CHAPTER V

EXPERIMENTS

The experimental works of the study of the alumina-supported platinum catalyst and titanium dioxide-supported platinum catalyst are divided into three parts:

1. Preparation of the catalysts
2. The catalytic activity measurements
3. Characterization of the prepared catalysts

The details of these experiments are explained in the following sections.

5.1 Preparation of the catalysts

5.1.1 Materials

The platinum precursor used for supplying the precious metal loading, and the supports are listed below:

1. Chloroplatinic Acid [$H_2PtCl_6 \cdot 6H_2O$] was obtained from Wako Pure Chemical Industries Co., Ltd., Japan.

2. Titanium oxide [TiO_2], used as support of catalyst, was obtained from Fluka., A Sigma-Aldrich Company., Switzerland.

3. Alumina pellet [γ-Al_2O_3, type KNH-3], used as support of catalyst, was obtained from Sumitomo Aluminum Smelting Co., Ltd., Japan.

5.1.2 Preparation of platinum on alumina catalyst

5.1.2.1 Preparation of platinum stock solution

The platinum complex solution was prepared by dissolving the prepared chloroplatinic acid in de-ionized water to the total volume of 25 ml.

5.1.2.2 Preparation of support

1. Alumina support

Alumina pellet, spherical shape, was grounded to the required mesh size of 40/60 and then washed with distilled water for 2-3 times. Followed by drying at 110°C overnight in the oven. Then the support was calcined at 300°C for 2 hours.

2. Titanium oxide support

Titanium oxide [TiO$_2$], was used in form of commercial supported.

5.1.2.3 Preparation of the alumina-supported platinum catalyst

1. The impregnation solution, for 2 grams of support, was prepared by calculating the amount of the chloroplatinic acid stock solution to yield the required metal loading. Then de-ionized water was added to the total volume of 2 ml.

2. Two grams of support was placed in flask and the aqueous solution of platinum precursor salt from step 1 was impregnated.

3. After impregnation, the catalyst was dried in the oven at 110°C in air over night and calcined at 380°C for 3 h in the flow of air 100 ml/min, at the heating rate of 10°C/min.

4. Repeat 1, 2, 3 and change the calcination emperature to 450, 500, 550 and 650°C.

5. Repeat 1, 2, 3, 4 and change the calcination in air flow to the calcination in flow of 10%H$_2$/N$_2$ 100 ml/min for 7 h, at the heating rate of 10°C/min.

5.1.2.3 Preparation of the titanium oxide-supported platinum catalyst

1. The impregnation solution, for 3 grams of support, was prepared by calculating the amount of the chloroplatinic acid stock solution to yield the required metal loading. Then de-ionized water was added to the total volume of 25 ml.

2. Heat aqueous solution to 80°C with a stirrer. Then, add three grams of TiO_2 powder to the heated aqueous solution.

3. The suspension was dried at 80°C. After impregnation, the catalyst was dried in an oven at 110°C in air over night and calcined at 380°C for 3 h in the flow of air 100 ml/min at the heating rate of 10°C/min.

4. Repeat 1, 2, 3 and change the calcination temperature to 450, 500, 550, 650°C.

5. Repeat 1, 2, 3, 4 and change the calcination in air flow to the calcination in flow of 10 %H_2/N_2 100 ml/min for 7 h, at the heating rate of 10°C/min.

5.2 Catalytic activity measurements

5.2.1 Chemical and reagents

The catalytic activity of catalysts were studied in the simulated exhaust gases that could be prepared by mixture of standard gases as follows:

Nitric oxide (1 vol.%), Propane (3 vol.%), Oxygen (10 vol.%), Carbon monoxide (5 vol.%) and balanced with ultra high purity helium (99.999 vol.%).

5.2.2 Instruments and apparatus

5.2.2.1 The activity of the catalyst was tested using an experimental set consisted of a gas quantity control section, a reactor section (quartz tube, inside diameter = 0.6 cm.), a gas chromatograph and a temperature controller.

5.2.2.2 Gas chromatograph:

- SHIMADZU GC-8ATP equipped with a MS-5A column and a gas sampling valve (2 ml Sampling loop) was used for analyzing oxygen, carbon monoxide and nitrogen.

- SHIMADZU GC-8AIT equipped with a Porapak-Q column was used for analyzing carbon dioxide, water, and propane.

The operation conditions for each gas chromatograph and the samples of chromatogram obtained from gas analysis are shown in Appendix E.

