

CHAPTER IV
EXPERIMENTAL SYSTEMS
AND EXPERIMENTAL PROCEDURES

This chapter describes the experimental systems and the experimental procedures applied in this research. A description of catalyst preparation method is given in section 4.1. The experimental system of propane dehydrogenation reaction is explained in section 4.2. The experimental system of infrared analysis (IR) is described in section 4.3. 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/ γ -Al₂O₃

The reaction conditions of the dehydrogenation reaction are as follows :

Catalyst Reduction Temperature : 500⁰ C
Reaction Temperature : 600⁰ C
Operating Pressure : 1 ATM
Time of Dehydrogenation : 2 - 240 min.

4.1 Preparation of Bimetallic Catalyst

4.1.1 Materials

The chemical used in this experiment is 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.

4.1.2 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 $10^{\circ}\text{C}/\text{min}$. until the temperature reach 500°C . Subsequently, the nitrogen was switched to air at the flow rate of 100 ml./min. (space velocity of about 2000 hour^{-1}). The material was held in this condition for 3 hours.

6. After calcination in air 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 1000°C under atmospheric pressure. 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 within the range between 0 to 800°C.

4.2.2.3 Electrical furnace

An electric 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. The 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.

4.2.3. Experimental System

The reactor 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 + 80 Vol.%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. During the experiment, the reaction temperature is monitored using a thermocouple and a digital temperature indicator.

4.2.4. Experimentation

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

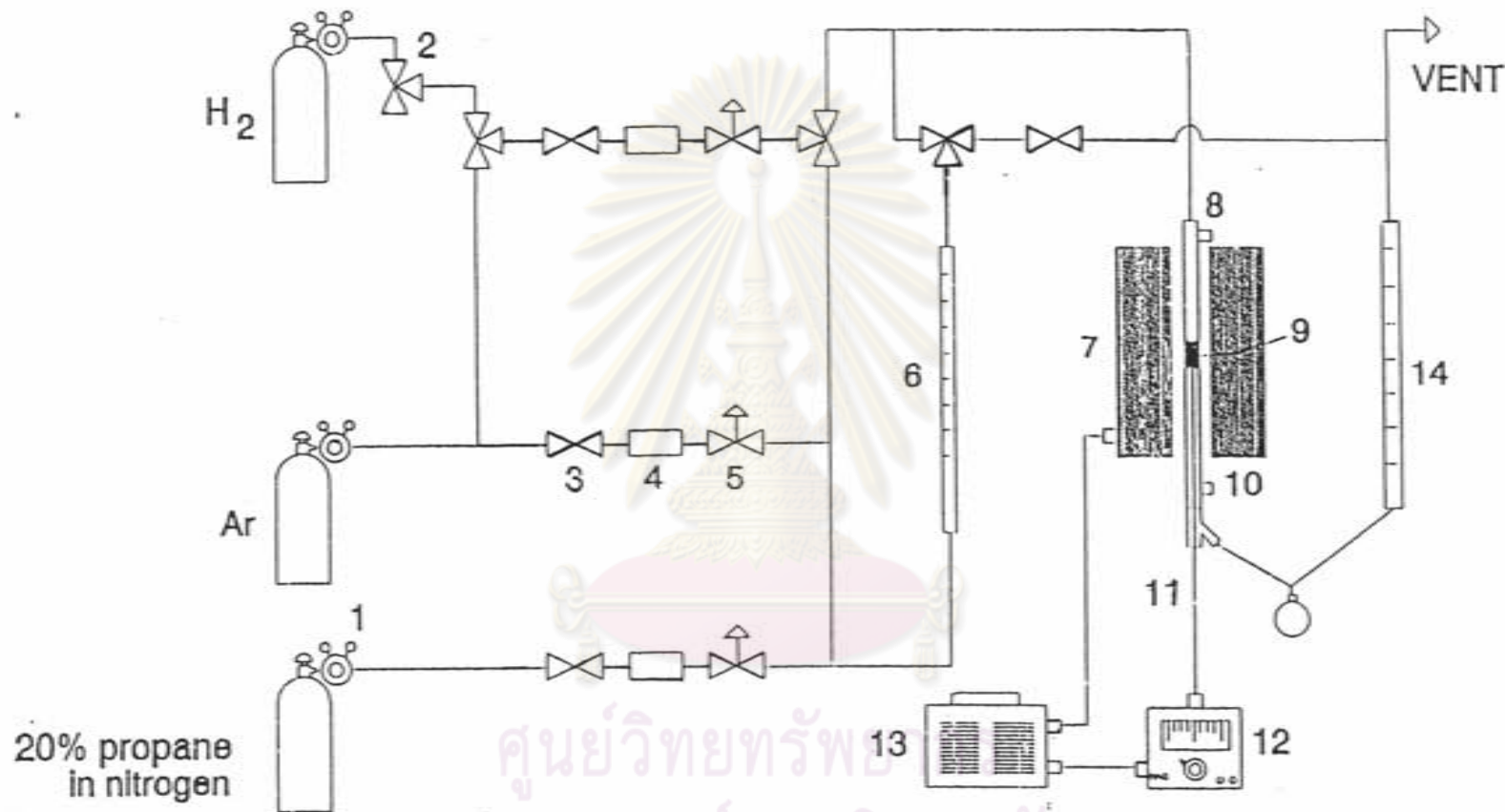
1. 0.1 gram of catalyst was packed in the middle of the quartz microreactor. The reactor was then placed in the furnace and the ultra high purity argon gas was introduced into the reactor at a flow rate of 30 ml./min.
2. The reactor was heated up at a constant heating rate of 10°C/min. until the catalyst 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 completed, the reactor was heated up again to a temperature of 600°C at 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. When desired time on stream was reached, the propane was changed to the ultra high purity argon gas. Then, the reactor was cooled down to room temperature in argon atmosphere.



