

## CHAPTER IV

### EXPERIMENTS

This chapter contains 2 parts, the first is about catalyst preparation, and the other is about experiment and catalyst characterization. The catalyst used in this study was prepared by the rapid crystallization method [12] developed by Prof. Tomoyuki Inui's laboratory, detail in section 4.1, and then loading the Cu by ion-exchange method, as in section 4.2. The reaction and the characterization are reported in sections 4.3 and 4.4, respectively. The section of reaction illustrates the nitric oxide reduction apparatus, reacting condition and procedure. The section of characterization reviews BET surface area measurement, TPO (Temperature Programmed Oxidation), Cu-sites measurement by N<sub>2</sub>O adsorption method, acid sites measurement by using pyridine as a probe molecule, and TPR (Temperature Programmed Reduction).

#### **4.1 Catalyst Preparation**

##### **4.1 Preparation of Na-ZSM-5 Catalysts**

The preparation procedure is shown in Figure 4.1, while reagents are shown in Table 4.1. As the source of metals, AlCl<sub>3</sub> were used. TPABr (Tetra-n-Propyl Ammonium Bromide) [(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N]Br] was used as organic template.

##### **4.1.1 Preparation of Gel Precipitation and Decantation Solution**

The source of metal was AlCl<sub>3</sub>. TPABr (Tetra-n-Propyl Ammonium Bromide) [(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N]Br] was used as organic template. The atomic ratio of silicon/aluminium was set at 50. The preparation of supernatant liquid was separated from that of gel, which was important to prepare the uniform crystals. The detailed procedures were as follows: Firstly, a gel mixture was prepared by

adding solution A-1 and solution B-1 into solution C-1 dropwise with vigorous stirring using magnetic stirrer at room temperature as shown in section 4.2. The pH of the mixed solution was maintained within 9-11, since it is expected that this pH value is suitable for precipitation. The gel mixture was separated from the supernatant liquid by centrifuge. The precipitated gel mixture was milled for totally 1 h by powder miller (Yamato-Notto, UT-22). The milling procedure was as follows: milled 15 min → centrifuge (to remove the liquid out) → milled 15 min → centrifuge → milled 30 min. Milling the gel mixture before the hydrothermal treatment was essential to obtain the uniform and fine crystals. Secondly, a decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2 as the same method of the preparation of gel mixture. The supernatant liquid from A-2, B-2, and C-2 was mixed altogether with the milled gel mixture, expecting that before mixing adjust the pH of solution between 9-11 with H<sub>2</sub>SO<sub>4</sub> (conc.) or 1 M NaOH solution. The reagents used for prepared the solution A, B and C are shown in figure 4.1.

#### 4.1.2 Crystallization

The mixture of the milling precipitate and the supernatant of decant solution was charged in an one litre stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized upto 3 kg/cm<sup>2</sup> gauge. Then the mixture in the autoclave was heated from room temperature to 160 °C in 90 min and then up to 210 °C with a constant heating rate of 12 °C/h while being stirred at 60 rpm, followed by cooling down the hot mixture to room temperature in the autoclave overnight. The temperature was programmed under the hydrothermal treatment to minimize the time which was necessary for the crystallization. The produced crystals were washed with de-ionized water about 8 times by using the centrifugal separator (about 15-20 min for each time), to remove Cl<sup>-</sup> out of the crystals, and dried in an oven at 110 °C for at least 3 h.

