

## CHAPTER IV

### EXPERIMENTAL

#### 4.1 Catalysts Preparation

##### 4.1.1 Na-ZSM-5

The parent Na-ZSM-5 was prepared by the rapid crystallization method according to Inui's method[129]. The preparation procedure is shown in Figure 4.1, while reagents are given in Table 4.1. As the source of metals,  $\text{AlCl}_3$  for Al and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  for Cu were used, respectively. TPABr (Tetra-n-Propyl Ammonium Bromide)  $[(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}]\text{Br}$  was used as organic template. Si/Al of the catalyst prepared for this study was about 50. The preparation procedure is described below:

##### 1) Preparation of Gel Precipitation and Decantation Solution

A supernatant liquid was separated from the gel, which is important for preparing the uniform crystals. A gel mixture was prepared by adding solution A-1 and solution B-1 into solution C-1 dropwise with vigorous stirring using a magnetic stirrer at room temperature as shown in Fig 4.2. The pH of the mixed solution was maintained within 9-11 because it was expected that this pH value is suitable for precipitation. The gel mixture was separated from the supernatant liquid by a centrifuge. The precipitated gel mixture was milled for 1 hr by a powder miller (Yamato-Notto, UT-22). The milling procedure was as follows: milled 15 min  $\rightarrow$  centrifuge (to remove the liquid out)  $\rightarrow$  milled 15 min  $\rightarrow$  centrifuge  $\rightarrow$  milled 30 min. Milling the gel mixture before the hydrothermal treatment was essential to obtain the uniform, fine crystals.

A decantation solution was prepared by adding solution A-2 and solution B-2 into solution C-2 same as for the preparation of the gel mixture. During the time the supernatant liquid from A-2, B-2, and C-2 was mixing

together. The pH of the solution was adjusted to between 9-11.  $\text{H}_2\text{SO}_4$  (conc.) or 1 M NaOH solution were used to adjust pH of the decant mixture to an appropriate level if it was necessary. The colourless supernatant liquid was separated from the mixture by sedimentation and centrifugation.

## 2) Crystallization

The mixture of the milling precipitate and the supernatant of decant solution was charged in a 500 ml Pyrex glass container. The glass container was placed in a stainless steel autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurised up to 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 of the hot mixture to room temperature in the autoclave overnight. The temperature was programmed to minimise the time necessary for the crystallization. The product crystals were washed with de-ionized water about 8 times using the centrifugal separator (about 15-20 min. for each time), to remove Cl<sup>-</sup> from the crystals, and dried in an oven at 110 °C for at least 3 hrs.

## 3) Calcination

The dry crystals were calcined in an air stream at 540 °C for 3.5 hrs, by heating them from room temperature to 540 °C in 60 minutes, to burn off the organic template and leave the cavities and channels in the crystals. The calcined crystals were finally cooled to room temperature in a desiccator. The obtained Na-ZSM-5 is the parent ZSM-5 zeolite which will be further transformed to the other appropriate forms for the experiments in this study.

Moreover, the Na-ZSM-5 given from each batch would be checked by using the X-Ray Diffraction (XRD) analysis to confirm the ZSM-5 structural and crystallinity of sample. If, unfortunately, the XRD pattern could not be acceptable, the sample would not be used and a new sample would have to be made.

**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>	0.8831 g	AlCl <sub>3</sub>	0.8831 g
TPABr	5.72 g	TPABr	7.53 g
NaCl	11.95 g	De-ionized water	60 ml
De-ionized 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
De-ionized water	45 ml	De-ionized water	45 ml
<u>Solution C1</u>		<u>Solution C2</u>	
TPABr	2.16 g	NaCl	26.27 g
NaCl	40.59 g	De-ionized water	104 ml
NaOH	2.39 g		
De-ionized water	208 ml		
H <sub>2</sub> SO <sub>4</sub> (conc.)	1.55 ml		

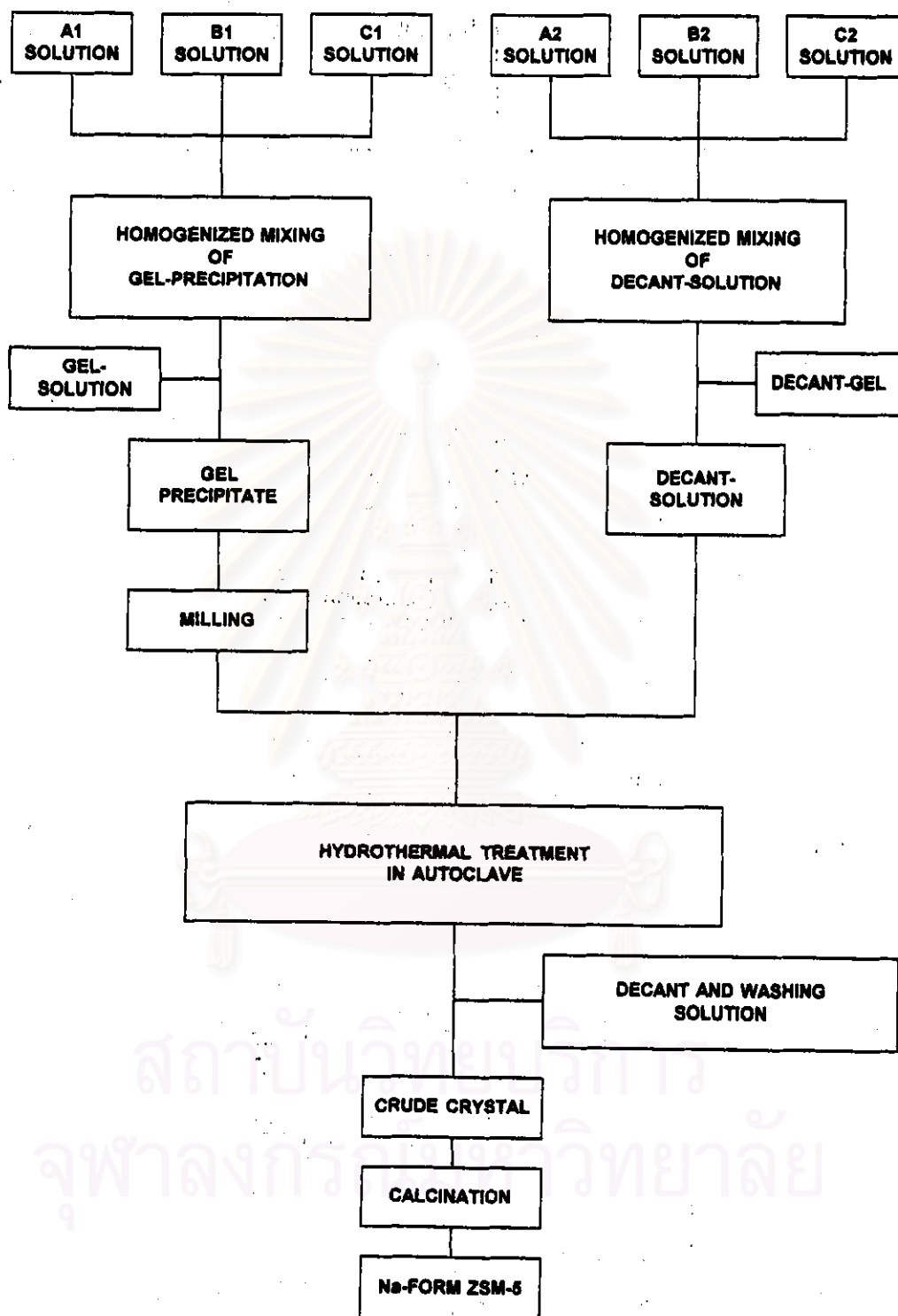


Figure 4.1 The preparation procedure of ZSM-5 by rapid crystallization method.

