

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 system are described in section 4.2 and 4.3 respectively. In each section, details of experimental procedures, including the materials and apparatus are described as the following.

The Scope of This Study

One type of propane dehydrogenation catalyst are used in this study

-(0.3 wt%) Pt/Al₂O₃

The reaction conditions of the dehydrogenation reaction are as follows:

Catalyst Reduction Temperature	: 500 °C
Reaction Temperature	: 550 °C, 600 °C, 650°C
Operating Pressure	: 1 atm.
Time of Dehydrogenation	: 40 min.

4.1 Preparation of catalyst

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

Apparatus

Unit for grinding and screening support

This unit which consists of a pestle, a mortar and sieves, is used for reducing size of the catalyst support to 60/80 mesh.

Unit for impregnation

This unit which consists of pipetes, flasks, droppers and volumetric flasks, is used for preparing aqueous solution and impregnating the solution onto the support.

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.

Preparation of support

Alumina support was ground 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.

Preparation of stock solution

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.

Preparation of Platinum 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 (appendix B). 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⁻¹). 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 cooldown to cooldown until the temperture decreased to room temperature.

4.2 Reaction of Propane Dehydrogenation

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 puring the system.

Apparatus

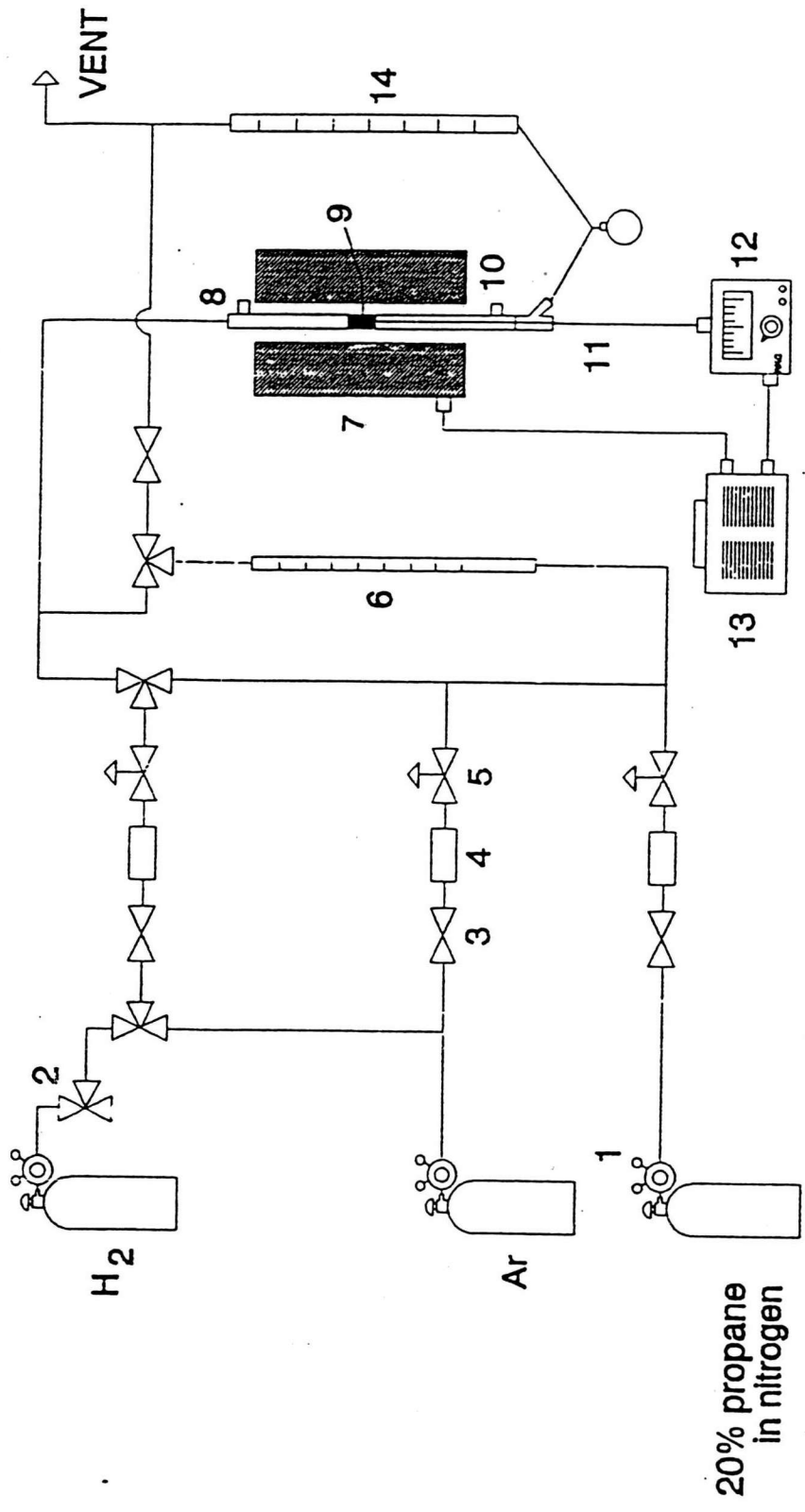
Flow diagram of the propane dehydrogenation system is shown in figure 4.1. The system consists of a reactor, an automatic temperature controller, an electrical furnace, and gas controlling system.

