

CHAPTER IV

EXPERIMENT

This work is divided into 3 parts:

- I. The preparation of catalysts.
- II. The benzene hydrogenation.
- III. Characterization of the catalysts.

In each part, the procedures, chemicals and reagents, and instruments used are described in detail.

4.1 Preparation of Catalysts.

4.1.1 Chemicals and Reagents.

The chemicals used in this experiment were normally of analytical grade, except some critical chemicals specify as follows :

- $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was manufactured by WAKO PURE CHEMICAL INDUSTRIES, LTD.
- $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was manufactured by E.MERCK, DARMSTADT
- Al_2O_3 Support (type KNH-3) was obtained from SUMITOMO ALUMINIUM SMELTING CO., LTD.
- N_2 gas from THAI INDUSTRIAL GASES LIMITED.

4.1.2 Instrument and Apparatus

4.1.2.1 Unit for grinding and Screening Support

This unit consists of pestil, mortar, and sieve trays. It was used for reducing the size of support down to 60/80 mesh (see Figure 4.1).



Fig. 4.1 Unit for grinding and Screening Support

4.1.2.2 Unit for catalyst impregnation

This unit consists of pipette, flask, dropper, and volumetric flask. It was used for preparing aqueous catalyst solution and for impregnating the solution onto the support. (see Figure 4.2)

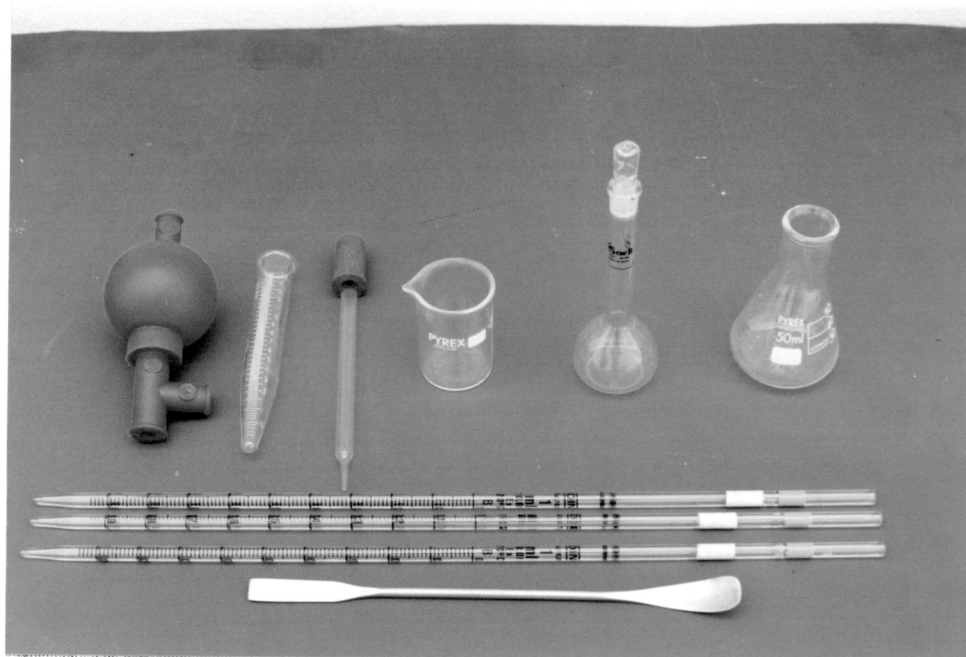


Fig. 4.2 Unit for impregnation

4.1.2.3 Unit for calcination

This unit is an electric furnace, consisting of heating coil and insulator, automatic temperature controller, and a variable voltage transformer. It was used for calcining catalysts at high temperatures (see Figure 4.3)



Fig. 4.3 Unit for calcination

4.1.3 Preparation of the catalyst

4.1.3.1 Preparation of Support and Stock Solution

4.1.3.1.1 Preparation of Support

Alumina support (Al_2O_3) was ground to the required size of 60/80 mesh and washed with distilled water 3-4 times in order to remove smaller particles and impurities. Then, the support was dried in an oven at 110°C overnight. Finally, it was calcined under air flow at 300°C for 3 hours.

4.1.3.1.2 Preparation of Stock Solution

1) Nickel stock solution

Nickel complex solution was prepared by dissolving nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 21.55 gm. in distilled water and then making total volume of the solution to 25 cm^3 (concentrated nickel solution)

2) Platinum stock solution

Platinum complex solution was prepared by dissolving chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) 1 gm. in distilled water and then making total volume of the solution to 25 cm^3 (concentrated platinum solution).

