loading was shown in Appendix A. The re-impregnation material was treated by the same procedure as step (c) to (f) in section 3.2.

## CATALYST CHARACTERIZATION

### 1. Metal active - site measurement

#### 1.1 Materials

The helium gas was used as a carrier gas. The hydrogen gas was used to reduce the catalyst. The carbon monoxide gas was used as an adsorbed gas and a standard gas.

#### 1.2 Apparatus

The metal active site was measured by CO adsorption technique on the basis that one CO molecule adsorbed on one metal active site (71). A flow diagram of the CO adsorption is shown in figure 4.1 , The amount of CO gas adsorbed on the catalyst was measured by the thermal conductivity detector (TCD). The operating conditions of the detector are shown in table 4.1. The sample tube was quartz tube .

Table 4.1 Operating condition of TCD gas detector.

Carrier gas and flow	He 30 ml./min.
Detector temperature	80 °C
Detector current	80 mA.

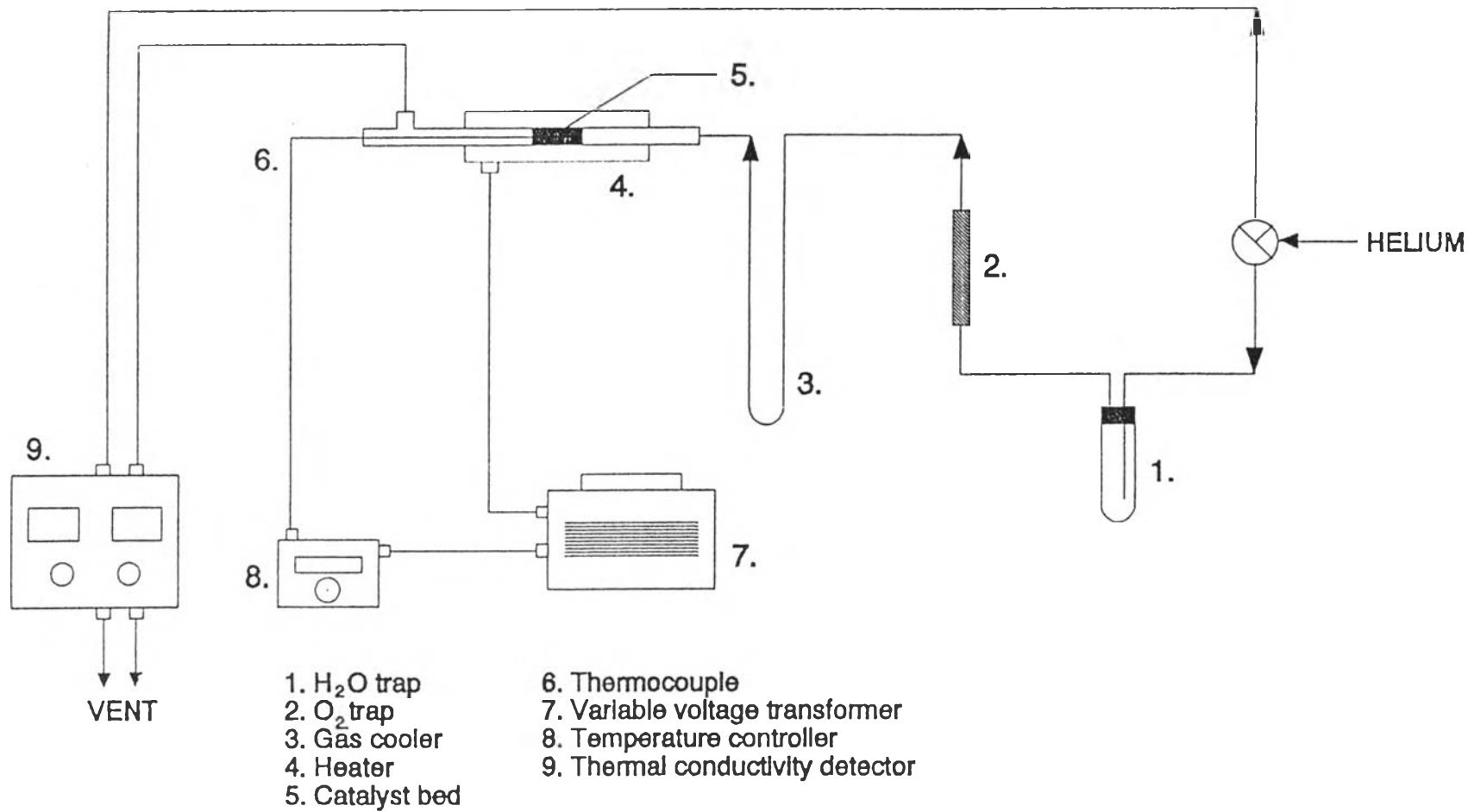


Figure 4.1 A flow diagram of the CO adsorption apparatus.