#### 4.1.2 $\text{NH}_4$ -and H- form ZSM-5

To make  $\text{NH}_4$ -ZSM-5, parent Na-ZSM-5 powder was firstly mixed with 1 M  $\text{NH}_4\text{NO}_3$  solution at 30 ml per gram of catalyst. In the procedure, catalyst amount did not exceed 5 grams to approach complete exchange. The slurry of zeolite and solution was then stirred and heated on a hot plate, maintained at  $80^\circ\text{C}$  by applying a condenser as shown in figure 4.3. After heating the mixture for about 1 hr, the mixture was cooled down to room temperature and centrifuged to remove the used solution. The remained crystals were mixed again with  $\text{NH}_4\text{NO}_3$  solution in the same amount. The previous step was repeated. The exchanged catalyst was then washed twice with deionized water using centrifuge. Subsequently, the exchanged crystals were dried in an oven at  $110$ - $120^\circ\text{C}$  for at least 3 hrs. The dried catalyst obtained is the  $\text{NH}_4$  -form of ZSM-5. The  $\text{NH}_4$ -ZSM-5 was converted to H-form ZSM-5 by removing  $\text{NH}_3$  species from the catalyst surface.  $\text{NH}_3$  can be removed by thermal treatment of the  $\text{NH}_4$ -ZSM-5 zeolite. This was done by heating a sample in a furnace from ambient temperature to  $540^\circ\text{C}$  in 1 hr and holding the sample at  $540^\circ\text{C}$  for 3.5 hrs. After the catalyst was cooled down, it was stored in a glass bottle in a desiccator for further use.

#### 4.1.3 Copper ion-exchanged ZSM-5

Either form (H or Na) of ZSM-5 was exchanged with copper to make Cu/ZSM-5. The procedure in the thesis of W. Engopasanan[108] was used to get a specified copper content in the ZSM-5. The catalyst powder was stirred with deionized water at 26.7 ml per gram of catalyst. The stock solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was added into the stirring slurry in the amount required. Normally, by this method, ratio of amount of copper loading and amount of copper exchanged into zeolite is about 1.1 - 1.2 depend on copper loading amount. Then, 10 %  $\text{NH}_4\text{OH}$  solution was gradually dropped into the mixture to get the appropriate pH level( pH~ 9-11)[108] to achieve a high loading. After the slurry had been well stirred for 12 hrs, the crystals were separated by centrifuge.

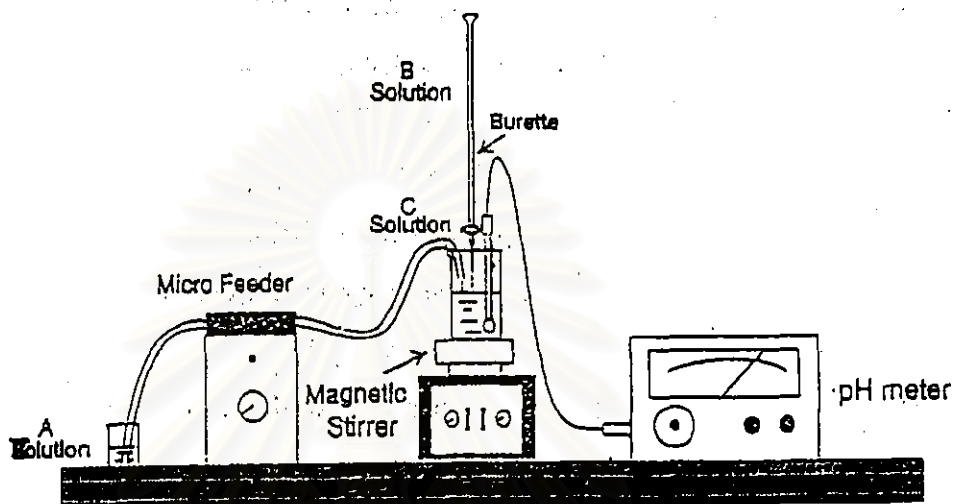


Figure 4.2 Apparatus used for the preparation of parent Na-ZSM-5 , Si/Al = 50

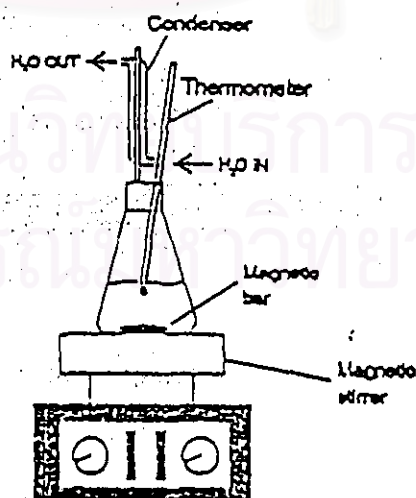


Figure 4.3 Apparatus used for ion-exchanging of ZSM-5 catalysts



The zeolite obtained was then washed with deionized water for 5-7 times to get rid of some ions. Finally, the catalyst was dried in an oven at 110 °C overnight and then calcined in air at 540 °C for 3.5 hrs as same as the Na-ZSM-5 preparation procedure.

#### **4.1.4 Pelletization**

All catalysts were pelletized by using a stainless steel die which has about a 1 cm diameter opening inside the die. The pelletization was performed at the pressure of about 3000 psi, by applying a manual press, for 3 minutes for the approximate 0.25 g. catalyst sample per one pellet. The pellets obtained then were cut by a clean cutter into small granular pieces and were sieved to acquire grain sized to 8-16 mesh for use in the steady state reaction experiments.