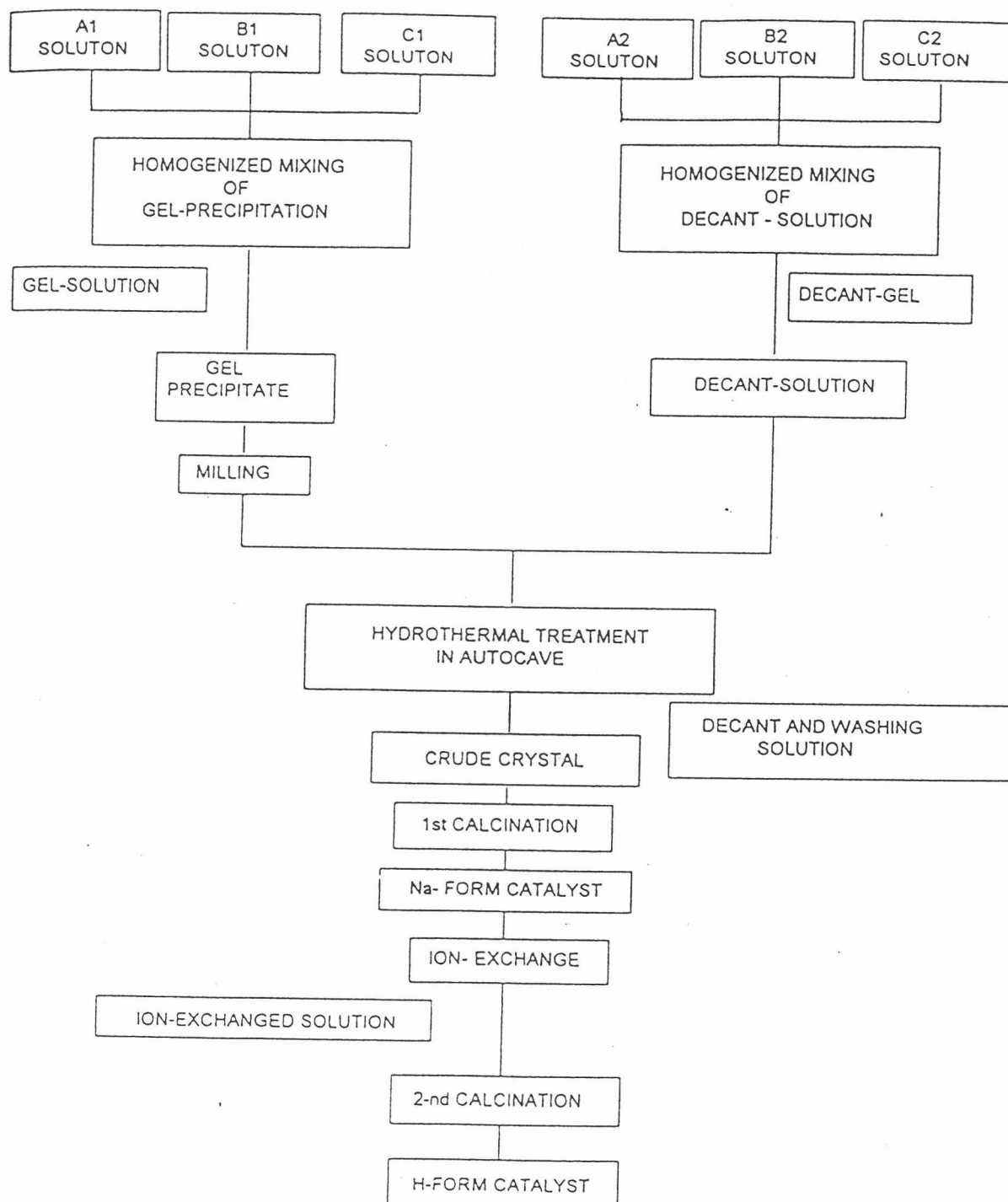


Figure 4.1 Preparation procedure of ZSM-5 by rapid crystallization method.

**Table 4.1** Reagents used for the preparation of Na-ZSM-5 (Si/Al =50)

Solution for the gel preparation	Solution for decant-solution preparation
<u>Solution A1</u>	<u>Solution A2</u>
AlCl <sub>3</sub> 0.8998 g	AlCl <sub>3</sub> 0.8998 g
TPABr                        5.72 g	TPABr                        7.53 g
NaCl                         11.95 g	Distilled water            60 ml
Distilled water            60 ml	H <sub>2</sub> SO <sub>4</sub> (conc.)            3.4 ml
H <sub>2</sub> SO <sub>4</sub> (conc.)            3.4 ml	
<u>Solution B1</u>	<u>Solution B2</u>
Sodium silicate            69 g	Sodium silicate            69 g
Distilled water            45 ml	Distilled water            45 ml
<u>Solution C1</u>	<u>Solution C2</u>
TPABr                        2.16 g	NaCl                         26.27 g
NaCl                         40.59 g	Distilled water            104 ml
NaOH                        2.39 g	
Distilled water            208 ml	
H <sub>2</sub> SO <sub>4</sub> (conc.)            1.8 g	

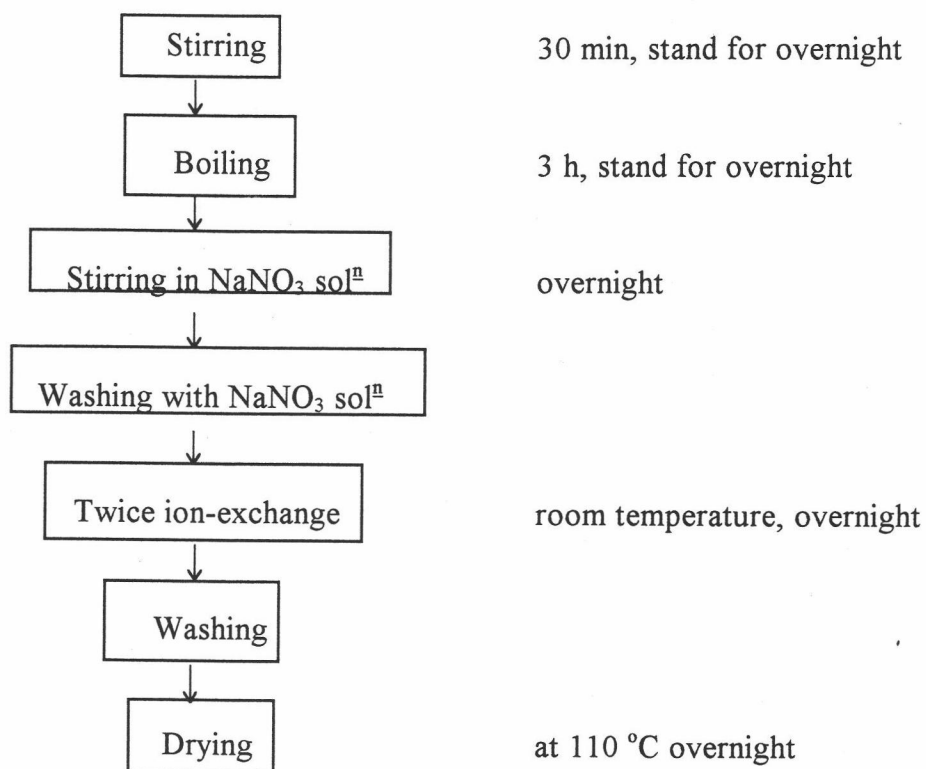
### 4.1.3 Calcination

The dry crystals were calcined in an air stream at 540 °C for 3.5 h, by heating them from room temperature to 540 °C in 60 min, to burn off the organic template and leave the cavities and channel in the crystals. The calcined crystals were cooled to room temperature in a dessicator. The obtained catalyst has been called Na-ZSM-5.

The Na-Zeolite was converted into the hydrogen form by using ion-exchange method. A 3.0 g portion of the calcined crystals was ion-exchanged twice in 90 ml of 1 M  $\text{NH}_4\text{NO}_3$  aqueous solution at 80 °C for 1 h, washed with de-ionized water, dried overnight at 110 °C, and calcined at 540 °C for 3.5 h.

## 4.2 Loading Cu by Ion-exchange Method

The zeolite was ion-exchanged at room temperature [52] with the procedure as shown in Figure 4.2. Approximately 2 g of ZSM-5 zeolite was stirred with 200 ml of de-ionized water about 30 min and standed for overnight, and then boiled for 3 h in new de-ionized water. This was stirred for overnight in 200 ml of 0.1 M  $\text{NaNO}_3$  solution and washed with 50 ml of  $\text{NaNO}_3$  solution. The metal exchange was carried out at room temperature for overnight with 100 ml of an aqueous copper nitrate solution of an adequate concentration. The wet cake obtained by separation from the solution was again ion-exchanged in new copper nitrate solution. Finally, the ion-exchanged zeolite was washed with de-ionized water and dried at 110 °C overnight.



