CHAPTER IV

EXPERIMENT

This research is divided into 4 parts : the catalyst preparation , the catalyst characterization, the catalyst deactivation by propane dehydrogenation, and the coked catalyst characterization. In each part, details of procedure, including the chemicals and apparatus, are described as the following.

4.1 Preparation of catalysts.

4.1.1 Materials.

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

1) Chloroplatinic Acid [$H_2PtCl_6 \cdot H_2O$] manufactured by Wako Pure Chemical Industries Co., Ltd., Japan.

2) Stannous Chloride Dihydrate [$SnCl_2 \cdot 2H_2O$] manufactured by Fluka Chemie AG, Switzerland.

3) Rhenium Oxide [Re_2O_7] manufactured by Nacalai Chemicals Co., Ltd., Japan.

4) Lithium Nitrate [LiNO$_3$] manufactured by E.Merck, Federal Republic of Germany.

5) Alumina [Al$_2$O$_3$] Support (type KNH-3) was obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan.

4.1.2 Apparatus.

4.1.2.1 Unit for grinding and screening support.

This unit which consists of pestle, mortar and sieve, is used for reducing size of the catalyst support to 60/80 mesh. Figure 4.1 shows the photograph of this unit.

Figure 4.1   Unit for grinding and screening support.

4.1.2.2 <u>Unit for impregnation</u>.

This unit which consists of pipette, flask, dropper and volumetric flask, is used for preparing aqueous solution and impregnating the solution onto the support. Figure 4.2 shows the photograph of this unit.

Figure 4.2 Unit for impregnation.

4.1.2.3 <u>Unit for calcination</u>.

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

4.1.3   Preparation of platinum catalysts.

4.1.3.1   Preparation of support and stock solution.

4.1.3.1.1   Preparation of support.

Support (Al_2O_3) was ground 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 impurities. Dried at 110 C overnight, the support was then calcined in air at 300°C for 3 hours.

4.1.3.1.2   Preparation of stock solution.

(1)   Platinum stock solution.

The platinum complex solution was prepared by dissolving 1 gram of Choroplatinic Acid in de-ionized water to the total volume of 25 ml.

(2)   Rhenium stock solution.

The rhenium complex solution was prepared by dissolving 1 gram of rhenium oxide in de-ionized water to the total volume of 25 ml.

(3)   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.

4.1.3.2 Preparation of platinum catalysts.

(1) The impregnating solution, for 2 grams of support, was prepared by calculating the amount of the stock solution to yield the required metal loading (Appendix A.1). 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) 2 g. of support was placed in 100 ml. Erlenmeyer flask and then the impregnating solution from (1) was slowly dripped into the support by dropper. Continuously stirring of the mixture in the flask while impregnating was required to obtain 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 over night.

(5) For calcination, the dried material was placed in a quartz tube. Nitrogen was introduced into the tube at the flow rate of 60 ml./min. The tube was heated at an increasing rate of 10 °C/min. until the temperature reached 500 °C. Then the nitrogen was changed to air at a flow rate of 100 ml./min. (space velocity of about 2,000 hours^{-1}). The material was held in this condition for 3 hours.

(6) For reduction, after calcined in air for 3 hours, the material was purged by nitrogen gas. Then switched to hydrogen gas for another 3 hours at the same space velocity and temperature.

4.1.3.3 Preparation of modified platinum catalysts.

4.1.3.3.1 Bimetallic catalysts.

Bimetallic catalysts were prepared in the same manner as platinum catalyst but there will be two metal components in impregnating solution. The second metal was chosen from tin and rhenium.

4.1.3.3.2 Trimetallic catalysts.

Trimetallic catalysts were prepared by the same method as described step 1 to 5 in section 4.1.3.2 but in this section there will be two metal components in the impregnating solution.

After calcination, the calcined material was reimpregnated by lithium impregnating solution (calculation of lithium loading shows in Appendix A.1). The reimpregnated material was treated by the same procedure as step 3 to 6 in section 4.1.3.2.

4.2 <u>Catalyst charaterization</u>.

  4.2.1 <u>Determination of metal content</u>.

    Percentage of each metal loaded onto the catalysts which were prepared in this reseach was analyzed by Atomic Absorption and Inductively Coupled Plasma Emission Spectrometry Method.