## **4.2 Steady State Reaction Test**

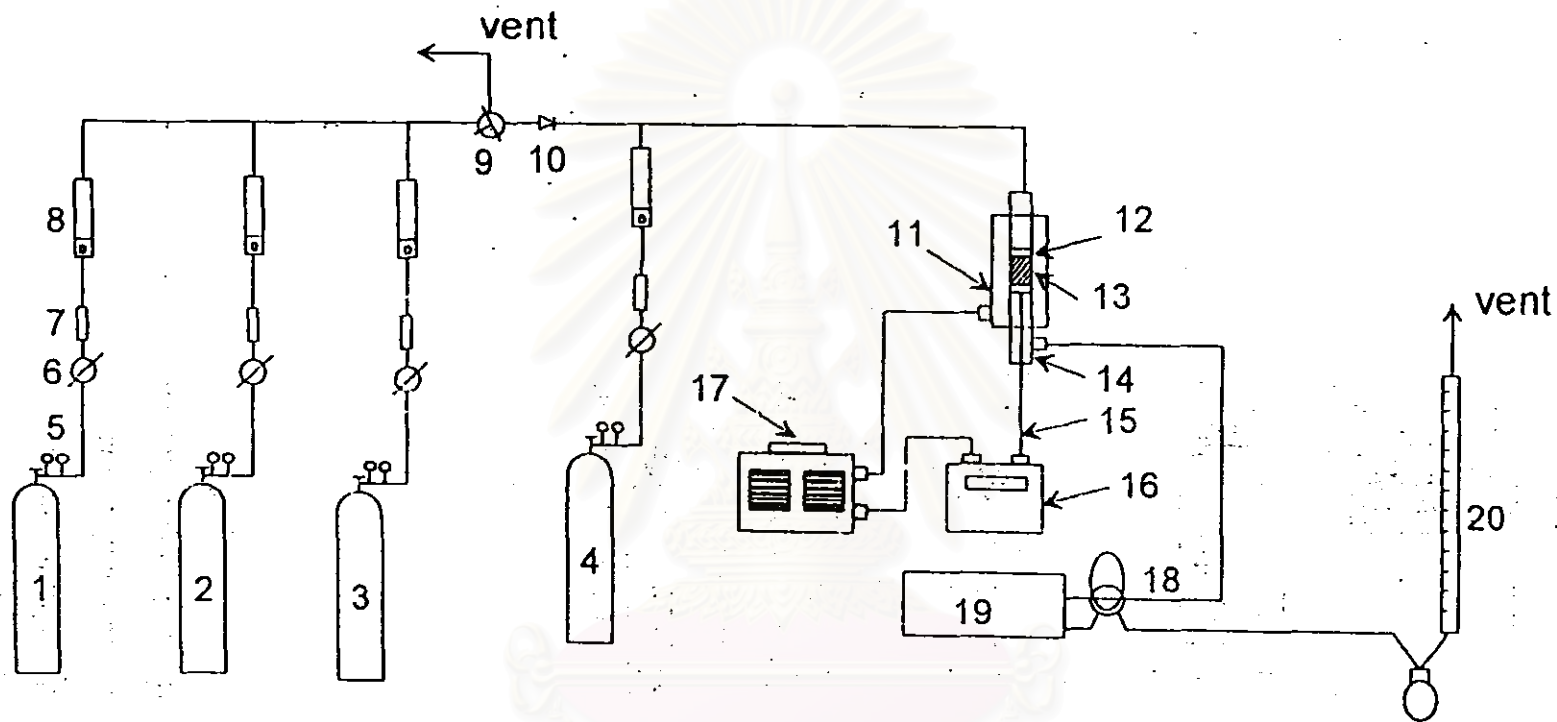
### **4.2.1 Chemicals and Reagents**

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.

### **4.2.2 Instruments and Apparatus**

A flow diagram of the steady state nitric oxide reduction system is shown in figure 4.4. The instruments used in this system is listed and explained below:

- 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.



- |                       |                    |                     |                                  |
|-----------------------|--------------------|---------------------|----------------------------------|
| 1) NO tank            | 6) On/off valve    | 11) Reactor furnace | 16) Temperature controller       |
| 2) Propane tank       | 7) Gas filter      | 12) Quartz wool     | 17) Variable voltage transformer |
| 3) Oxygen tank        | 8) Flow meter      | 13) Catalyst bed    | 18) Sampler                      |
| 4) He tank            | 9) Three way valve | 14) Reactor         | 19) Gas chromatography           |
| 5) Pressure regulator | 10) Check valve    | 15) Thermocouple    | 20) Bubble flow meter            |

Figure 4.4 Flow diagram of the steady state experiment for the NO reduction by propane



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 the NO reduction reaction. The reactor can be operated from room temperature up to 700 °C at a maximum voltage of 200 volts.

4) Gas control system : Nitric oxide, hydrocarbon, oxygen and helium cylinders; each equipped with a pressure regulator (0-120 psig), a set of needle valves was used to adjust the flow rate of gases. A sampling valve was used to take sample of effluent gas into a gas chromatograph analyzer.

5) Gas Chromatography : consisted of thermal conductivity detector (TCD) equipped gas chromatographs, SHIMADZU GC-8APT and SHIMADZU GC-8AIT Operating condition used are given in Table 4.2.

**Table 4.2** Operating conditions of 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	70 °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> , CO	C <sub>3</sub> H <sub>8</sub> , CO <sub>2</sub>

### 4.2.3 Reaction Procedure

A 0.5 g portion of the catalyst was packed in the quartz tube reactor. Before the experiment, the catalyst was heated in He flow at room temperature to 500 °C in 1 hr. and then held at this temperature for 1 hr. After that, the reactor was cooled down to 100 °C. The catalytic reaction was then started. A gas mixture containing NO, C<sub>3</sub>H<sub>8</sub>, and O<sub>2</sub>, 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) columns. The concentration of hydrocarbons in the inlet and outlet streams were analysed for hydrocarbon combustion. The catalytic activity for NO removal was evaluated by the extent of conversion into N<sub>2</sub>.

## 4.3 Transient Experiment

This experiment was under taken at the Reactor Engineering Laboratory, Department of Chemical Engineering, University of Waterloo, Canada.

### 4.3.1 Chemicals and Reagents

1.2 % Nitric oxide in nitrogen, compressed air and pure propane which were provided by Praxair Canada were used in this study.

