

**CHAPTER IV**  
**EXPERIMENTAL SYSTEMS**  
**AND EXPERIMENTAL PROCEDURES**

This chapter describes the experimental systems and the experimental procedures used in this work. A description of catalyst preparation method is presented in section 4.1. The experimental system and the Temperature-Programmed Oxidation (TPO) system are described in sections 4.2 and 4.3 respectively. Finally, support and metal digestion method and surface area measurements are included in sections 4.4 and 4.5. In each section, details of experimental procedures, including the materials and apparatus are as follows.

**The Scope of This Study**

One type of propane dehydrogenation catalyst is used in this study

: (0.3 wt%) Pt-(0.3 wt%)Sn/Al<sub>2</sub>O<sub>3</sub>

The reaction conditions of the dehydrogenation reaction are as follows:

Catalyst Reduction Temperature	: 500 °C
Reaction Temperature	: 600 °C
Operating Pressure	: 1 atm.
Time of Dehydrogenation	: 5-360 min.

## 4.1 Preparation of Bimetallic Catalyst

### 4.1.1. Materials

The chemicals used in this experiment are normally Analytical Grade, but only some critical chemical have to be specified as follows:

1. Chloroplatinic acid [ $\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ ] manufactured by Wako Pure Chemical Industries CO.,Ltd.,Japan.
2. Stannous Chloride Dihydrate [ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ] manufactured by Fluka Chemie AG, Switzerland.
3. Alumina [ $\text{Al}_2\text{O}_3$ ] support (type NKH-3) obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan.

### 4.1.2. Apparatus : Unit for calcination

This unit which consists of an electrical furnace, an automatic temperature controller, a variable voltage transformer, is used for calcining the impregnating catalysts at high temperature.

### 4.1.3. Preparation of support

Alumina support was grounded to the require mesh size of 60/80 followed by washing with distilled water 3-4 times to remove the very fine particles and other impurities, then dried at 110 °C for overnight. Subsequently, the support was calcined in air at 300 °C for 3 hours.

### 4.1.4. Preparation of 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.

#### 4.1.5. Preparation of Platinum-Tin catalyst

1. The concentration of impregnating solution, for 2 grams of catalyst support, was prepared by calculating the amount of the stock solution to yield the required metal loading. The second metal, tin, was followed the calculation to yield the required tin loading, and hydrochloric acid, 5 weight percent of support, was then added to the solution. De-ionized water was finally added until 2 ml. of the solution was obtained.

2. Two grams of support was placed in a 100 ml. Erlenmeyer flask and then the impregnating solution from (1.) was slowly dropped to the support using a dropper. Continuously stirring of mixture in the flask while impregnating was required in order to achieve the homogeneously distributed metal component on the support.

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

4. The impregnated support was dried at 110 °C in air overnight.

5. The calcination step was carried out by placing the dried material obtained from (4) in a quartz tube. Nitrogen was firstly introduced into the tube at a flow rate of 60 ml/min. Then the tube was heated up at an increasing rate of 10 °C/min. until the temperature reach 500 °C. Subsequently, the nitrogen was changed to air at a flow rate of 100 ml./min. (space velocity of about 2,000 hour<sup>-1</sup>). The material was held in this condition for 3 hours.

6. For reduction, after calcination in air for 3 hours, the tube was purged with nitrogen for about 5 min. to remove air. Then switched to hydrogen gas for another 3 hours at the same space velocity and temperature.

7. After reduction in hydrogen gas for 3 hours, the tube was purged by nitrogen to cool down until the temperature decreased to room temperature.