**Figure 4.2** A diagram for metal ion-exchanged on catalyst.

The catalysts were tabletted by a tablet machine, then crushed and sieved in a grain-size of 8-16 mesh to provide for the reaction.

### 4.3 Nitric Oxide Reduction

#### 4.3.1 Chemicals and Reagents

Nitric oxide (1%) in helium, Hydrocarbon (3%) in helium, and oxygen of ultra high purity grade (99.999%) were provided by Thai Industrial Gases Limited.

### 4.3.2 Instruments and Apparatus

1) Reactor : The NO reduction reactor is a conventional microreactor made from a quartz tube with 6 mm. inside diameter. The reaction was carried out under ordinary gas flow and atmospheric pressure. The effluent gas was sampled and analyzed by on-line gas chromatography.

2) Automation Temperature Controller : This consists of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller series REX-C900 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 ° C to 1000 ° C.

3) Electrical furnace : This supplies the required heating to the reactor for NO reduction reaction. The reactor can be operated from room temperature up to 700 °C at maximum voltage of 200 volts.

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

5) Gas Chromatography : thermal conductivity detector (TCD) gas chromatographs, SHIMADZU GC-8APT and SHIMADZU GC-8AIT, and flame ionization detector (FID) gas chromatograph, GOW-MAC Series 750 were used to analyze feed and effluent gas. Operating conditions used are shown in Table 4.3.

### 4.3.3 Procedure

A 0.5 g portion of the catalyst was packed in a quartz tube reactor. Before the reaction, the catalyst was heated in He flow at room temperature to 500 °C in 1 h, held at this temperature for 1 h and then cooled

**Table 4.2** Operating conditions of gas chromatograph for Nitric oxide reduction

## a) Thermal conductivity detector gas chromatograph

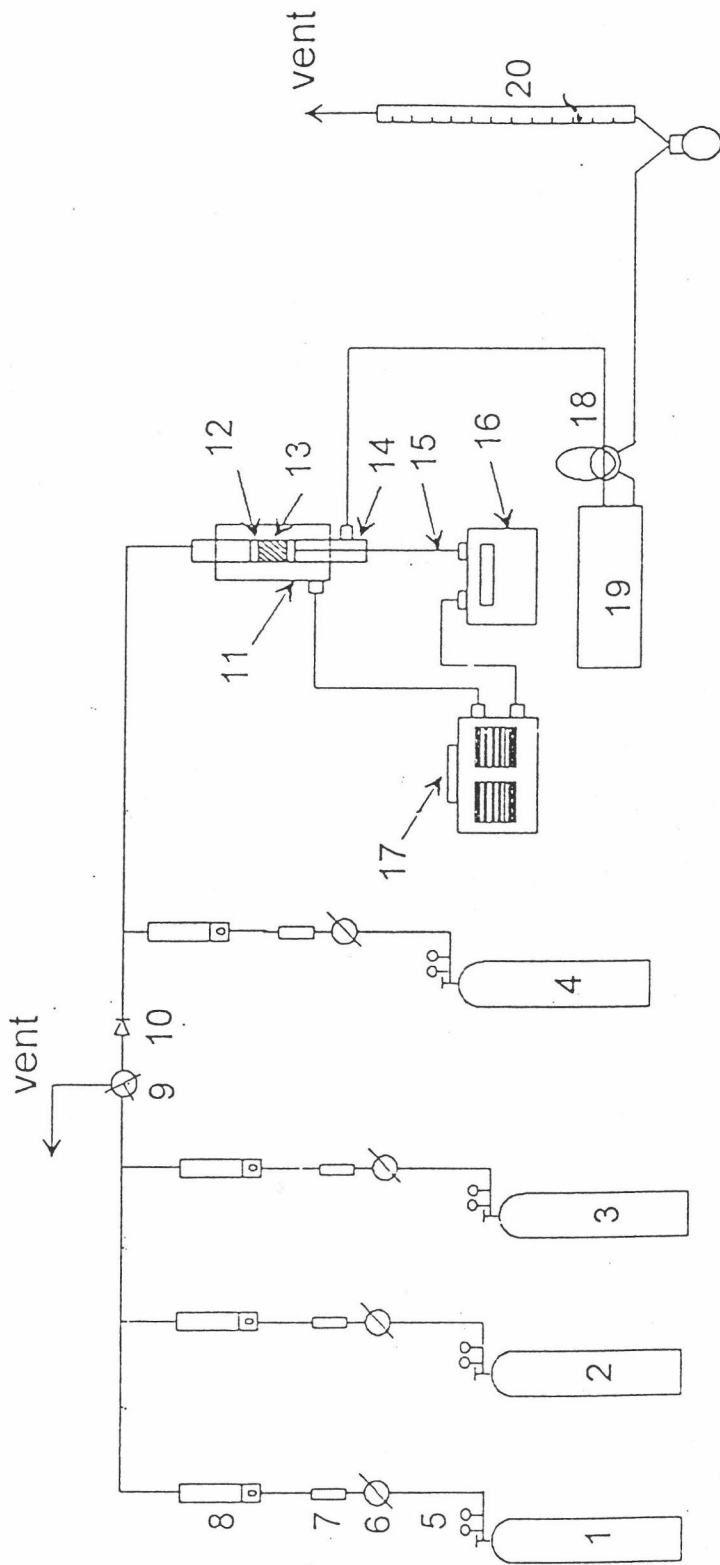
Gas chromatography	SHIMADZU GC-8APT	SHIMADZU GC-8AIT
Detector	TCD	TCD
Packed column	MS-5A	PORAPAK - Q
Carrier gas	He (99.999%)	He (99.99%)
Flow rate of carrier gas	30 ml/min	60 ml/min
Column temperature	60 °C	90 °C
Detector temperature	100 °C	100°C
Injector temperature	100 °C	100 °C
Analyzed gas	O <sub>2</sub> , N <sub>2</sub> , CH <sub>4</sub> , CO	C <sub>3</sub> H <sub>8</sub> , CO <sub>2</sub>

