

## CHAPTER IV

### EXPERIMENTS

#### 4.1 Preparation of Na-ZSM-5 and Cu,Al-silicate

The preparation procedure of Na-ZSM-5, Cu,Al-silicate by rapid crystallization method [58] was shown in Figure 4.1, while reagents were shown in Tables 4.1 and 4.2. This method could advantageously and rapidly prepare the uniform and fine zeolitic crystals [58,59] with the following improvements : (i) the preparation of supernatant liquid was separated from that of gel, which was important to prepare the uniform crystals, (ii) the precipitated gel was milled before the hydrothermal treatment, which was essential to obtain the uniform and fine crystals, and (iii) the temperature under the hydrothermal treatment was programmed to minimize the time which was necessary for the crystallization. The detailed preparation procedures of Cu,Al-silicate and ZSM-5 were described below.

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

The source of metals for preparation of decantation and gel solutions were  $\text{AlCl}_3$  for Al and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  for Cu, 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. 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

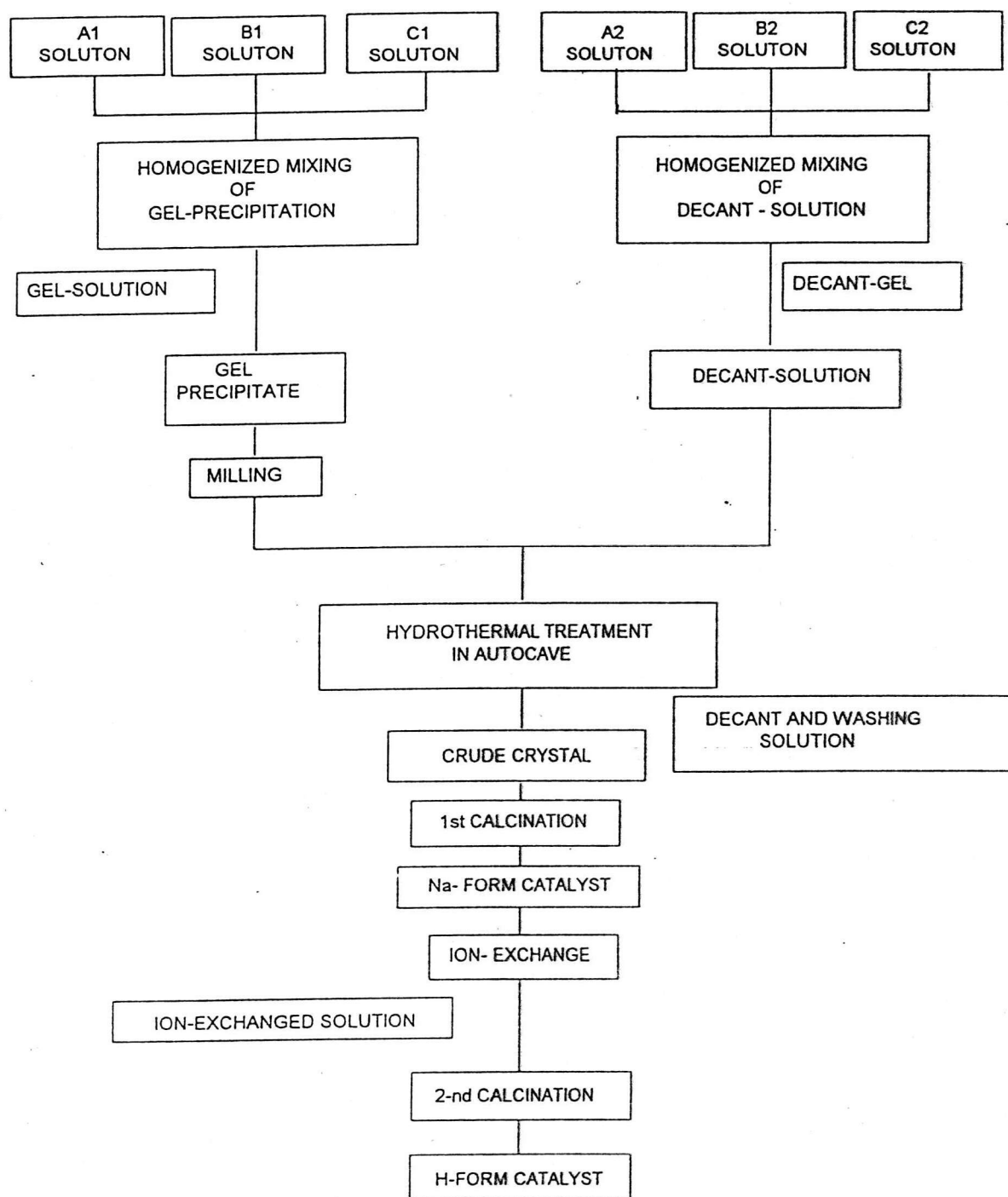


Figure 4.1 Preparation procedure of ZSM-5 and Cu,Al-silicate by rapid crystallization method [58]

Table 4.1 Reagents used for the preparation of Na-ZSM-5

| Solution for the gel preparation  | Solution for decant-solution preparation   |
|---|--|
| <u>Solution A1</u><br><br>AlCl <sub>3</sub> 0.8998 g<br>TPABr                    5.72 g<br>NaCl                      1 g<br>De-ionized water      60 ml<br>H <sub>2</sub> SO <sub>4</sub> (conc.)        3.4 ml           | <u>Solution A2</u><br><br>AlCl <sub>3</sub> 0.8998 g<br>TPABr                    7.53 g<br><br>De-ionized water      60 ml<br>H <sub>2</sub> SO <sub>4</sub> (conc.)        3.4 ml |
| <u>Solution B1</u><br><br>Sodium silicate        69 g<br>De-ionized water      45 ml  | <u>Solution B2</u><br><br>Sodium silicate        69 g<br>De-ionized water      45 ml   |
| <u>Solution C1</u><br><br>TPABr                    2.16 g<br>NaCl                      51.54 g<br>NaOH                    2.39 g<br>De-ionized water      208 ml<br>H <sub>2</sub> SO <sub>4</sub> (conc.)        1.55 ml | <u>Solution C2</u><br><br>NaCl                      26.27 g<br><br>De-ionized water      104 ml  |

Table 4.2 Reagents used for the preparation of Cu,Al-silicate catalyst.

| 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                               |
| Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O X g | Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O X g |
| TPABr 5.72 g   | TPABr 7.53 g   |
| NaCl 1 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 51.54 g   | NaCl 26.27 g   |
| NaOH 2.39 g  |  |
| De-ionized water 208 ml                                  | De-ionized water 104 ml                                  |
| H <sub>2</sub> SO <sub>4</sub> (conc.) 1.55 ml           |  |

vigorous stirring using a magnetic stirrer at room temperature . The pH of the mixed solution was maintained within 9-11, since it was expected that this pH value was suitable for precipitation [58]. The gel mixture was separated from the supernatant liquid by centrifugation. The precipitation gel mixture was milled for totally 1 hr . The milling procedures were 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 with the same method of the preparation of gel mixture. The supernatant liquids from A-2, B-2 and C-2 were mixed together with the milled gel mixture. However, before mixing, the pH of solution was adjusted to be between 9-11 with H<sub>2</sub>SO<sub>4</sub> (conc.) or 1 M NaOH solution.

#### 4.1.2 Crystallization

The mixture of the milling precipitate and the supernatant of decant solution were mixed together in a glass vessel in an autoclave. The atmosphere in the autoclave was replaced by nitrogen gas and pressurized up to 3 kg/cm<sup>2</sup> gauge. Then, 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, followed by cooling down the hot mixture to room temperature 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.

#### 4.1.3 First 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. This step was to burn off the organic template and to leave the cavities and channels in the crystals. Then, the calcined crystals were cooled to room temperature in a dessicator. After this step the catalysts formed were called Na-ZSM-5 and Na-Cu,Al-silicate, respectively.

#### 4.1.4 Ammonium ion-exchange

The ion-exchange step was carried out by mixing 3 g of the calcined crystal with 90 ml of 1 M  $\text{NH}_4\text{NO}_3$  and heated on a stirring hot plate at 80 °C for 1 h. Then, the mixture was cooled down to room temperature. Then, the ion exchange step was repeated again. After that, the ion-exchanged crystal was washed twice with deionized water by using centrifuge separator. Then, ion-exchanged crystal was dried at 110-120 °C for at least 3 h in oven. The dried crystals ( "NH<sub>4</sub>-ZSM-5" and "NH<sub>4</sub>-Cu,Al-silicate" ) were then obtained.

