

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. Finally, the experimental system and the Temperature Programmed Oxidation (TPO) system are described in sections 4.2 and 4.3, respectively.

The Scope of This Study

Two type of reactants are used in this study

- : paraffins have carbon atom between 3 - 9 atom
- : olefin have carbon atom between 3 - 9 atom

One type of propane dehydrogenation catalyst is used in this study

: (0.3 wt%)Pt-(0.3 wt%)Sn-(0.6 wt%)K/Al₂O₃

The reaction conditions of the dehydrogenation reaction are as follows:

- Catalyst Reduction Temperature : 500 °C
- Reaction Temperature : 200-600 °C
- Operating Pressure : 1 atm.

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 [Al_2O_3] support (type NKH-3) obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan

4. Potassium Nitrate (KNO_3) was manufactured by E.Merck, Federal Republic of Germany

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

(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) Potassium stock solution

The potassium nitrate solution was prepared by dissolving 1 gram of sodium nitrate in de-ionized water to the total volume of 25 ml.

4.1.5 Preparation of Trimetallic Catalyst

(a) 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 impregnation solution from (1) was slowly dropped to the support using a dropper. Continuously stirring of mixture in the flask while impregnation 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 200 °C. Subsequently, the nitrogen was changed to air at a flow rate of 100 ml/min (space velocity of about 2,000 hour⁻¹). The material was held in this condition for 3 hours.

6. For reduction, after calcination in air for 3 hours the catalyst was allowed to cool down until the temperature decreased to 200 °C. After that air was switched to nitrogen.

(b) Preparation of Platinum-Tin-Potassium catalyst

After calcination the Pt-Sn catalyst, the calcined material was reimpregnated by potassium impregnation solution. The reimpregnated material was treated by the same procedure as steps 2-6 in section (a)

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4.2 Reaction of Propane Dehydrogenation

4.2.1 Material

(a) Gas

Gas mixture of 20 % propane and propene 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.

(b) liquid

Table 4.1 Chemical specified of liquid

Reactant	Analytical Grade (GC), %	Manufactured by
n-Pentane	99.5	Fluka Chemie AG, Switzerland
1-Pentene	97.0	Fluka Chemie AG, Switzerland
n-Hexane	99.5	Ajax chemicals, Australia
1-Hexene	98.0	Fluka Chemie AG, Switzerland
n-Heptane	99.5	Carlo ERBA Reagenti
1-Heptene	98.19	Trade Mark, Japan
n-Octane	99.0	Carlo ERBA Reagenti
1-Octene	95.0	Wako pure chemical industries Co., Ltd.

4.2.2 Apparatus

Flow diagram of the propane and propene dehydrogenation system is shown in Figure 4.1. The system consists of a reactor, two automatic temperature controller, an electrical furnace, and gas controlling system. Flow diagram of n-pentane, 1-pentene, n-hexane, 1-hexene, n-heptane, n-octane and 1-octane dehydrogenation system is shown in Figure 4.2. The system consists of a saturator, a reactor, two automatic temperature controllers, an electrical furnace, and a 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.

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 set point is adjustable with in 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 form 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 or propene 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. A cylinder of ultra high purity nitrogen, equipped with a pressure regulator (0-120 psig), an on-off valve and a fine-metering valve, are used for adjusting the flow rates of N₂ that pass through the liquid reactant saturator.
3. The cylinders of ultra high purity argon and hydrogen, equipped with pressure regulators (0-120 psig), an on-off valve and a fine-metering valve, are used for purging the system and reducing catalyst.