    The catalyst was prepared in solution form by the method described below :

    A certain amount of catalyst (about 50 mg.) was digested by digesting solution; 20 ml. of concentrated hydrochloric acid, 10 ml. of nitric acid, and 10 ml. of de-ionized water. The mixture was heated until the color of the support changed to white. During digestion, water was added into the solution to maintain the volume of the solution. Afterward, 2 drops of hydrofluoric acid were added into the mixture to digest the support. Heating step was proceeded until all of catalyst was dissolved. Then, the volume of the solution was made up to 50 ml. by de-ionized water.

    The prepared solution was analyzed for Platinum, Tin, and Rhenium content by Inductively Coupled Plasma Emission Spectrometry (ICPES, Perkin-Elmer PLASMA-1000) and for Lithium content by Atomic Absorption (AA, Varian Model Spectra AA-300). The measurements were performed by the Scientific and Technological Research Equipment Center, Chulalongkorn University.

4.2.2 Metal active sites measurement.

4.2.2.1 Materials.

The 99.99 % helium was used as a carrier gas. The hydrogen was used to reduce the catalyst. The carbon monoxide was used as an adsorbed gas and a standard gas.

4.2.2.2 Apparatus.

The metal active sites was measured by CO adsorption technique on the basis that one CO molecule adsorbed on one metal active site [49]. The flow diagrm of the CO adsorption is shown in Figure 4.3. The amount of CO 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 made of quartz tube.

Table 4.1 Operating condition of TCD gas detector.

Carrier gas and flow	He 30 ml.^{3}/min.
Temperature of detector	80 °C
Detector current	80 mA.

4.2.2.3 Procedure.

(1) 100 mg of catalyst was placed in the sample tube. The temperature was raised to 400°C at the rate of

HELIUM

1. H_2O trap
2. O_2 trap
3. Gas cooler
4. Heater
5. Catalyst bed

6. Thermocouple
7. Variable voltage transformer
8. Temperature controller
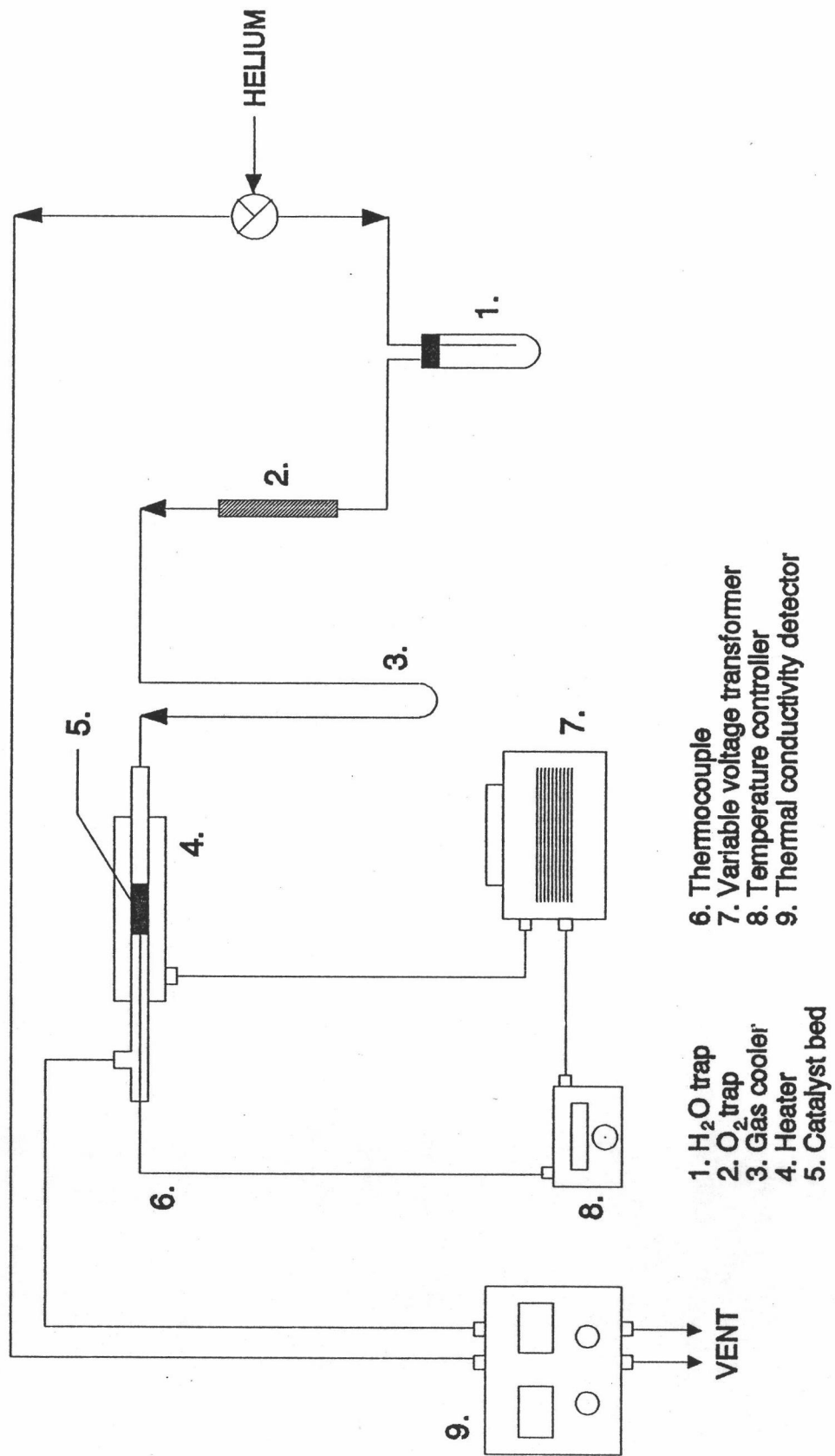9. Thermal conductivity detector

