CHAPTER IV

EXPERIMENTAL

The study catalysts for automotive pollution control with transition metals the catalysts were devided into three parts:

1. The preparation of catalysts
2. The redox reaction of simulated exhaust gases
3. Characterization of these catalysts.

The details of the experiments are explained in the following section

4.1 The preparation of catalyst

4.1.1 Materials

- Gamma alumina [γ-Al_2O_3,type KN - 324] was used as the catalysts support. It has approximately a surface area of 300 m^2/g. and comes from Sumitomo LTD.

- The metal complexes used for supported catalysts are metal components. The deposit metals on the support are of analytical grade. They are listed as follows.

Cerium [III] nitrate	$Ce[NO_3]_3 . 6H_2O$
Cobalt [II] nitrate	$Co[NO_3]_2 . 6H_2O$
Palladium [II] nitrate	$Pd[NO_3]_2$

4.1.2 Preparation of support and stock solution of metal complexes.

- Support Alumina was ground to the required mesh size of 40/60 and then washed with distilled water to remove the dust particles. Followed by drying at 110°C overnight, the support was then calcined at 300 °C, for 2 hours.

- Preparation of stock solution

Stock solution was mainly used with transition metals are especially group VIII B and lanthanide group.

- Cerium stock solution

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

-Cobalts and palladium stock solution. Similar to, the preparation of cerium complex solution, cobalt-nitrate 1 g. was dissolved in de-ionized water and palladium nitrate 0.1 g. with 4.0 ml. of hydrochloric acid. De-ionzed water was added for a total volume of 25 ml.

4.1.3 Procedure of preparation

In the experiment ,the catalysts were metal supported on an alumina catalyst. They were prepared by dried impregnation. The preparation is described below.

- The impregnation solution for 3 g. of support was prepared by calculating the amount of stock solution to yield the required metal loading. De-ionized water was finally added until 3 ml. of the solution was obtained.

- 3 g. of support was placed in a flask. The aqueous solution of the metal complex solution was impregnated.

First, cerium nitrate was slowly impregnated on the alumina support. Then the catalyst was dried at 110°C in an air over night, and calcined at 500°C for 2 hours in air atmosphere. After that, the cerium supported catalyst was impregnated by cobalt nitrate and palladium nitrate, respectively. For calcination of a cobalt supported catalyst and palladium supported catalyst, after drying, the cobalt supported catalyst and the palladium-cobalt supported catalyst were calcined at 400°C, for 3 hours. and at 500°C, for 2 hours. respectively.

The description of the calculation of the amount of the stock metal complex solution and the preparing catalyst are illustrated in **Appendix A.**

4.2 The redox reaction of simulated exhaust gases.

4.2.1 Chemical and reagents

Investigation performance of catalysts were used the simulated exhaust gases could be assumed by mixture of standard gases as follows.

1% Nitric Oxide: 3% Propane: 10% Oxygen: 5% Carbon monoxide balance in ultra high purity helium (99.999%)

Catalyst for study is 4 gram. each.

4.2.2 Apparatus

For the activity measurement the experimented set consists of a gas control quantity section by a rotameter, followed by reactor section (quartz tube diameter = 0.6 cm.) , gases analysis section and the temperature control.

Gas chromotography (type TCD), with a MS-5A column was used for analysis of oxygen, hydrogen, methane, carbon monoxide and nitrogen, equipped with a sampling loop (2.5 ml.). A Porapak-Q column was used for the analysis of carbon dioxide, water and propane. The operating conditions for chromotograph and the chromatograph obtained from the gas analysis are shown in **Appendix B.**

The catalytic activity was measured in a temperature programmed experiment. Standard conditions for these experiments are given in table 1.

Table 1 : Standard conditions for the activity measurement.

Temperature range	150 - 700°C
Gas flow rate	141 ml./min.
GSHV	15,000 h^{-1}
Catalyst	0.40 gm.

The simulated exhaust gases were used at the stoichiometry that was characterized by formula the " Stoichiometric number ",(S) formula It is taken as ref.

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

where parenthesis indicates concentrations in volume percent.

The composition of the simulated exhaust gases to achieve a stoichiometric mixture is 0.05% NO, 0.30%CO, 0.215%C_3H_8, 1.20%O_2 balance helium (%by volume). The stoichiometric number range could be accepted ± 0.05. The catalysts were screened by heating the sample at 10°C/min from 150°C-700°C. To ensure steady - state condition each reaction temperature was held for 10 minutes and analyzed the effluent gases by gas chromatography. The conversion is defined as the difference between the amount of inlet and outlet gas composition and divided by the inlet gas composition. In this experiment, the NO, CO and propane gases are considerate for comparison of the activity of the catalyst. Then, each part of the results in chapter V presents three conversions (as NO, CO and propane conversion) in each the performance tests. The schematic diagram of the reactor system is shown in figure 4.1.