Table 5.1 Standard condition for the activity measurement

Condition	Pt/Al$_2$O$_3$	Pt/TiO$_2$
Temperature range	25-600 °C	25-600 °C
Gas flow rate	141 ml/min	118 ml/min
GHSV	15,000 h^{-1}	15,000 h^{-1}
Catalyst	0.30 g	0.30 g

"Stoichiometric number (S)" of the simulated exhaust gas is calculated using the following equation:

$$S = \frac{2[O_2] + [NO]}{[CO] + [H_2] + 3n[C_nH_{2n}] + (3n+1)[C_nH_{2n+1}]}$$

where quantity in parenthesis indicated concentration in volume percent.

The composition of the simulated exhaust gas to achieve a stoichiometric mixture (S = 1.0) is shown in Table 5.2 and excess 5% O$_2$ is shown in Table 5.3.

Table 5.2 The composition of simulated exhaust gas at stoichiometric mixture (S=1)

Gas	concentration
NO	0.05 vol.%
CO	0.30 vol.%
C$_3$H$_8$	0.215 vol.%
O$_2$	1.2 vol.%
He	Balance

Table 5.3 The composition of simulated exhaust gas at excess 5 % oxygen

Gas	concentration
NO	0.05 vol.%
CO	0.30 vol.%
C_3H_8	0.215 vol.%
O_2	5.0 vol.%
He	Balance

The stoichiometric condition accepted on this experiment should be in the range $S = 1 \pm 0.025$. The catalysts were screened by heating the sample at a heating rate of $5°C/min$ and the effluent gases were analyzed by gas chromatography technique. The conversion was defined as the difference between an amount of inlet and outlet gas concentration and divided by the inlet gas concentration. In this experiment, the NO, CO and C_3H_8 gases were considered for comparison of the catalytic activity. The schematic diagram of the reactor system is shown in Figure 5.1.

5.3 Characterization of prepared catalysts

5.3.1 Active site measurement

Quantity of catalyst used is 0.1 g. Helium 99.99% was used as a carrier gas. Hydrogen was used to reduce the catalyst. Carbon monoxide was used as an adsorbent and a standard gas.

a) Apparatus

The number of metal active sites were measured by CO adsorption technique on the assumption that only one CO molecule adsorbed for one metal active site. The flow diagram of the CO adsorption apparatus is shown in Figure 5.2. The amount of adsorbed CO was measured by a thermal conductivity detector.
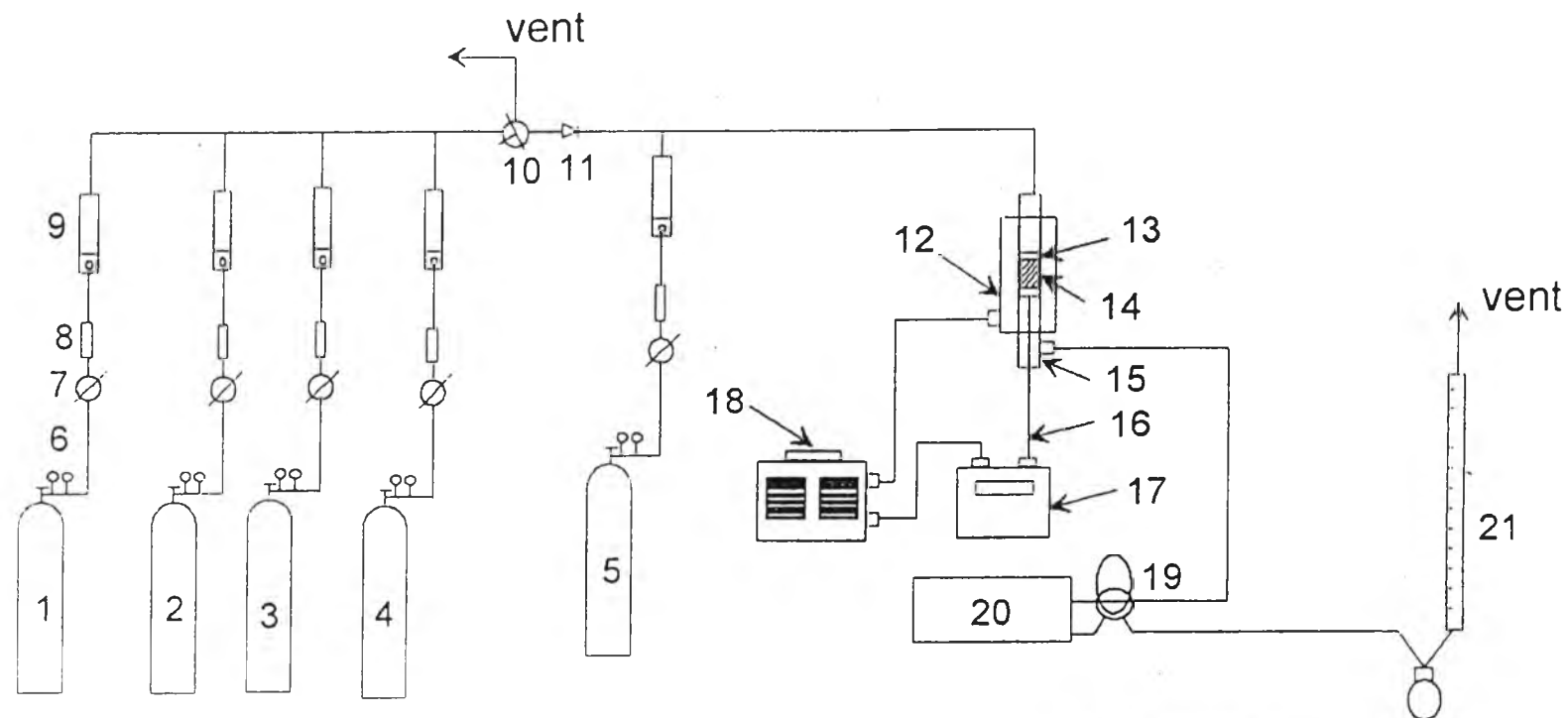
1. NO Tank	6. Pressure regulator	11. Check value	16. Thermocouple
2. C_3H_8 Tank	7. On-off valve	12. Reactor furnace	17. Temperature controller
3. O_2 Tank	8. Gas filter	13. Quartz wool	18. Variable voltage transformer
4. CO Tank	9. Flow meter	14. Catalyst bed	19. Sample
5. He Tank	10. Three way valve	15. Reactor	20. G.C. 21. Soap film flow meter

