

## CHAPTER IV

### EXPERIMENTS

#### 4.1 Preparation of ZSM-5 and Co,Al-silicate [12]

The preparation procedure of ZSM-5, and Co,Al-silicate by rapid crystallization method was shown in Figure 4.1, while reagents were shown in Table 4.1. This method could advantageously and rapidly prepare the uniform and fine zeolite crystals 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 detail preparation procedures of Co,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  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  for Co, respectively. TPABr (Tetra-*n*-Propyl Ammonium Bromide,  $(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NBr}$ ) 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

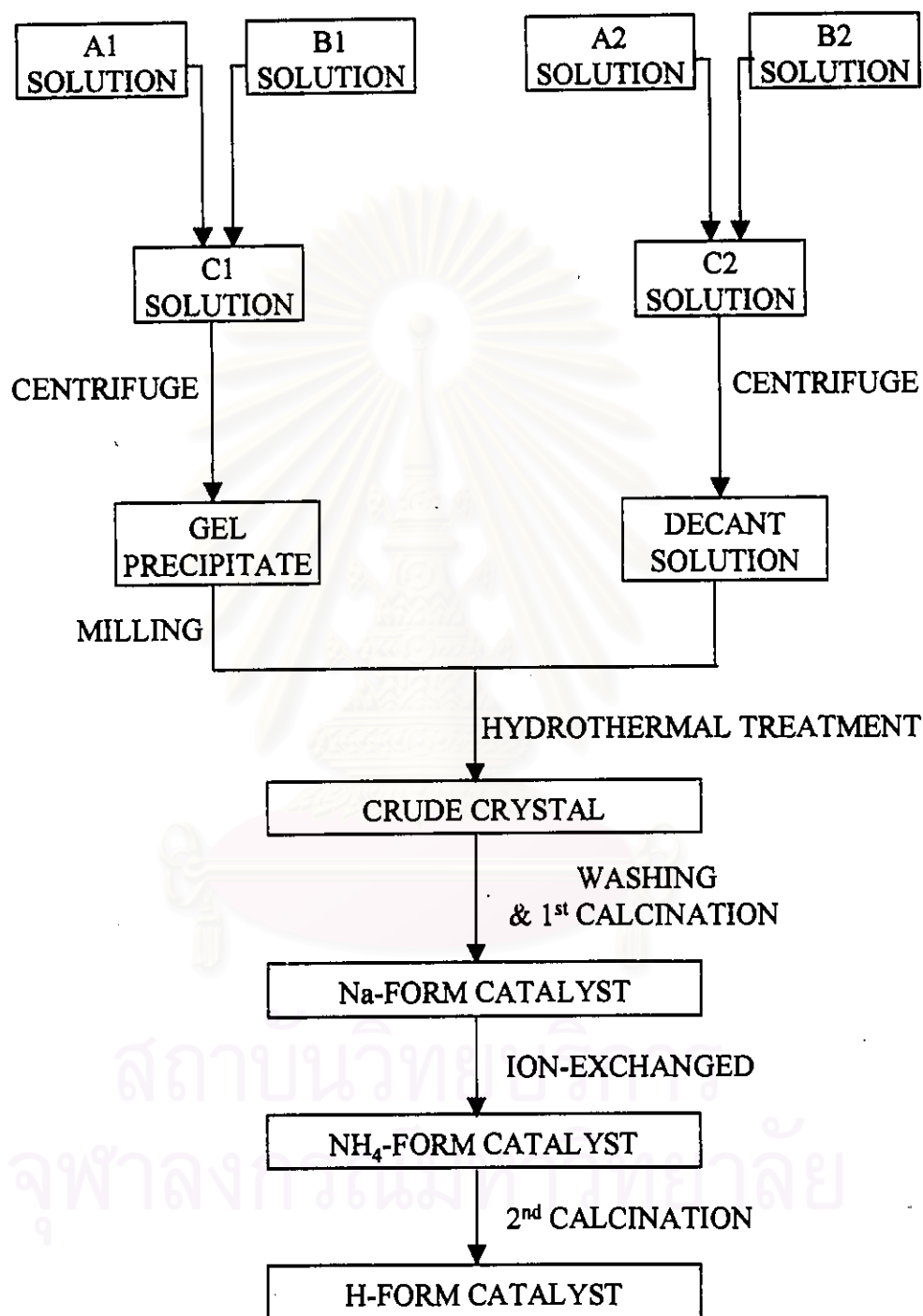


Figure 4.1 preparation procedure of ZSM-5 and Co,Al-silicate by rapid crystallization method [12]