4.1.3.2 Preparation of 8% nickel on alumina support, 8%Ni/ Al_2O_3

1. Nickel solution for 2 gm. of alumina

support was prepared by using 1 cm³ of nickel stock solution and making volume to 2 cm³.

2. In order to impregnate the nickel onto support, 2 gm of support was placed in 50- ml flask and then the nickel solution from (1) was slowly dripped into the support while gently shaking the flask for the homogeneous distribution of metal component on support.

3. The impregnated support was left to stay for 12 hours. Then, the support was dried at 110 °C for 12 hours.

4. The dry impregnated support was placed in a calcinator under nitrogen flow with a space velocity of about 2000 hr⁻¹ while heating the support at 10 °C/min to attain the temperature of 300 °C. The catalyst were held under these conditions for 1 hour.

4.1.3.3 Preparation of Pt promoted 8% nickel on alumina support (0.5-2.0%Pt/8%Ni/Al₂O₃, % Pt:Ni)

4.1.3.3.1 Co-impregnation (for 0.5% Pt on nickel catalyst)

1. Mixed nickel and platinum solution (mixed solution) for 2 gm alumina support was prepared by using 1 cm³ of nickel stock solution plus 0.03 cm³ of platinum stock solution. Then the volume of mixture was made to 2 cm³ by adding distilled water.

2. Impregnation, 2 gm of support was placed in 50 ml flask and then the mixed solution from (1) is slowly dripped into the support while gently shaking the flask, for the homogeneous distribution of metal component on support.

3. Left the impregnated support for 12 hours for good distribution of metal complex in alumina support. Then the support was dried at 110 °C for 12 hours.

4. Calcination. The dried impregnated support was placed in a calcinator under nitrogen flow with a space velocity of about 2000 hr⁻¹, while heating the support at a rate of 10 °C/min to attain the temperature of 300 °C. The catalyst were held under this condition for 1 hour

4.1.3.3.2 Impregnate platinum before nickel

1. Prepared platinum solution for 2 gm alumina support by used 0.03 of platinum stock solution (for 0.5% Pt loading) and used distilled water to made volume of solution to 2 cm³.

2. Impregnation, 2 grams of support were placed in 50 ml flask and then the platinum solution from (1) was slowly dripped into the support while it was gently shacking, for the homogeneously distributed metal component on support.

3. Left the impregnated support for 12 hr. for good distribution of platinum complex in alumina

support. Then, impregnation support was dried at 110 °C 12 hours.

4. Calcination, nitrogen was passed over the dried catalyst with a space velocity of about 2000 hr⁻¹, heating rate of 10 °C/min was used to attain the temperature of 300 °C. The catalyst was held in this condition for 1 hour.

5. Prepared nickel solution by using 1 cm³ of nickel stock solution and used distilled water to make volume of solution to 2 cm³.

6. Impregnation, catalyst from (4) was placed in 50 ml flask and then the nickel solution from (5) was slowly dripped into the support while it was gently shecking for the homogeneously distributed metal component on support.

7. like (3), (4) at above-mentioned.

4.1.3.3.3 Impregnate nickel before platinum

1. Prepared nickel solution for 2 gm. alumina support by using 1 cm³ of nickel stock solution and using distilled water to make volume of the solution to 2 cm³.

2. Impregnation, 2 grams of support was placed in 50 ml. flask and then the nickel solution from (1) was slowly dripped into the support while it was gently shecking for the homogeneously distributed metal component on support.

3. Left the impregnated support for 12 hr. for good distribution of nickel complex in alumina support. Then, impregnation support was dried at 110 °C 12 hours.

4. Calcination, nitrogen was passed over the dried catalyst with a space velocity of about 2000 hr⁻¹, heating rate of 10 °C/min was used to attain the temperature of 300 °C. The catalyst was held in this condition for 1 hour.

5. Prepared platinum solution by using 0.03 of platinum stock solution (for 0.5% Pt loading) and used distilled water to make volume of the solution to 2 cm³.

6. Impregnation, catalyst from (4) was placed in 50 ml flask and then the platinum solution from (5) was slowly dripped into the support while it was gently shecking, for the homogeneously distributed metal component on support.

7. like (3), (4) at above-mentioned.

4.2 Benzene Hydrogenation

4.2.1 Chemicals and reagents

- Benzene (C₆H₆) of Analytical grade manufactured by E.MERCK, DARMSTADT.

