CHAPTER IV

EXPERIMENT

In the present study of the automotive emission control of three-way catalyst, the experiment was divided into three parts :

1. The noble metal supported catalyst preparation,
2. The catalytic activity measurement,
3. Characterization of the noble metal catalyst prepared.

The details of the experiments would be explained in the following section.

4.1 Preparation of Catalysts

4.1.1 Materials.

The metal complexes used for supplying the metal components required to be deposited on the support are of extra grade. They are listed below :

1. Cerium (III) Nitrate [$Ce(NO_3)_3$] manufactured by Wako Pure Chemical Industries Co., Ltd., Japan.
2. Rhodium Nitrate Anhydrous [$Rh(NO_3)_3$] from Mitsuwas Pure Chemicals Co., Ltd., Japan.
3. Chloroplatinic Acid [$H_2PtCl_6 \cdot H_2O$] was supplied by Wako Pure Chemicals Industries Co., Ltd., Japan.

4. Alumina [γ-Al_2O_3] Support (type KNH-3) was obtained from Sumitomo Aluminium Smelting Co., Ltd., Japan

4.1.2 Preparation of three-way catalysts

4.1.2.1 Preparation of Support.

Alumina support (γ-Al_2O_3) 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, the support was then calcined in an air stream at 300 °C for 2 hours.

4.1.2.2 Preparation of stock Solution.

1. Cerium stock solution

The cerium complex solution was prepared by dissolving 10 gram of cerium nitrate in de-ionized water to the total volume of 25 ml.

2. Rhodium stock solution

The rhodium complex solution was prepared by dissolving 0.5 gram of rhodium nitrate anhydrous in de-ionized water to the total volume of 50 ml.

3. Platinum stock solution

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

4.1.2.3 Preparation of three-way catalysts

The automotive emission control catalysts investigated in this research are based on the noble metals Pt and Rh. The preparation of catalyst was modified from the previous studies [42, 43, 44]. The preparation procedures are described below.

1. The impregnating solution, for 4 grams of support, was prepared by calculating the amount of the stock solution to yield the required metal loading. De-ionized water was finally added until 4 ml. of the solution was obtained.

2. 4 g. of support was placed in a 100 ml erlenmeyer flask The aqueous solutions of cerium nitrate, rhodium nitrate, and chloroplatinic acid were impregnated, respectively. After impregnating, the catalysts were dried and calcined at 500 °C for 4 h in air. The description of calculating the amount of the stock solution. and the method of preparing catalyst were illustrated in Appendix A.

4.2 The Activity Measurements

The objective of this experiment is the prepared catalytic activity measurement. The detail of the chemical reagent, the instruments and apparatus, and the procedure of the experiment are described below.

4. 2.1 Chemicals and Reagents

Nitric oxide (1%) in helium, Propane (3%) in helium, Carbon monoxide (5%) in helium, Oxygen (10%) in helium, and Helium of ultra high purity grade (99.999%) were supplied by Thai Industrial Gas Co., Ltd., Thailand.

4.2.2 Instruments and Apparatus

4.2 2.1 Reactor : The reactor is a conventional microreactor made from quartz tube with 0.6 mm. inside diameter, therefore it can be operated at high temperatures. The reaction was carried out under ordinary gas flow rate and atmospheric pressure. The effluent gas was sampled and analyzed on-line by gas chromatograph.

4.2.2.2 Temperature Controller : this consists of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller series REXC900 connected to a thermocouple attached to the catalyst bed in reactor. A dial setting establishes a set pointed at any temperature within the range between 0^{o} C to 1000^{o} C.

4.2.2.3 Electrical furnace : This supplies the required heating to the reactor for the reaction. The reactor can be operated from room temperature up to about 700^{o} C at the maximum voltage of 220 voltage.

4.2.2.4 Gas Controlling System : Nitric Oxide, propane, oxygen, carbon monoxide and helium each cylinders is equipped with a pressure regulator (0 - 120 psig), an on-off valve and needle valve were used to adjust flow rate of gas. A sampling valve was used to take sample of the effluent gas.

4.2.2.5 Gas Chromatograph : SHIMADZU GC-8APT and SHIMADZU GC-8AIT each equipped with a thermal conductivity detector (TCD) were used to analyze the composition of the reactant and effluent gases. Operating conditions used are shown in Table 4.1 below.

Table 4.1 Operating conditions for gas chromatograph

Gas chromatograph	SHIMADZU GC-8APT	SHIMADZU GC-8AIT
Detector	T.C.D.	T.C.D.
Packed column	MS - 5A	PORAPAK - Q
Carrier gas	He (99.999%)	He (99.99%)
Flow rate of carrier gas	30 cc/min.	60 cc/min.
Column temperature	90° C	90° C
Detector temperature	100° C	100° C
Injector temperature	100° C	100° C
Analyzed gas	O_2, N_2, CH_4, CO	CO_2, H_2O, C_3H_8

The chromatograms obtained from gas analysis are shown in Appendix B.