VENT

Figure 4.3 Flow diagram of the CO adsorption apparatus.

10 °C/min. The catalyst was reduced by the hydrogen at this temperature for 1 hour.

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

(3) The sample was then ready to measure its metal sites. 0.18 ml. of CO was injected to the injection port. The CO injection was repeated until the catalyst did not adsorb CO gas.

(4) The amount of CO adsorbed was measured. The amount of metal site was calculated (Appendix A.2).

4.2.3 Surface area measurement.

4.2.3.1 Materials.

The helium and nitrogen were used as carrier gases. The liquid nitrogen was used to cool the sample to boiling temperature of nitrogen.

4.2.3.2 Apparatus.

The apparatus consisted of two gas feed lines for helium and nitrogen. The flow rate of gas was adjusted by means of a fine-metering valve. The sample cell was made of pyrex glass. The four-port valve was used to direct the flow of gas to pass or by-pass the sample. The flow diagram of the BET surface area measurement is shown in Figure 4.4. The operating condition of the gas detector is the same as shown in Table 4.1.
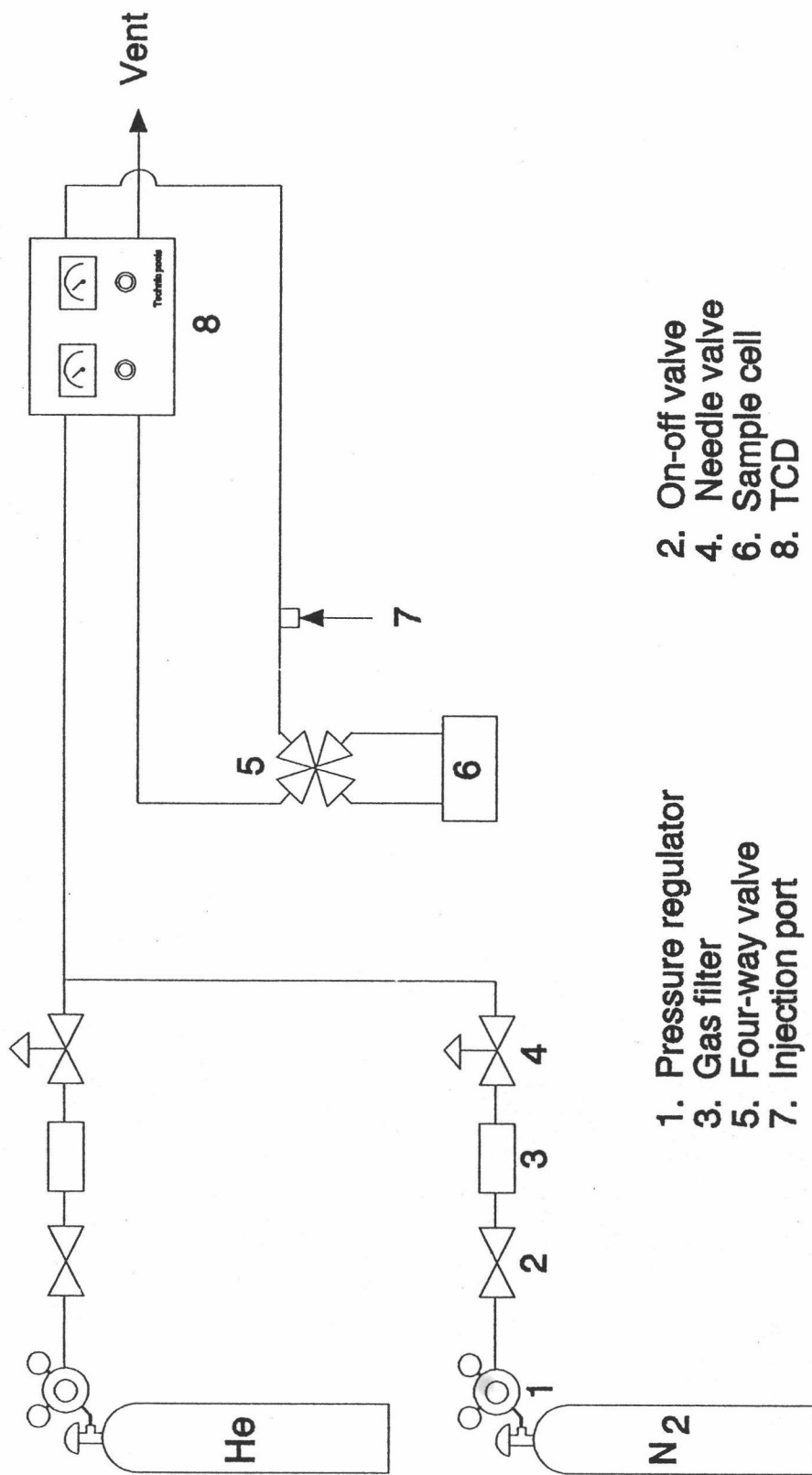
1. Pressure regulator   2. On-off valve
3. Gas filter   4. Needle valve
5. Four-way valve   6. Sample cell
7. Injection port   8. TCD

Figure 4.4 Flow diagram of the BET surface area measurement.

4.2.3.3 Procedure.