- Hydrogen was bought from THAI INDUSTRIAL GASES LIMITED.

4.2.2 Instuments and Apparatus.

4.2.2.1 Reactor

The reactor is a conventional microreactor made from quartz tube. It can be operated at high temperatures.

4.2.2.2 Automatic Temperature Controller

It consists of a magnetic switch connected to a variable voltage transformer and is controlled by a RKC temperature controller of PF-4 series. The controller receives signal from thermocouple in the bed of catalyst in the reactor. A dial setting of the controller establishes a set point of any temperature within the range between 0 °C to 800 °C.

4.2.2.3 Electric Furnace

Electric furnace was used to heat the reactor for reducing the catalyst and then for benzene hydrogenation. the heating rate was controlled by variable voltage transformers. By using with automatic temperature controller, the furnace could generate heat for the reactor ranging from room temperature up to 800 °C.

4.2.2.4 Gas Controller System

The system consists of :

1. A hydrogen cylinder equipped with a

pressure regulator (0-120 psig), an on-off valve , and a needle valve used to adjust hydrogen flow rate.

2. Benzene vaporizer was used for producing diluted benzene vapour. The hydrogen from (1) was directed to flow pass through the benzene vaporizer and then carried benzene vapour to the reactor.

4.2.2.5 Gas chromatograph (GC)

Gas chromatograph was used to analyse the quantity of benzene and cyclohexane in the sample obtained from reactor. This GC is FID* of SHIMADZU GC 14A with capillary column OV-1 (50 m)(see Figure 4.4). The operating conditions of Gas Chromotograph are shown in Table 4.1.

Table 4.1 Operating Conditions of Gas Chromotograph

SHIMADZU GC 14 A, FID	
Detector Type	FID*
Detector Temperature	100 °C
Column Type	Capillary Silicon OV-1, 0.25 mm.x50 m.
Column Temperature	60 °C
Carrier Gas	Nitrogen
Integrator	Chromatopac C-R6A

*FID = Flame Ionization Detector

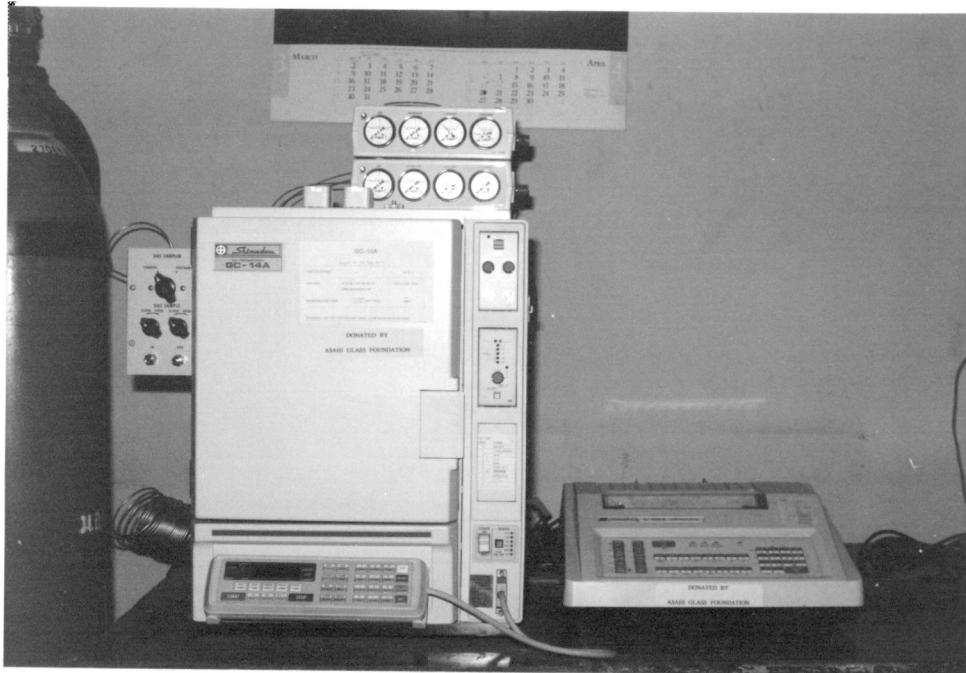


Fig. 4.4 Gas chromatograph (GC)