### 4.3.2 Instrument and Apparatus

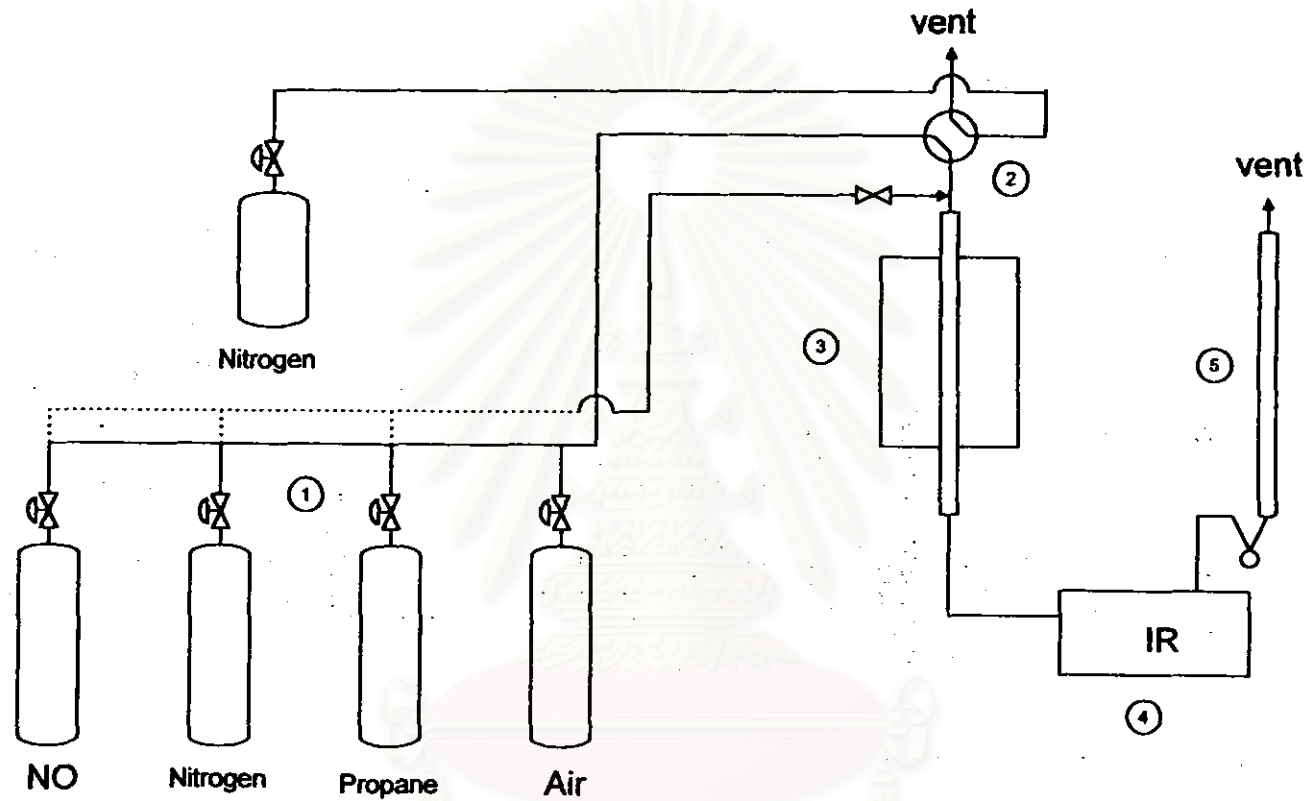
A simple process flow diagram is shown in figure 4.5. Each gas tank was equipped with a needle valve and a set of on-off valves to choose gases for the experiment and adjust their flow rate to a switching valve or to the reactor bed. Actual flow rate of each gas was measured and adjusted by a bubble flow meter and needle valves. A GC sampling valve was adapted to serve as

switching valve located above the reactor section in order to alternate reactant mixed gas or inert, nitrogen gas, passing through the reactor. The reactor used in this experiment was a quartz tube, 10 mm outside diameter. A K type thermocouple was located at the bottom of catalyst bed, inside of the quartz tube. The reactor heater was controlled by an on/off temperature controller and a variac transformer. In order to reduce void volume as much as possible, the reactor tube was filled with glass beads. Moreover, the 1/16" stainless tube, about 30 cm in length, was connected from the outlet of the quartz reactor to the IR gas cell to bring the outlet gas from the reactor to IR analyzer as fast as possible. Concentration of each gas was measured by FT-IR continuously. The exhaust gas from the IR gas cell then came to a bubble flow meter and was finally vented to a fume hood.

#### **4.3.3 On-line Detector FT-IR**

##### **1) FT-IR**

Fourier Transform-IR, Mattson model Galaxy 5022, was used to measure the concentration of gases continuously. The analyser was connected with a 386 personal computer and used the First Enhanced version 1.6 program with a Time Evolved Analysis option which is enabled the IR to measure and show the absorbance of each peak with time. For high detection efficiency, a Mercury Cadmium Telluride(MCT) detector cooled with liquid nitrogen was used. In addition, to study the dynamic behaviour of the reaction, the IR must measure gas outlet as fast as possible. Consequently, the FT-IR was operated at resolution  $16\text{ cm}^{-1}$  and a single scan. It spent a few seconds per detection. Nevertheless, signal was adequate for interpretation.



- 1) Alternative reactant gases
- 2) Switching valve
- 3) Reactor

- 4) FT-IR Analyzer
- 5) Bubble flow meter

Figure 4.5 Flow diagram of transient experiment

## 2) IR gas Cell

The quartz reactor outlet was directed to a small IR gas cell mounted on the FT-IR and referred to as a light pipe (LP). The IR gas cell used in this study was designed by Khodadadi[130]. The body of the light pipe shown in figure 4.6 was made of aluminium. A 3.5 x 70 mm (0.67 ml ) cavity and cavities for O-rings and windows were provided in the cell body. Two 13 mm diameter x 2 mm of water resistant CaF<sub>2</sub> windows were sealed with O-rings at both ends of the cavity by three bolts. The 1/16" OD. inlet and outlet of the cell was soldered to small nozzles attached to the cell body. As shown in figure 4.7, the light pipe was held in a cylinder by two set of screws. The cylinder, including the light pipe, fastened to the sample holder of FT-IR so that a rough XY position of the light pipe could be made. Fine adjustment of the gas cell was done by the two sets of the screws as suggested by the figure 4.7.

### 4.3.4 Dynamic Behaviour of the System

To study the reactor dynamic, the blank test would be carried out. The dynamic respond of switching from N<sub>2</sub> to 1.2 % NO, as tracer, in only a glass beads filled reactor is depicted in figure 4.8. The transit time of a total gas flow of around 50 ml/min. at room temperature from the switching valve to the IR analyzer is approximately 12 sec. whereas at 400 °C it is about 10 sec. The FT-IR can measure NO, NO<sub>2</sub>, N<sub>2</sub>O, CO<sub>2</sub> and propane simultaneously but neither N<sub>2</sub> nor O<sub>2</sub> can be detected. Graphs in this study show as absorbance. This is simply related to the gas concentration, although, relationship differs for each gas because the intensity of absorbance spectra of each gas depends on its molecular structure. Nevertheless, the absorbance signals can be used for a rough comparison among experiments. The absorbance band for each gas detected by the FT-IR used in this study are summarised in Table 4.3.

