

CHAPTER IV

EXPERIMENTS

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

1. Preparation of the platinum-based metal catalyst,
2. The catalytic activity measurements,
3. Characterization of prepared platinum-based metal catalysts

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

4.1 Preparation of the platinum-based metal catalyst

4.1.1 Materials

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

1. Platinum tetrammine dichloride(II) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$ was obtained from Mitsuwa's Pure Chemicals Co., Ltd., Japan.
2. Chloroplatinic Acid $[\text{H}_2\text{PtCl}_6]$ was obtained from Wako Pure Chemicals Industries Co., Ltd., Japan.
3. Alumina pellet ($\gamma\text{-Al}_2\text{O}_3$, type KNH -3), used as support of catalyst, was obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan.
4. Alumina powder ($\gamma\text{-Al}_2\text{O}_3$, size 5μ), used for washcoat monolith, was obtained from Sumitomo Co., Ltd., Japan.

5. Cordierite Monolith, used as substrate, was obtained from N-COR, Ltd., Nagoya, Japan.

4.1.2 Preparation of platinum-supported metal catalyst.

4.1.2.1 Preparation of platinum stock solution

1. Platinum tetrammine dichloride (II) stock solution

The platinum complex solution was prepared by dissolving 1 gram of platinum tetrammine dichloride (II) in de-ionized water to the total volume 25 ml.

2. Chloroplatinic acid stock solution

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

4.1.2.2 Preparation of platinum supported on pelleted-alumina

1. 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 over night in the oven then the support was calcined at 300 °C, for 2 hours.

2. The impregnating solution was prepared by calculating the amount of the stock solution to yield the metal loading. Then adding de-ionized water to the total volume 2 ml.

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

4. After impregnating, the catalyst was dried in the oven at 110 °C in air over night and calcined at 500 °C for 4 hr. in air atmosphere.

The description of calculating the amount of the stock solution and the method of catalyst preparation were illustrated in Appendix A.

4.1.2.3 Preparation of platinum supported on washcoat monolith

1. Preparation of slurry for washcoat

Alumina powder (TA) 1.5-2 grams was added to aqueous solution of acetic acid (2.5 wt%, 5 ml) and stirred for 5 min. The final slurry for washcoat has pH 5-6 and viscosity in range of 10-100 cp.

2. Monolith coating procedure

The catalyst test samples used was a cylindrical cordierite honeycomb structure (400 cell/in²). First, cordierite monolith was cut into bar shape, 3 mm Width x 3 mm Height x 20 mm Long. Then the bar was dipped into the prepared slurry for 1-2 min. and blowed by compressed air in order to remove extra slurry in cells of the monolith, followed by drying at 110 °C over night in the oven and calcining at 500 °C for 2 hours in air atmosphere.

3. Platinum loading procedure

The impregnating solution for dry impregnation was prepared by calculating the amount of the stock solution to yield the required metal loading. De-ionized water was added up to 0.1 ml which was used on one bar of cut-monolith.

The activated washcoat monolith was impregnated with the prepared platinum precursor salt solution. After that, the catalyst samples were dried at 110 °C over night in the oven and calcined at 500 °C 4 hr. in air atmosphere.

The description of calculating the amount of the stock solution and the method of preparing catalyst were illustrated in Appendix A.

4.1.2.4 Pretreatment of prepared catalyst in simulated exhaust gas

1. The impregnated and dried catalyst, 0.4 g. for Pt supported on alumina or one bar of Pt supported on washcoat monolith, was packed into quartz reactor (inside diameter 0.6 cm.). Then the quartz tube was connected to the reaction system.

2. The concentration of each reactant gases for pretreatment was adjusted to rich gas mixtures by using flow meter. Then the total flow rate was balanced to 141 cc./min. (GHSV = 15,000 h⁻¹).

3. The sample was heated to 300 °C with heating rate of 10 °C/min. and was holding at constant temperature for 2 h. After that, the sample was cooled down to room temperature in the reactant gases.