## b) Flame ionization detector gas chromatograph

Gas chromatography	GC GOW-MAC Series 750
Detector	FID
Packed column	VZ-10
Nitrogen flow rate	25 ml/min
Hydrogen flow rate	30 ml/min
Air flow rate	250 ml/min
Column temperature	50°C
Detector temperature	80°C
Injector temperature	80°C
Analyzed gas	hydrocarbons



down to 100 °C. The catalytic reaction was then started. A gas mixture containing NO (1000 ppm), C<sub>3</sub>H<sub>8</sub> (3000 ppm), and O<sub>2</sub> (10 volume%), diluted with He, was allowed to flow through the catalyst bed at a flow rate of 50 ml/min (GHSV ~ 4,000 h<sup>-1</sup>). For studying the effect of hydrocarbons, the number of carbon atom was kept constant in all cases by adjusting the hydrocarbon concentration. The reaction temperature was increased stepwise from 150 to 600 °C. The catalysts were heated up every 20 min (50 °C per time interval). At each of the reaction temperatures, the gas composition was analyzed by gas chromatography using Porapak-Q (CO<sub>2</sub> and C<sub>3</sub>H<sub>8</sub>), Molecular Sieve-5A (O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and CO) and VZ-10 (hydrocarbons) columns. The concentration of hydrocarbons at the inlet and outlet stream was therefore analyzed for hydrocarbons combustion. The catalytic activity for NO removal was evaluated by extent of conversion into N<sub>2</sub>. The flow diagram of nitric oxide reduction system was shown in figure 4.3.



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

Figure 4.3 Flow diagram of the nitric oxide reduction system

## 4.4 Characterization of the Catalysts

### 4.4.1 BET Surface Area Measurement.

#### a) Apparatus

Specific surface area of the catalyst was measured by a BET surface area analyzer (model ASAP 2000) at Analysis Center of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. The method was a physical adsorption of  $N_2$  on surface of catalyst to find the specific surface area.

**Table 4.3** Operating condition of BET surface area measurement

The catalyst weight	0.3 g.
Degas temperature	150 °C
Vacuum pressure	10 $\mu$ Hg.
Pressure table	5 points.

#### b) Procedure

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

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

3. The amount of  $N_2$  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.

#### 4.4.2 Chemical Analysis

##### a) Apparatus

Percentage of metals loading was analyzed by atomic absorption spectrometry (AAS) method. The copper content of the prepared solution was analyzed by atomic absorption spectrometry (AAS) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University.

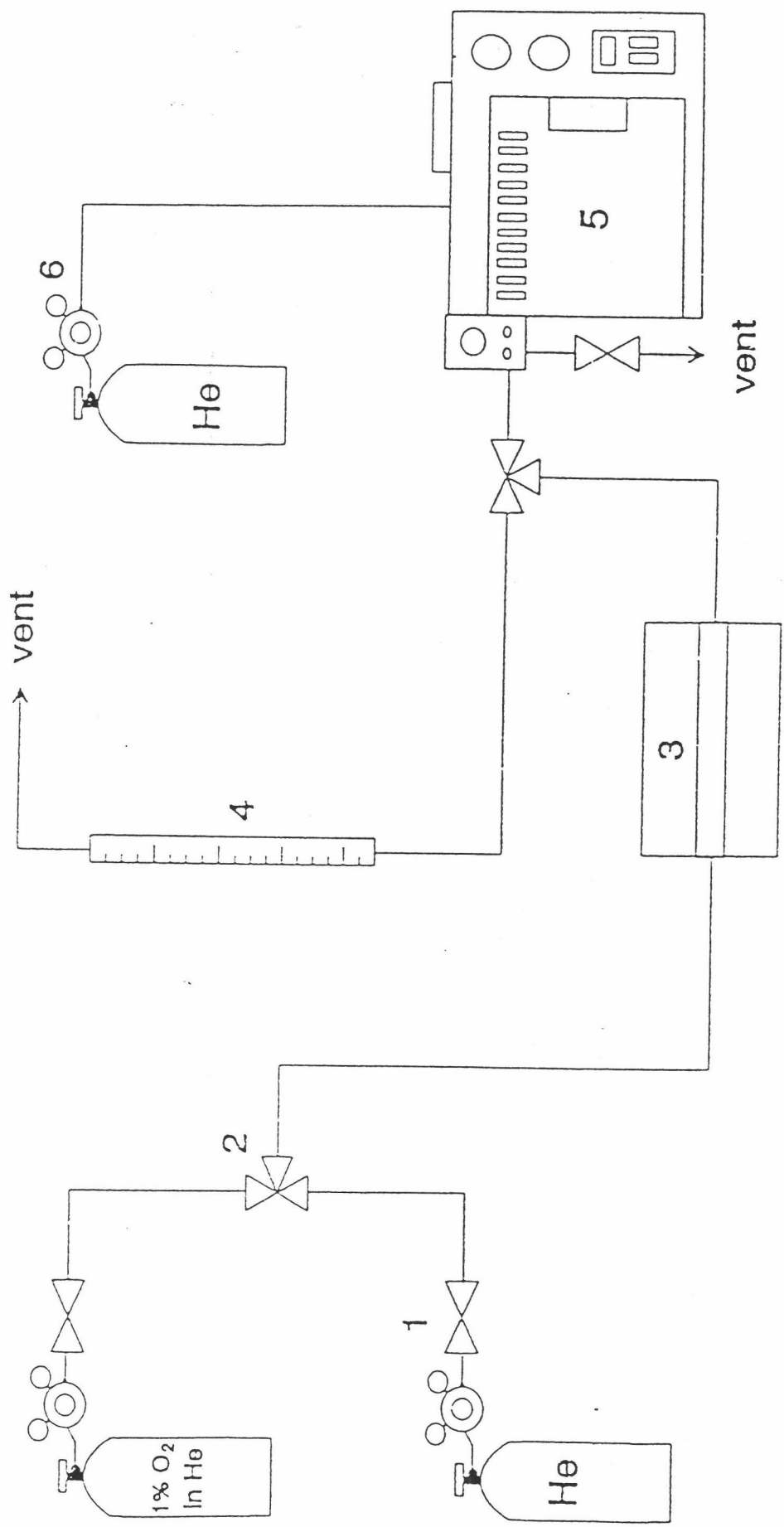
##### b) Procedure

The catalyst was dissolved by the following procedure. A certain amount of catalyst (about 100 mg) was digested by digesting solution containing solution of 20 ml of conc. HCl, 10 ml of conc. HNO<sub>3</sub>, and 10 ml of H<sub>2</sub>O. The mixture was heated up until the color of the support changed into white. During the heating step, water had to be added into the mixture to maintain the volume of mixture. Then, 5 drops of HF were added into the mixture in order to digest the support. Heating step was repeated until the solution became clear. Then volume of the solution was made up to 50 ml by adding de-ionized water.