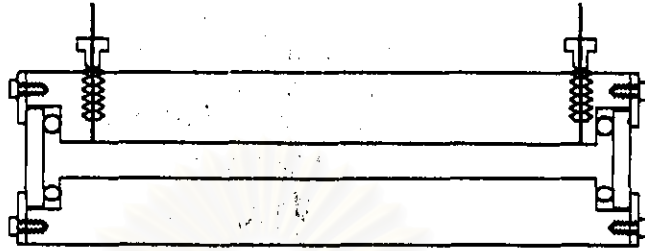


Figure 4.6 Body of IR gas cell ( Light Pipe) for transient experiment

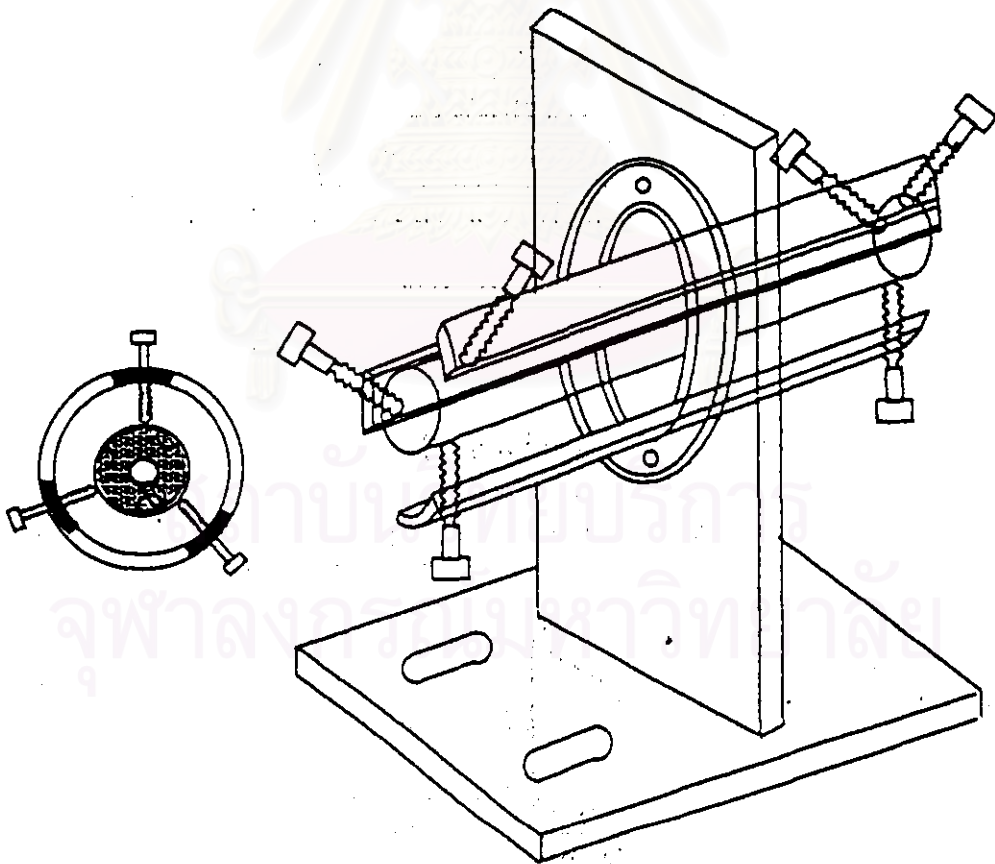


Figure 4.7 Adjustment mechanism of IR gas cell for transient experiment



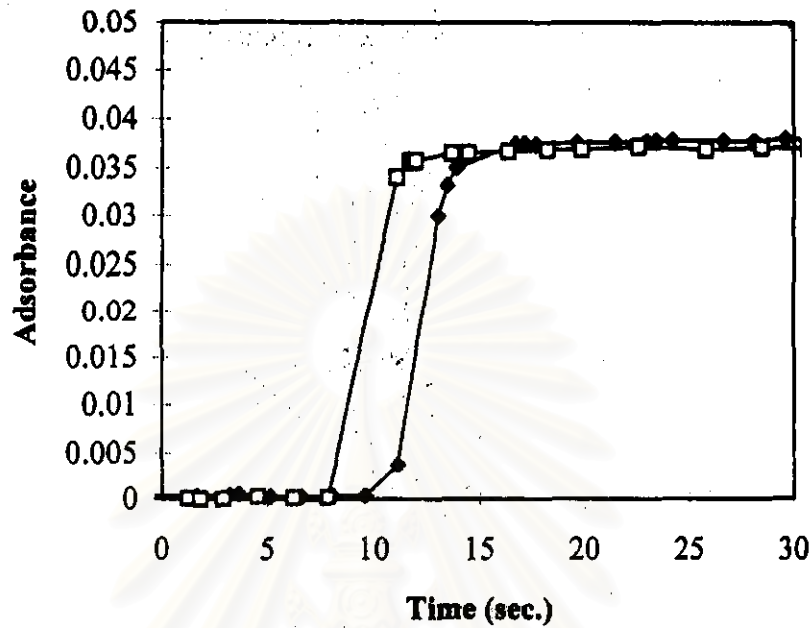


Figure 4.8 Dynamic response of NO signal in switching from  $N_2$  to 1.2 % NO ; flow rate 50 ml/min ; at 24 °C(♦) and at 400 °C (□)

Table 4.3 IR Band of gases

Gas species	appearance peak ( $cm^{-1}$ )
NO	1905(xl), 1850(l)
NO <sub>2</sub>	1630(xl), 1600(xl), 1750(l), 1263(l)
N <sub>2</sub> O	2225(xl), 1290(l)
C <sub>3</sub> H <sub>8</sub>	2970
CO <sub>2</sub>	2362

xl = extra large

l = large

#### 4.3.5 Reaction Procedure

The 1.2 g. of 10-20 mesh granular zeolite catalyst was added to the quartz reactor. Reactants balanced with nitrogen or pure nitrogen could be selected as feed to the reactor. Flow rate of each gas was adjusted by a needle valve. Flow rate of each gas and the total gas flow rate was measured by a bubble flow meter. The total gas flow rate passing the reactor is 50 ml/min corresponding to a GHSV of about  $2000 \text{ hr}^{-1}$ . The composition of gas streams in the experiment are :

1.2 % NO	N <sub>2</sub> Balanced
0.5 % NO + 12 % O <sub>2</sub>	N <sub>2</sub> Balanced
0.5 % NO + 0.4 % C <sub>3</sub> H <sub>8</sub>	N <sub>2</sub> Balanced
0.5 % NO + 0.4 % C <sub>3</sub> H <sub>8</sub> + 12 % O <sub>2</sub>	N <sub>2</sub> Balanced

The reaction was investigated at temperature between 300 - 400 °C. Before starting each experiment, the catalyst bed was flushed with nitrogen at a flowrate of 50 ml/min. at 450 °C for about 1 hr to remove water and residue species from the catalyst surface. Then, the catalyst bed was cooled to the reaction temperature. After the FT-IR was turn on, the gas stream was switched from inert to reactant feed. After the FT-IR absorbance of gases detected became constant, the feed to the reactor bed was abruptly changed into nitrogen again in order to investigate dynamics in both step up as well as step down of the reactant feed.

## **4.4 FT-IR Pyridine Adsorption**

### **4.4.1 Chemical and Reagents**

High purity (99.99 % ) nitrogen supplied by TIG Ltd. and Pyridine , analytical grade supplied by Univar or Ajax Chemical were used in these experiments.