The mixture of helium and nitrogen gas flowed through the system at the nitrogen relative partial pressure of 0.3. The sample was placed in a sample cell which was then heated up to 150 °C and held at this temperature for 1 hour. Afterwards it was cooled down to room temperature. The sample was then ready to measure its surface area. There were three steps in the surface area measurement : adsorption, desorption and calibration.

(1) Adsorption step : the sample cell was dipped into liquid nitrogen. The nitrogen in the gas mixture was adsorbed onto the surface of the catalyst sample until equilibrium was reached.

(2) Desorption step : the sample which adsorbed with nitogen was dipped into water at room temperature. The adsorbed nitrogen was desorbed from the surface of the catalyst sample. This step would be completed when the recorder line returned to the base line.

(3) Calibration step : 4 ml.^{3} of nitrogen gas at atmospheric pressure was injected at the calibration port. The reference nitrogen peak appeared in the same direction of desorption peak.

(4) The BET surface area was calculated (APPENDIX A.3).

4.3 Catalyst deactivation by propane dehydrogenation.

4.3.1 Materials.

Mixture of 20 % propane in nitrogen supplied by Thai Industrial Gases 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.

4.3.2 Apparatus.

Flow diagram of the propane dehydrogenation system is shown in Figure 4.5. The system consists of a reactor, an automatic temperature controller, an electrical furnace, and gas controlling system.

4.3.2.1 Reactor.

The dehydrogenation microreactor is made from 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.