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. Catalyst is placed between quartz glass wool layer.

Automatic temperature controller

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.



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|----------------------------------|-----------------------|----------------------------|
| 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.

Electrical furnace

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

Gas controlling system.

The 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. The cylinders of ultra high purity argon and hydrogen, equipped with pressure reguratures (0-120 psig), an on-off valves and fine-metering valves, are used for adjusting the flow rates of these gases.

Gas chromatograph

A gas chromatograph 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	75 °C

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.% C₃H₈ +Vol. 80% N₂) 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 for 40 min. During the experiment, the reaction temperature is monitored using a thermocouple and a digital temperature indicator. The effluent gas is analysed by a gas chromatography equipped with a flame ionization detector. The operating condition of the GC. are shown in table 4.1. Blank runs show that at this operating temperature, the thermal cracking of the reactant gas and / or the reaction between propane and the equipment are insignificant.

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 replace by hydrogen gas at allow 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 H₂/HC = 0).

4. The gas sampling was taken at 5, 10,20, 30 and 40 minutes.

5. When time on stream was 40 minutes, the propane was changed to the ultra high purity argon gas. The reactor temperature was held at 600 °C for at least 2 hours under this ultra high argon atmosphere before the reactor was cooled down to room temperature. This step was to remove all the reactant that might still remain on the catalyst surface. The purpose of these experimental procedures was to confirm whether the adsorbed reactant contributed to the peak observed at low temperatures during the Temperature-Programmed Oxidation or not.

6. Repeat steps 1 to 5 but the ratio of hydrogen: hydrocarbon is changed to 1 and 3. (calculation of flow rate of propane and hydrogen shows in appendix C)