4.3 Characterization of the catalyst

4.3.1 Material active site measurement

Quantity of catalyst is 0.4 g. 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 adsorped gas and a standard gas.

a. Apparatus

The metal active sites were measured by CO adsorption technique on the basis that one CO molecule adsorbed on one metal active. The flow diagram of the CO adsorption is shown in figure 4.2. The amount of CO adsorbed was measured by the thermal conductivity detector.

Operation conditions of TCD gas detector.

Carrier gas and flow : He 30 ml./min

Temperature of detector : 80° C

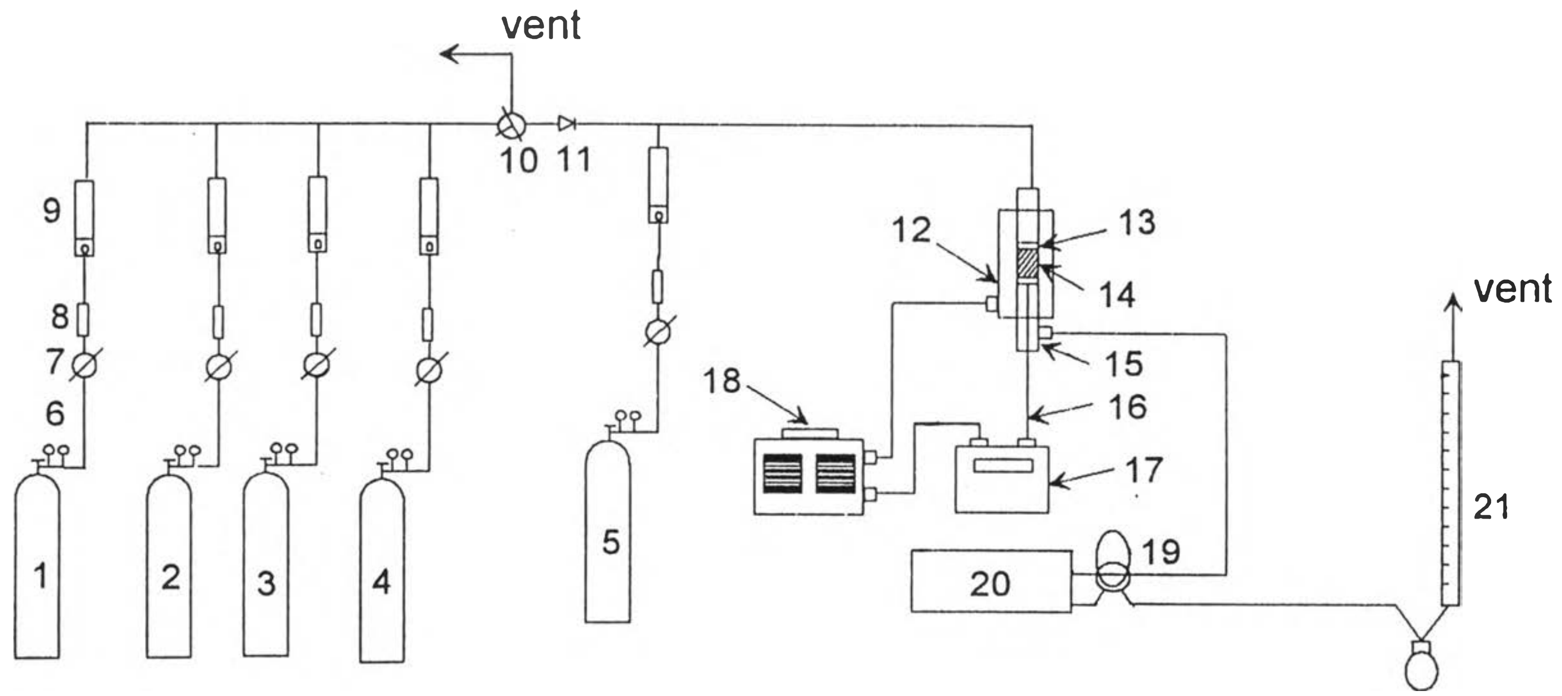
Detector current : 80 mA

b. Procedure

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

-The sample tube was cooled down to room temperature.

-The sample was then ready for measurement of its metal sites. 0.18 ml. of CO was injected to the injection port. The CO injection was repeated until the catalyst did not adsorp CO gas.



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 Quart wool
14. Catalyst bed
15. Reactor
16. Thermccouple
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.