The schematic diagram of the preparation of Pt-based metal catalyst was shown in Figure 4.1 and the gas composition for pretreatment catalyst in rich condition (S=0.8) was shown in Table 4.2.

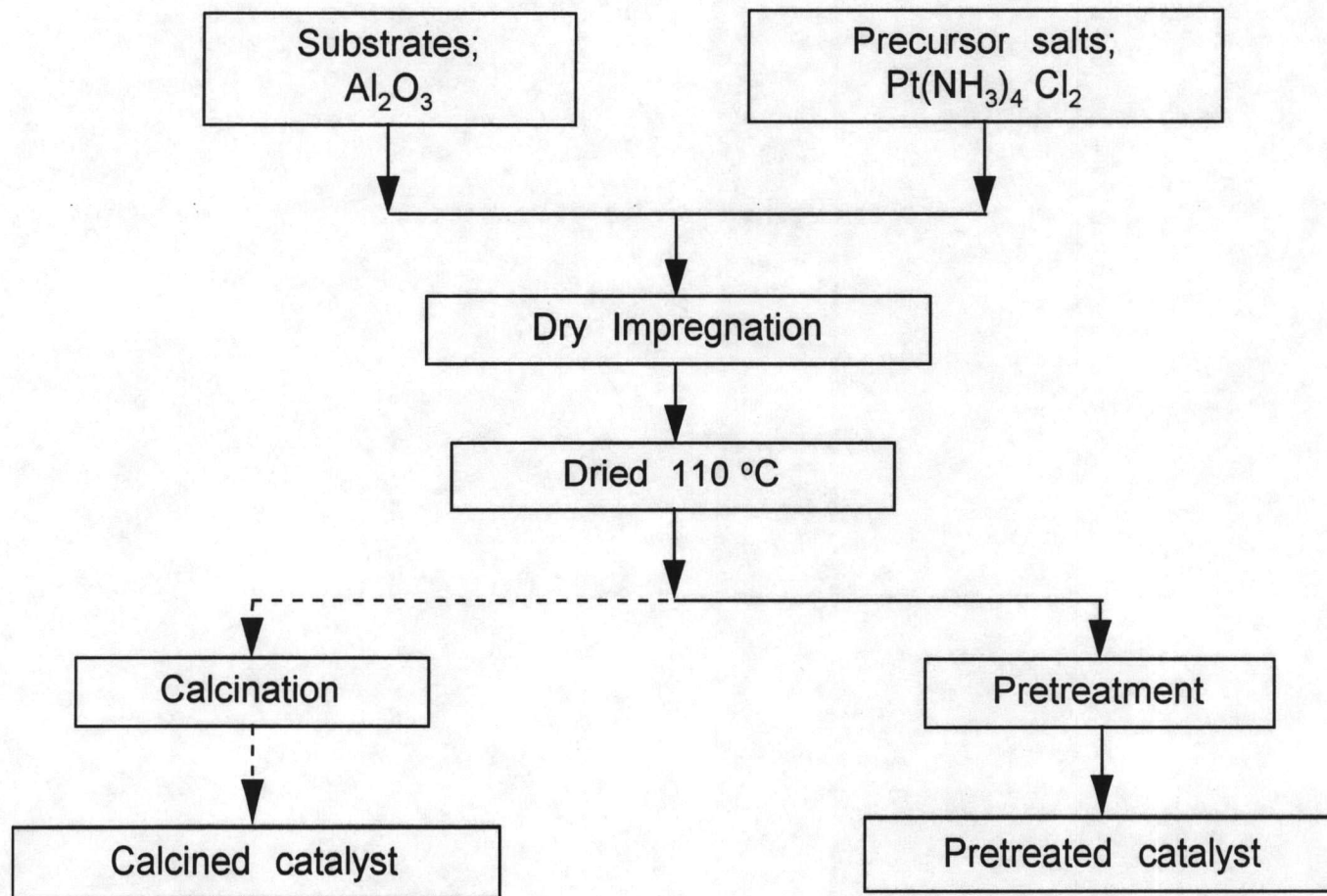


Figure 4.1 Schematic diagram of the catalyst preparation procedure.