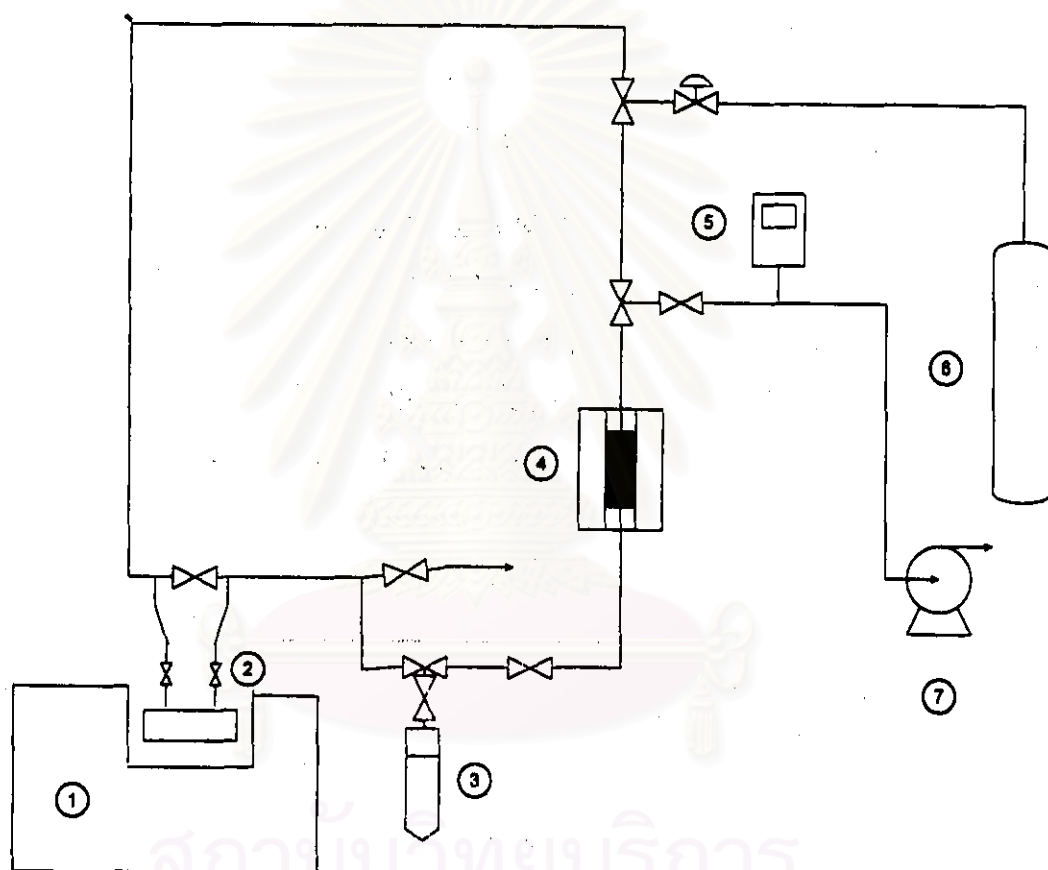
### **4.4.2 Instruments and Apparatus**

#### **1) Flow diagram**

The flow diagram of the in-situ FT-IR apparatus is depicted in figure 4.9. All gas lines, valves and fitting in this apparatus are made of Pyrex glass except for the IR gas cell and the sample disk holder which are made of quartz glass in order to avoid the adsorption of any gas species which may remain on the inner surface of glass tube while the system was evacuated. Nitrogen was used for purging before starting the experiment. Pyridine was added to a glass tube connected with a valve which can open to the gas line system. A home-made electro-magnetic pump, fixed in the gas line, was used for circulating the gas (including the pyridine vapour) through the sample in order to accomplish the adsorption of gases or pyridine specie on the sample surface. A Labconco 195 - 500 HP vacuum pump, which theoretically has capacity at  $10^{-4}$  Torr, was used. Furthermore, a digital pressure indicator, attached to the gas line, measured the pressure of the system and checked leaking of the apparatus as well.

#### **2) FT-IR**

A Nicolet model Impact 400 FT-IR equipped with a deuterated triglycine sulfate (DTGS) detector and connected to a personal computer with Omnic version 1.2a on Windows software (to fully control the functions of the IR analyzer) were applied to this study. The analyzer was place on a movable table for conveniently adjustment.



- |                                      |                               |
|--------------------------------------|-------------------------------|
| 1) FT-IR Analyzer                    | 5) Digital pressure indicator |
| 2) IR quartz gas cell                | 6) Vacuum pump                |
| 3) Pyridine tube                     | 7) Nitrogen gas cylinder      |
| 4) Electro magnetic circulating pump |                               |

Figure 4.9 Flow diagram of instrument for pyridine adsorption experiment

### 3) IR gas cell

IR gas cell used in this experiment (Fig. 4.10) was made of quartz glass and covered with a 32 x 3 mm KBr windows at each ends of the cell. The windows were sealed by two O-ring and a stainless flange fasten by a set of screws.

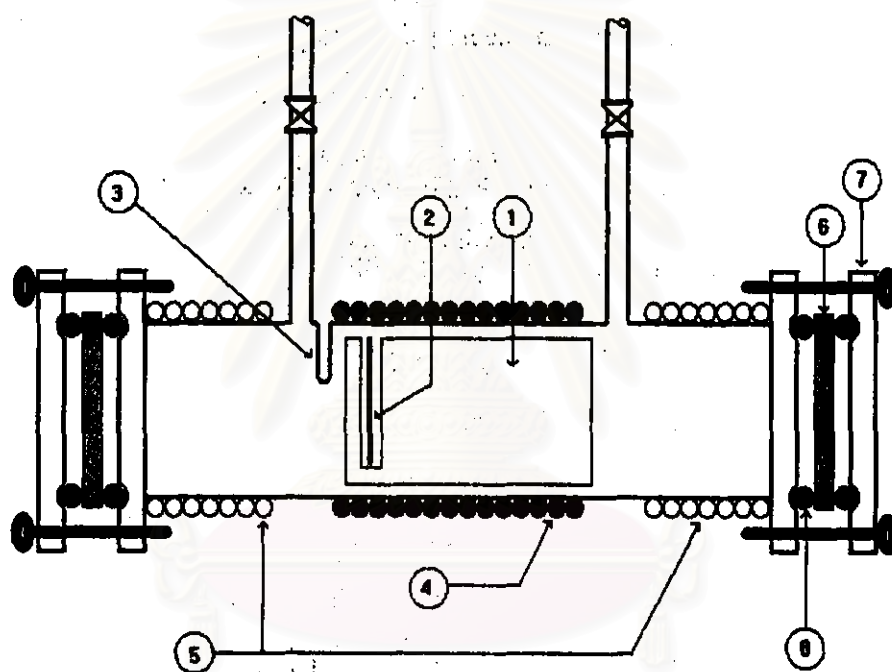
The cell is roughly divided into two zones; heating and cooling with respect to their temperature. The function of the heating zone at the middle of the IR cell is to increase the temperature for the sample disk. The quartz sample holder for the sample disk to keep it perpendicular to the IR beam, is arranged inside the IR cell in the heating zone. A thermocouple is used to measure the sample disk temperature. The temperature is controlled by a variable voltage transformer and a temperature controller. At both ends of the IR cell were water cooled. They were applied to reduce the excessive heating, which may damage O-ring seals and the windows.