### 1.3 Procedure

(a). 300 mg. of catalyst or spent catalyst was placed in the sample tube. Helium gas was introduced into the tube at the flow rate of 30 ml./min. The tube was heated at an increasing of 10 °C/min. until the temperature reached 200 °C, then the helium gas was changed to hydrogen gas at a flow rate of 100 ml./min. The tube was continuously heated at the same rate until the temperature reached 500 °C . The tube was held in this temperature for 1 hour.

(b). Sample tube was cooled down to room temperature .

(c). The sample was then ready to measure metal active sites, 0.18 ml of the CO gas was injected to TCD at the injection port. The CO gas injection was repeated until the sample did not adsorb the CO gas.

(d). The amount of CO gas adsorbed was measured , the amount of metal active site was calculated (Appendix B).

## 2. Temperature programmed oxidation (18)

### 2.1 Materials

The 1 % oxygen in helium gas mixture supplied by Thai Industrial Gas Limited was used for oxidation reaction. The helium gas was used for purging the system. The ultra-high purity argon gas was used for cooling down the reaction.

## 2.2 Apparatus

The apparatus included two gas feed lined for helium gas and 1 % oxygen in helium gas. The proper gas was chosen by means of three-way valve. A fine metering valve was used for controlling the flow rate of the feed stream. The reactor was made of quartz glass. The temperature of the catalyst bed was measured by a thermocouple. The reactor was placed in a furnace which various heating rate was controlled by a programable temperature controller (PC-600, Shinko). A flow diagram of this system is shown in figure 4.2.

The operating conditions of gas chromatograph (GC-8 AIT, Shimadzu) used for analysing the effluent stream were shown in Table 4.2.

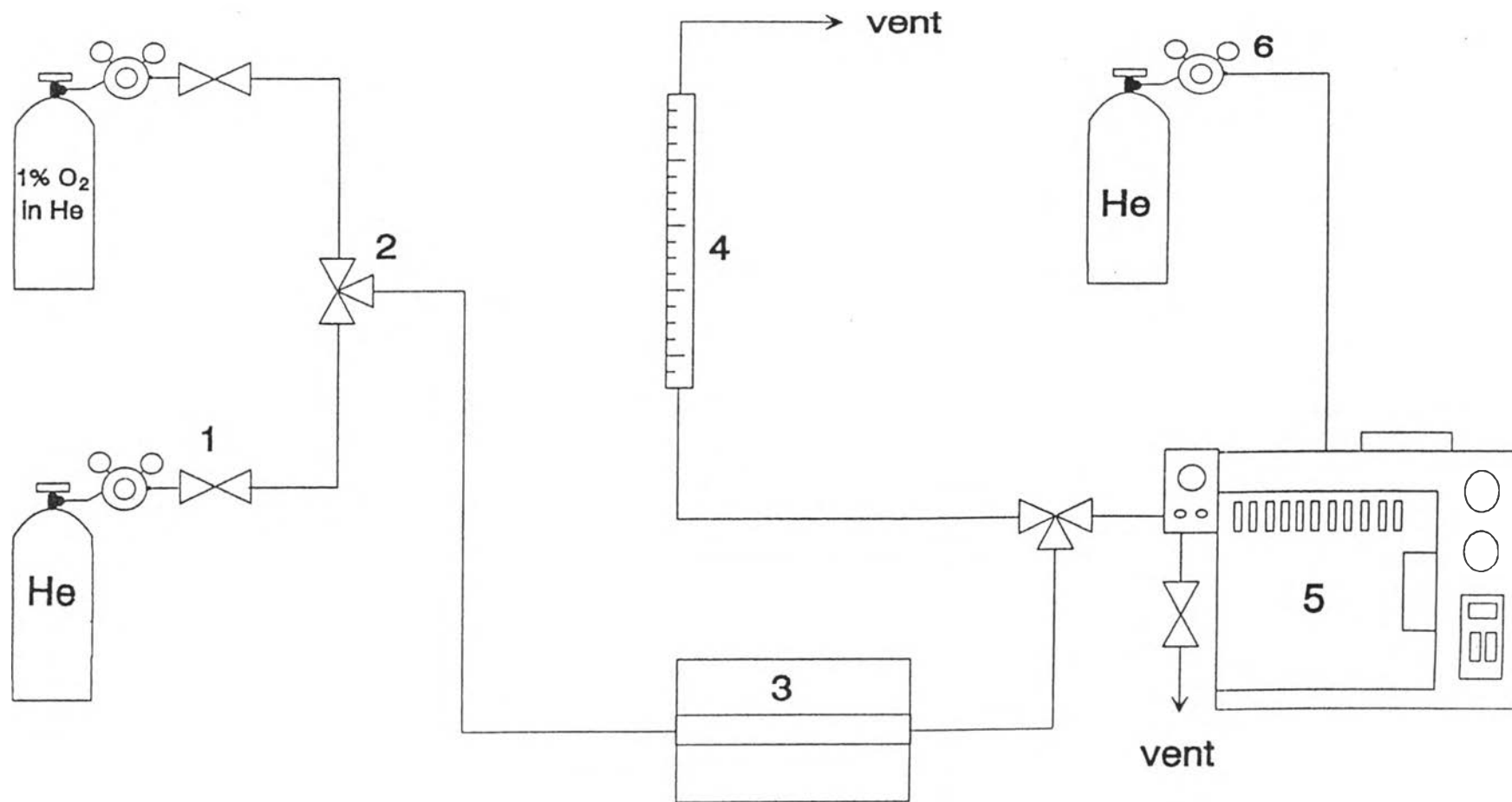
Table 4.2 Operating condition of gas chromatograph (GC-8 AIT).