4.2.3 Procedure

Catalyst activities were evaluated by studying their light-off behaviour in non-oscillating exhaust gas mixtures, with a constant flow rate of the simulated exhausted gas from 150 - 600 °C at a heating rate of 5 deg. min^{-1} and GHSV of 15,000 h^{-1}. At each reaction temperature the conversion was observed when the catalyst activity become constant.

The stoichiometry of the feedstream was characterized by the formula for the “Stoichiometry number”, S. The stoichiometric number is taken as

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

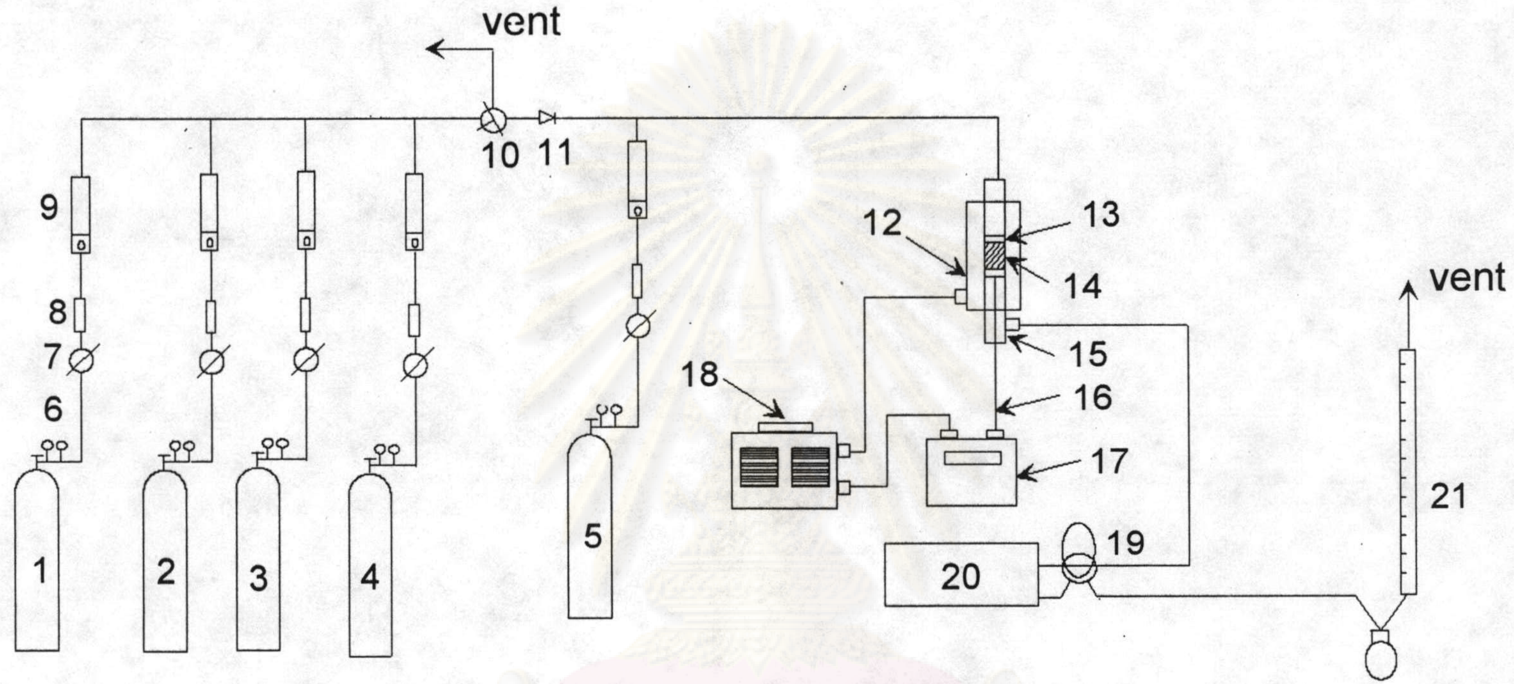
where parentheses indicate concentrations in volume percent. This is simply the inverse of the formula used by Gandhi et al [45]. On the “S” scale, a value of unity represents a stoichiometric mixture ; small values reflect rich conditions, larger value indicate lean conditions.

The composition of the simulated exhaust gas to achieve a stoichiometric mixture is shown in Table 4.2.