Table 4.1 Reagent required for the preparation of ZSM-5 and Co,Al-silicate

Solution for the gel preparation	Solution for the decant preparation
<b><u>A1 Solution</u></b>	<b><u>A2 Solution</u></b>
AlCl <sub>3</sub> 0.8998 g	AlCl <sub>3</sub> 0.8998 g
Co(CH <sub>3</sub> COO) <sub>2</sub> .4H <sub>2</sub> O 0-7.2442 g	Co(CH <sub>3</sub> COO) <sub>2</sub> .4H <sub>2</sub> O 0-7.2442 g
TPABr 5.72 g	TPABr 7.53 g
H <sub>2</sub> O 60 ml	H <sub>2</sub> O 60 ml
conc. H <sub>2</sub> SO <sub>4</sub> 3.4 ml	conc. H <sub>2</sub> SO <sub>4</sub> 3.4 ml
NaCl 1.0 g	
<b><u>B1 Solution</u></b>	<b><u>B2 Solution</u></b>
Na <sub>2</sub> O.SiO <sub>2</sub> .H <sub>2</sub> O 69 g	Na <sub>2</sub> O.SiO <sub>2</sub> .H <sub>2</sub> O 69 g
H <sub>2</sub> O 45 ml	H <sub>2</sub> O 45 ml
<b><u>C1 Solution</u></b>	<b><u>C2 Solution</u></b>
TPABr 2.16 g	
NaCl 51.54 g	NaCl 26.27 g
NaOH 2.39 g	
H <sub>2</sub> O 208 ml	H <sub>2</sub> O 104 ml
conc. H <sub>2</sub> SO <sub>4</sub> 1.55 ml	

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 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. The gel mixture was separated from the supernatant liquid by centrifugation. The precipitation gel mixture was milled for totally 45 min. The milling procedures were as follows: milled 15 min → centrifuge (to remove the liquid out) → milled 15 min

→ centrifuge → milled 15 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 liquid from A-2, B-2 and C-2 was mixed together with the milled gel mixture. However, before mixing, the pH of solution was adjusted to be between 9-11 with  $\text{H}_2\text{SO}_4(\text{conc.})$  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  $\text{kg/cm}^2$  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/hr, 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 time by using the centrifugal separator (about 15 min for each time) to remove  $\text{Cl}^-$  out of the crystals, and dried in an oven at 110 °C for at least 3 hr.

#### 4.1.3 First Calcination

The dry crystals were calcined in an air stream at 540 °C for 3.5 hr 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-Co,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 hr. Then, the mixture was cooled down to room temperature. After that, the ion-exchange step was repeated twice. Next, the ion-exchanged crystal was washed twice with de-ionized water by using centrifuge separator. Then, ion-exchanged crystal was dried at 110-120 °C for at least 3 hr in oven. The dried crystals (“ $\text{NH}_4$ -ZSM-5” and “ $\text{NH}_4$ -Co,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-Co,Al-silicate” for ZSM-5 and Co,Al-silicate, respectively.

## 4.2 Co Loading by Ion-exchange

A suitable metal-exchange technique comprises contacting the zeolite with a solution which contains the salt of the desired replacing cation. Examples of suitable salts include the halides such as chlorides, nitrates, carboxylates and sulfates. A preferred exchange solution is cobalt(II) acetate [13]. Approximately 3 g of Na-form catalyst was stirred with 150 ml of a dilute (0.01 M) cobalt(II) acetate solution. The metal exchange was typically carried out at 80 °C for 24 hr. More repeats of ion-exchanged step were required upon the amount of cobalt needed. The wet cake obtained by separation from the solution was washed with de-ionized water and dried at 110 °C overnight. The Co ion-exchanged H-form zeolite was made by exchanging  $\text{Co}^{2+}$  into an  $\text{NH}_4$ -form catalyst followed by heating a metal exchanged  $\text{NH}_4$ -form zeolite in helium at 500 °C for 1 hr [3].