Detector	TCD
Packed column	Poropak QS (200 x 0.32 cm.)
He flow rate	60 ml./min.
Column temperature	90 °C
Detector/injector temperature	110 °C
Detector current	90 mA

## 2.3 Procedure

(a). 90 mg. of coked catalyst was packed in quartz reactor, the reactor was purged by a helium gas stream at room temperature, the temperature was raised to 105 °C for desorbing CO<sub>2</sub> gas and water which might be adsorbed when the catalyst was exposed to air. Afterwards, the reactor was cooled down to





- |                        |                       |
|------------------------|-----------------------|
| 1. On-Off Valve        | 2. Three Way Valve    |
| 3. Furnace and Reactor | 4. Flow Meter         |
| 5. Gas Chromatography  | 6. Pressure Regulator |

Figure 4.2 A flow diagram of temperature programmed oxidation.

room temperature and the gas stream was switched from helium gas to 1 % oxygen in helium gas, the flow rate of the gas stream was 30 ml./min.

(b). When the flowrate of the gas stream was steady, the temperature programmed oxidation of coke was started. The temperature was raised to 700 °C at the heating rate of 5 °C/min. When the temperature was 50 °C , the effluent stream was sampled every 5 min. by an on-line gas sampler. The amount of oxygen consumed and carbon dioxide produced were measured and calculated.

### **3. Electrical conductivity measurement**

The nitrogen gas was used for carrier gas . The hydrogen gas was used to reduce the catalyst.

#### **3.1 Apparatus**

The electrical conductivity was measured by PM 6303 automatic RCL meter (philips) with the value of a electrical resistance.

#### **3.2 Procedure**

(a). The catalyst was grounded to finely powder and placed in a calcinator. Then nitrogen gas was introduced into the calcinator at a flow rate of 60 ml./min.

(b). The calcinator was heated up at an increasing rate at 10 °C/min. until the temperature reached 200 °C. Then nitrogen gas was changed to the hydrogen gas at a flow rate of 100 ml./min. while the calcinator was continuously

heated at the same rate until the temperature reached 300 °C. The calcinator was held at this temperature for 1 hour.

(c). When the reduction time was completed, the calcinator was cooled down to room temperature.

(d). Removed the finely powder of catalyst and pressed it in a pellet die at 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 electrical conductivity could be calculated (72).