Table 4.2 The composition of the synthetic exhaust gas

GAS	Units	S = 1
NO	%	0.05
CO	%	0.30
C_3H_8	%	0.215
O_2	%	1.20
He		Balance

For activity test, the catalysts were heated up every 20 min (50 °C per time interval). At each reaction temperatures, the gas composition was analyzed by gas chromatograph using Parapak-Q (CO_2 and C_3H_8) and Molecular Sieve-5A (O_2, N_2 and CO) columns. The concentration of CO and C_3H_8 at the inlet and outlet stream were therefore analyzed for CO oxidation



1. NO Tank
2. C3H8 Tank
3. O2 Tank
4. CO Tank
5. He Tank
6. Pressure regulator
7. On-off valve
8. Gas filter
9. Flow meter
10. Three way valve
11 Check valve
12. Reactor furnace
13 Quartz wool
14. Catalyst bed
15. Reactor
16. Thermocouple
17. Temperature controller
18. Variable voltage transformer
19. Sampler
20. G.C.
21. Soap film flow meter

Figure 4.1 Flow Diagram of the Reaction System.

and C_3H_8 combustion. The catalytic activity for NO removal was evaluated by extent of conversion into N_2. The schematic diagram of the reactor system is shown in Figure 4.1

4.3 Characterization of the Catalysts

Characterization of the prepared catalysts consists of metal active sites measurement and BET surface area measurement techniques. Each step of the characterization method is depicted as follows.

4.3.1 Metal active sites measurement.

4.3.1.1 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.

4.3.1.2 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 diagram of the CO adsorption is shown in Figure 4.2. 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 4.3. The sample tube was made of quartz tube.

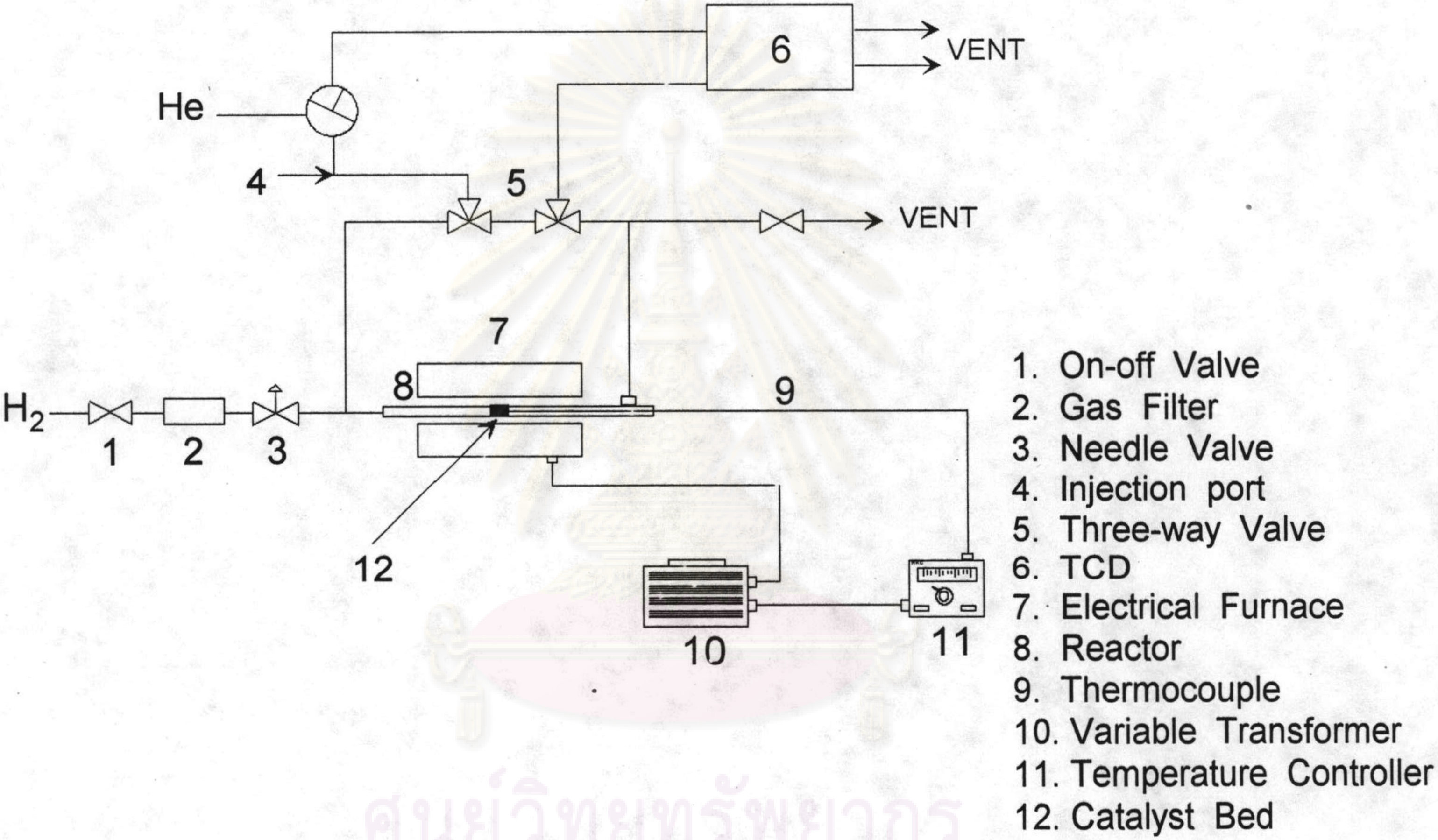


Figure 4.2 Flow Diagram of the CO adsorption apparatus.