4.2.3 Procedure

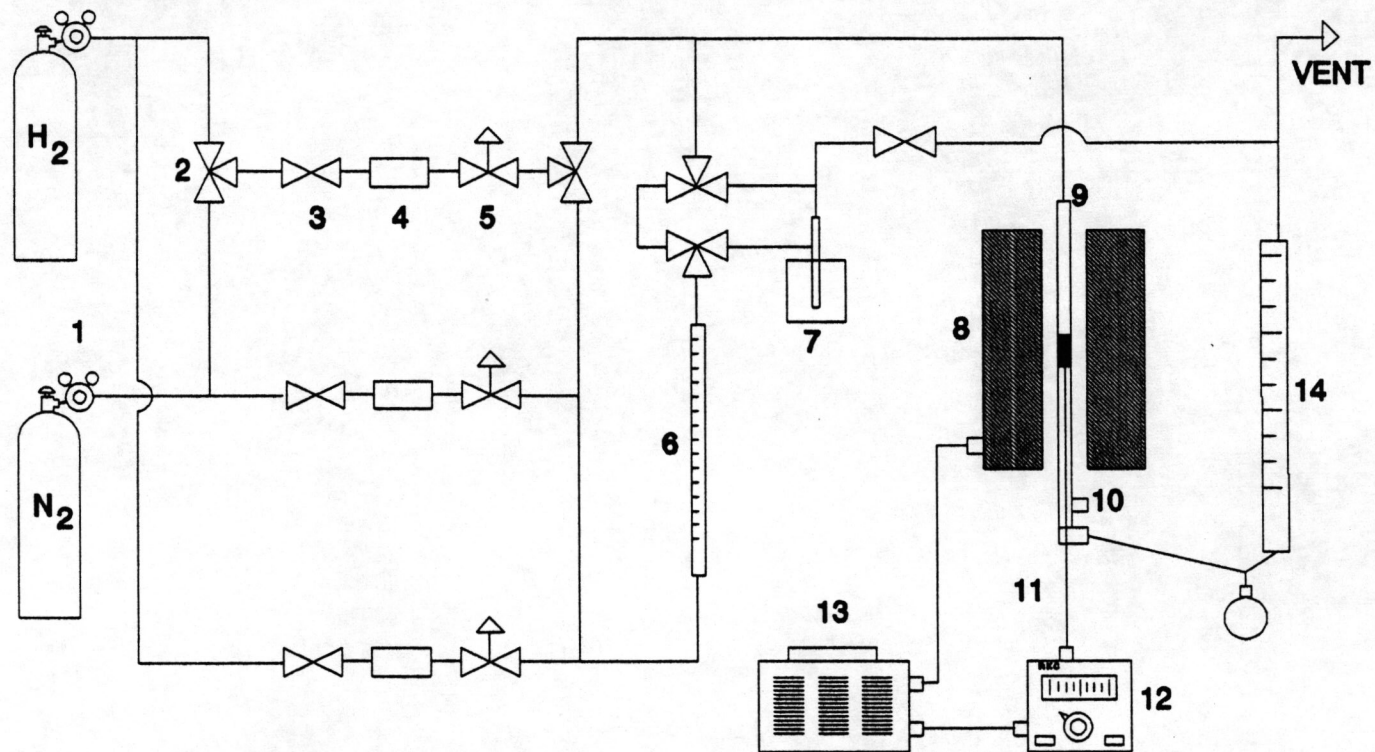
The activity of catalyst for benzene hydrogenation was measured in conventional microreactor made from quartz tube. Reaction was carried out in an ordinary flow under atmospheric pressure.

1) 50 mg of catalyst was packed in reactor and reduced by hydrogen gas which was made to flow over the catalyst at a rate of 60 cm³ per minute. The reactor was heated up from room temperature to 400 °C and maintained at this temperature for 1.5 hours.

2) The reactor was cooled down from 400 °C to reaction temperature of 100 °C and held at this temperature for 10 minutes. Then hydrogen-benzene mixture, from another line, with the same flow rate of 60 cm³ per minute was fed into the reactor, replacing the flow of pure hydrogen. This mixture was obtained from passing hydrogen through the benzene vapourizer. The benzene thus reacted hydrogen to produce cyclohexane.

3) Gas Chromatograph was used to analyze the quantity of benzene and cyclohexane in the sample from the reactor. The conversion of the reaction was then calculated from the data obtained.

The flow diagram of the benzene hydrogenation system was shown in Figure 4.5.