#### 4.1.5 Second Calcination

The removed species, i.e.  $\text{NH}_3$ ,  $\text{NO}_x$ , were decomposed by thermal treatment of the ion-exchanged crystal in a furnace at 540 °C, with the temperature same operating line as the first calcination. The catalyst formed in this step were called "H-ZSM-5" and "H-Cu,Al-silicate" for ZSM-5 and Cu,Al-silicate, respectively.

### 4.2 Cu Loading by Ion-exchange

The zeolite was ion-exchanged at room temperature using the procedure shown in Figure 4.2 [60]. Approximately 3 g of ZSM-5 zeolite was stirred with

300 ml of de-ionized water about 30 min and stand overnight, and then boiled for 3 h in new de-ionized water. This was stirred overnight. The metal exchange was carried out at room temperature overnight with 150 ml of an aqueous copper acetate solution of an adequate concentration. Example of calculation was shown in Appendix A-2. The wet cake obtained by separation from the solution was again ion-exchanged in new copper acetate solution. Finally, the ion-exchanged zeolite was washed with de-ionized water and dried at 110 °C overnight.

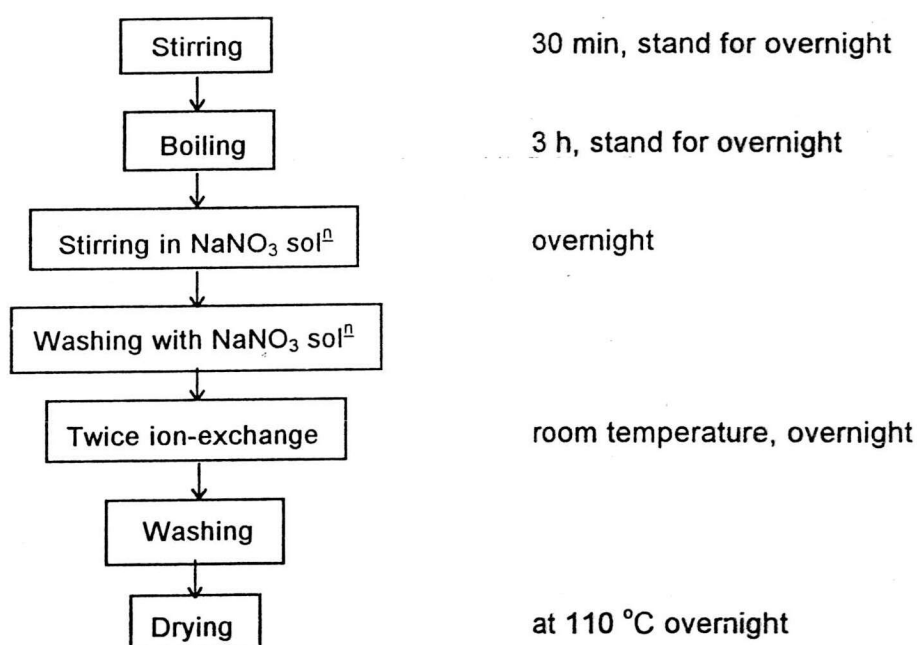


Figure 4.2 A diagram for metal ion-exchanged on catalyst [60].

### 4.3 Preparation of Coated Cu/Cu,Al-silicate on Monolith.

Activated alumina powder was mixed together with Cu/Cu,Al-silicate. The ratio of activated alumina to Cu/Cu,Al-silicate was adjusted to investigate activity of NO removal. Acetic acid solution ( 2.5 % wt. acetic acid ) was added to mixed powder with vigorous stirring at room temperature for about 1-2 minutes. Then, ceramic monolith was dipped into mixture for about 1 minute. The coated monolith was dried at 110-120 °C overnight, after blowing off extra slurry in cell of monolith by compressed air. Then, dried monolith was calcined in an air stream at 450 °C for 0.5 h by heating it from room temperature to 450 °C in 60 min.

### 4.4 Nitric Oxide Reduction

#### 4.4.1 Chemicals and Reagents

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

#### 4.4.2 Instruments and Apparatus

1. Reactor : The NO reduction reactor was a conventional microreactor made from quartz tube with 0.6 cm inside diameter. The reaction was carried out under ordinary gas flow and atmospheric pressure. The effluent gas was sampled and analyzed by an on-line gas chromatograph.