## 4.3 Nitric Oxide Reduction

### 4.3.1 Chemicals and Reagents

Nitric oxide (1% by vol.) in helium, Methane (10% by vol.) in helium, Oxygen of ultra high purity grade (99.999% by vol.) and Helium with the same grade as Oxygen (99.999% by vol.) were provided by Thai Industrial Gases Limited.

### 4.3.2 Instruments and Apparatus

1. Reactor: The NO reduction reactor was a conventional micro-reactor 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 to 999 °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 600 °C at maximum voltage of 220 volts.

4. Gas Controlling System: Nitric oxide, methane, 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-ATP was used to analyze feed and effluent gas. Operating condition used was shown in Table 4.2.

Table 4.2 Operating condition of gas chromatograph SHIMADZU 8ATP

Detector	TCD
Packed column	MS-5A
Carrier gas	He (99.999 %)
Flow rate of carrier gas	40 ml/min
Column temperature	70 °C
Detector temperature	100 °C
Injector temperature	100 °C

#### 4.3.3 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 about 35 mm. It was heated at room temperature to 500 °C in 1 hr under He stream (35 cm<sup>3</sup>/min), held at this temperature for 1 hr, and then cooled down to room temperature. A gas mixture containing NO (1000 ppm), CH<sub>4</sub> (1 vol %), O<sub>2</sub> (10 vol %), and He balance was fed at a total flow rate of 50 cm<sup>3</sup>/min (GHSV ~ 4000 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 gas chromatograph with Molecular Sieve-5A (for O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO) columns. The gas chromatograph was equipped with Shimadzu C-R6A integrator. The concentration of CH<sub>4</sub> before and after the reaction were analyzed for CH<sub>4</sub>



consumption. The conversion of NO was calculated based on the concentration of N<sub>2</sub> formed.

#### **4.4 Characterization of the catalysts**

##### **4.4.1 X-ray Diffraction patterns**

X-ray powder diffraction (XRD) was used to obtain information about the structure, composition, and state of polycrystalline materials. Before testing, the sample was mounted in a sample holder. 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-ray 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.

XRD patterns of the prepared catalysts were performed by using SIEMENS XRD D5000 diffractometer, accurately measured in the 4-40° 2θ angular region, at laboratory of Petrochemical Research group, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

##### **4.4.2 Morphology**

The shape and size of the crystals of prepared catalysts were observed by using JEOL JSM-35 CF Scanning Electron Microscope (SEM) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC).

#### 4.4.3 Chemical Analysis

Atomic absorption spectroscopy (AAS) was a technique for determining the concentration of metallic elements in solution.

The prepared catalysts were dissolved by following procedure: A certain amount of catalyst (about 0.1 g) was digested by digesting solution containing 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 to white. During heating, H<sub>2</sub>O had to be added into the mixture in order to maintain the volume of the 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. Finally, the volume of the solution was made up to 50 ml by adding 1 % by vol of HCl in volumetric flask.

The prepared solution was tested by spectrometer (Shimadzu atomic absorption/flame emission spectrometer AA-640-01) at the Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC). 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.

#### 4.4.4 FT-IR pyridine adsorption [73]

Infrared spectroscopy and temperature programmed desorption of pyridine have been used to investigate the acidic properties of MFI-type zeolites.

The catalyst (0.06 g) was pressed into self-supporting wafer and placed into a quartz in situ IR gas cell with sample disk holder. The gas cell was attached with two KBr windows at both ends. Prior to adsorption the sample was evacuated to about  $10^{-4}$  torr at 500 °C for 1 hr and then cooled down to room temperature in vacuum. Pyridine was introduced into the IR cell by self vaporizing in vacuum condition and was circulated through the system by an electromagnetic pump. After 1 hr of adsorption, the excess and weakly adsorbed pyridine was removed by evacuating at 100 °C for 30 min to ca.  $10^{-4}$  torr. Presumably only the chemisorbed pyridine remained on the surface. Desorption was then continued by evacuation at progressively higher temperature, every 50 °C, and IR spectra were recorded on a Nicolet Impact 400 FT-IR equipped with a deuterated triglycine sulfate (DTGS) detector at the various stages of desorption. Each spectrum consisted of 500 scans at a resolution of  $4\text{ cm}^{-1}$ . Background spectra, i.e., prior to adsorption, were subtracted from all spectra such that the effects of adsorption and thermal treatments could be more clearly seen. All of these procedures were conducted at laboratory of Petrochemical Research group, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University.