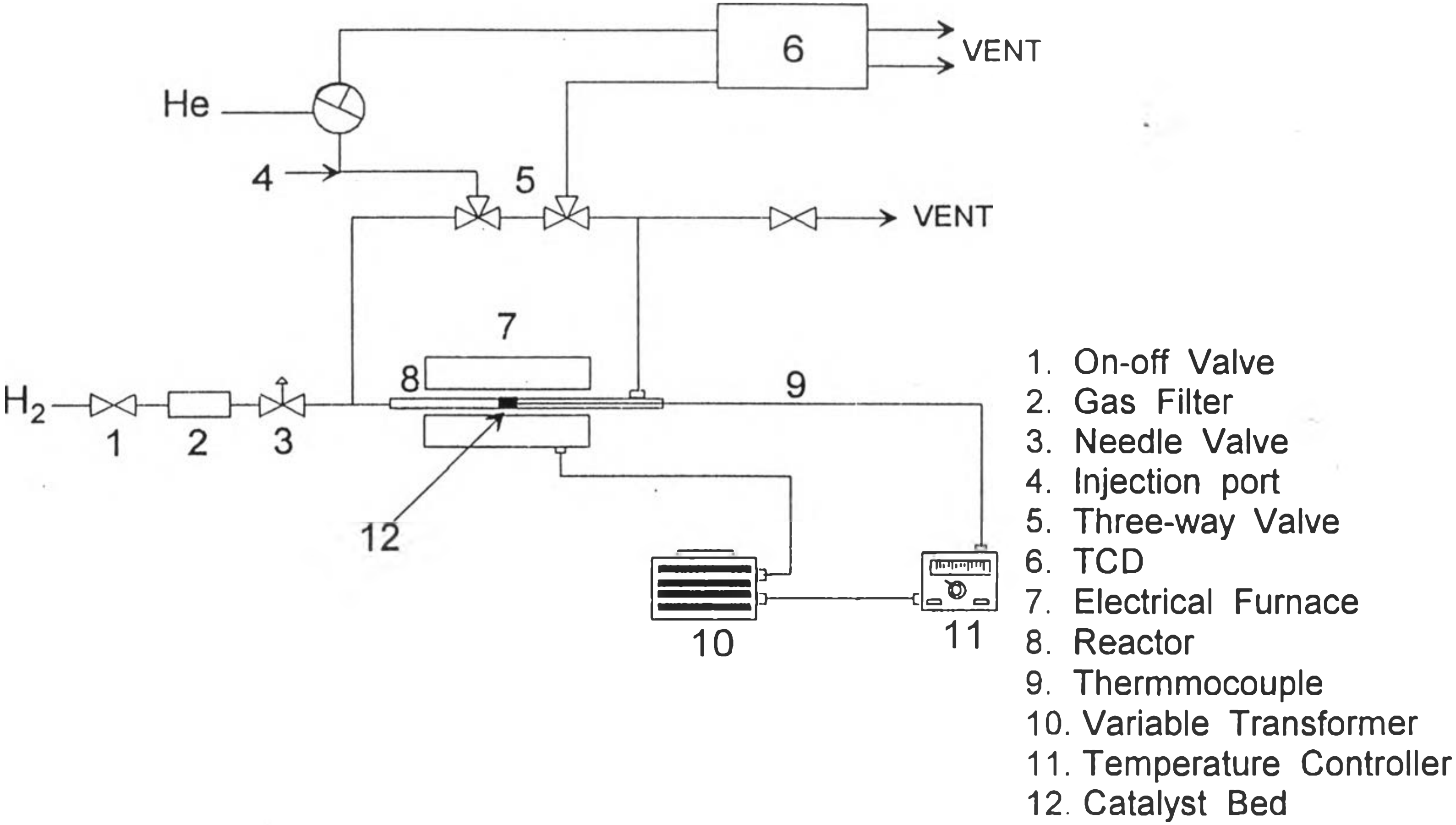


Figure 4.2 Flow Diagram of the CO adsorption apparatus.

-The amount of CO adsorbed was measured. The amount of metal site was calculated in Appendix A. Each catalyst was degassed in the stream of He, (30m./min) at 150°C for 30 minutes and then reduced in a hydrogen stream (100ml./min) at 400°C for 1 hour.

4.3.2 BET Surface area measurement.

Specific surface area of the catalyst was measured by a BET surface area analyzer (model ASAP 2000). This method was a physical adsorption of N_2 on the surface of the catalyst to find the specific area.

BET surface was measured by a BET analyzer at the Analytical center of Chemical Engineering Department , Chulalongkorn University.

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 point.

4.3.3 Temperature Program Reduction.

a. Introduction .

Temperature Program Reduction, TPR studies showed that these ions are strongly associated with support. The reducible site was measured by H_2 reduced oxide on the surface. And the product of this reaction is water vapor which is trapped by a molecular sieve (3A - type). The amount of reducible H_2 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.

b. Procedure.

The experiment TPR system is exhibited schematically in figure 4.3.

Operation condition of TCD gas detector.