Figure 5.1 Flow Diagram of the reaction system
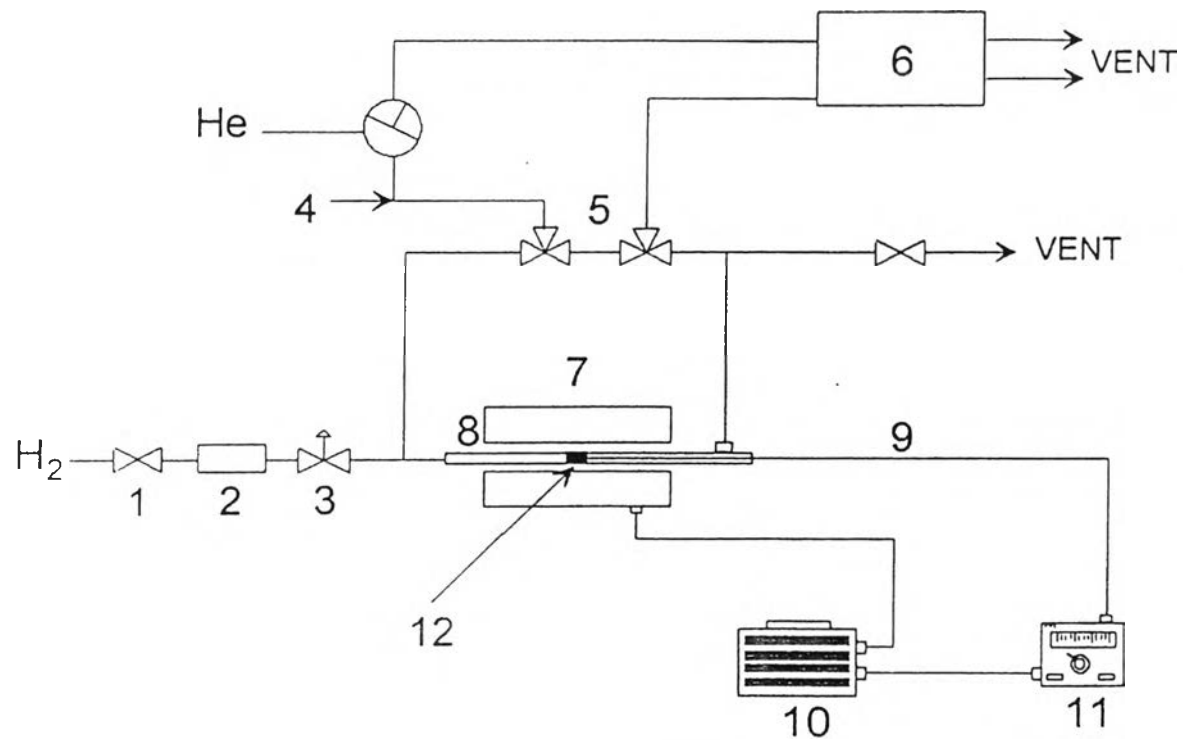
1.On-off valve	4. Injection port	7. Electrical furnace	10. Variable transformer
2. Gas filter	5. Three way valve	8. Reactor	11. Temperature controller
3.Needle valve	6. TCD	9. Thermocouple	12. Catalyst bed