4.3.2.2 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 is measured at the bottom of the bed of catalyst in the reactor. The temperature

Figure 4.5 Flow diagram of the propane dehydrogenation system.
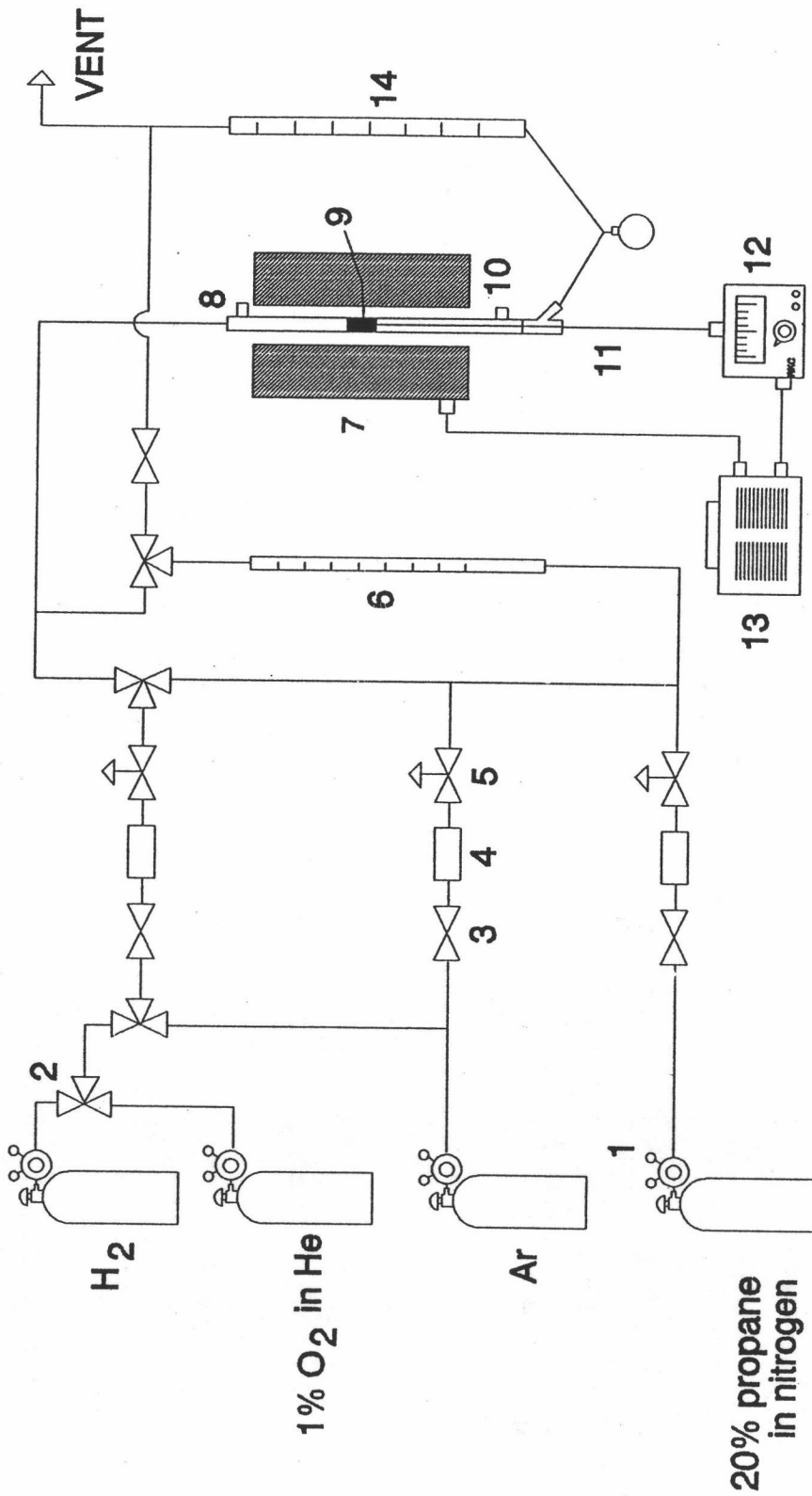
1. Pressure Regulator
2. Three-way Valve
3. On-off Valve
4. Gas Filter
5. Needle Valve
6. Flow Meter
7. Furnace
8. Reactor
9. Catalyst Bed
10. Sampling Port
11. Thermocouple
12. Temperature Controller
13. Variable Voltage Transformer
14. Bubble Flow Meter

control setpoint is adjustable within the range between 0 to 800 °C.