4.2.2.5 Gas chromatograph

Gas chromatograph (Shimadzu GC-14A and Shimadzu GC-14B) equipped with a flame ionization detector (FID) was used to analyze the composition of hydrocarbons in the feed and product streams. The operating conditions are illustrated in Table 4.2

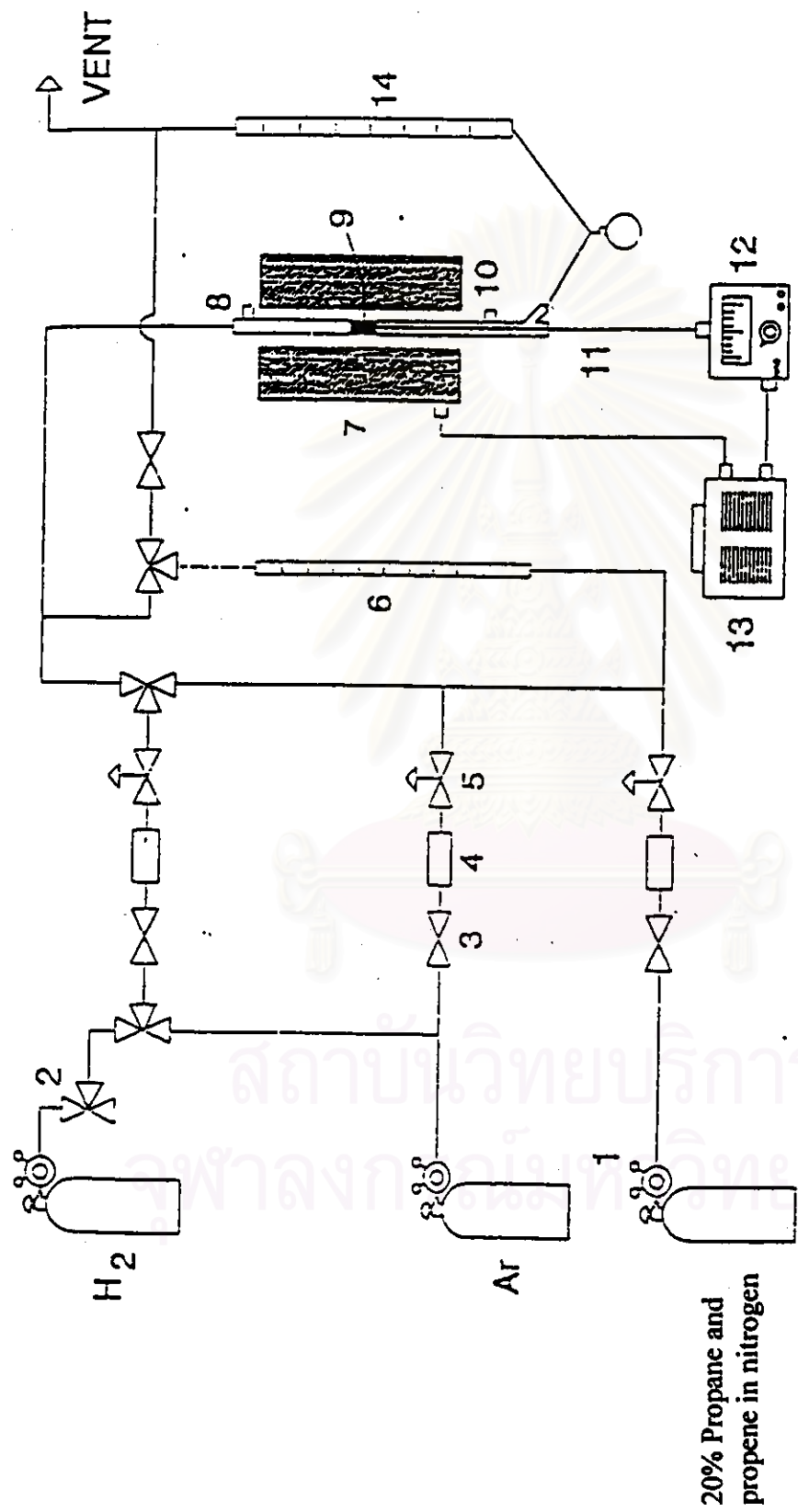
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Table 4.2 Operating condition for gas chromatograph