#### 4.4.3 Temperature-Programmed Oxidation (TPO)

##### a) Apparatus

An inevitable phenomenon when a catalyst is used with a hydrocarbon feed stock is the deactivation by the deposition of some carbonaceous compounds, commonly called "coke". However, coke removal can be accomplished by burning the coked catalyst, using a gas mixture containing oxygen, at a suitable temperature over a period of time. The temperature-programmed oxidation technique can give information of the total amount of coke by measuring the amounts of carbon dioxide produced. The flow diagram of the system is shown in Figure 4.4.



- 1. On-Off Valve
- 2. Three Way Valve
- 3. Furnace and Reactor
- 4. Flow Meter
- 5. Gas Chromatography
- 6. Pressure Regulator

**Figure 4.4** Flow diagram of Temperature-Programmed Oxidation system.

**Table 4.4** Operating condition of gas chromatograph for TPO

Gas chromatography	SHIMADZU GC-8AIT
Detector	TCD
Packed column	PORAPAK - QS
Helium flow rate	60 ml/min
Column temperature	90 °C
Detector / injector temperature	110 °C
Detector current	90 mA

#### b) Procedure

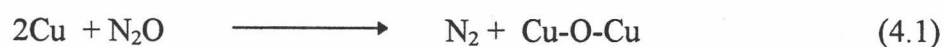
The temperature-programmed oxidation of the catalyst was carried out in a quartz tube reactor with an outside diameter of 6 mm packed with spent catalyst. The reactor was placed in a furnace which various heating rates was controlled by a programmable temperature controller (PC-600, Shinko). The temperature-programmed oxidation process began by heating up the catalyst with 1% oxygen in helium gas 30 ml/min from room temperature to 700 °C at a constant heating rate of 5 °C/min. Gas chromatograph (Shimadzu GC-8AIT) with Porapak QS column was used to measure the amount of CO<sub>2</sub> produced from coke combustion. The operating condition of the GC is shown in Table 4.4. When the catalyst temperature reached 50 °C, the effluent stream was first analysed at an interval of about 5 min until the temperature was raised to 700 °C. The catalyst sample was then cooled down in He stream.

#### 4.4.4 Cu-sites measurement by N<sub>2</sub>O adsorption method

##### a) Apparatus

The number of metal active sites were measured by N<sub>2</sub>O adsorption technique on the assumption that only one N<sub>2</sub>O molecule adsorbed and reacted with

two Cu-site, as the equation 4.1. Quantity of catalyst used is 0.1 g. Helium 99.99 % was used as a carrier gas. Nitrous oxide was used as an adsorbent and a standard gas. The reaction temperature was 90°C. The flow diagram of the N<sub>2</sub>O adsorption apparatus was shown in Figure 4.5. The amount of adsorbed N<sub>2</sub>O was measured by a thermal conductivity detector.



**Table 4.5** Operating condition of gas chromatograph for Cu-sites measurement

Gas chromatography	GC GOW-MAC Series 750
Detector	TCD
Packed column	PORAPAK - QS
Helium flow rate	30 ml/min
Column temperature	80 °C
Detector / injector temperature	80 °C
Detector current	80 mA