2. Automation Temperature Controller : This unit consisted 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 established a set point at any temperature within the range between 0 °C to 1000 °C.

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

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

5. Gas Chromatography : Thermal conductivity detector (TCD) gas chromatograph, SHIMADZU GC8-APT and SHIMADZU GC8-AIT, were used to analyze feed and effluent gas. Operating conditions used were shown in Table 4.3. Example of the chromatograms obtained from gas analysis was shown in Appendix B, respectively.

#### 4.4.3 Procedure

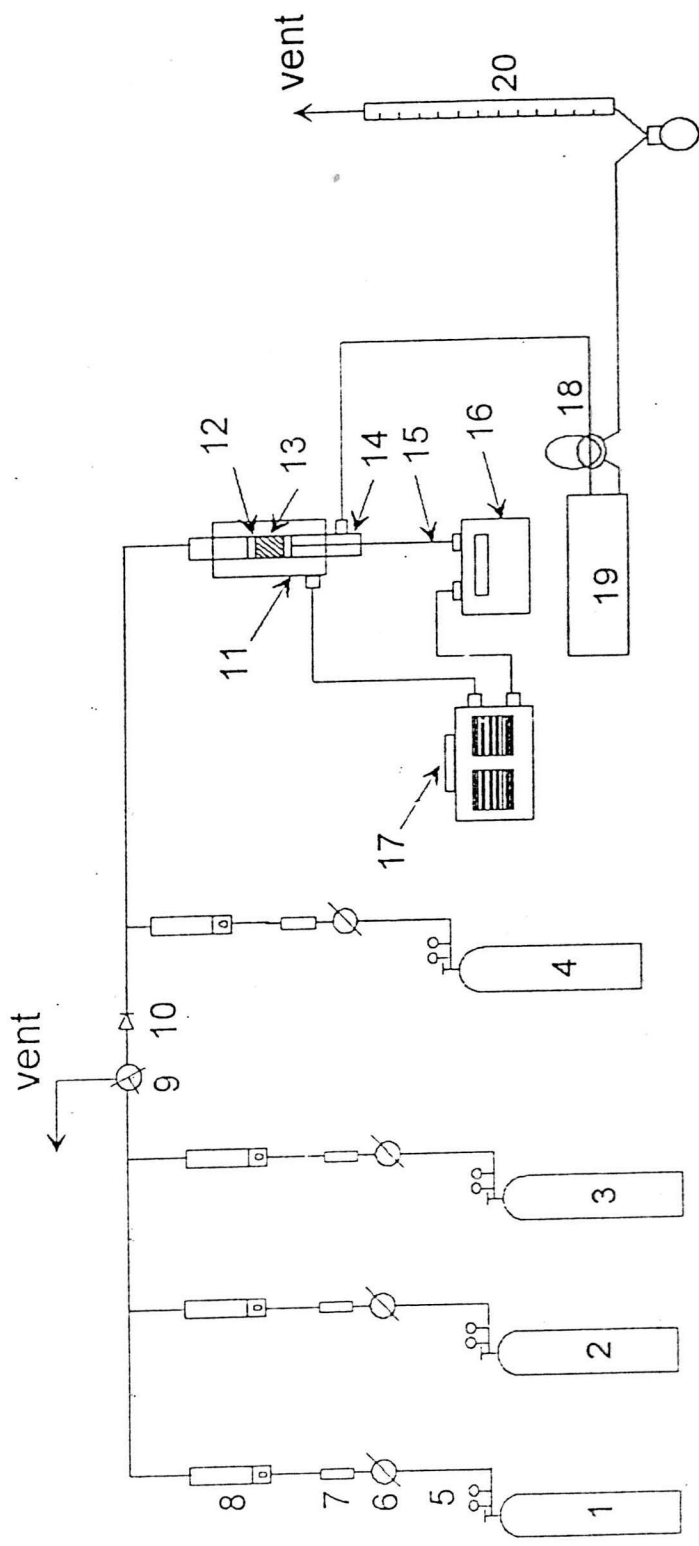
The catalytic test was carried out by using a conventional microreactor. The catalyst in powder form was tabletted with a tablet machine. It was crushed and sieved to 8-16 mesh to be used for the reaction. A 0.5 g portion of the catalyst was packed in a quartz tube reactor and the catalyst-bed length was 30 mm. It was heated at room temperature to 500 °C for 1 h under a He stream (35 cm<sup>3</sup>/min), held at this temperature for 1 h, and then cooled down to room temperature. A gas mixture containing NO (1000 ppm), C<sub>3</sub>H<sub>8</sub> (1000 ppm), O<sub>2</sub> (10 volume %) , and He balance was fed at a flow rate of 50 cc/min (GHSV ~ 4,000 h<sup>-1</sup>). The reaction gas was introduced at temperature range from 150 to 600 °C. The samples of reaction