Gas chromatographs	Shimadzu GC-14A	Shimadzu GC-14B
Detector	FID	FID
Column	Capillary	VZ-10
Carrier gas	N ₂ (99.99%)	N ₂ (99.99%)
Flow rate of carrier gas	25 ml/min.	25 ml/min.
Column temperature		
-Initial	35	65
-final	140	80
Detector temperature	150	150
Injector temperature	50	100
Analyzed gas	Hydrocabon C ₄ -C ₁₀	Hydrocabon C ₁ -C ₄
Split ratio	50	-

4.2.3 Experimental System.

The reactor system consists of a micro reactor installed in a tube furnace. The diagram of the systems for gaseous and liquid reactants are exhibited schematically in Figures 4.1 and 4.2 respectively. The furnace and saturater temperature are controlled by temperature controllers. the micro reactor is constructed from a quartz tube. The gas mixtures used as the reactants gas are showed in Table 4.3 Coked catalysts were prepared by passing the gas mixture through the catalyst bed which was maintained at a temperature monitored using a thermocouple and a digital temperature indicator.



- 1. Pressure Regulator
- 2. Three-way Valve
- 3. On-of 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 short chain hydrocarbon(C₃) dehydrogenation system.

Table 4.3 Concentration and Control temperature of Reactants.

Reactant	% vol in N ₂ balance	Control temperature in saturater (°C)*
Propane	20	-
Propene	20	-
n-Pentane	12	-14.2
1-Pentene	12	-19.5
n-Haxane	10	10.2
1-Hexene	10	5.6
n-Heptane	8.6	32.4
1-Heptene	8.6	28.1
n-Octane	7.5	52.9
1-Octene	7.5	48.8

*The calculation of temperature control in saturater and the values of constant are summerized in appendix A

4.2.4 Experimentation

The deactivation of catalyst was performed by the alkane/alkene dehydrogenation reactions. The experimental procedures is 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 constant heating rate of 10 °C/min. until the catalyst temperature reached 200°C. Then, ultra high purity argon was replaced by hydrogen gas at a rate of 100ml./min. followed by heating up the reactor at 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 complete, hydrogen was replaced by argon. After that, the reactor was heated up or cooled down to the reaction temperature of 200-600 °C. The temperature was held constant at reaction temperature for 5 min. before the argon gas was switched to the gas mixture at a flow rate of 30 ml/min. (ratio H₂/HC=0).

4. When desired time on stream was reached, the reactants were changed to the ultra high purity argon gas. Then, the reactor was cooled down to room temperature in argon atmosphere.



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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 helium was used for purging the system.

4.3.2 Experimental System

Temperature programmed oxidation of the catalyst was carried out in a quartz tube(8 mm. O.D.) located in a tube a furnace. The furnace temperature was controlled by a microprocessor base temperature controller (PC 600, Shinko). A gas mixture 1 vol.% oxygen in helium was used as an oxidizing gas. The 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 CO₂ in the effluent gas was first analyzed 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 flow diagram of this system is shown in Figure 4.3. The operating conditions of the GC. are reported in Table 4.4. The purpose of these experimental procedures was to observe TPO curve of varying coked catalyst samples.