- 1. Regulator
- 3. On-off Valve
- 5. Needle Valve
- 7. Benzene Vaporizer
- 9. Reactor
- 11. Thermocouple
- 13. Variable Voltage Transformer

- 2. Three-way Valve
- 4. Filter
- 6. Flow Meter
- 8. Furnace
- 10. Sampling Port
- 12. Temperature Controller
- 14. Bubble Flow Meter

Fig. 4.5 Flow diagram of the benzene hydrogenation system

4.3 Characterization of the Catalysts

4.3.1 Metal Site Measurement

4.3.1.1 Introduction

Generally, activity of catalyst is a function of metal site. Therefore, in order to describe changing of activity of catalyst, the metal site measurement was necessary to characterize the catalyst. CO-adsorption technique was used for the measurement. It was assumed that the ratio of adsorbed CO:site was 1:1 and adsorption of CO was irreversible.

4.3.1.2 Procedure

The CO-adsorption was detected by TCD detector and diagram of this apparatus is shown in Figure 4.6 and procedure is followed as below :

1. 100 mg of catalyst was packed in the sample tube and reduced with 60 cm³/min of the hydrogen. The sample tube was heated up from room temperature to 400 °C with heating rate 10 °C per minute and maintained at this temperature for 90 minutes.

2. When the time reached 90 min, The catalyst was cooled down to 30 °C. While cooling the catalyst, TCD detector was turned on and set at the condition as shown in Table 4.2.

