

CHAPTER IV

EXPERIMENTAL

4.1 Catalyst Preparation

In this study, four of Co-ZSM-5 catalysts, having different Si/Al ratio (50,80,50,150). Co-ZSM-5 was prepared for methanol conversion to light olefins. This catalyst used for selected the best catalyst for various particle sizes. The preparation of Co-ZSM-5 was described as follows:

4.1.1 Chemicals

The details of chemicals used in the preparation procedure of ZSM-5 were shown in Table 4.1

Table 4.1 The chemicals used in the catalyst preparation

Chemical	Supplier
-Tetrapropyl ammonium bromide (TPABr)	Aldrich
-Sodium silicate Solution (SiO ₂ 25.5-28.5)	Merck
-Sodium hydroxide [NaOH]	Merck
-Aluminium chloride [AlCl ₃]	Aldrich
-Cobalt (II) nitrate	Aldrich
-Sodium hydroxide (NaOH)	Merck
-Sulfuric acid (98.08%)	J.T. Baker

4.1.2 Preparation of Na-ZSM-5 (MFI)

The preparation procedure of Na-ZSM-5 by rapid crystallization method was shown in Figure 4.1, while reagents were shown in table 4.2. This method can

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 Na-ZSM-5 were described below.

Table 4.2 Reagents used for the preparation of Na-ZSM-5: Si/Al = 50

Solution for the gel preparation		Solution for the decant-solution preparation	
<u>Solution A1</u>		<u>Solution A2</u>	
AlCl ₃	0.8831g	AlCl ₃	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 ₂ SO ₄	3.4 ml
H ₂ SO ₄	3.4 ml		
<u>Solution B1</u>		<u>Solution B2</u>	
De-ionized water	45 ml	De-ionized water	45 ml
Sodium silicate	69 g	Sodium silicate	69 g
<u>Solution C1</u>		<u>Solution C3</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 ₂ SO ₄	1.55 ml		