Table 4.3 Operating condition of TCD gas detector.

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

4.2.2.3 <u>Procedure</u>.

1. 100 mg of catalyst was placed in a sample tube. The temperature was raised to 400 °C at heating rate of 10 °C/min. The catalyst was reduced by the hydrogen at this temperature for 1 hour.

2. The 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).

Each catalyst was degassed in He stream (30 cc/min.) at 150° C for 30 min. and then reduced in hydrogen stream (30 cc/min.) at 400° C for 1 hour.

4.3.2 BET Surface Area Measurement [46]

4.3.2.1 Introduction

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.

4.3.2.2 Procedure

BET surface was measured by an area analyzer as shown in Fig.4.3. The gas mixture of He and N_2 flowed through the system at N_2 partial pressure of 0.3. The gas detector used was thermal conductivity type (T.C.D.). The detector temperature of 80° C and filament current of 80 mA were used.

The analysis began by placing sample in a sample cell and connected to the surface area analyzer. The sample was then heated up to 120° C, held at this temperature for 1 hour and cooled down to room temperature. There were three steps in this surface area measurement : adsorption, desorption, and calibration.

- 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.

- 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.

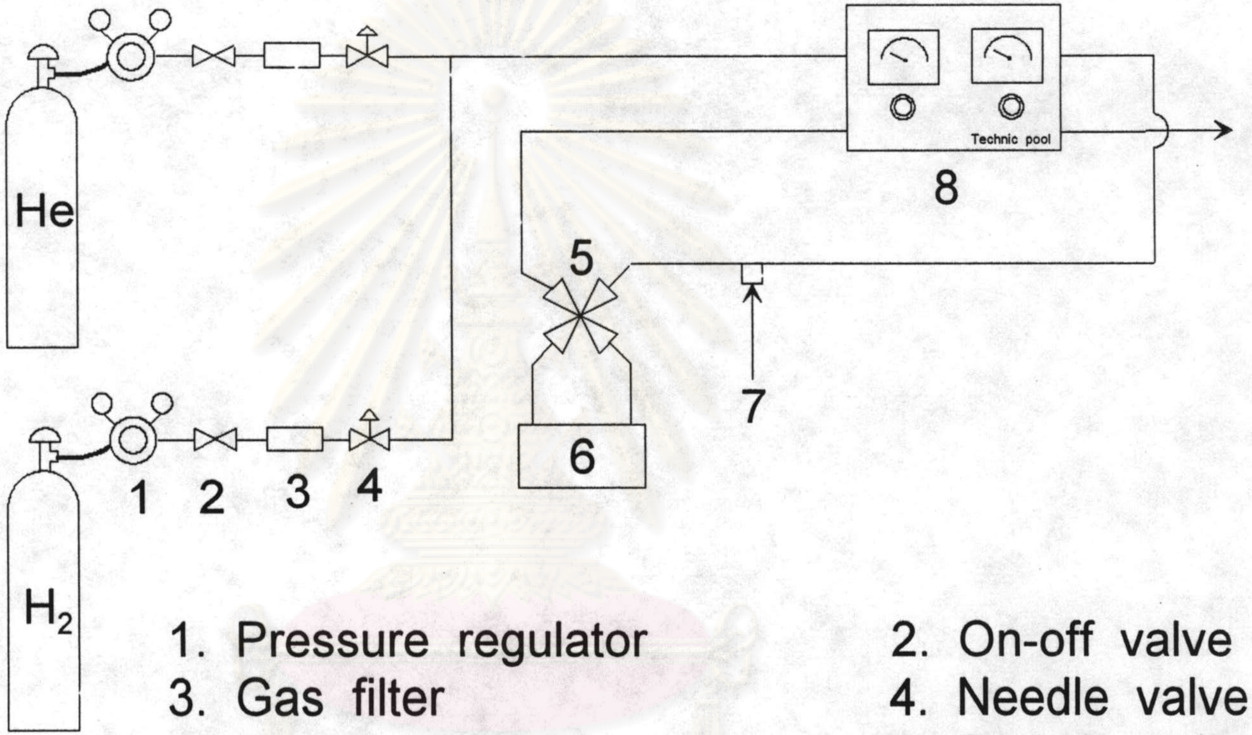


Figure 4.3 Flow diagram of the BET surface area analyzer.

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