## **4.2 Reaction of Propane Dehydrogenation**

### **4.2.1. Material**

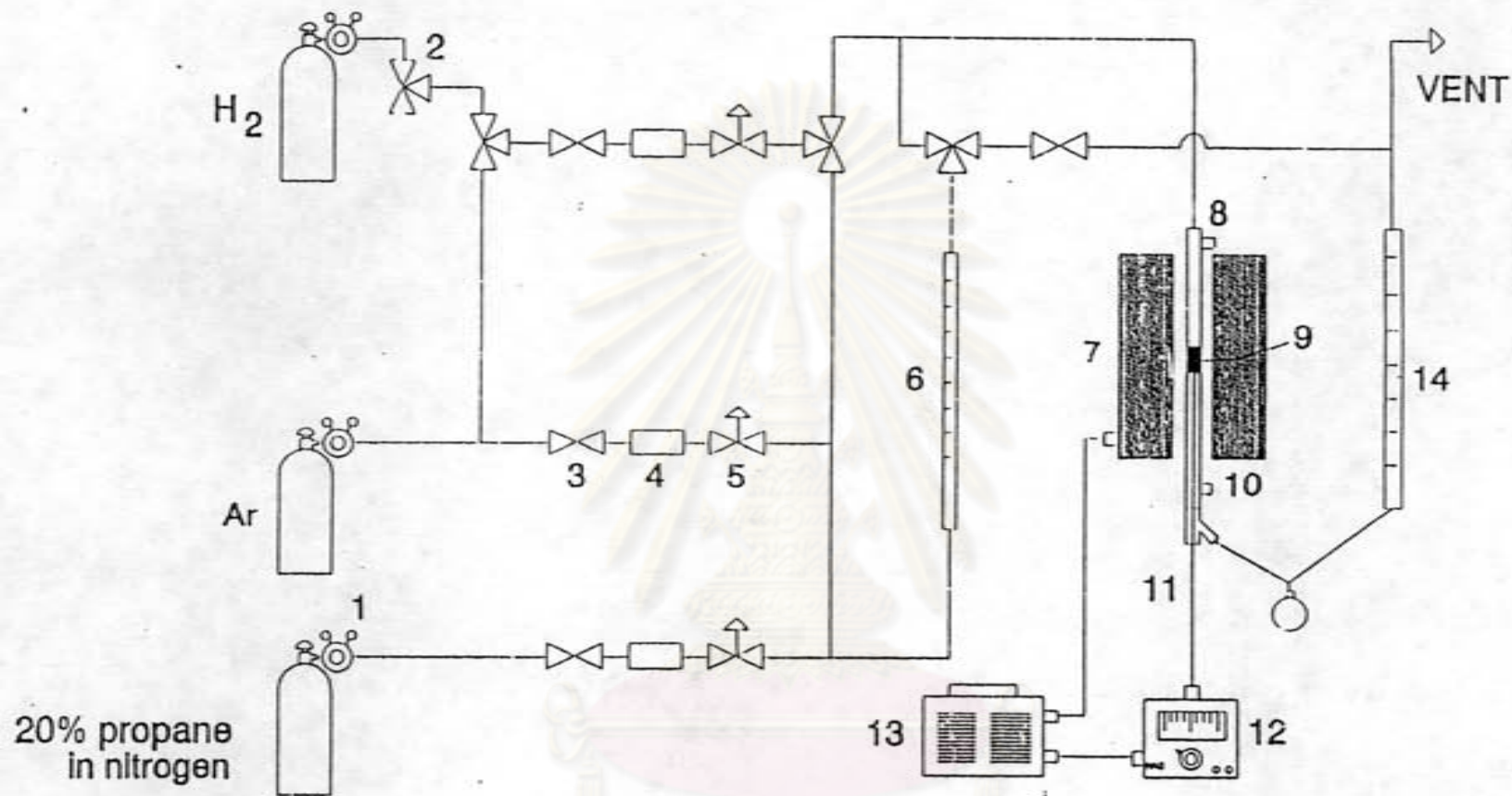
Gas mixture of 20 % propane in nitrogen supplied by Thai Industrial Gas Limited was used as feed stream for the dehydrogenation in this study. The hydrogen was used for reducing the catalyst. The ultra - high purity argon was used for purging the system.

### **4.2.2. Apparatus**

Flow diagram of the propane dehydrogenation system is shown in figure 4.1. The system consists of a reactor, an automatic temperature controller, an electrical furnace, and gas controlling system.