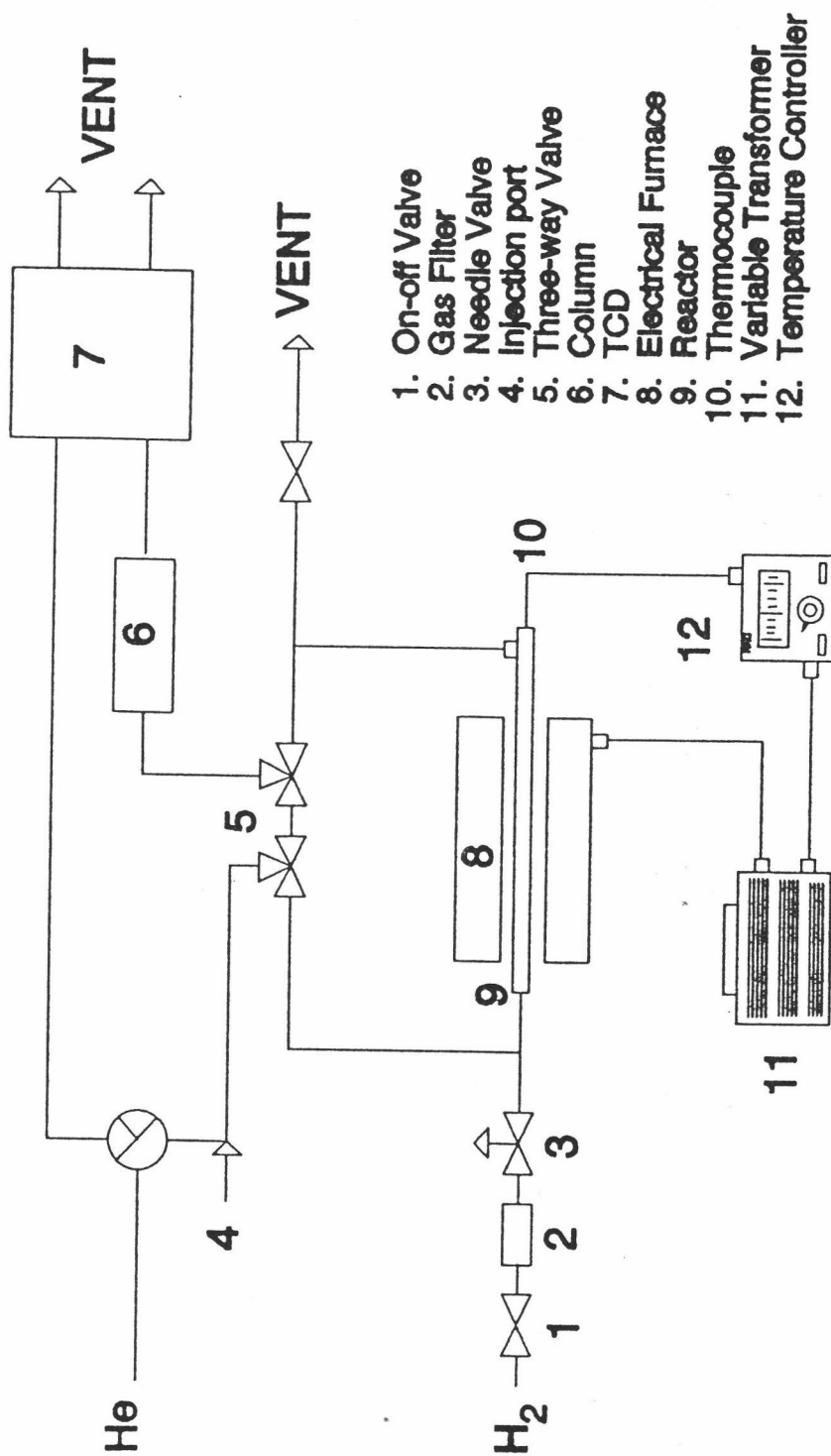
#### b) Procedure

1. Catalyst sample 0.1 g. was placed in a sample tube. The temperature was raised to 400 °C at rate of 10°C/min in 30 ml/min. flowed He. Then the catalyst was kept at this temperature for 1 hour.

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

3. Inject N<sub>2</sub>O 50 µl to the injection port. The N<sub>2</sub>O injection was repeated until the catalyst did not adsorb N<sub>2</sub>O by observed that the chromatogram area, after N<sub>2</sub>O adsorption in the first injection had occurred, was kept nearly constant for the following others injection.

4. Measure the amount of N<sub>2</sub>O adsorbed. The amount of metal site can be calculated using the procedure described in detail in Appendix A.



**Figure 4.5** Flow Diagram of the nitrous oxide reaction for measurement of copper surface area



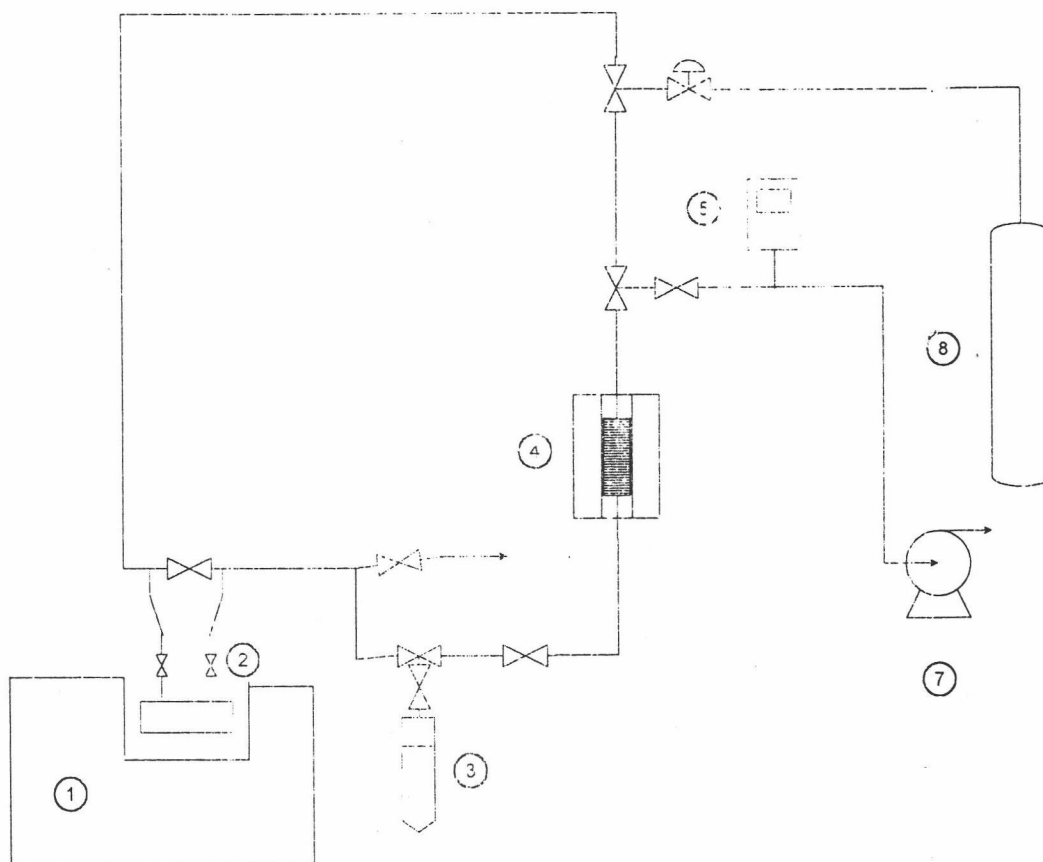
#### 4.4.5 FT-IR pyridine adsorption

##### a) Apparatus

The flow diagram of in situ FT-IR apparatus is depicted in Fig. 4.6 . All of gas lines, valves and fitting set in this apparatus is made of pyrex glass excepted for IR gas cell and sample disk holder which are made of quartz glass in order to avoid adsorption of any gas species which may remain on the inner surface of gas lines while the system was evacuated. High purified (99.99 % ) nitrogen supplied by TIG Ltd. was used for purging the process before start doing an experiment. Pyridine , Analytical grade supplied by Univar, Ajax Chemical, was filled in a glass tube connected with a valve which can open to the gas line system. A home-made electromagnetic pump was fixed in the gas line for circulating the gas including the pyridine vapour through the system in order to accomplish the adsorption of gases or pyridine specie on the sample surface thoroughly. A Labconco model 195 - 500 HP vacuum pump ,which theoretically has capacity in evacuation down to  $10^{-4}$  Torr, was used in this experiment. Furthermore, a digital pressure indicator was attached to line to measure the pressure of the system and used to check the leaking of the system line as well.