4.3.2.3 Electrical furnace.

Electrical furnace supplies heat to the reactor for propane dehydrogenation. So the reactor can be operated from room temperature up to 800 °C at maximum voltage of 220 volt.

4.3.2.4 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 fine-metering valve is used for adjusting the flow rate of the propane.

(2) The cylinders of ultra high purity argon, hydrogen, and 1 % oxygen in helium, equipped with a pressure regulators (0-120 psig), on-off valves and fine-metering valves, are used for adjusting the flow rates of these gases.

4.3.2.5 Gas chromatograph.

Flame ionization detector gas chromatograph was used to analyse the compositions of hydrocarbons in the feed and product stream. The operating conditions are illustrated in Table 4.2.

Table 4.2 Operating conditions of gas chromatograph (GC-14A).

Model	GC-14A (Shimadzu)
Detector	FID
Packed Column	23 % SP-1700 on 80/100 Chromosorp P AW
Nitrogen Pressure	2 kg/cm^2 (flow rate 25 ml./min.)
Hydrogen Pressure	0.5 kg/cm^2 (flow rate 30 ml./min.)
Air Pressure	0.3 kg/cm^2 (flow rate 240 ml./min.)
Column Temperature	30 °C
Injection Temperature	60 °C
Detector Temperature	70 °C

4.3.3 Procedure.

The deactivation of catalysts was performed by propane dehydrogenation reaction.

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

(2) The reactor was heated up at an increasing rate of 10 °C/min. until the temperature reached 500°C. The temperature was held at 500 °C for 10 min. before switching from argon gas to hydrogen gas to reduce the catalyst. The flow rate of the hydrogen gas was 100 ml./min., and the catalyst reduction time was 1 hour.

(3) When the reduction time was completed, the hydrogen gas was switched back to the argon gas for 5 min.

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

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

(6) When the time on stream was 20 hours, the diluted propane was switched back to the argon gas. The reactor temperature was held at 500°C for 5 minutes before the reactor was cooled down.

4.4 Characterization of coke on catalysts.

4.4.1 Weight of coke measurement.

In this section, the weight of coke formed on catalyst was measured by Differential Thermal Analyser (DTG-40, Shimadzu). The photograph of this system is shown in Figure 4.6. The procedure was divided into two parts.

4.4.1.1 Moisture removal.

The deactivated catalyst was placed in platinum cell. Helium gas was introduced at a flow rate of 30 ml./min. The temperature was increased at the rate of 10°C/min. up to 105°C and held at this temperature for 1 hour before cooled down to room temperature.

4.4.1.2 <u>Measurement of weight loss</u>.

The helium gas was switched to the 1 % oxygen in helium at a flow rate of 30 ml./min. The temperature was increased at 5°C/min. up to 650°C. The weight loss of the catalyst was measured.
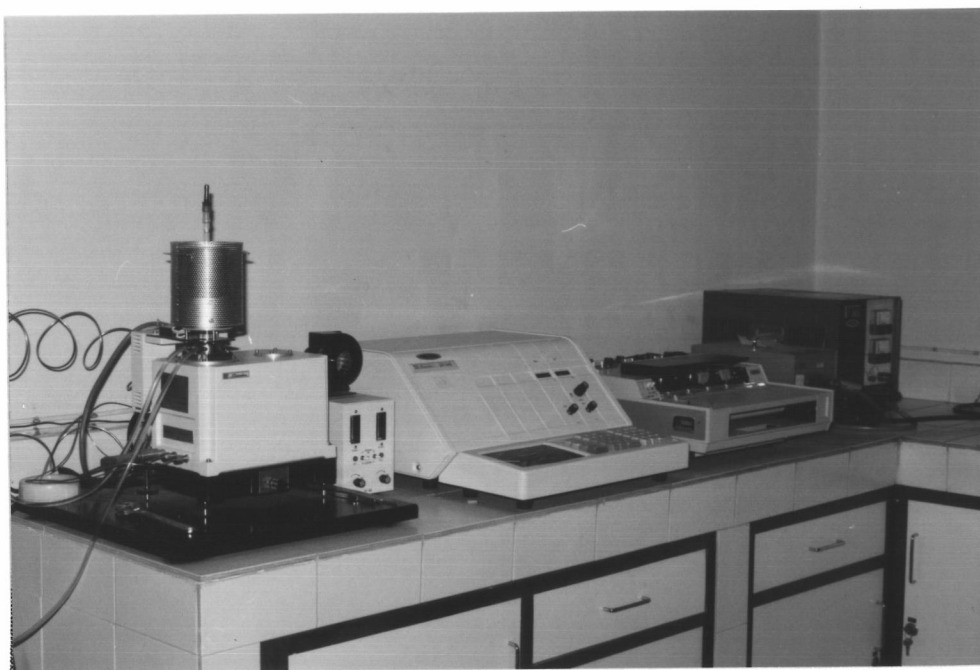