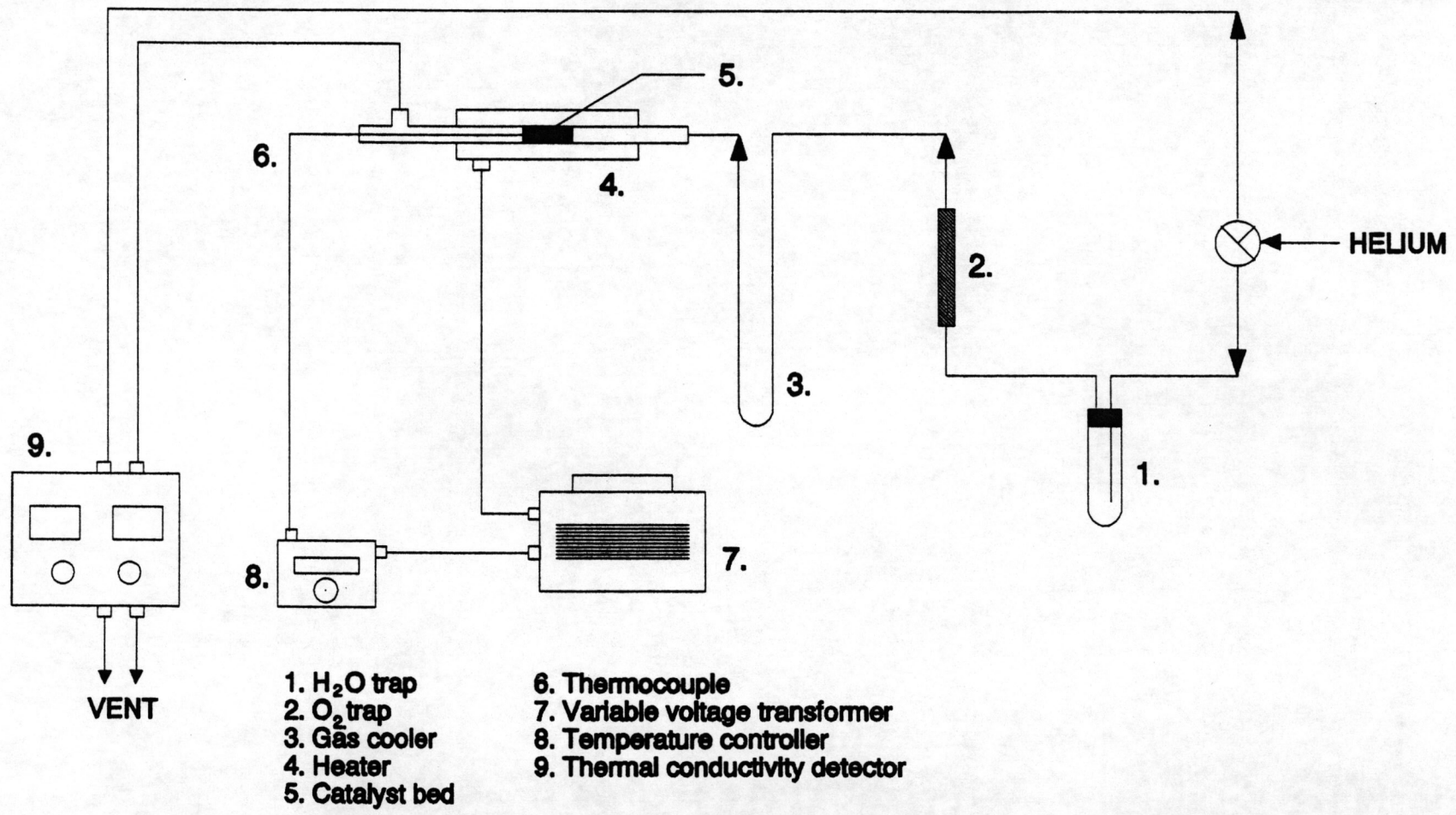


Fig. 4.6 Flow diagram of CO adsorption apparatus.

Table 4.2 Condition of TCD detector

variable	condition
Carrier gas and flow	He 30 cm ³ /min
Temperature of detector	80 °C
Amp. of detector	80 mA.

3. 0.18 cm³ of CO was injected to the injection port, the result was shown by recorder, repeated injection of CO until the sample did not adsorb CO gas, size of CO peak did not change.

4.3.2 Hydrogen adsorption

4.3.2.1 Introduction

The hydrogen adsorption was measured by application of the CO adsorption technique and the adsorbed hydrogen which was measured by this method was the irreversible adsorbed hydrogen.

4.3.2.2 Procedure

The procedure of the hydrogen adsorption measurement was the same as the method of the site measurement in section 4.3.1 and used the CO-adsorption apparatus.

4.3.3 Measurement of reactive adsorbed benzene

4.3.3.1 Introduction

There are two type of the adsorbed benzene occurred on surface of nickel catalyst, reactive and non-reactive adsorbed benzene. In this study, the benzene pulse experiment was made in order to find out the amount of reactive adsorbed benzene.

4.3.3.2 Procedure

The amount of reactive adsorbed benzene was measured by GC which is on line with the reactor. The flow diagram of this apparatus is shown in Figure 4.7. The procedure is as follows:

1. 100 mg of catalyst was packed in the reactor and reduced with hydrogen flow of 60 cm³/min at 400 °C. The heating rate was 10 °C/minute. The catalyst was held at 400 °C for 90 minutes.

2. While heating the reactor in (1), GC was turned on and set at the conditions as shown in table 4.3. After reaching the reaction time of 90 minutes, the hydrogen valve was shut off and helium line of GC was switched to the reactor, helium gas was passed over the catalyst in the reactor before moving into GC. The reactor was cooled down to 150 °C and stayed at this temperature for 10 minutes.

