

## CHAPTER IV

### EXPERIMENTAL

#### 4.1 Catalyst preparation

For this study, synthesized five of ZSM-5 zeolite catalyst such as Si/Al, Si/Ga, Si/Fe, Si/Zn and Silicalite by using the same Si/Al or Si/Metal ratio (Si/Al = 25 or Si/Metal =25) and used aluminosilicate (Al / HZSM-5) and metal silicate (Me / HZSM-5) were prepared for the hydrothermal treatment, scanning electron microscope and X-ray diffraction. The preparation of Al / HZSM-5 and Me / HZSM-5 were described as follow.

##### 4.1.1 Preparation of Na-ZSM-5

The procedure of preparation of ZSM-5 by rapid crystallization method [71, 72] was shown in Figure 4.1 and the chemical reagent were shown in Table 4.1. That this method could be rapidly prepare the uniform and fine zeolite crystals with the following in these methods (i) the preparation of supernatant liquid was separated from gel, which was important to prepare the uniform crystal (ii) the precipitated gel was milled before the hydrothermal treatment which was essential to obtain the uniform and fine crystals and (iii) the hydrothermal treatment is under temperature program to minimize time which was necessary for the crystallization. The detail of preparation procedure of ZSM-5 were described below.

##### 4.1.1.1 Preparation of gel precipitation and decantation solution

Gel mixture was separated from supernatant liquid that is important for preparing the uniform crystals and gel mixture was prepared by adding solution A-1 and solution B1 into solution C-1 by dropping and vigorous stirring using magnetic stirrer at room temperature. The pH must be controlled within the range 9-11 because of it was expected that this pH range is suitable for precipitation after that gel mixture

was separated from supernatant liquid by centrifuge. The precipitated gel mixture was milled for 1 hr. by a powder miller (Yamato-Notto, UT-22) by procedure as this follows: centrifuge 15 min – milled 15 min – centrifuge 15 min – milled 15 min – centrifuge 15 min – milled 30 min – centrifuge 15 min. So, gel mixture must be milling before the hydrothermal treatment because of it was essential to obtain the uniform and got fine crystal.

For the decantation solution was prepared by adding solution A-2 and solution B-2 into C-2 by using same method gel mixture preparation. At the same time the supernatant liquid from A-2, B-2, C-2 was mixing together. And it must be control pH between 9-11 by using  $\text{H}_2\text{SO}_4$  (conc.) or 1M NaOH solution and supernatant liquid was separate from mixture by sedimentation and centrifuge

#### 4.1.1.2 Crystallization

Milled precipitate mixture and supernatant of decant solution was charged in 500 ml of pyrex glass container. The glass container was placed in a stainless steel autoclave. The air in the autoclave was replaced by nitrogen gas by pressure up to 3  $\text{kg/cm}^2$  gauge. The mixture in the autoclave was heated from room temperature to  $160^\circ\text{C}$  with the heating rate  $2^\circ\text{C}/\text{min}$  and then up to  $210^\circ\text{C}$  with the heating rate  $12^\circ\text{C}/\text{hr}$  ( $2^\circ\text{C}/10\text{ min}$ ) while stirred at 50 rpm. After that, cooling hot mixture to room temperature in the autoclave overnight. The crystallization is under temperature program. The crystal products were washed with de-ionized water about 8 times using the centrifuge separator (about 15 min for each time) to remove  $\text{Cl}^-$  from the crystals and dried in an oven at  $110^\circ\text{C}$  for at least 3 hr.

#### 4.1.1.3 Calcination

The dry crystals were calcined in air steam at  $540^\circ\text{C}$  for 3.5 hr by heating from room temperature to  $540^\circ\text{C}$  in 1 hr to burn off the organic template and leave the cavities and channels in the crystals. The calcined crystals were cooled to room temperature. Finally, 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.

For each batch, Na-ZSM5 was checked by X-ray diffraction (XRD) analysis to confirm the ZSM-5 structure and crystallinity of the sample. If, unfortunately, the XRD pattern could not be acceptable, the sample would be discarded and a new sample has to be made.