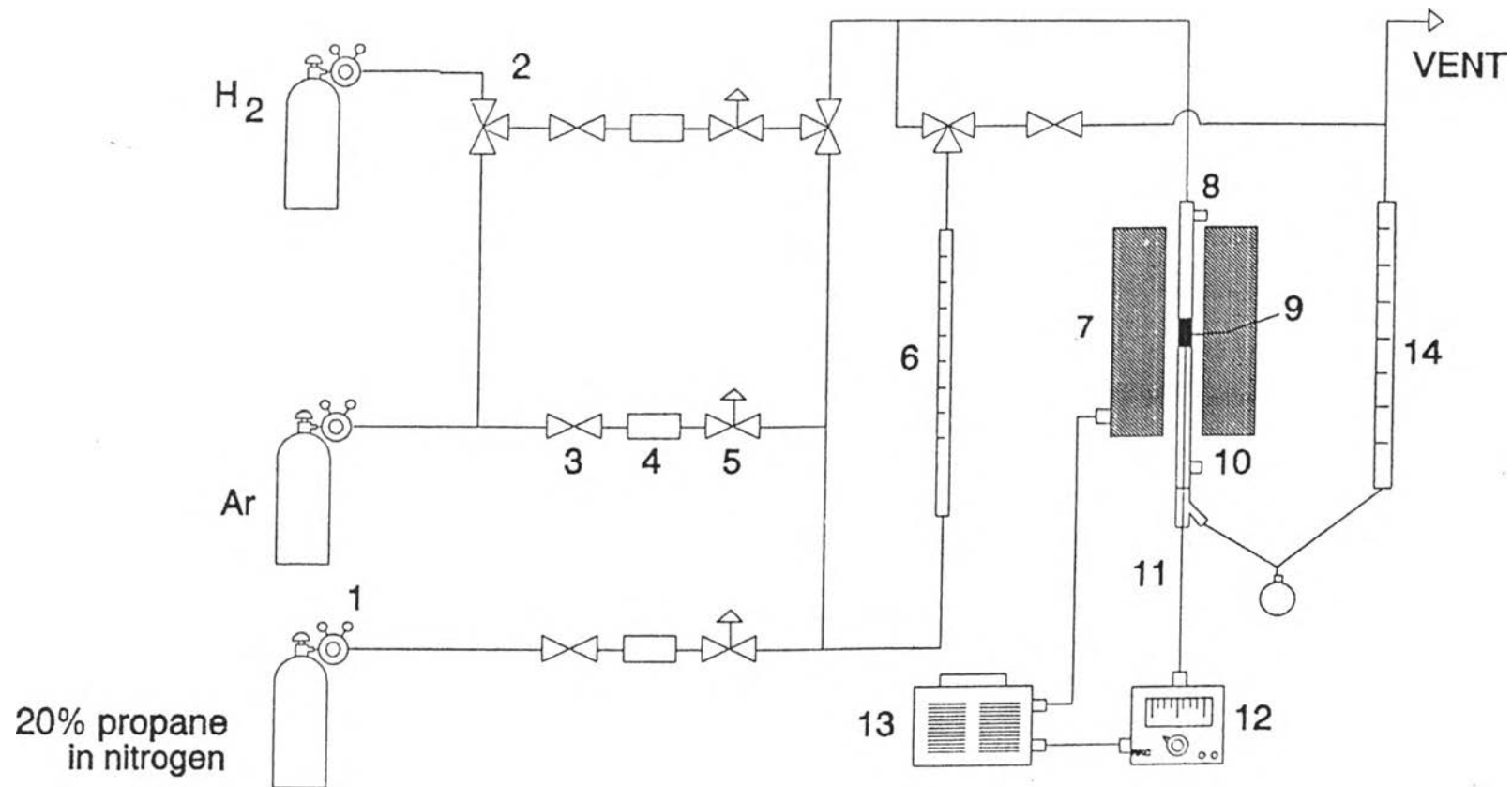
## **THE CATALYST DEACTIVATION BY PROPANE DEHYDROGENATION**

### **1. Materials**

Mixture of 20% propane in nitrogen gas supplied by Thai Industrial Gases Limited was used as feed stream for propane dehydrogenation. The hydrogen gas was used for reducing the catalyst and as feed stream in case of operating condition at hydrogen/hydrocarbon = 2. The ultra-high purity argon was used for purging the system.