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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.

4.3 Infrared Analysis

4.3.1 Sample Preparation for Infrared Analysis

The general approach of sample preparation method for solids where in-situ qualitative identification is required, is a compressed self-supporting disk technique. The thickness of a disk in practice may vary between 20-30 mg./cm⁻¹ depends on properties of each sample. Below this value the disk is likely to be mechanically weak, above it the IR radiation losses due to scattering will be excessive. The procedures to obtain a thin disk for IR study are

1. The sample is finely ground to the smallest obtainable particle size to avoid scattering, especially in the high wave number region, and to result in high quality spectrum.

2. The die used is made of stainless steel as shown in figure 4.2. The most important part of the die which its surface directly contacts with the sample is so-called the support disk. They compose of upper and lower support disks, they both are 20 mm. in diameter. The support disks are essential to be highly polished in their surfaces like mirror finish in order to overcome the sticking of sample to the surface of the die, the main problem arises in pressing disk.

3. Transfer the grind sample to the die and spread the grind sample to totally cover the surface of the lower support disk.

4. Then apply pressure 140 -180 kg./cm² for 2 to 3 minutes . From past experience, too high pressure may simply cause the disk to crack or stick to the die.

5. Carefully remove the thin disk from the die, the sample disk is readily for in-situ IR experiment.

For $\gamma\text{-Al}_2\text{O}_3$, fresh catalyst and coked catalyst at 2,5,and 10 min. on stream, the samples are formed into disks without mixing with $\gamma\text{-Al}_2\text{O}_3$. Otherwise, for the coked catalyst of higher time on stream,using only the coked

catalyst itself to form the disk results in almost totally obstruct the transmission of IR radiation. To solve the above difficulty, the coked catalyst were mixed with $\gamma\text{-Al}_2\text{O}_3$ to dilute the coked catalyst. The ratio of coked catalyst to $\gamma\text{-Al}_2\text{O}_3$ is in the range of 1: 1.