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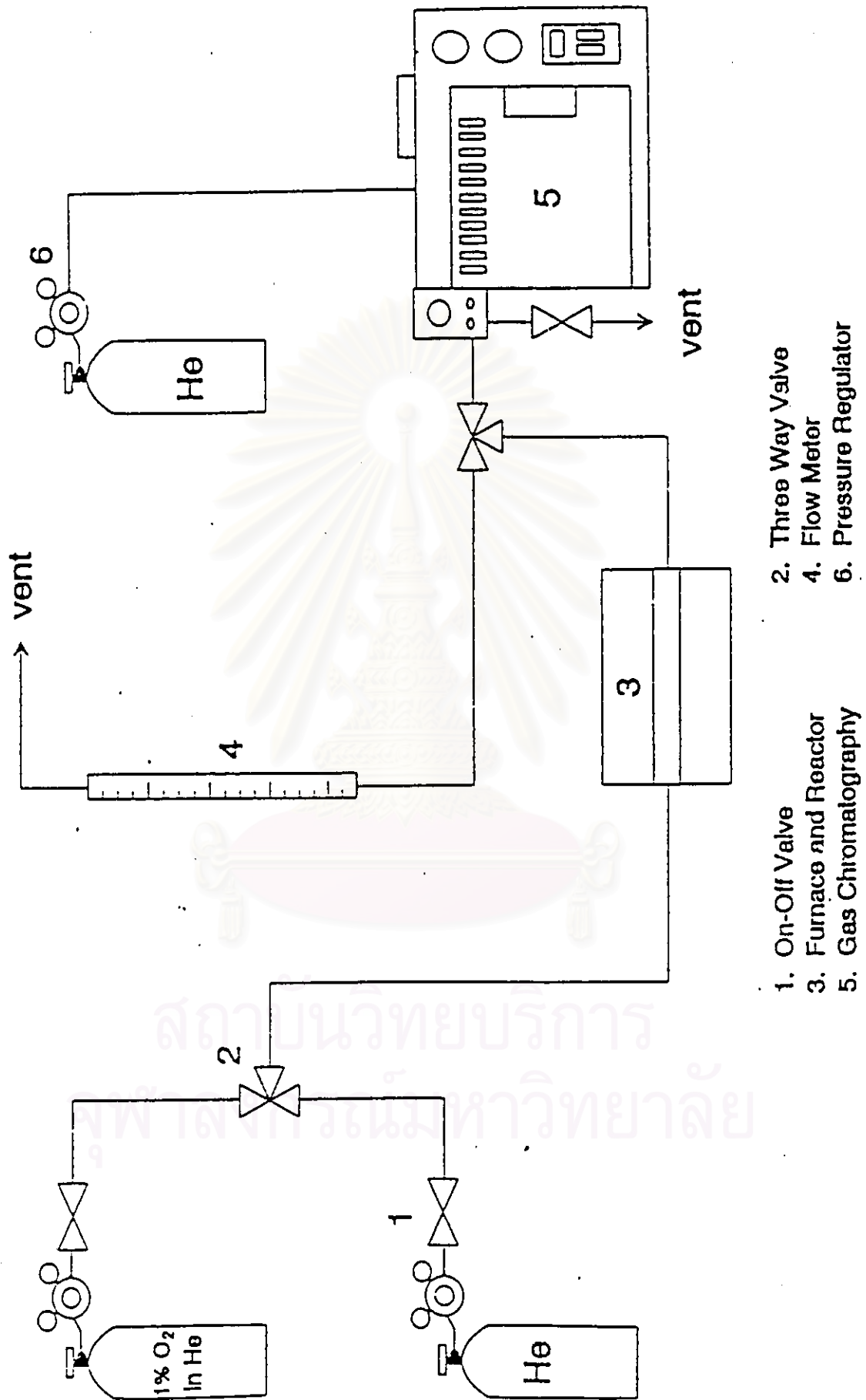


Figure 4.3 Flow diagram of temperature programmed oxidation system.

Table 4.4 Operating condition of gas chromatograph (GC-8AIT, Shimadzu)

Model	GC-8AIT (Shimadzu)
Detector	TCD
Packed column	porapack QS (200x0.32 cm.)
Helium flow rate	60 ml./min.
Column temperature	90 °C
Detector/injector temperature	110 °C
Detector current	90 mA.

4.3.3. 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 sampled every 5 minutes by the on-line gas sampler

4. The amount of oxygen consumed and carbondioxide produced was measured.

5. After the catalyst temperature reached 700 °C., the 1 Vol.% oxygen in helium gas was changed to ultra high purity helium and the reactor was cooled down.