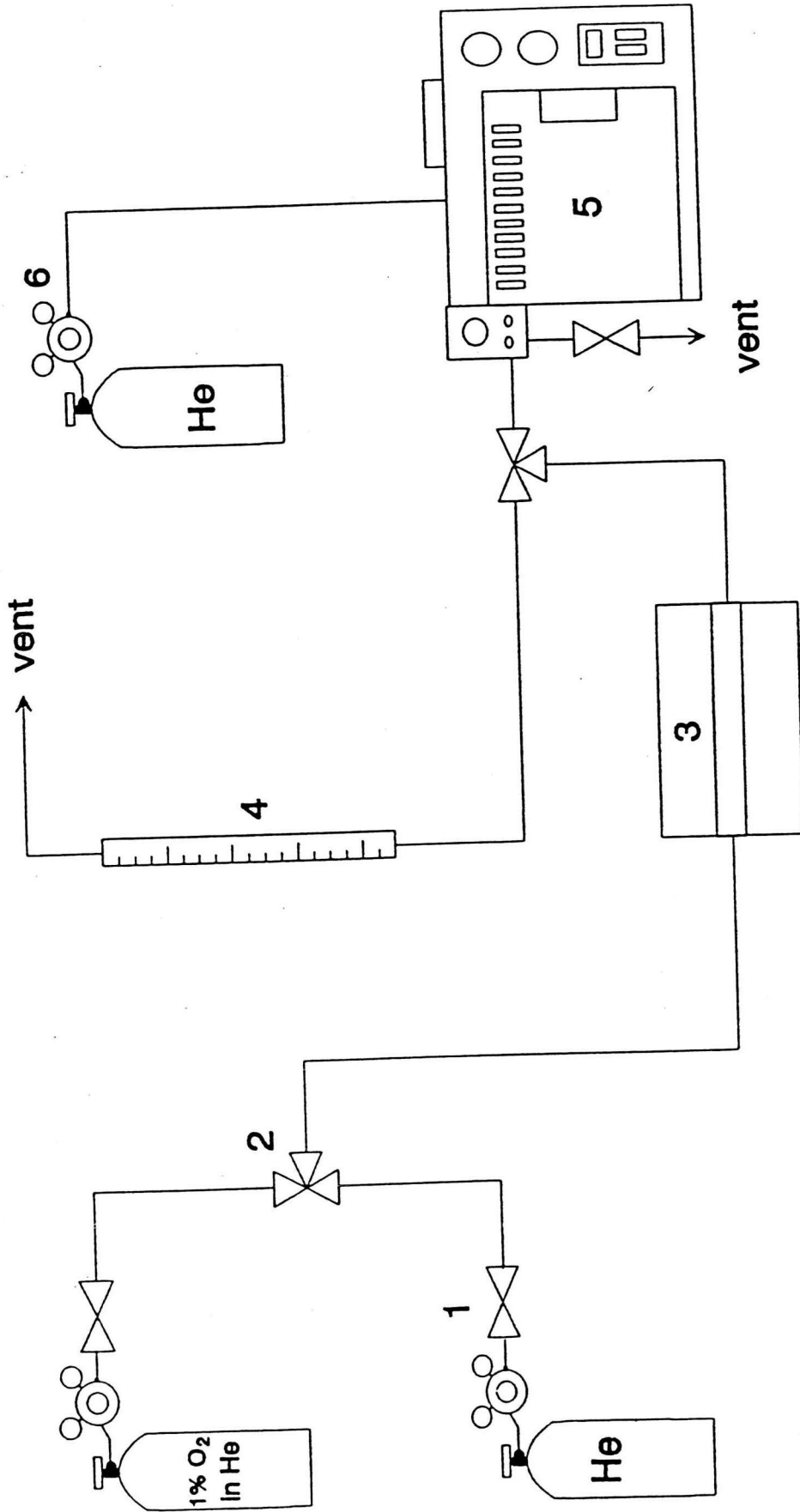
4.3 Temperature - Programmed Oxidation

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.

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.



- 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.

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

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

Model	GC- 8AIT (Shimadzu)
Dectector	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.

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 CO₂ 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. While in the other experiments, the Temperature - Programmed Oxidation process was run at constant temperature. The purpose of these experimental procedures was to find out the rate of coke combustion.

Procedure

Constant increasing rate experiment

1. The coked catalyst was packed in the middle of quartz microreactor before placing the reactor in the furnace.
2. The 1Vol.% 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 on-line gas sampler.
4. The amount of oxygen consumption and carbondioxide production 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.

Constant temperature experiment.

1. The coked catalyst was packed in the middle of the quartz microreactor. The reactor was packed in the furnace and the ultra high purity argon gas was introduced into the reactor.

2. The reactor was heated up until the catalyst temperature reached a select temperature of reaction. The temperature was held at that temperature for 5 minutes before switching from ultra high purity argon gas to 1 Vol.% oxygen in helium to start the Temperature - Programmed Oxidation of coke. The flow rate of 1 Vol.% oxygen in helium is 30 ml./min..

3. When the 1 Vol.% oxygen in helium gas was flowed into system, the effluent stream was sampled every 5 minutes by an on - line gas sampling valve until the amount of carbondioxide was zero or become very small.

4. The reactor was cooled down by switching from 1 Vol.% oxygen in helium gas to ultra high purity argon gas.