#### **4.2.2.1 Reactor**

The dehydrogenation microreactor is made from a quartz tube, it can be operated from room temperature up to 1,000 °C under atmospheric pressure. Sampling points are provided above and below the catalyst bed. Catalyst is placed between quartz glass wool layer.



- |                                  |                       |                            |
|----------------------------------|-----------------------|----------------------------|
| 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 4.1 Flow diagram of the propane dehydrogenation system.

#### 4.2.2.2 Automatic temperature controller

An automatic temperature controller consists of a magnetic switch, a variable voltage transformer, a temperature controller( PF - 96, RKC ), and a thermocouple. Temperature control setpoint is adjustable within the range between 0 to 800 °C.

#### 4.2.2.3 Electrical furnace

An electrical furnace supplies heat to the reactor for propane dehydrogenation. Therefore, the reactor can be operated from room temperature up to 800 °C at the maximum voltage of 220 volts.

#### 4.2.2.4 Gas controlling system.

The gas controlling system consists of :

1. A cylinder of 20 % propane in nitrogen, equipped with a pressure regulator (0-50 psig), an on-off valve and a fine-metering valve, are used for adjusting the flow rates of these gases.
2. Cylinders of ultra high purity argon and hydrogen, equipped with pressure regulators (0-120 psig), on-off valves and fine- metering valves, are used for adjusting the flow rates of these gases.

#### 4.2.2.5 Gas chromatograph

A gas chromatograph (GC GOW MAC series 750) equipped with a flame ionization detector (FID) was used to analyse the composition of hydrocarbons in the feed and product streams. The operating conditions are illustrated in table 4.1.

Table 4.1 Operating condition of gas chromatograph (GC Gow-MAC Series 750)

Model	GC Gow-MAC Series 750
Detector	FID
Packed column	VZ-10
Nitrogen flow rate	25 ml./min.
Hydrogen flow rate	30 ml./min.
Air flow rate	250 ml./min.
Column temperature	45 °C
Injector temperature	75 °C
Detector temperature	100 °C

#### 4.2.3. Experimental System.

The reaction system consists of a micro reactor installed in a tube furnace. The diagram of the system is exhibited schematically in figure 4.1. The furnace temperature is controlled by a temperature controller. The micro reactor is constructed from a quartz tube. A gas mixture (20Vol.%  $C_3H_8$  + Vol. 80%  $N_2$ ) is used as a reactant gas. Coked catalysts were prepared by passing the gas mixture through the catalyst bed which was maintained at a temperature of 600°C. During the experiment, the reaction temperature is monitored using a thermocouple and a digital temperature indicator. The effluent gas is analysed by the gas chromatograph.

#### 4.2.4. Experimentation.

The deactivation of catalysts was performed by propane dehydrogenation reaction. The experimental procedures are described in detail below.

1. 0.1 gram of catalyst was packed in the middle of the quartz microreactor. The reactor was then placed in the furnace and the ultra high purity argon gas was introduced into the reactor at a flow rate of 30 ml./min.

2. The reactor was heated up at a heating rate of 10 °C / min. until the catalyst temperature reached 200°C. Then, ultra high purity argon gas was replaced by hydrogen gas at a flow rate of 100 ml/min. followed by heating up the reactor at a heating rate of 10 °C / min. until the catalyst temperature reached 500 °C. The catalyst was reduced at this temperature for 1 hour.

3. When the reduction process was completed, the reactor was heated up again to a temperature of 600 °C at a heating rate of 10 °C/min. The temperature was held constant at 600 °C for 5 min. before the hydrogen gas was switched to the 20 % propane in nitrogen gas at a flow rate of 30 cc./min. (ratio  $H_2/HC = 0$ ).

4. The gas sample was taken every 5 minutes to the whole reaction intervals.

5. When desired time on stream was reached, the propane was changed to the ultra high purity argon gas. Then, the reactor was cooled down without the holding step at 600°C for 2 hours due to the recent investigator ( Atchara,1995) who proved that there were no significant difference between purging and no purging system. TPO peak still remained its characteristic for both different system.