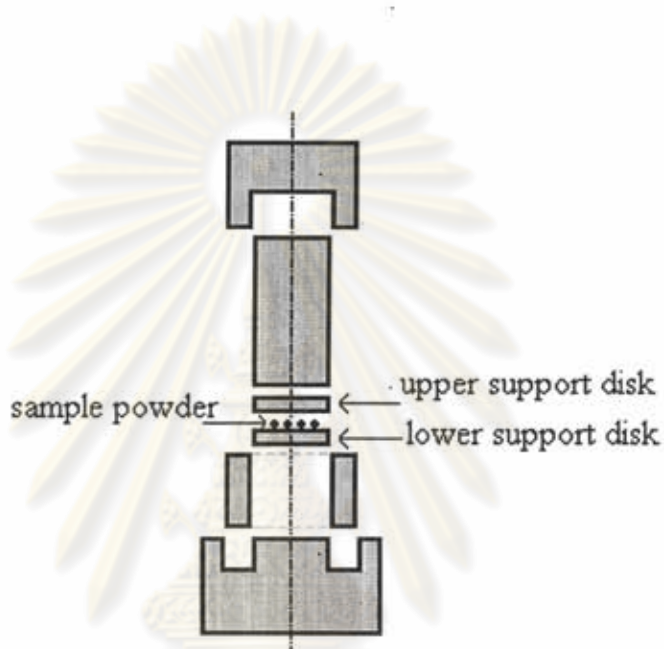
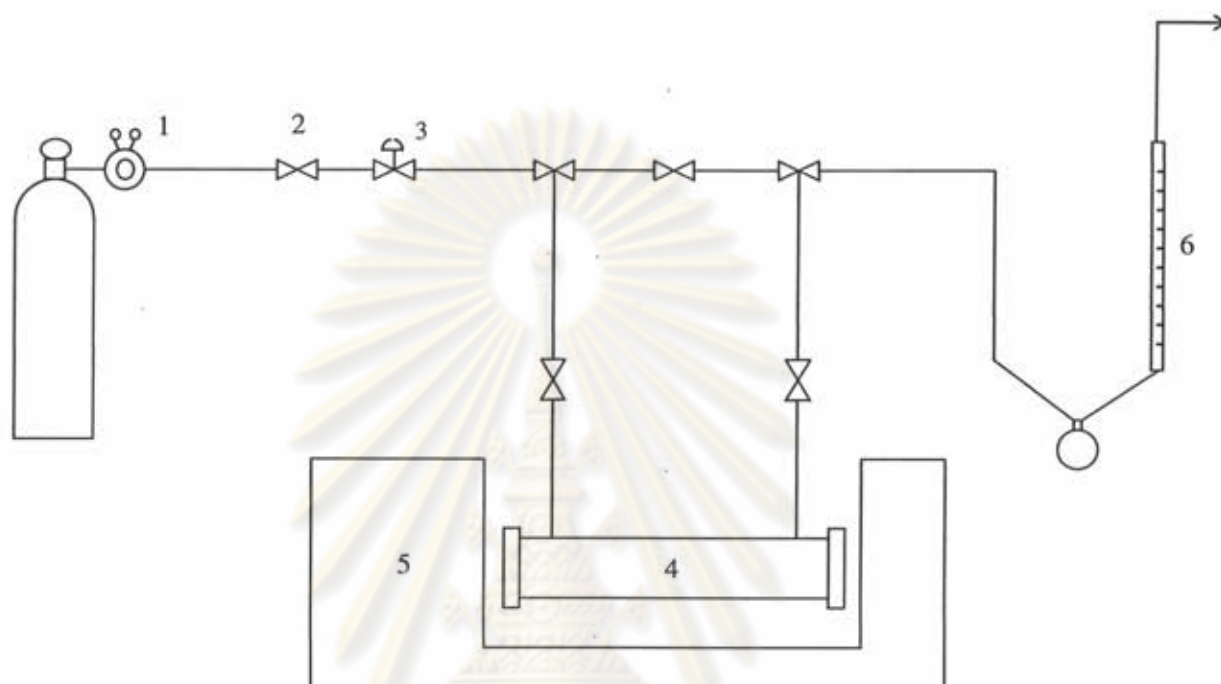


Figure 4.2 A Die for Pressed Disk

4.3.2 in-situ IR Experiment

The in-situ IR glass apparatus is illustrated in figure 4.3. The flow system (open loop) is applied in this study. Dry inert gas (N_2 , 99.999 %) supplied by Thai Industrial Gas Limited is the purge gas for the system. The relative humidity in the laboratory is controlled to be between 30 - 40 %



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| 1. Pressure Regulator | 4. IR Quartz Cell |
| 2. On-off Valve | 5. FT-IR Spectroscopometer |
| 3. Needle Valve | 6. Bubble Flow Meter |

Figure 4.3 Flow Diagram of in-situ IR (open loop) System

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4.3.2.1 The in-situ IR cell

The quartz IR cell used in this experiment is shown in figure 4.4. The cell is roughly divided into two zones; heating and cooling zone, in respect to their temperature. Some description of their features may be summarized as follows

1. The function of heating zone at the middle of the IR cell is to give rise in the temperature for the sample disk. The quartz sample holder for the sample disk to keep it perpendicular to the IR beam, is arranged inside the IR cell in the heating zone. A thermocouple is used to measure the sample disk temperature, and this temperature is controlled by a variable voltage transformer and a temperature controller.