Figure 5.2 Flow diagram of the CO adsorption apparatus

Operating condition of TCD gas detector were:

Carrier gas and flow	He 30 ml/min
Temperature of detector	80°C
Detector current	80 mA

b) Procedure

1. Catalyst sample of 0.1 g was placed in a sample tube. The temperature was raised to 500°C at a rate of 10°C/min. Then the catalyst was reduced by hydrogen at the flow rate of 100 ml/min for 1 h.

2. The sample tube was cooled down to room temperature.

3. Inject CO 50 μl to the injection port. The CO injection was repeated until the catalyst did not any longer adsorb CO by observed that the chromatogram area, after CO adsorption in the first injection had occurred, was kept nearly constant for the following others injection.

4. Measure the amount of CO adsorbed. The amount of metal site can be calculated using the procedure described in detail in Appendix B.

5.3.2 BET surface area measurement

a) Apparatus

Specific surface area of the catalyst, was measured by a BET Surface Area Analyzer. This method uses a physical adsorption of N_2 on the surface of catalyst to find the specific surface area.

b) Procedure

BET surface was measured by an area analyzer as shown in Figure 5.3. The gas mixture of He and N_2 flowed through the system

The analysis began by placing sample in a sample cell and connected to the surface area analyzer. The sample was then heated up to 150°C. held at this temperature for 1 h and cooled down to room temperature. There were three steps in this surface area measurement.

1. Adsorption step: The sample cell was dipped into a liquid nitrogen bath. The N_2 in gas mixture would be adsorbed on the surface of the catalyst sample, shown as a peak on the recorder, when the equilibrium was reached, a straight line was shown on the recorder.

2. Desorption step: The sample cell was taken out of the liquid nitrogen bath and then dipped into a water bath. The adsorbed N_2 would be desorbed from the surface of the catalyst sample until the equilibrium was reached, shown as a peak in the opposite direction to adsorption.

3. Calibration step: 1ml of nitrogen gas of 1 ml. At atmospheric pressure was injected at the sampling point. The standard nitrogen peak would appear at the same side of desorption peak.

5.3.3 Temperature programmed reduction

a) Apparatus

Temperature Programmed Reduction, TPR studies show that these ions are strongly associated with support. The reducible site was measured by investigating the amount of CO which reduced oxide species on the surface. And the product of this reaction is CO_2 which is trapped by sodium hydroxide [NaOH]. The amount of CO was measured by the thermal conductivity detector. The TPR traces show that the capable of oxide adsorbed over the catalyst site varied in strength different. The flow diagram of the TPR apparatus is shown in Figure 5.4.

Operating condition of TCD gas detector were:

Carrier gas and flow	5 %CO/He, 30 ml/min
Temperature of detector	$80^\circ C$
Detector current	80 mA

b) Procedure

There were two steps in this measurement.

- Oxidation step

0.2 g of catalyst sample was placed in a sample tube. 10%O_2/He was fed into the sample at the flow rate of 30 ml/min and the sample was heated up to 500°C at a heating rate of 10°C/min and held for 15 min to ensure that the surface was covered with oxygen. Then the gas was switched into the system to replace 10%O_2/He at the flow rate of 30 ml/min and the system was cooled down to room temperature.

- Temperature Programmed Reduction Step

1. After oxidation: Switch to the mixture gas 5%CO/He flow into the sample at the flow rate 30 ml/min and wait until the baseline of the TCD signal was constant.