GC. SHIMUDZU	: 8A - TP
Carrier gas and flow	: 5%H_2 / Ar ; 50 ml./ min.
Temperature of detector	: 80 °C
and column chamber	: 80 °C.
Detector current	: 60 mA.

Attenuation : 4 , Slope : 100 , Speed chart : 1 mm/min.

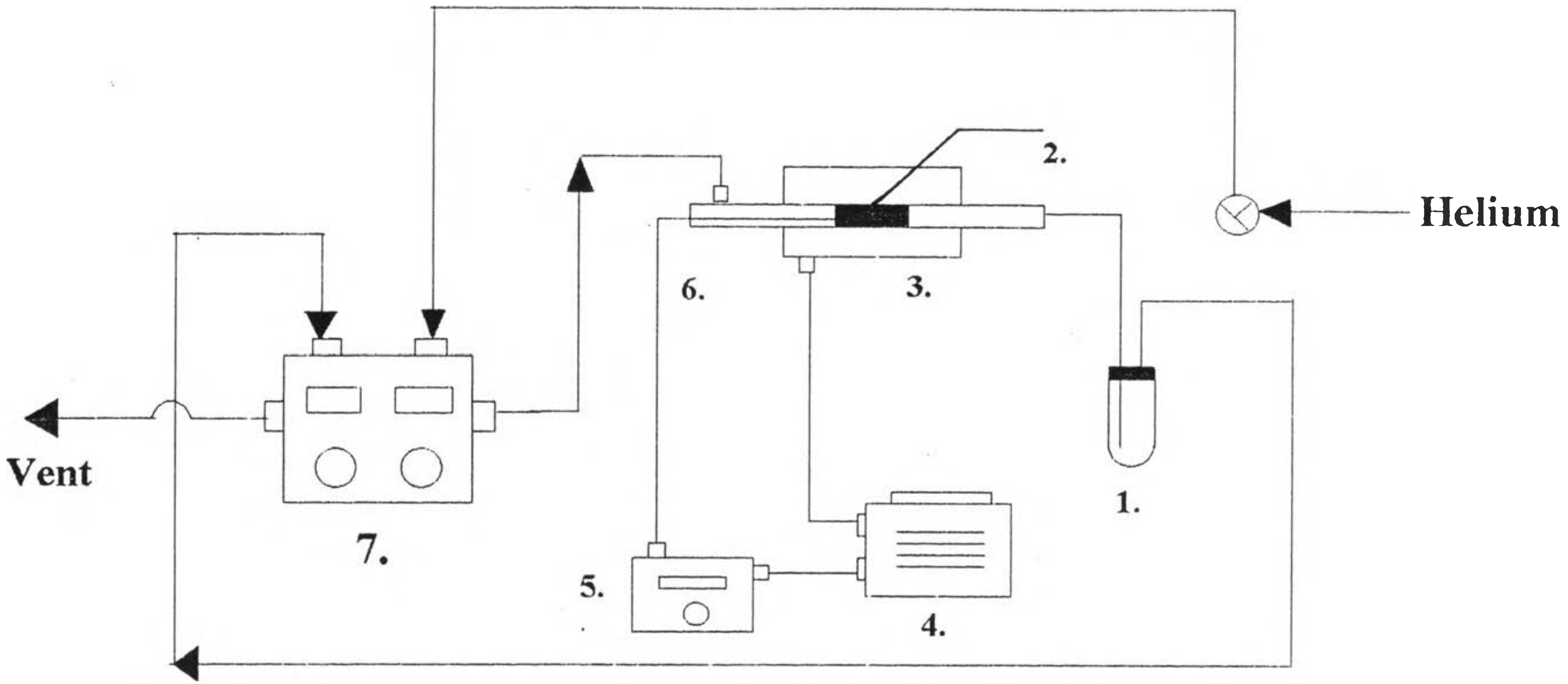
0.2 g. of catalyst was placed in a quartz reactor. The temperature was increased to 500 °C at a rate 10 °C/min. There were two steps in this measurment.

b.1. Calcining step.

The sample (0.2 g) was placed on a quartz tube. Air flow air through the sample was at 100 ml./min and was heated up to 500°C at a rate 10 °C/min, held for 1 hour. to ensure the surface was covered with oxide form.

b.2. Temperature Progammed Reduction Step.

After calcining : Switch to the mixture gas 5%H_2 /Ar. Flow through the sample, 50 ml./min. The temperature increased to 500°C, at a rate 5°C/min. The rise in temperature, was done in steps of 100°C. Waiting for the signal of 500°C to be reported , cool down system until the baseline was constant. Repeat that step, for baseline compensation of the first chromatogram.



1. H_2O Trap.
2. Catalyst bed.
3. Heater.
4. Variable voltage transformer.
5. Temperature controller.
6. Thermocouple .
7. Thermal conductivity detector.

FIGURE 4.3 Flow diagram of the TPR apparatus.