4.2 The catalytic activity measurements

4.2.1 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 followed:

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

4.2.2 Instruments and apparatus

4.2.2.1 The activity of the catalysts 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 analysis section, and a temperature controller.

4.2.2.2 Gas chromatograph :

- SHIMADZU GC-8ATP equipped with a MS-5A column and a gas sampling valve (2.5 ml sampling loop) was used for analyzing oxygen, hydrogen, methane, carbonmonoxide and nitrogen.

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

The operating conditions for each gas chromatography machine and the samples of chromatogram obtained from gas analysis were shown in Appendix B.

Table 4.1 : Standard condition for the activity measurement.

Temperature range	150 - 700°C
Gas flow rate	141 ml./min.
GHSV	15,000 h ⁻¹
Catalyst	0.40 gm.

“Stoichiometric number (S)” of the simulated exhaust gas was calculated using the following equation:

$$S = \frac{2[\text{O}_2] + [\text{NO}]}{[\text{CO}] + [\text{H}_2] + 3n[\text{C}_n\text{H}_{2n}] + (3n+1)[\text{C}_n\text{H}_{2n+2}]} \quad (4.1)$$

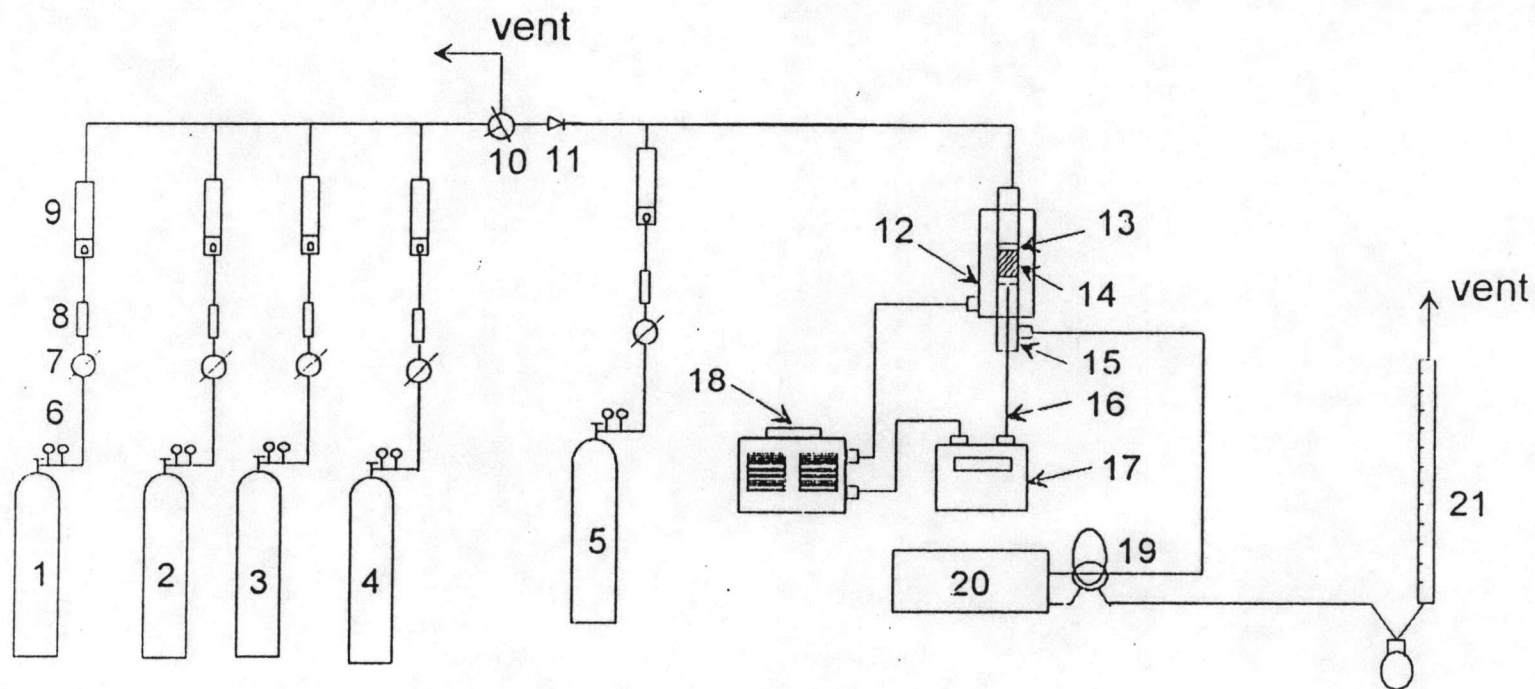
where quantity in parenthesis indicated concentration in volume percent.