The Nicolet model Impact 400 FT-IR equipped with a deuterated triglycine sulfate (DTGS) detector connected to a computer using Omnic version 1.2a on windows software owing to fully control the functions of the IR analyzer. The analyzer is standed on a movable desk for conveniently adjustment to appropriate position. IR gas cell used in this experiment (Fig. 4.7) is made of quartz glass attached with two of 32 x 3 mm KBr windows at both ends of the cell. At each end of the quartz cell, the window is sealed by two O-rings and a stainless flange fasten by a set of screws.

The cell is roughly divided into two zones; heating and cooling zone, in respect to their temperature. The function of heating zone at the middle of the IR cell is to give rise in the temperature for the sample disk. The quartz sample holder for the sample disk to keep it perpendicular to the IR beam, is arranged inside the IR cell in



**Figure 4.6** Flow Diagram of insitu FT-IR apparatus

the heating zone. A thermocouple is used to measure the sample disk temperature, and this temperature is controlled by a variable voltage transformer and a temperature controller. At both ends of the IR cell are water cooling zones. They are applied to reduce the excessive heating which may damage O-ring seals and the windows.

#### b) Procedure

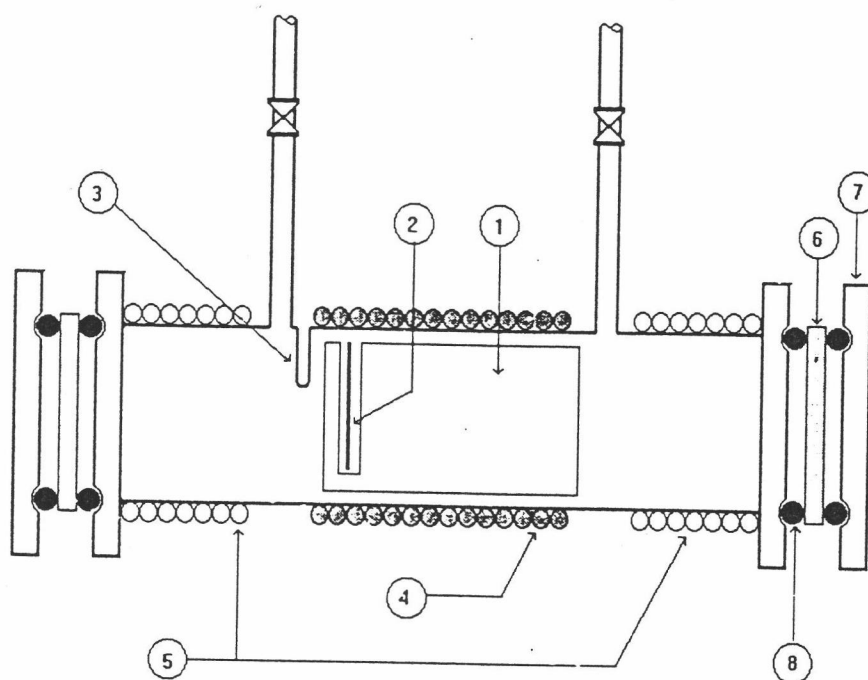
To produce a self-supporting catalyst sample disk for an in-situ experiment, firstly, catalyst sample, which in this study are ZSM-5 zeolite, was milled thoroughly in a tiny quartz mortar to obtain the very fine powder of sample because the scattering of infrared can be avoid to get high quality of spectrum and the sample disk can be easily made.

The die used is made of stainless steel as shown in fig. 4.8. , The powder sample was put into the die and spread the catalyst powder to totally cover the surface of the lower support disk. All parts of die then were integrated and was pressed by a manual hydraulic press pressure 140 -180 kg./cm<sup>2</sup> for 5 minutes. Finally, carefully remove the thin disk from the die, the sample disk is readily for in-situ IR experiment.

For the time we got a well-formed sample disk, it would ready for start experiment. Firstly, the sample disk was placed in the sample holder and then put the sample holder including sample disk into the middle of IR gas cell via locating the sample disk close to the thermocouple probe hole as much as possible. After the KBr windows were sealed at both ends of the IR gas cell and leaking was not observed, the IR gas cell through the gas line system was evacuated by a vacuum pump for at least 30 minutes to make the system under vacuum. The sample disk was pretreated at 300 - 400 C for 1 hr. under evacuating. However, due to the changing of IR spectra of sample was not found during the pretreatment, this step sometimes would be ignored. The sample disk adsorbed pyridine vapour at room temperature. Under well vacuum condition, pyridine would self evaporize from the pyridine tube into gas line through the IR gas cell. Besides, the pyridine vapour was circulated through the system by an electromagnetic pump for about 1 hr or until the IR spectra of pyridine peak did not change at further time to achieve the perfect adsorption of pyridine. After that, the IR

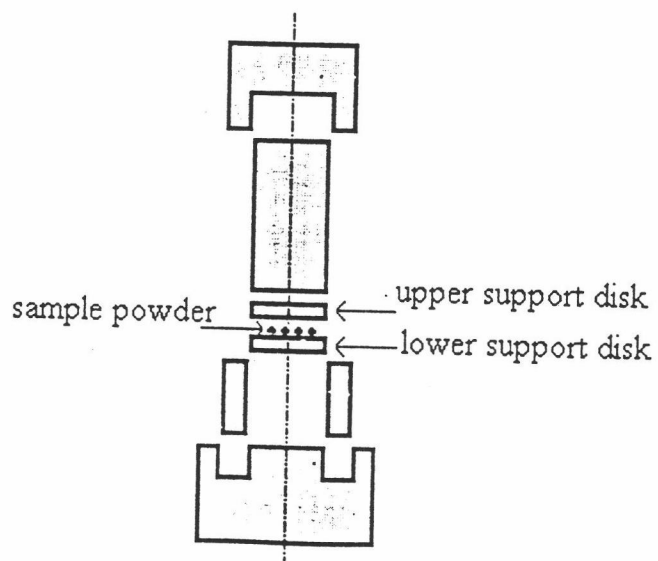
cell and gas line were evacuated to remove not only pyridine vapour remained in the cell and gas line but also the physisorbed pyridine species from the catalyst surface. The vacuum pump was operated till the IR spectra peaks of vapour pyridine and physisorbed pyridine was totally vanished and there was no change in any other peaks of the spectra which normally spent around 1.5 hr. FT-IR began measure spectra of pyridine-adsorbed sample at room temperature and then at elevated temperature at every 25 C.