### 4.3 Temperature - Programmed Oxidation

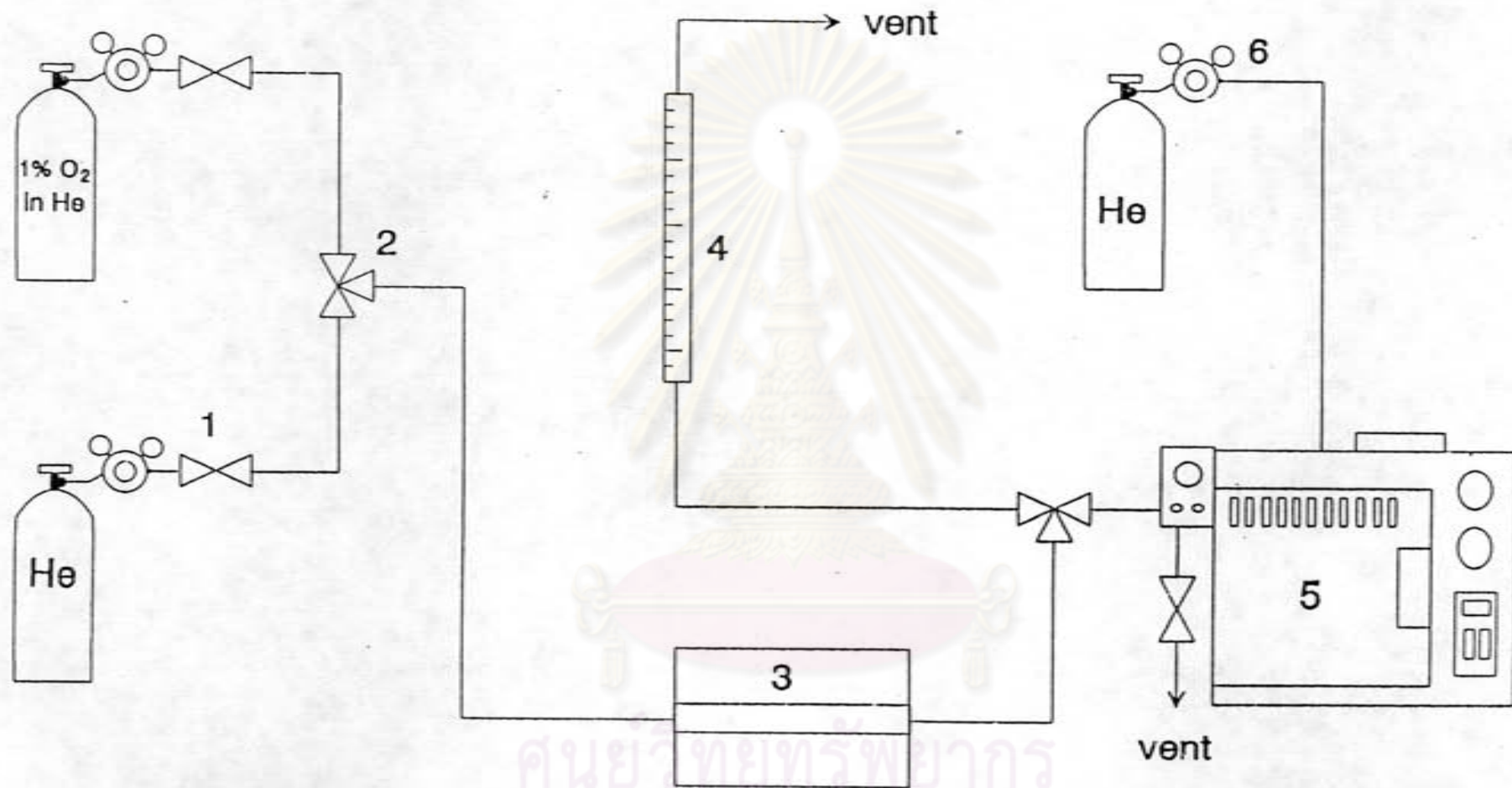
#### 4.3.1. Materials

The 1 Vol.% oxygen in helium gas mixture supplied by Thai Industrial Gas was used as oxidizing agent. The ultra high purity argon was used for purging the system.