The composition of the simulated exhaust gas to achieve a stoichiometric mixture (S=1.0) was shown in Table 4.2.

Table 4.2 The composition of simulated exhaust gas

Gas	S=0.8	S=1.0
NO	0.05 vol. %	0.05 vol. %
CO	0.03 vol. %	0.03 vol. %
C ₃ H ₈	0.215 vol. %	0.215 vol. %
O ₂	1.0 vol. %	1.2 vol. %
He	Balance	Balance

The stoichiometric condition could be accepted in this experiment with the range $S = 1 \pm 0.025$. The catalysts were screened by heating the sample at a heating rate of 10 °C/min from 150-700 °C. To ensure steady - state condition, each reaction temperature was hold for 10 minutes 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 propane gases were considered for comparison of the catalytic activity. The schematic diagram of the reactor system was shown in Figure 4.2.



- | | | | |
|---------------------------------------|-----------------------|---------------------|----------------------------------|
| 1. NO Tank | 6. Pressure regulator | 11 Check valve | 16. Thermocouple |
| 2. C ₃ H 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. Sampler |
| 5. He Tank | 10. Three way valve | 15. Reactor | 20. G.C. |
| | | | 21. Soap film flow meter |

Figure 4.2 Flow Diagram of the Reaction System.

4.3.1 Material active site measurement

Quantity of catalyst used is 0.4 g. Helium 99.99% was used as a carrier gas. Hydrogen was used to reduce the catalyst. Carbonmonoxide 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 was shown in Figure 4.3. The amount of CO adsorbed was measured by a thermal conductivity detector.

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

-Catalyst sample was placed in a sample tube. The temperature was raised to 400°C at rate of 10 °C/min. Then the catalyst was reduced by hydrogen at this temperature for 2 hours.

-The sample tube was cooled down to room temperature.

- 0.18 ml. of CO was injected to the injection port. The CO injection was repeated until the catalyst did not adsorb CO. It was observed that the chromatogram area, after CO adsorption in the first injection had occurred, was kept nearly constant for the following others injection.