Figure 4.6 Photograph of the Differential Thermal Analyser system.

4.4.2 <u>Temperature programmed oxidation [13]</u>.

4.4.2.1 <u>Materials</u>.

The 1 % oxygen in helium gas mixture supplied by Thai Industrial Gas was used for oxidation reaction. The 99.99 % helium was used for purging the system.

4.4.2.2 Apparatus.

The apparatus included two gas feed lines for helium and 1 % 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 fine metering valve. The reactor was made of quartz glass with an outside diameter of 8 mm. The temperature of the catalyst bed was measured by a thermocouple. The reactor was placed in a furnace which various heating rates was controlled by a programmable temperature controller (PC-600, Shinko). The flow diagram of this system is shown in Figure 4.7.

The operating condition of gas chromatograph (GC-8AIT, Shimadzu) used for analysing the effluent stream is shown in Table 4.3.

Table 4.3 Operating condition of gas chromatograph (GC-8AIT).

Model	GC-8AIT (Shimadzu)
Detector	TCD
Packed column	Porapak QS (200x0.32 cm.)
He flow rate	60 ml./min.
Column temperature	90 °C
Detector/injector temperature	110 °C
Detector current	90 mA.
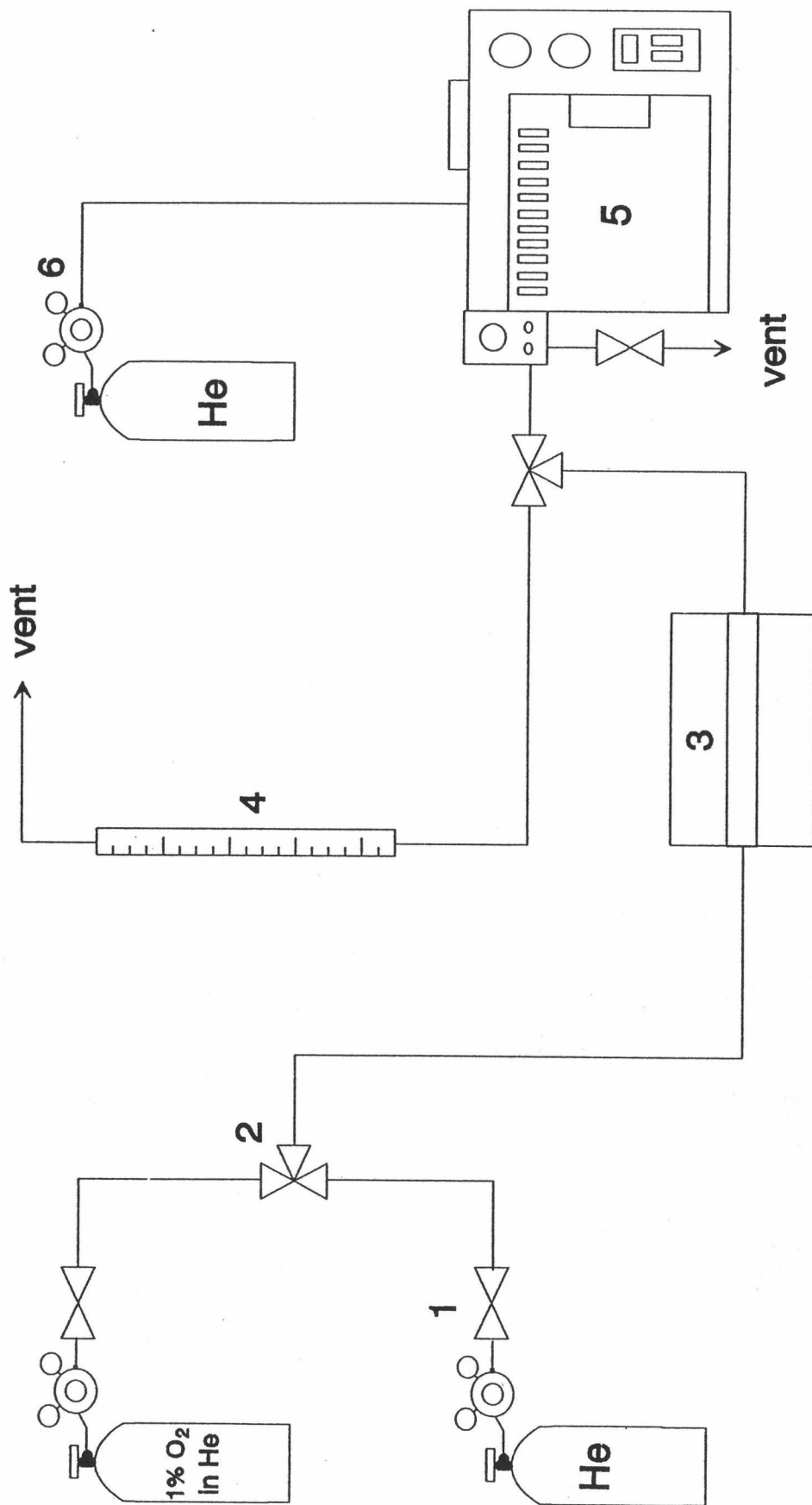
1. On-Off Valve   2. Three Way Valve
3. Furnace and Reactor   4. Flow Meter
5. Gas Chromatography   6. Pressure Regulator