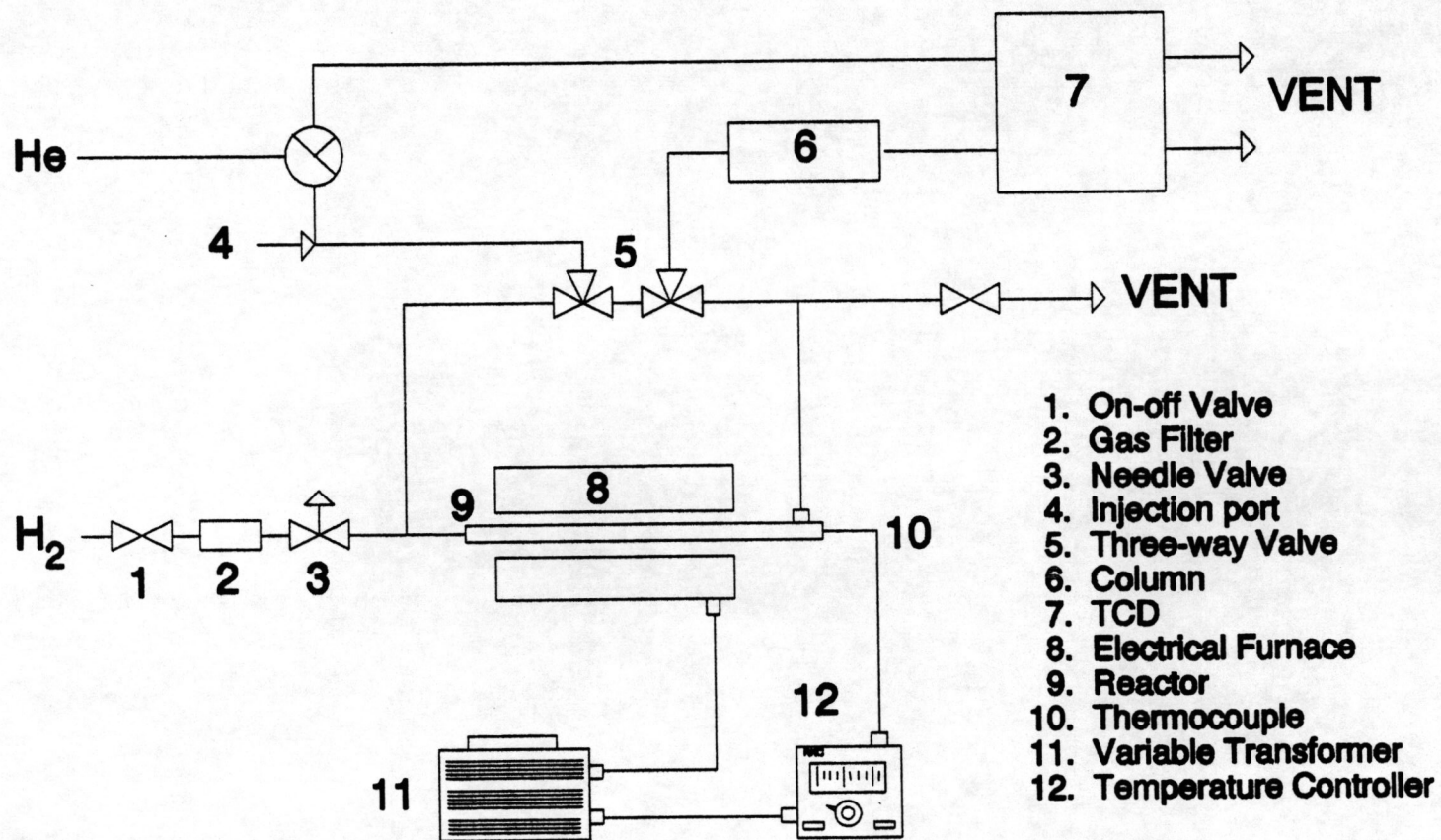


Fig. 4.7 Flow diagram of apparatus of reactive adsorbed benzene measurement

Table 4.3 Operating Condition of GC with TCD Detector.

GC GOWMAC WITH TCD DETECTOR

Operating Conditions of GC

Column	30% PEG on chromasorb PA
Column temperature	50 °C
TCD temperature	50 °C
Ampere	90 mA
Carrier gas	He
Flow of carrier gas	50 cm ³

3. 1 cm³ of hydrogen benzene mixture with a ratio of 5:1 was injected at the inlet of the reactor. This resulted in the peaks of benzene and cyclohexane at GC recorder. The injection of the mixture was repeated several times until the heights of peaks were steady.

4. 1 cm³ of hydrogen was then injected into the reactor several times until the cyclohexane peak disappeared.

4.3.4 BET Surface Area Measurement

4.3.4.1 Introduction

Specific surface area of the catalyst was measured by a surface area analyzer using BET method. This method

use the concept of physical adsorption of nitrogen on the surface of catalyst to find the specific surface area.

4.3.4.2 Procedure

BET surface area was measured by a surface area analyzer as shown in Figure 4.8. The gas mixture of helium and nitrogen was made to flow through the system at nitrogen partial pressure of 0.3. The gas detector was of thermal conductivity type (TCD) operated at detector temperature of 80 °C and filament electric current of 80 mA.

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

1) Adsorption : The sample cell was dipped into liquid nitrogen. The nitrogen in gas mixture would be adsorbed onto the surface of the catalyst sample, shown as peak on the recorder, until equilibrium was reached, shown as a straight line on the recorder. This step took about 10-15 minutes.

2) Desorption : The liquid nitrogen in adsorption step was replaced by water at room temperature. Adsorbed nitrogen would be desorbed from the surface of the catalyst sample, shown as peak in the opposite direction to adsorption. This step was completed when the recorder pen came back at the base line.