### **2. Apparatus**

The apparatus consists of a reactor, an automatic temperature controller, an electrical furnace and gas controlling system. A flow diagram of the system is shown in figure 4.3.



- |                                  |                       |                            |
|----------------------------------|-----------------------|----------------------------|
| 1. Pressure Regulator            | 2. Three-way Valve    | 3. On-off Valve            |
| 4. Gas Filter                    | 5. Needle Valve       | 6. Flow Meter              |
| 7. Furnace                       | 8. Reactor            | 9. Catalyst Bed            |
| 10. Sampling Port                | 11. Thermocouple      | 12. Temperature Controller |
| 13. Variable Voltage Transformer | 14. Bubble Flow Meter |                            |

Figure 4.3 A flow diagram of the propane dehydrogenation unit.

(a). Reactor. The propane dehydrogenation reactor was made from quartz tube, it could be operated from room temperature up to  $1,000^{\circ}\text{C}$  under atmospheric pressure. Two positions of sampling points were provided. Catalyst was placed between quartz wool layer.

(b). Automatic temperature controller. Automatic temperature controller consisted of a magnetic switch, a variable voltage transformer, a temperature controller (PF-96, RKC) and a thermocouple. Temperature was measured at the bottom of the bed of catalyst in the reactor. The temperature control set point was adjustable within the range between 0 to  $800^{\circ}\text{C}$ .

(c). Electrical furnace. Electrical furnace supplied heat to the reactor for propane dehydrogenation. Therefore, the reactor could be operated from room temperature up to  $800^{\circ}\text{C}$  at the maximum voltage of 220 volt.

(d). Gas controlling system. The system consisted of

1. A cylinder of 20 % propane in nitrogen, equipped with a pressure regulator (0-50 psig), an on-off valve and fine-metering valve was used for adjusting the flow rate of the propane.

2. A cylinders of ultra high purity argon gas and hydrogen gas equipped with a pressure regulator (0-120 psig), an on-off valves and a fine-metering valve were used for adjusting the flow rate of these gases.

(e). Gas chromatograph. Flame ionization detector gas chromatograph was used to analyze the compositions of hydrocarbons in the feed

and product stream. The operating conditions were illustrated in table 4.3.

Table 4.3 Operating conditions of gas chromatograph (Shimadzu GC-14A).

Detector	FID
Pack column	23% SP-1700 on 20/100 Chromosorp P AW
Nitrogen pressure	2 Kg/cm <sup>2</sup> (flow rate 25 ml./min.)
Hydrogen pressure	0.5 Kg/cm <sup>2</sup> (flow rate 30 ml./min.)
Air pressure	0.3 Kg/Cm <sup>2</sup> (flow rate 240 ml./min.)
Column temperature	30 °C
Injection temperature	60 °C
Detector temperature	70 °C

### 3. Procedure

#### 3.1 The operating temperature at 500 °C and H<sub>2</sub>/HC = 0

(a). 0.1 gram of catalyst was packed in the middle of quartz reactor. The reactor was placed in the furnace and then argon gas was introduced into the reactor at a flow rate of 30 ml./min.

(b). The reactor was heated up at an increasing rate of 10 °C/min until the temperature reached 200 °C, then argon gas was changed to hydrogen gas at a flow rate of 100 ml./min., the reactor was continuously heated at the same rate until the temperature of 500 °C. The reactor was held at this temperature for 1 hour.

(c). When the reduction time was completed, the hydrogen

gas was changed back to the argon gas for 5 min.

(d). To start the propane dehydrogenation reaction, the argon gas was changed to the 20% propane in nitrogen gas at a flow rate of 30 ml./min.

(e). The first sampling was started at 5 minutes after the diluted propane was fed to the reactor.

(f). When the reaction time was completed, the diluted propane was changed to argon gas for 5 min. then changed to hydrogen gas for 1 hour, and cooled down the reactor to room temperature.

### **3.2 The operating temperature at more than 500 °C and H<sub>2</sub>/HC - 0**

After step (b) in section 3.1, the reactor was heated to a desired temperature, then the hydrogen gas was changed to the argon gas for 5 min and changed to the 20 % propane in nitrogen gas to start up propane dehydrogenation reaction. When the reaction time was completed, the diluted propane was changed to the argon gas for 5 min. then changed to the hydrogen, the reactor was cooled down to the temperature of 500 °C and held for 1 hour. Finally the reactor was cooled down to room temperature.