#### 4.1.2 Ammonium ion-exchanged

To make the parent Na-ZSM5 powder to  $\text{NH}_4$ -ZSM5 by using 1M  $\text{NH}_4\text{NO}_3$  solution at 30 ml per 1 g of catalyst. In the procedure, the catalyst did not use exceed 5 grams to approach complete exchange. The slurry of zeolite and solution was stirred and heated on a hot plate, then maintained at  $80^\circ\text{C}$  by reflux and maintain this temperature 1 hr. After that the mixture was cooled down to room temperature and centrifuged to removed the used solution. In the same amount of  $\text{NH}_4\text{NO}_3$  solution were mixed again with remained crystals by the previous step was repeated. The exchanged crystals were washed twice with deionized water using centrifuge. After that the exchanged crystals were dried in an oven at  $110$ - $120^\circ\text{C}$  for at least 3 hr. The dried catalyst obtained is the  $\text{NH}_4$ - form of ZSM-5. The  $\text{NH}_4$ -ZSM5 was converted to H- form ZSM-5 by removing  $\text{NH}_3$  species from the catalyst surface. The thermal treatment was removed  $\text{NH}_3$  from  $\text{NH}_4$ -ZSM-5 seolite by using furnace from ambient temperature to  $540^\circ\text{C}$  in 1 hr. for heating the crystals and hold the sample at  $540^\circ\text{C}$  for 3.5 hr. After that the crystal was cooled down and it was stored in a glass bottle for further use

#### 4.2 Pretreatment condition

In this study concerns the pretreatment procedure by using the hydrothermal treatment condition. The catalyst were pretreated in He while temperature up from room temperature to  $600^\circ\text{C}$  with heating rate  $10^\circ\text{C}/\text{min}$ . The catalyst samples were kept at  $600^\circ\text{C}$  for 24 hr. while adding 10% mole of water vapor and the catalysts were cooled down to room temperature in the He stream.

**Table 4.1** Reagents used for the preparation of Na-ZSM-5 : Si/Al = 25

Solution for the gel Preparation		Solution for decant – solution Preparation	
<u>Solution A1</u>		<u>Solution A2</u>	
AlCl <sub>3</sub>	1.654 g	AlCl <sub>3</sub>	1.654 g
Silicalite	w g	Silicalite	w g
Zn (NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	x g	Zn (NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	x g
FeCl <sub>3</sub> .6H <sub>2</sub> O	y g	FeCl <sub>3</sub> .6H <sub>2</sub> O	y g
Ga (NO <sub>3</sub> ) <sub>3</sub>	z g	Ga (NO <sub>3</sub> ) <sub>3</sub>	z 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		