#### 4.3.2. Apparatus

The apparatus included two gas feed lines for the ultra high purity argon and the 1 Vol.% oxygen in helium. The proper gas was chosen by means of a three way valve. The flow rate of the feed stream is controlled by a needle valve. The reactor was made of quartz glass with an outside diameter of 8 mm. The temperature of the catalyst bed was measured by using a thermocouple. The reactor was placed in a furnace which various heating rate was controlled by a programmable temperature controller (PC -600, Shinko) at temperatures between 50-700 °C and was controlled by an automatic temperature controller when operated at a constant temperature. The flow diagram of this system is shown in figure 4.2.

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



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

Figure 4.2 Flow diagram of Temperature-Programmed Oxidation system.

Table 4.2 Operating condition of gas chromatograph ( GC 8AIT, Shimadzu)

Model	GC- 8AIT (Shimadzu )
Detector	TCD
Packed column	porapack QS (200x 0.32 cm.)
Helium flow rate	60 ml./min.
Column temperature	90 °C
Detector / injector temperature	110 °C
Detector current	90 mA.

#### 4.3.3. Experimental System.

Temperature - Programmed Oxidation of the catalyst was carried out in a quartz tube located in a tube (8 mm.O.D.) furnace. The furnace temperature was controlled by a microprocessor base temperature controller. A gas mixture consisted of 1 Vol.% oxygen in helium was used as an oxidising gas. In one experiment, the Temperature - Programmed Oxidation process began by heating up the catalyst at a rate of 5 °C/min. The oxidation process was performed until the furnace temperature reached 700 °C. During the oxidation, the amount of CO<sub>2</sub> in the effluent gas was first analysed when the catalyst temperature reached 50 °C, then at an interval of about 5 minutes, using a gas chromatograph (Shimadzu 8 AIT) equipped with a gas sampling valve (1 ml. sampling loop) and a thermal conductivity detector. The operating conditions of the GC. are reported in table 4.2. The purpose of these experimental procedures was to observe TPO curve of varying coked catalyst samples.

#### 4.3.4. Experimentation.

##### Procedure of constant increasing rate experiment on TPO

1. The coked catalyst was packed in the middle of quartz microreactor before placing the reactor in the furnace. The catalyst section was placed in the constant temperature zone of the furnace.
2. The 1 Vol.% oxygen in helium gas was flowed through the system at a flow rate of 30 ml./min.
3. 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 sampling every 5 minutes by an on-line gas sampler.
4. The amount of oxygen consumed and carbon dioxide produced was measured.
5. After the catalyst temperature reached 700 °C., the 1 Vol.% oxygen in helium gas was changed to ultra high purity argon and the reactor was cooled down.

จุฬาลงกรณ์มหาวิทยาลัย

#### 4.4 Support and Metal Digestion Method

##### Procedures

##### (1) Digestion

Approximately 0.5 grams of spent catalyst was preweighed and put into an evaporating dish with 20 ml of hydrochloric acid, 10 ml of nitric acid and 10 ml of water. Then, the evaporating dish was closed by a watch glass and start to heat with the low heating rate. After waiting for 2 h, 5 drops of hydrofluoric acid was added to dissolve  $\text{SiO}_2$ . Wait for another 30 minutes. Finally, cool down the obtained solution to room temperature and add 50 ml of water.

##### (2) Coke Separation

The mixture of coke acid from the first step had to be diluted by water and separated by a centrifugal separator (about 10 minutes, 3000 RPM) for five times in order to wash out the acid. Finally, the coke was put into an oven which was operated at  $110^\circ\text{C}$  and dried it for over night.

#### 4.5 BET surface area and pore size distribution

Micromeritic ASAP 2000 is used as the surface area analysis measurement. It provides a convenient means for mainly BET surface area measurement. A wide variety of reports are available for the ASAP 2000, which include:

- Single and multi-point BET surface area
- Langmuir surface area
- Micropore volume and area
- Full adsorption and desorption isotherms
- Mesopore volume and area distributions
- Total pore volume