#### 4.4.5 Temperature Programmed Reduction, TPR [23,38]

Temperature programmed reduction, TPR, is used to investigate the reducibility of catalyst and also can use to evaluate the extra-lattice oxygen on the catalyst surface by observing the amount of hydrogen used. The main product, water vapor, is trapped before the reaction gas entering the detector. The amount of hydrogen consumption is monitoring by the thermal conductivity detector, TCD. The operating condition of the TCD apparatus which was set up at laboratory of Petrochemical Research group, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University is shown in table 4.3

Table 4.3 Operating condition of the TCD for TPR

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

Catalyst sample, 0.2 g, was placed in a sample tube. Prior to the measurement the sample was in situ pretreated in air with flow rate of 100 ml/min and with the temperature ramped rate of 10 °C/min to 500 °C. Hold for 1 hr to ensure the surface was covered with oxide form. Then switch to He gas flow through the sample, 100 ml/min, at 500 °C for 10 min then cooled down (in He) to room temperature. After calcination, the sample was purged with the mixture gas of H<sub>2</sub>/Ar, 50 ml/min, until

reach the steady state. After that, the TPR program was started by mean at 100 °C, and allowed the temperature to increase up to 750 °C at ramped rate of 10 °C/min

#### 4.4.6 CO adsorption for determination of catalyst active site

the active sites was measured by CO adsorption technique on the basis that one CO molecule adsorbed on one active site. The amount of CO adsorbed on the catalyst was measured by the thermal conductivity detector at laboratory of Petrochemical Research group, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University. The operating condition of the TCD is illustrated in table 4.4

Table 4.4 Operating condition of the TCD for CO adsorption

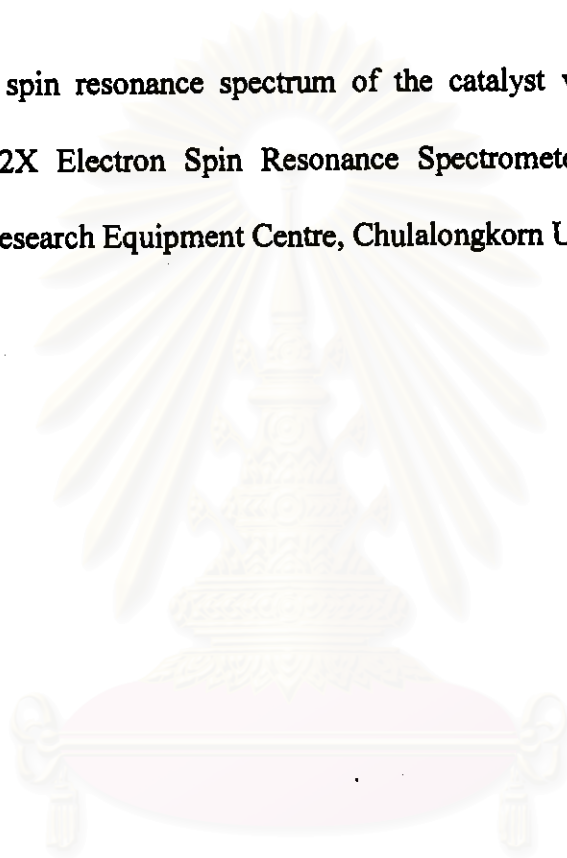
Helium carrier gas flow rate	30 ml/min
Detector temperature	80 °C
Detector current	80 mA

0.1 g of catalyst was placed in the stainless tubular reactor. Helium gas was introduced into the reactor at the flow rate of 30 ml/min. The reactor was heated with an increasing rate of 10 °C/min unit the temperature reached 500 °C and hold at this temperature for 1 hr. After cooling down to room temperature, the catalyst was ready to measure active sites. 40 µl of the CO was injected to reactor at the injection port located before the catalyst bed. The CO gas injection was repeated until the sample

did not adsorb the CO gas. The amount of active sites of catalyst was calculated by the amount of adsorbed CO gas ( see Appendix A ).

#### 4.4.7 Electron Spin Resonance, ESR

Electron spin resonance spectrum of the catalyst was conducted by using JEOL JES-RE 2X Electron Spin Resonance Spectrometer at the Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC).



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