#### 4.4.3 Sample Disk Preparation

To produce a self-supporting catalyst sample disk for an IR experiment, the ZSM-5 zeolite was milled thoroughly in a small quartz mortar to obtain a very fine powder. This minimized the scattering of infrared radiation and provided a high quality of spectrum.

The die used was made of stainless steel and is shown in figure 4.11. The most important part of the die, which is directly in contact with the sample is the so-called the support disks. These are composed of upper and lower disks, each 20 mm. in diameter. Support disks are highly polished to a mirror like finish in order to overcome the sticking of sample to the surface of the die, the main problem in pressing disks. The powder sample, about 0.05 - 0.06 g, was spread to totally cover the surface of the lower support disk placed in the die to make a sample having a weight 15-20 mg/cm<sup>3</sup>. If a thick sample disk was used, a poor IR scan result and if a too thin sample disk was employed, it would be easily cracked by thermal treating as well as broken itself. All parts of die were put together and were pressed by a manual hydraulic press at pressures of 140 -180 kg./cm<sup>2</sup> for 5 minutes. The pressure should

not be too low so that a self-supporting cannot be made. After pressing, the well-formed disk was carefully removed from the die and mounted in the IR cell.



- |                          |                       |
|--------------------------|-----------------------|
| 1. Sample Holder         | 5. Water Cooling Line |
| 2. Sample Disk           | 6. KBr Window         |
| 3. Thermocouple Position | 7. Flange             |
| 4. Heating Rod           | 8. O-ring             |

Figure 4.10 IR gas cell used for the pyridine adsorption experiment



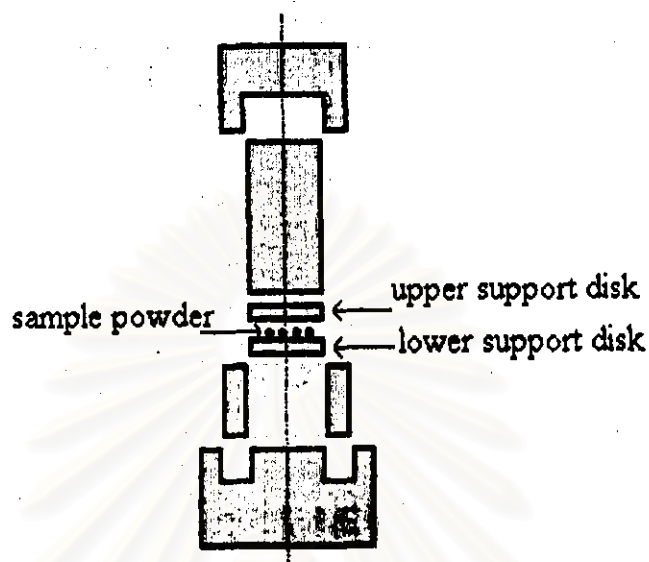


Figure 4.11 Body of the die for preparation of a self-supporting catalyst disk

#### 4.4.4 Experimental Procedure

After a well-formed sample disk is obtained, it was placed in the sample holder and then the sample holder, including sample disk, was placed into the middle of IR gas cell, locating the sample disk close to the thermocouple probe hole as possible. Once the KBr windows were sealed at both ends of the IR gas cell and leaks were not observed, the IR gas cell was evacuated by a vacuum pump through the gas line for at least 30 minutes to place the system under vacuum. The sample disk was pre-treated at 300 - 400 °C for 1 hr. under evacuation. However, since no change of the IR spectrum of the sample was found during the pre-treatment, this step sometimes ignored. Pyridine vapour was brought into contact with the disk at room temperature. Under vacuum, liquid pyridine evaporates from a pyridine tube into gas line leading through the IR gas cell. To achieve the maximum adsorption of pyridine, pyridine vapour was circulated through the system by the electro-magnetic pump for about 1 hr or until the IR spectra of pyridine peak did not change. After that, the IR cell and gas line were evacuated to remove not only pyridine vapour remaining in the

cell and gas line but also the physisorbed pyridine from the catalyst surface. The vacuum pump was operated till the IR spectra peaks of vapour pyridine and physisorbed pyridine totally vanished and there was no change in any other peaks of the spectra. This normally took spent around 1.5 hrs. Then, FT-IR measurement of the spectra of the pyridine-adsorbed sample started at room temperature and were repeated at elevated temperature in 25 °C steps.

The vacuum pump was kept running while the sample disk and the IR gas cell were heating to suck 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 hand, since the vibration would occur and bring about bad scans, the vacuum was switched off while the temperature was held constant for IR detection. The measurement was completed when all peaks of adsorbed pyridine disappeared so that the IR spectra of the sample was identical to the one before pyridine dosing.

## **4.5 Characterization of Catalysts**

### **4.5.1 X-ray diffraction patterns**

X-ray diffraction (XRD) patterns of the catalysts were performed by a X-ray diffractometer SEIMENS D5000 connected with a personal computer with Diffrac AT version 3.3 program for fully control of the XRD analyzer. The experiments was carried out by using  $\text{CuK}\alpha$  radiation and the operating condition of measurement are shown below:

2 $\theta$ range of detection	:	4 - 60°
Resolution	:	0.02°
Number of Scan	:	12

The functions of base line subtraction and smoothing were used in order to get the well formed XRD spectra.

#### 4.5.2 Specific Surface Area Measurement

Specific surface areas of the catalysts were measured by physical adsorption based on BET assumption, with nitrogen as the adsorbent using a Micromeritics model ASAP 2000 at liquid-nitrogen temperature. This unit is located at Analysis Centre of Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. The operating condition are listed as follows:

Sample weight	:	0.1 g
Degas temperature	:	150 °C
Vacuum pressure	:	< 10 $\mu$ Hg
Pressure table	:	5 points

#### 4.5.3 Chemical Analysis

##### 1) Atomic Adsorption Spectrometry(AAS)

Metal content was analyzed by the atomic absorption spectrometry (AAS) method. The catalyst was digested into solution before analysis by AAS.

About 100 mg of catalyst was digested in a 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 until the colour of the zeolite support changed to white. During the heating step, H<sub>2</sub>O had to be added to the mixture to maintain the volume. Then, 5 drops of HF were added into the mixture in order to digest the support. The heating step was repeated until the solution became clear. Then the volume of the solution was made up to 50 ml by adding de-ionized water.

The concentration of copper in the prepared solution was analyzed by AAS. The unit is located at the Scientific and Technological Research Equipment Centre, Chulalongkorn University. The obtained concentration was converted to convenient % wt. of copper per weight of catalyst by applying the calculation shown in Appendix A-3.