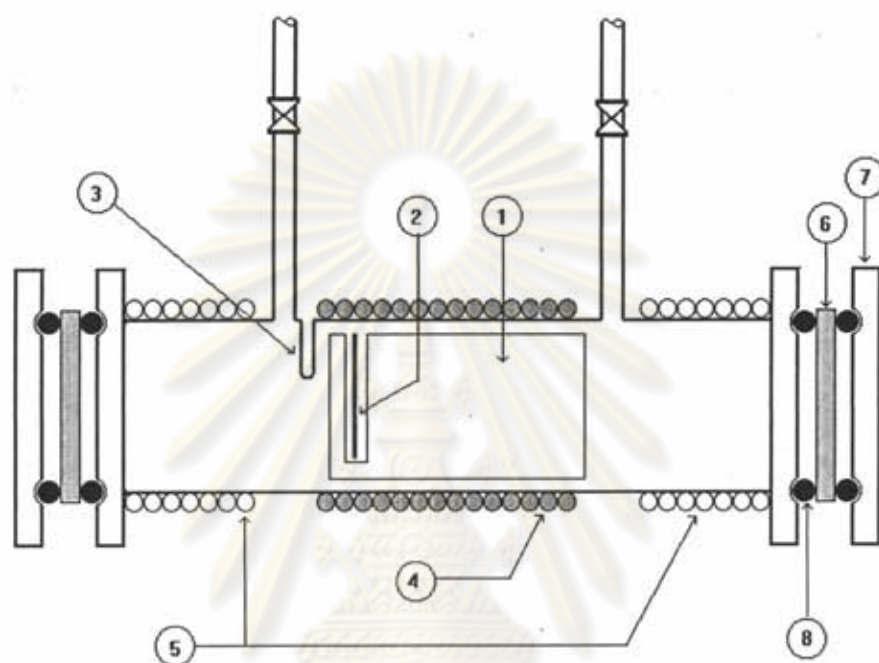
2. At both ends of the IR cell are water cooling zones. They are applied to reduce the excessive heating which may damage O-ring seals and NaCl windows. A NaCl window, located at each side, is attached to the IR cell by screwing between two stainless steel flanges, adjacent to rubber o-ring seal.

4.3.2.2 FT-IR Spectroscopometer

The Nicolet model Impact 400 equipped with a deuterated triglycine sulfate (DTGS) detector is used to qualitatively analyze the molecular structure of carbon deposits on catalyst. It stands above a movable desk for conveniently adjustment to the appropriate position. The resolution of 4 cm^{-1} with 500 scans is employed for every experiment.

4.3.2.3 Experiment

Generally, a background spectrum is collected prior to a sample spectrum. The experimental procedures for collecting the background spectra are described in detail below.



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| 1. Sample Holder | 5. Cooling Zone |
| 2. Sample Disk | 6. NaCl Window |
| 3. Thermocouple Position | 7. Flange |
| 4. Heating Zone | 8. O-ring |

Figure 4.4 The Assembly of an in-situ IR Quartz Cell

1. The background system for this experiment includes of the IR cell, the sample holder, and NaCl windows. These are installed together into readily examined IR cell as shown in figure 4.4.

2. The FT-IR spectrometer is then move until the position of IR cell is located in sample compartment. The suitable position should allow the maximum signal from optics compartment to pass through IR cell and reach the detector compartment . Mark this position once the system is properly adjusted.

3. The first background spectrum is measured at room temperature in ambient air.

4. The following background spectrum is taken at room temperature under dry inert gas flow.

5. The temperature is then gradually elevated to desired temperatures at 100, 200, 300, and 400°C. in inert atmosphere. At each temperature, the background spectrum is monitored.

All experiments are performed at atmospheric pressure.

In accordance with the above procedures, the sample spectrum which will be examined in analogous to the same temperature and atmosphere of the background spectrum, is supposed to diminish the effects which may be generated from these background systems.

FT-IR examination of sample disk is operated after collecting background spectrum in similar to those of background. The sample disk is vertically held by the sample holder and is placed into IR cell. The sample spectrum is analyze by following the procedures of collecting background spectrum as mention before. After the sample spectrum is analyzed at temperature up to 400°C, the IR cell is cooled down to room temperature in dry inert gas flow. The final sample spectrum is taken at this condition.