and product gases were taken for the concentration measurement. The gas samples were analyzed by using a gas chromatograph, using Porapak-Q ( $\text{CO}_2$  and  $\text{C}_3\text{H}_8$ ) and Molecular Sieve-5A ( $\text{O}_2$ ,  $\text{N}_2$  and  $\text{CO}$ ) columns. Each gas chromatograph was equipped with Shimadzu C-R6A integrator. The concentration of  $\text{C}_3\text{H}_8$  at the inlet and outlet stream were therefore analyzed for  $\text{C}_3\text{H}_8$  combustion. The conversion of NO was calculated based on the concentration of  $\text{N}_2$  formed. Examples of calculation were shown in Appendix A-4. The flow diagram of nitric oxide reduction system was shown in Figure 4.3 .

Table 4.3 Operating conditions of gas chromatograph

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             | $\text{O}_2$ , $\text{N}_2$ , $\text{CH}_4$ , $\text{CO}$ | $\text{C}_3\text{H}_8$ , $\text{CO}_2$ |



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

Figure 4.3 Flow diagram of the nitric oxide reduction system

## 4.5 Characterization of the Catalysts

### 4.5.1 X-ray Diffraction Patterns

X-ray powder diffraction (XRD) was used to obtain information about the structure, composition, and state of polycrystalline materials. Schematic of an x-ray diffractometer was illustrated in Figure 4.4 [61]. Before testing, the sample was mounted in an automatic sample changer. After that, the sample was placed in X-ray diffractometer. The beam of monochromatic x-radiation was directed at the sample. The reflection or diffraction of the x-rays was observed at various angles with respect to the primary beam. The diffraction pattern of the prepared catalyst was compared with the standard diffraction pattern. In this study, the standard diffraction pattern was XRD patterns of H-ZSM-5 of Mobil Oil Corporation [64].

X-ray Diffraction (XRD) patterns of the prepared catalysts were performed by using Rigaku-Denki Geigerflex-2013 with Ni-filtrated monochromatic  $\text{CuK}\alpha$  radiation. Unit cell parameters were obtained by least square fit to the interplanar spacing of 25-28 reflections, accurately measured in the  $13\text{-}46^\circ$   $2\theta$  angular region, using  $\alpha$ -alumina as an internal standard. XRD patterns were analyzed at Sedimentology laboratory of Department of Geology, Faculty of Science, Chulalongkorn University.

### 4.5.2 Specific Surface Area and Pore Size Distribution Measurement

BET surface area and pore size distribution measurement were determined by using gas adsorption techniques. Flow diagram of continuous flow gas adsorption apparatus was depicted in Figure 4.5 [61]. The surface area of the catalysts were measured by nitrogen adsorption with continuous flow method at the liquid nitrogen temperature. Helium was used as the carrier gas. The steps of

- A: Collimation Assembly
- B: Sample
- C: Slit
- D: Exit Beam Monochromator
- E: Detector
- X: Source of X-Rays