### **3.3 The operating temperature at 500 °C and H<sub>2</sub>/HC = 2**

After the reduction time completed , the hydrogen gas flow rate was changed to 5 ml./min. and 20 % propane in nitrogen gas with the flow rate of 25 ml./min. was fed together. When the reaction time was completed, the

diluted propane was stop and the reactor was held at  $500^{\circ}\text{C}$  for 1 hour then the reactor was cooled down to room temperature.

## **DETERMINATION OF COKE DEPOSITION ON CATALYSTS BY METAL ACTIVE SITE REGENERATION**

In this section , the  $\text{Pt}/\text{Al}_2\text{O}_3$ ,  $\text{Pt-Sn}/\text{Al}_2\text{O}_3$  and  $\text{Pt-Sn-Na}/\text{Al}_2\text{O}_3$  catalyst were determined.

### **1. Materials and apparatus**

The materials and apparatus used for this section were the same as used in metal active sites measurement unit.

### **2. Procedure**

#### **2.1 The reation at $500^{\circ}\text{C}$ and $\text{H}_2/\text{HC} = 0$**

The procedure was divided into 4 parts : metal active site of fresh catalyst, of spent catalyst, of regenerated catalyst after coke combustion at  $250^{\circ}\text{C}$  and of regenerated catalyst after coke combustion at  $500^{\circ}\text{C}$ .

(a). Metal active site of fresh catalyst. The procedure was as the same as metal active site measurement.

(b). Metal active site of spent catalyst. The reactor was heated up to  $150^{\circ}\text{C}$  in a helium gas stream and held for 30 min. to desorb  $\text{CO}$  gas. The reactor was heated to  $500^{\circ}\text{C}$  , when the temperature was  $200^{\circ}\text{C}$ , helium gas



was changed to hydrogen gas and at 500 °C the hydrogen gas was changed to the helium gas for 5 min. and changed to 20 % propane in nitrogen to start the dehydrogenation reaction with a certain period. When the reaction time was completed, the dilute propane was changed to the helium gas for 5 min. then changed to hydrogen gas and held at this temperature for 1 hour. Finally the reactor was cooled down to room temperature. CO gas was injected to the system. The amount of CO gas adsorbed on the catalyst was measured by the thermal conductivity detector. The number of metal active site was calculated.

(c). Metal active site of regenerated catalyst after coke combustion at 250 °C. The reactor was heated up to 150 °C in a helium gas stream and held for 30 min. to desorb CO gas. The reactor was heated to 250 °C and changed helium gas to 1 % oxygen in helium gas at the flow rate of 90 ml./min. the reactor was held at this temperature for 30 min. the diluted oxygen gas was changed to the hydrogen and the reactor was heated up to 500 °C and held at this temperature for 1 hour. Finally the reactor was cooled down to room temperature. CO gas was injected to the system. The amount of CO gas adsorbed on the catalyst was measured by the thermal conductivity detector. The number of metal active site was calculated.

(d). Metal active site of regenerated catalyst after coke combustion at 500 °C. The reactor was heated up to 150 °C in a helium gas stream and held for 30 min. to desorb CO gas. The reactor was heated to 200 °C and changed the helium gas to 1 % oxygen in helium gas. The reactor was still heated to 500 °C and held for this temperature for 30 min. Then the diluted oxygen was changed to the hydrogen and held for 1 hour. Finally the reactor was cooled down to room temperature. CO gas was injected to the system. The amount of CO gas adsorbed on the catalyst was measured by the thermal conductivity detector. The

number of metal active site was calculated.

### **2.2 The reaction at not 500 °C and $H_2/HC = 0$**

Only step (b) of section 2.1 was changed in the heating step from 500 °C to desired temperature.

### **2.3 The reaction at 500 °C and $H_2/HC = 1$**

Only step (b) of section 2.1 was changed in feed gas from 20% propane in nitrogen gas at the flow rate of 90 ml./min. to the gas mixture between the diluted propane at the flow rate of 75 ml./min. and the hydrogen gas at the flow rate of 15 ml./min.

### **2.4 The reaction at not 500 °C and $H_2/HC = 1$**

Only step (b) of section 2.1 was changed to section 2.2 plus section

2.3