2. The TPR runs were started at 50°C, by allowing the temperature to increase to 500°C at a rate of 10°C/min.

5.3.4 Temperature programmed desorption

a) Apparatus

Temperature Programmed Desorption of Carbon Dioxide, CO_2-TPD studies to measure the adsorbable strength and the amount of carbon dioxide adsorbed on catalysts. Based on the mechanism of contact catalysis, desorption of the reaction product from the catalyst particle is an important step of this mechanism adsorbed on the catalyst surface. The flow diagram of the TCD apparatus was shown in Figure 5.3.

Operating condition of TCD gas detector were:

| Carrier gas and flow	He 30 ml/min
Temperature of detector	80°C
Detector current	80 mA

b) Procedure

1. 0.2 g of catalyst sample was placed in a sample tube. He was fed into the sample at the flow rate of 30 ml/min and the sample was heated up to 500°C at a heating rate of 10°C/min and held for 60 min. Then, the system was cooled down to room temperature.

2. Switch to the pure gas CO_2 flow into the sample at the flow rate 30 ml/min and held for 60 min. After that, switch to He flow into the sample at the flow rate 30 ml/min wait until the baseline of the TCD signal was constant.

3. The TPD runs were started at 30°C, by allowing the temperature to increase to 500°C at a rate of 10°C/min.

5.3.5 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of the catalysts were performed using X-ray diffractor model JDX, Jeol, Japan at Scientific And Technological Research Equipment Center, Chulalongkorn University.
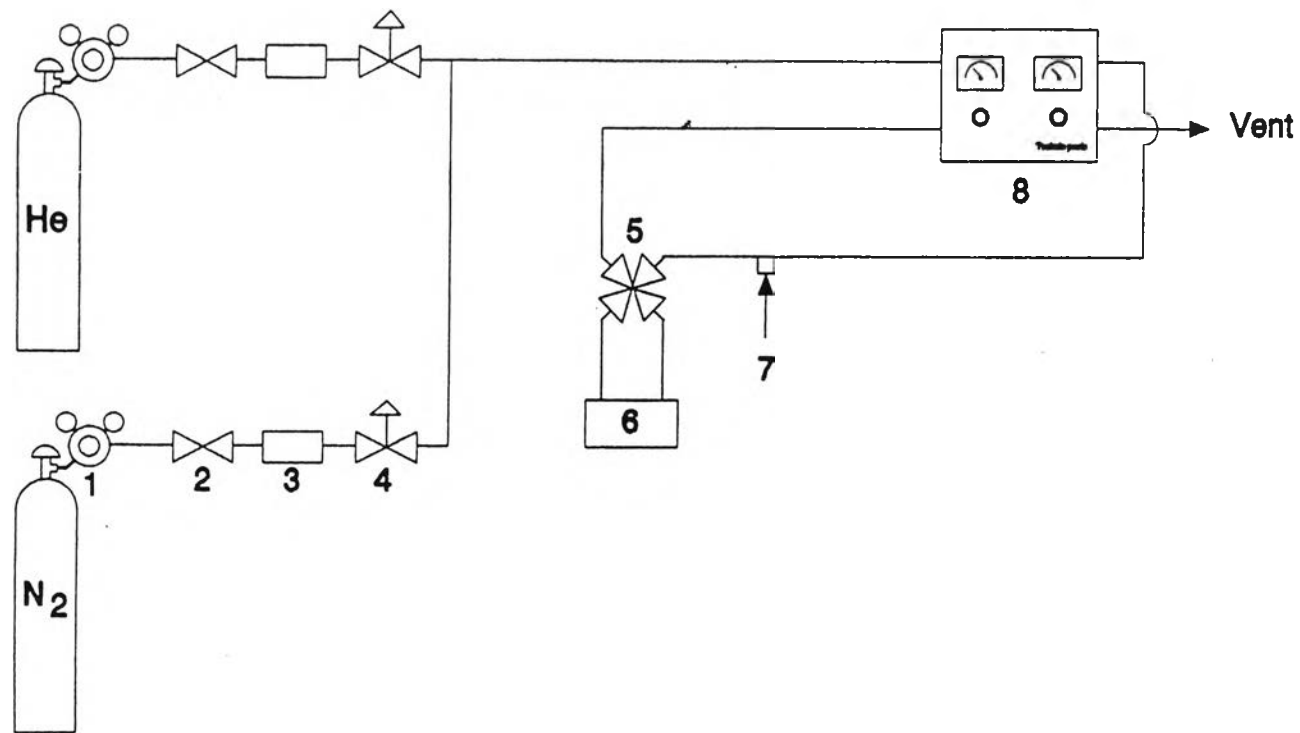
1. Pressure regulator   3. Gas filter   5. Four-way valve   7. Injection port