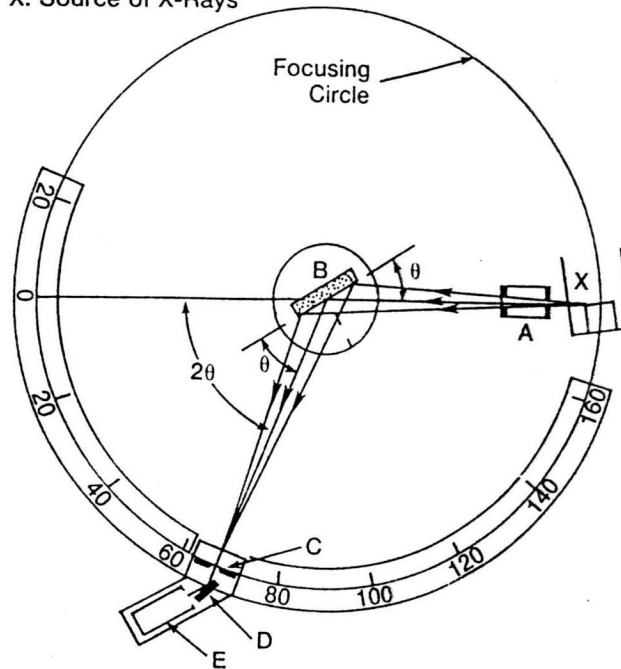


Figure 4.4 Schematic of an x-ray diffractometer[61].

measurement were as follows : The sample was heated and placed under vacuum to remove the moisture and the other contaminants before analysis. After this step, the catalyst was weighted. Then, the sample was automatically analyzed and it must have an information file assigned to it. The amount of gas needed to form a monomolecular layer on the surface of sample could be determined from measurements of the volume of gas adsorbed. The BET (Brunauer, Emmett, and Teller) equation was used for surface area calculation.

The BET surface areas and pore size distribution of the prepared catalysts were measured by a micrometrics model ASAP 2000 at Analysis Centre of Department of Chemical Engineering , Faculty of Engineering , Chulalongkorn University.

#### 4.5.3 Chemical Analysis

Atomic absorption spectroscopy (AAS) was a technique for determining the concentration of metallic elements in solution. Schematic of an atomic absorption spectrometer was shown in Figure 4.6 [61].

The prepared catalysts were dissolved by 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 heating step, H<sub>2</sub>O had to be added into the mixture in order 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 continued until the solution became clear. Then volume of the solution was made up to 50 ml by adding de-ionized water.

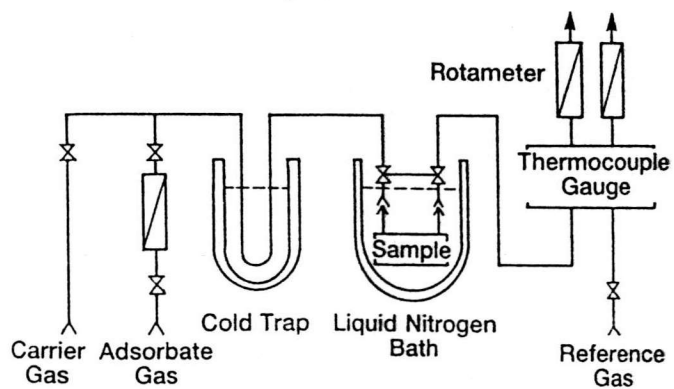


Figure 4.5 Continuous flow gas adsorption apparatus [61]

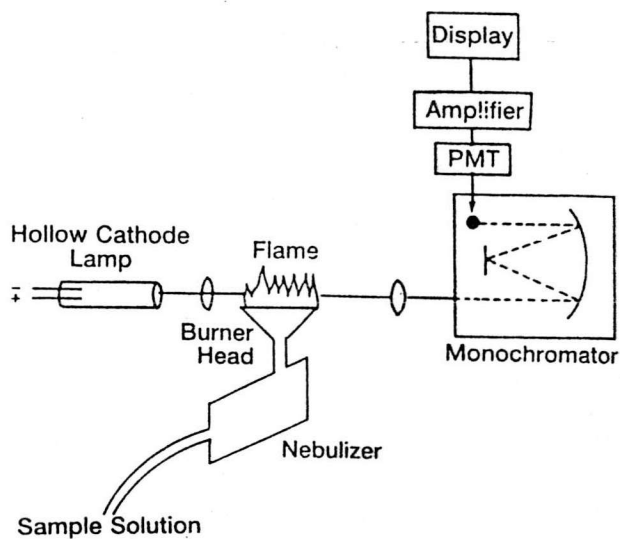


Figure 4.6 Schematic of an atomic absorption spectrophotometer [61]

The prepared solution was tested by spectrophotometer (Shimadzu atomic absorption / flame emission spectrophotometer AA-640-01) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University. An emission source, a hollow cathode lamp, produced the line spectrum of a particular element. The prepared solution was vaporized. When a specific wavelength of this radiation was passed through the vapor, some of this radiation was absorbed. The decrease in the signal observed by the photomultiplier tube was a function of the quantity of the element in the vapor.