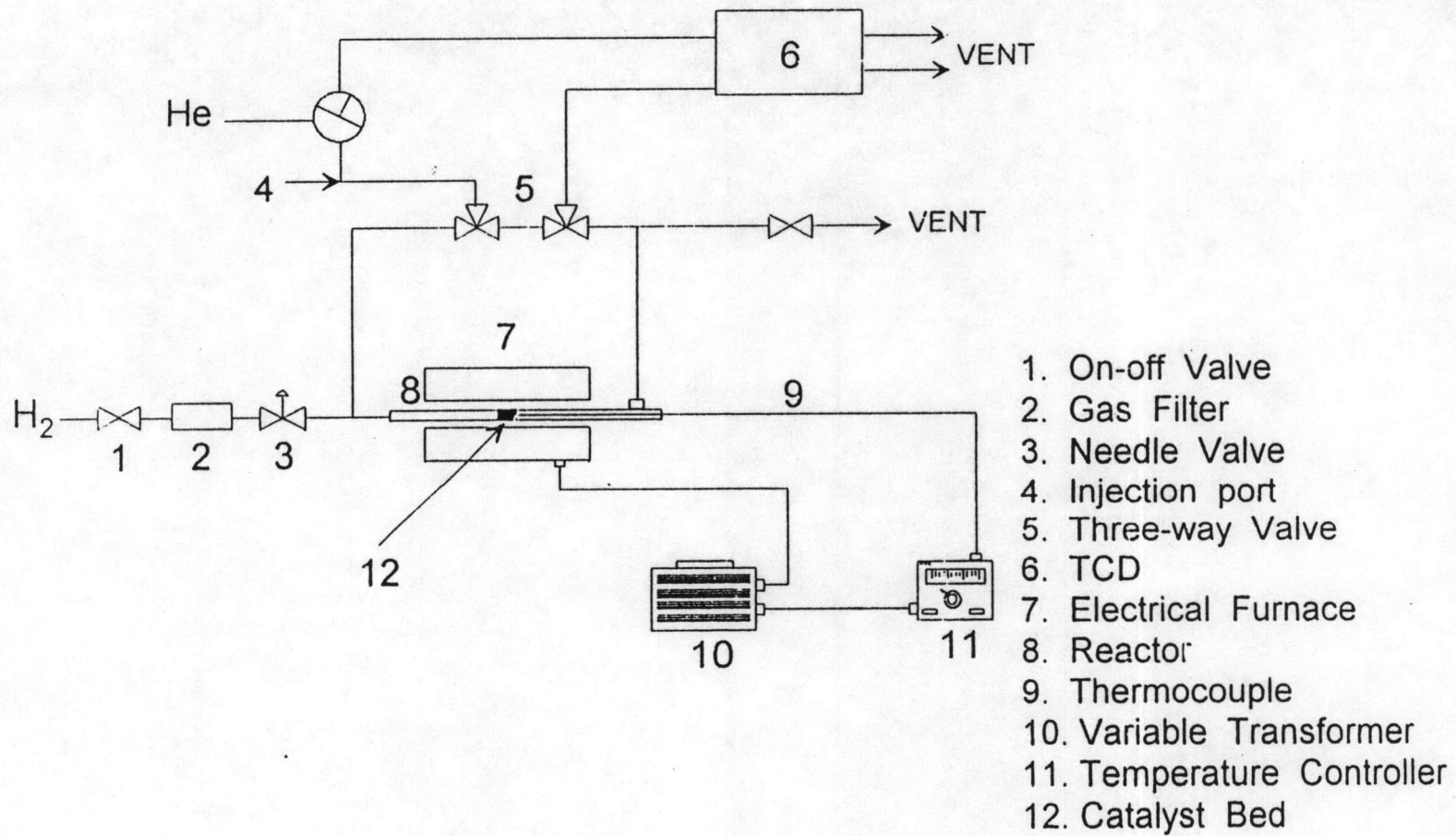


Figure 4.3 Flow Diagram of the CO adsorption apparatus.

-Measure the amount of CO adsorbed. The amount of metal site can be calculated using the procedure described in detail in Appendix A. Each catalyst was degassed in the stream of He (30 ml./min) at 150 °C for 30 minutes and then reduced in hydrogen stream (100 ml./min) at 400 °C for 1h.

4.3.2 BET Surface area measurement.

Specific surface area of the catalyst was measured by a BET surface area analyzer (model ASAP 2000) at Analytical center of Chemical Engineering Department, Chulalongkorn University. The method was a physical adsorption of N₂ on surface of catalyst to find the specific surface area.

Operating condition :

1. The catalyst weight = 0.3-0.5 g.
2. Degas temperature = 150 °C
3. Vacuum pressure = 10 μHg.
4. Pressure table = 5 points.

Procedure :

- The sample was heated and placed under vacuum to remove the moisture and other contaminants before analysis.

- The catalyst sample was weighted. After that, the sample was automatically analyzed.

- The amount of N₂ gas needed to form a monolayer on the surface of sample could be determined from measurements of the volume of gas adsorbed. The BET (Brunnauer, Emmett, and Teller) equation was used for calculation in the specific surface area.