2. On-off valve   4. Needle valve   6. Sample cell   8. TCD

Figure 5.3 Flow diagram of the BET surface area analyzer
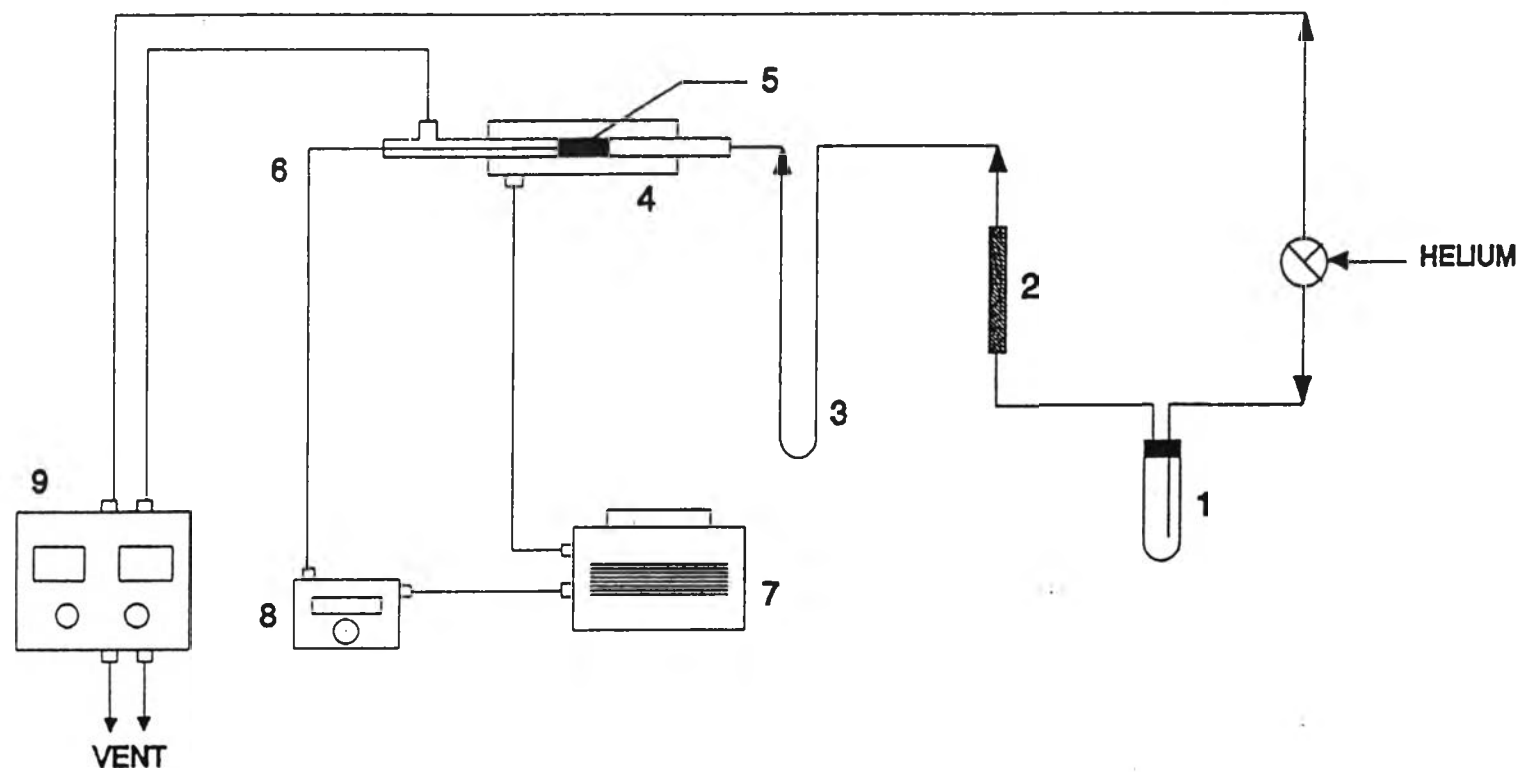
1. H₂O trap	4. Heater	7. Variable voltage transformer
2. O₂ trap	5. Catalyst bed	8. Temperature controller
3. Gas cooler	6. Thermocouple	9. Thermal conductivity detector

Figure 5.4 Flow diagram of TPD and TPR units