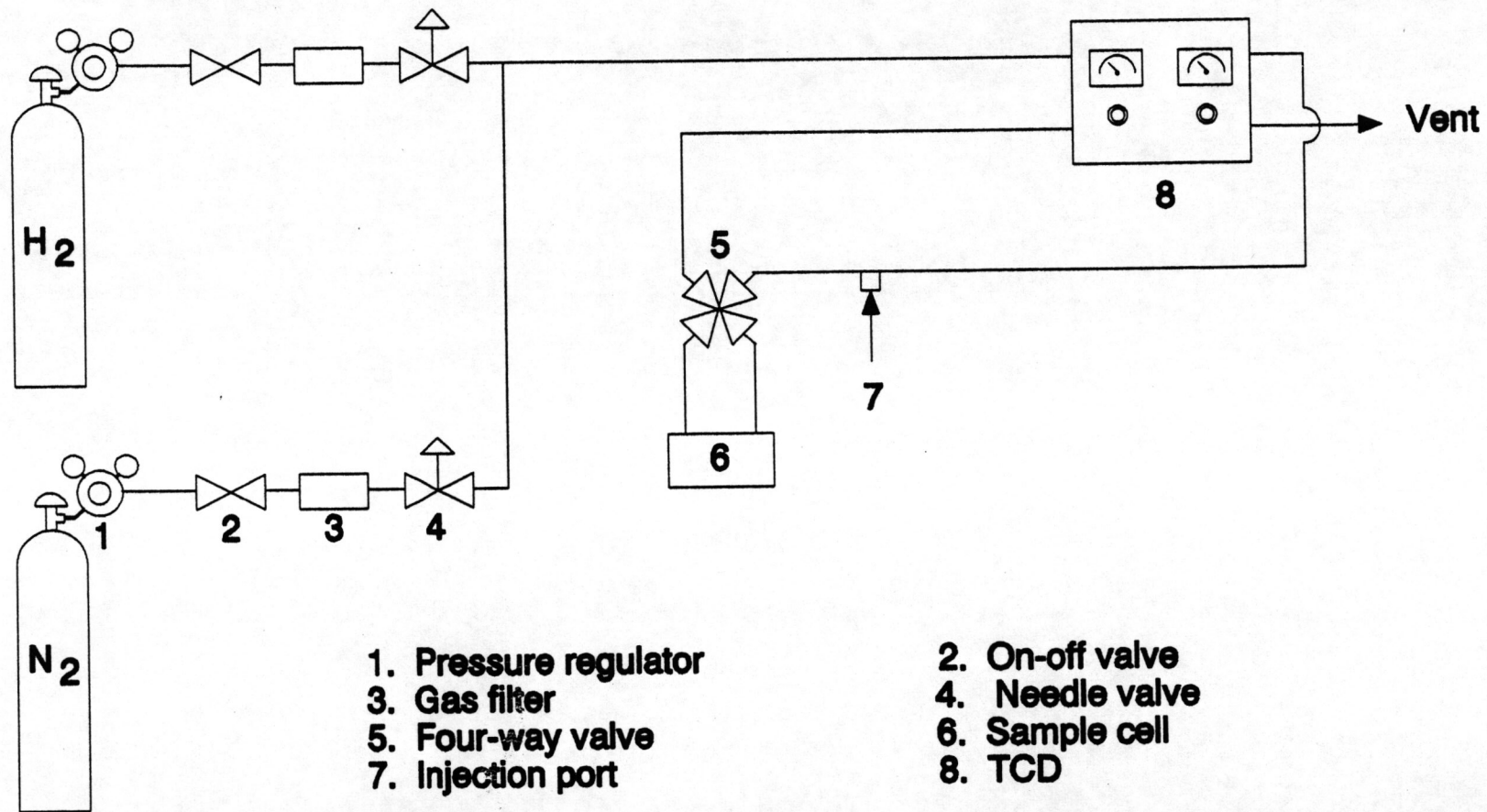


Fig. 4.8 Diagram of surface area analyzer

3) Calibration Step : nitrogen gas of 5 cm³ at atmospheric pressure was injected at the sampling port. The standard nitrogen peak would appear at the same direction of desorption peak.

4.3.5 Chemical Analysis

Percentage of metal loading was analyzed by Atomic Absorption and Inductively Coupled Plasma Spectrometry Method. Catalyst was prepared in solution form by the following procedure :

A certain amount of catalyst (about 200 mg.) was digested by digesting solution, the solution of 20 ml of concentrated HCl, 10 ml of HNO₃, and 10 ml of distilled water. The mixture was heated up until the color of support was changed to white. During digestion water must have been added into the mixture to maintain the volume of mixture. Then, 2 drops of HF were added into the mixture in order to digest the support. Heating was going on until the color of solution was clear. Then the volume of the solution was made up to 100 ml by using de-ionized water.

The prepared solution was analyzed for nickel by Atomic Absorption (AA) and for platinum by Inductively Coupled Plasma Spectrometry (ICPS).