w, x, y, z are shown in Appendix A-1

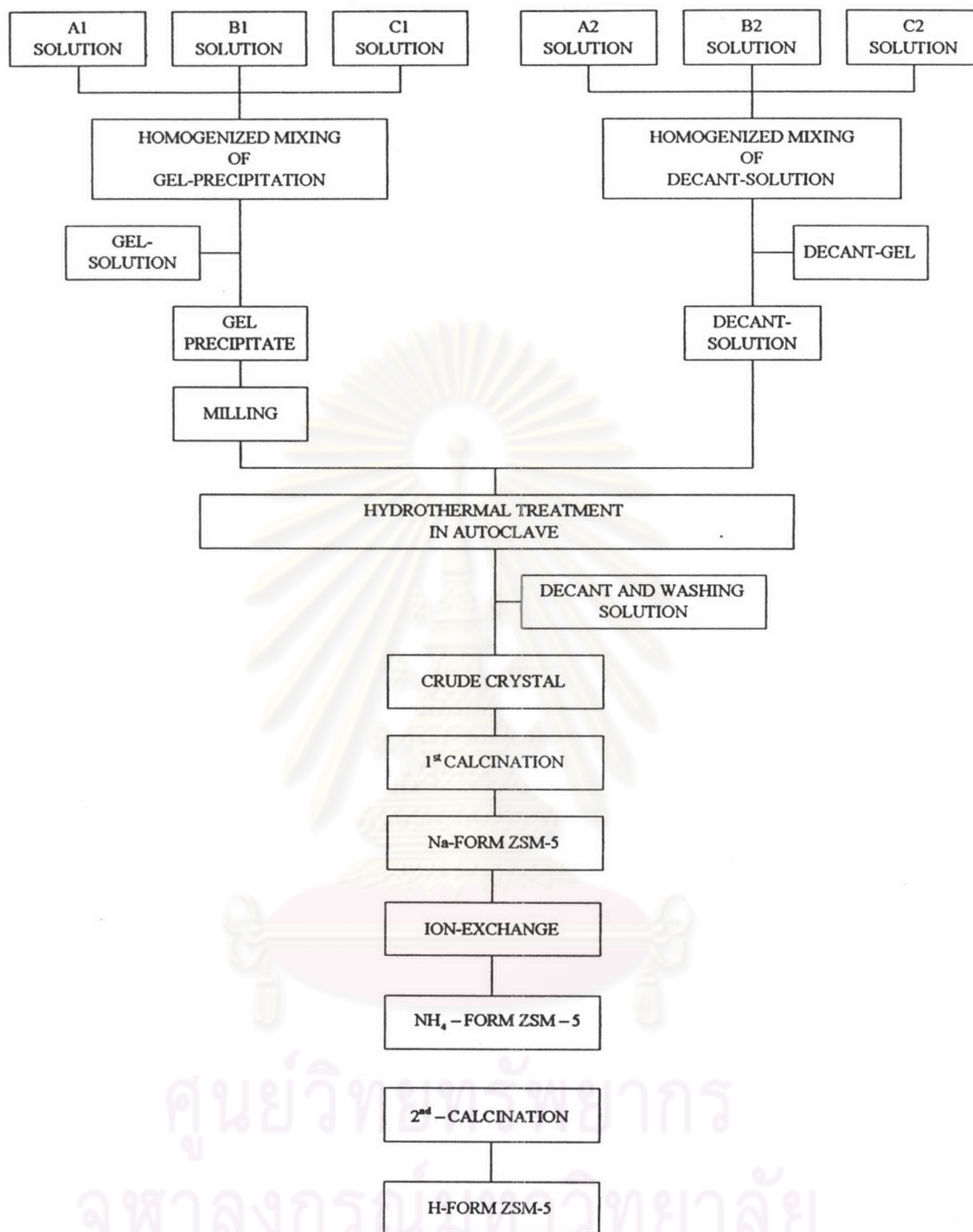


Figure 4.1 The preparation procedure of ZSM-5 by rapid crystallization method.

### 4.3 Characterization of the catalysts

#### 4.3.1 X-ray Diffraction analysis (XRD)

The crystallinity and X-ray diffraction (XRD) patterns of the catalyst were performed by X-ray diffractometer SEIMENS D 5000 connected with a personal computer with diffract AT version 3.3 program for fully control of the XRD analyzer. The experiments was carried out by using  $\text{CuK}\alpha$  radiation with Ni filter and the operating condition of measurement are shown below:

$2\theta$  range of detection : 4-60°  
Resolution : 0.04°  
Number of scan : 10

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

#### 4.3.2 Scanning Electron Microscope (SEM)

JEOL JSM-35 CF Scanning Electron Microscope (SEM) at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC) analyzed shape and size of the crystal of the prepared catalysts.

#### 4.3.3 X-Ray Fluorescence analysis (XRF)

Quantities of Al, Si, Zn, Fe and Ga 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.

#### 4.3.3 FT-IR Infrared Spectroscopy

The vibrational spectroscopy of the catalyst was measured by FT-IR Infrared spectroscopy at Nation Metal And Materials Technology Center.

#### 4.3.4 $^{29}\text{Si}$ and $^{27}\text{Al}$ Magnetic Angle Spinning Nuclear Magnetic Resonance ( $^{29}\text{Si}$ , $^{27}\text{Al}$ MAS NMR)

Quantitative analysis of silicon tetrahedral in zeolites was conformed by  $^{29}\text{Si}$  and  $^{27}\text{Al}$  magnetic angle spinning nuclear magnetic resonance ( $^{29}\text{Si}$ ,  $^{27}\text{Al}$  MAS NMR, BRUKER DPX-300 spectroscopy operating at 78.2 MHz) at National Metal and Materials Technology Center (MTEC) Paholyothin Road, Pathumthani. The signal of Silicon tetrahedral could be detected at around 50 ppm.

#### 4.3.5 TPD ( $\text{NH}_3$ ) curve

TPD ( $\text{NH}_3$ ) curve of metallosilicate catalysts were measured at PTT.

#### 4.3.6 FT-Raman Spectroscopy

The vibration spectroscopy of the catalyst was measured by FT-Raman Spectroscopy at Nation Metal and Materials Technology center.



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