Figure 4.7 Flow diagram of temperature programmed oxidation.

4.4.2.3. Procedures.

In a typical analysis, the reactor was purged by a helium gas stream at room temperature, then the temperature was raised to 105°C for desorbing CO_2 and water which might be adsorbed when the catalyst was exposed to air. Afterwards, the reactor was cooled down to room temperature and the gas stream was switched from helium to 1 % oxygen in helium, the flow rate of the gas was adjusted to 30 ml./min.

When the flow rate of the 1 % oxygen in helium gas 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 sampling every 5 min. by on-line gas sampler. The amount of oxygen consumption and carbon dioxide production were measured. The hydrogen/hydrocarbon ratio was calculated (APPENDIX A.4).

4.4.3. Determination of location of irreversible coke deposited on catalysts by regeneration method.

In this section, the Pt/Al$_2$O$_3$, Pt-Sn/Al$_2$O$_3$, and Pt-Sn-Li/Al$_2$O$_3$ catalysts were determined for the location of irreversible coke by regeneration method described below.

4.4.3.1. Materials and apparatus.

The apparatus and materials used for determining the location of irreversible coke on catalysts were the same as those used in the propane dehydrogenation reaction

(described in section 4.3).

4.4.3.2. Procedure.

The determination was divided into two parts :
combustion of coke on catalyst at 250 °C and combustion of coke on
catalyst at 500 °C.

4.4.3.2.1. Combustion of coke on catalysts at 250 °C.

After the propane dehydrogenation
reaction was performed, as described in section 4.3, and the reactor
was cooled down to ambient temperature, the reactor was heated up to
250 °C and held at this temperature for 5 minutes before changing
from argon to 1 % oxygen in helium gas mixture at the flow rate of
30 ml./min. to remove coke for 30 minutes. Then, the 1 % oxygen in
helium gas mixture was switched back to argon. The reactor was
heated up to 500 °C and held at this temperature for 5 minutes. The
argon was switched to the dilute propane to start the
dehydrogenation again for 2 hours.

4.4.3.2.2. Combustion of coke on catalysts at 500 °C.

After the propane dehydrogenation
reaction was performed, as described in section 4.3, the argon was
switched to 1 % oxygen in helium gas mixture at the flow rate of 30
ml./min. to remove coke for 30 minutes. Then, the 1 % oxygen in
helium gas mixture was switched back to argon for 5 minutes. Then,

argon was switched to the dilute propane to start the dehydrogenation again for 2 hours.