The vacuum pump was kept running while the sample disk via IR gas cell was heating to remove all species desorbed from the sample surface out of the system in order to avoid disturbing the result spectra by such species. On the other hands, since the vibration would occur and may bring about the bad scan of IR measuring, the vacuum was switched off when the temperature was held for IR detection. The measurement would complete when all of peaks of adsorbed pyridine were disappeared corresponding to the IR spectra of the sample would be identical with the one before pyridine dosing.



- |                          |                 |
|--------------------------|-----------------|
| 1. Sample Holder         | 5. Cooling Zone |
| 2. Sample Disk           | 6. NaCl Window  |
| 3. Thermocouple Position | 7. Flange       |
| 4. Heating Zone          | 8. O-ring       |

**Figure 4.7** The assembly of an in-situ IR quartz Cell



**Figure 4.8** A die for pressed disk

#### 4.4.6 Temperature Programmed Reduction.

##### a) Apparatus

Temperature programmed reduction, TPR, was used to investigate the oxygen on the catalyst surface by observing the amount of H<sub>2</sub> used. The product of this reaction is water vapour which is trapped by dried ice mixed with isopropanol. The amount of H<sub>2</sub> was measured by the thermal conductivity detector, TCD. The flow diagram of the TPR apparatus is shown in figure 4.9.

**Table 4.6** Operating condition of TCD

Carrier gas and flow	5% H <sub>2</sub> /Ar 50 ml/min.
Temperature of detector	80 °C
Detector current	80 mA.

##### b) Procedure

There were two steps in this measurement.

##### 1) Calcining step

1. Catalyst sample, 0.2 g, was placed in a sample tube. Flow rate of air through the sample was at 100 ml/min. and was heated up to 300 °C at a rate of 10 °C/min., held for 1 hour to ensure the surface was covered with oxide form.

2. Switch to helium flow through the sample 100 ml/min. at 300 °C for 5 minutes, then cooled down (in helium) to room temperature.

##### 2) Temperature programmed Reduction step

1. After calcining : switch to the mixture gas H<sub>2</sub> flow through the sample, 50 ml./min. Waiting until the baseline was constant.

2. The TPR runs were started at 50 °C, by allowing the temperature to increase to 700 °C at rate 10 °C/min.

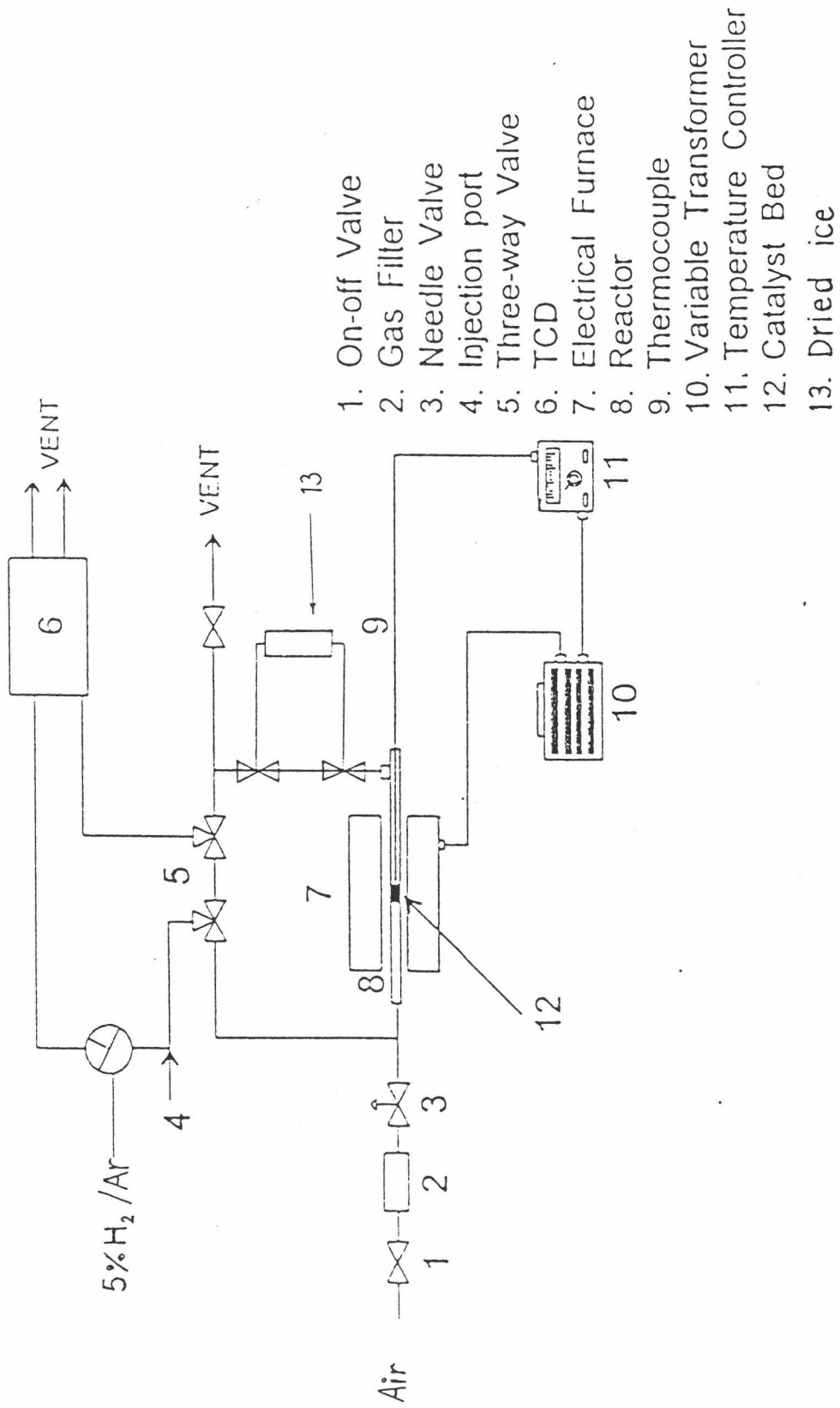


Figure 4.9 Flow Diagram of the Temperature-Programmed Reduction System