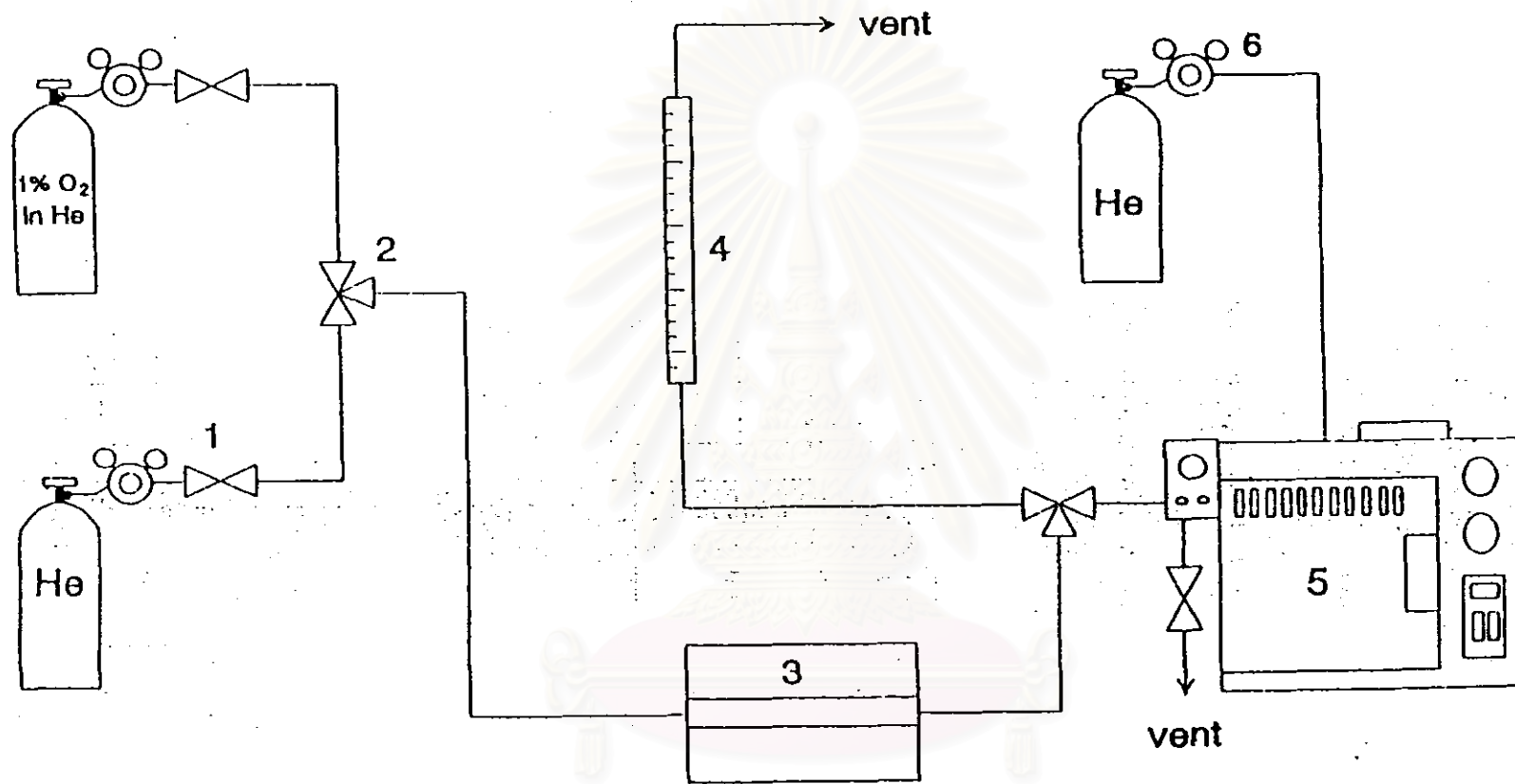
## 2) X-Ray Fluorescence Analysis (XRF)

Quantities of Na, Al, Si, and also Cu in the samples were determined by using XRF analyzer at the Science Service Department, Rama VI Road, Bangkok. About 0.5 g of catalyst sample was used for one measurement.

### 4.5.4 Temperature-Programmed Oxidation (TPO)

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 the total amount of coke on the sample by measuring the amounts of carbon dioxide produced.

The flow diagram of the TPO system is shown in Figure 4.12. The TPO 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 was controlled by a programmable temperature controller (Shino DB 1000F). The catalyst was pre-treated in the reactor with 30 ml/min. of He at 250 °C for about 4 hrs. and then cooled down to ambient temperature before starting the experiment. Then, the TPO process began by heating up the catalyst with 1% oxygen in helium gas at 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 and then at intervals of about 5 min until the temperature reached 700 °C. The catalyst sample was then cooled in argon stream.



- |                        |                       |
|------------------------|-----------------------|
| 1) On-off valve        | 4) Flow meter         |
| 2) Three way valve     | 5) Gas chromatography |
| 3) Furnace and reactor | 6) Pressure regulator |

Figure 4.12 Flow diagram of temperature-programmed oxidation experiment

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

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

#### 4.5.5 Oxygen Adsorption

The amount of oxygen adsorbed on the surface of catalysts was determined at room temperature. The chemisorp apparatus was shown in figure 4.12. The amount of oxygen in gas outlet was measured by a thermal conductivity detector(TCD) which performed under operating condition given in Table 4.5.

0.3 g of catalyst sample was placed in a stainless steel sample tube. The catalyst bed was flushed in 50 ml/min. of ultra high purity(UHP) He gas at 450 ° C for 1 hr to remove all adsorbed species from the catalyst surface. Then, the catalyst was cooled in He to room temperature. When the TCD detector was well function, 30 µl of UHP oxygen was injected to the injection port. The oxygen injection was repeated until the adsorption was complete. The chromatogram area obtained from the first injection and the constant area from the following others injections were used to determine the adsorption capacity of oxygen by the calculation method mentioned in Appendix A-6.



**Table 4.5** Operating condition of TCD gas detector for oxygen adsorption

Carrier gas flow rate (UHP He)	30 ml/min.
Detector temperature	80 °C
Detector current	80 mA

#### 4.5.6 CO Adsorption

The amount of  $\text{Cu}^{1+}$  was determined by CO adsorption based on the confirmation of Iwamoto et al.[11, 131]. The apparatus of the experiment is the same as the gas adsorption above which showed in figure 4.12. 0.2 g of the catalyst sample was packed in an 4 mm. stainless steel tube. The catalyst bed was pre-treated in 50 ml/min. of He at 450 °C for 1hr. Then, the catalyst bed was cooled down to room temperature for adsorption. Injections of 0.2 ml of CO to the bed were carried out until the adsorption was complete. Unadsorbed CO in downstream of the catalyst bed was detected by TCD. The quantity of  $\text{Cu}^{1+}$  was calculated on the basis that one site of  $\text{Cu}^{1+}$  can adsorb one molecule of CO (see Appendix A-6).

#### 4.5.7 Dealumination by Al-NMR

Quantitative analysis of alumina tetrahedral in zeolites was conformed by Al-Nuclear magnetic Resonance(Al-NMR) at National Metal and Materials Technology Center (MTEC) Rammer VI Road, Bangkok. The signal of alumina tetrahedral could be detected at around 50 ppm.