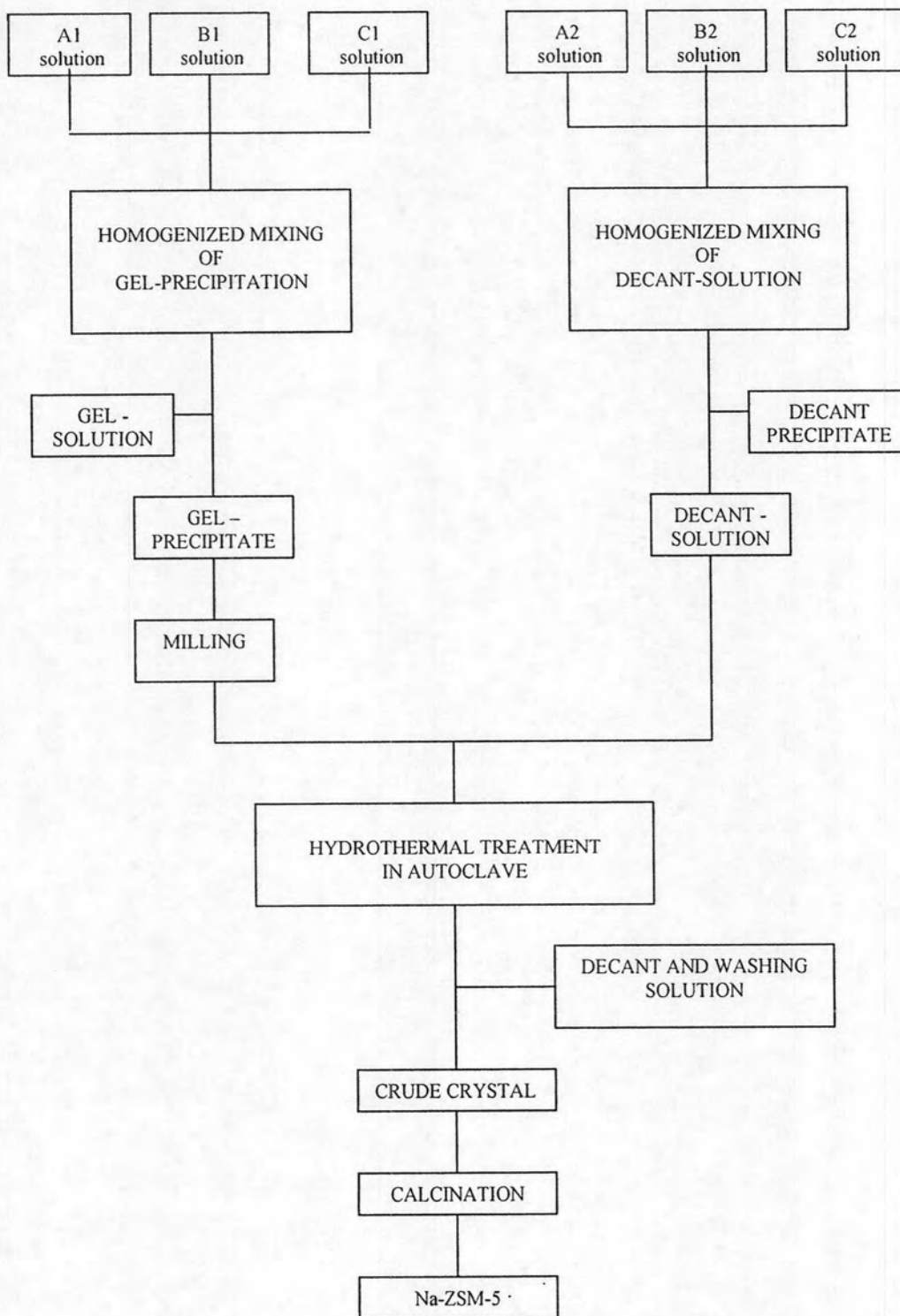


Figure 4.1 The preparation procedure of Na-ZSM-5 by rapid crystallization method.

4.1.2.1 Preparation of Gel Precipitation and Decantation Solution

A supernatant liquid was separated from the gel, which was important for preparing the uniform crystals. A gel mixture was prepared by adding solution A-1 and solution B-1 into solution C-1 drop wise with vigorous stirring using a magnetic stirrer at room temperature. The pH of the mixed solution was maintained within the range 9-11 because it was expected that this pH range was suitable for precipitation. The gel mixture was separated from the supernatant liquid by a centrifuge. The precipitated gel mixture was milled for 1 h by a powder miller. The milling procedure was 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, 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 is mixing together. The pH of the solution was adjusted to between 9-11. H_2SO_4 (conc.) or 1 M NaOH solution were used to adjust pH of the decant mixture to an appropriate level if it is necessary. The colorless supernatant liquid was separated from the mixture by sedimentation and centrifugation.

4.1.2.2 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 pressurized up to 3 kg/cm² gauge. Then the mixture in the autoclave was heated from room temperature to 160 °C with various heating rate for various particle sizes 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 minimize 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^- from the crystals, and dried in an oven at $110\text{ }^\circ\text{C}$ for at least 3 h.

4.1.2.3 Calcination

The dry crystals were calcined in an air stream at $540\text{ }^\circ\text{C}$ for 3.5 h, by heating them from room temperature to $540\text{ }^\circ\text{C}$ in 1 h, 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 desiccators. The obtained Na-MFI was the parent ZSM-5 zeolite which was further transformed to the other appropriate forms for the experiments in this study.

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

4.1.2.4 NH_4^- and H- form ZSM-5

To make NH_4 -ZSM-5, the parent Na-ZSM-5 powder was firstly mixed with 1 M NH_4NO_3 solution at 30 ml per gram of catalyst. In the procedure, the catalyst amounts 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 $80\text{ }^\circ\text{C}$ by reflux. After heating the mixture for about 1 h, the mixture was cooled down to room temperature and centrifuged to remove the used solution. The remained crystals were mixed again with NH_4NO_3 solution in the same amount. The previous step was repeated. The exchanged catalyst was then washed twice with deionized water by using a centrifugal separator. Then, the ion exchange crystal was dried at $110\text{ }^\circ\text{C}$ for at least 3 h. in oven. The dried catalyst was obtained the NH_4 -form of ZSM-5. The NH_4 / ZSM-5 was converted to H-form ZSM-5 by removing NH_3 species from the catalyst surface. NH_3 can be removed by thermal treatment of the NH_4 -ZSM-5 zeolite. This was done by heating a sample in a furnace from ambient temperature to $540\text{ }^\circ\text{C}$

in 1 h and holding the sample at 540 °C for 3.5 h. After this step, the obtained crystals were H-zeolite.

4.1.2.5 Cobalt loading

In this experimental, the incipient wetness impregnation method had been used for cobalt loading. Selected this method because can be easy control amount of cobalt than ion exchange method. Cobalt nitrate was used as precursor in this method. The incipient wetness impregnation procedure was as following:

1. Cobalt nitrate (1%, 5%, 10% loading) was dissolved in deionized water which its volume equals to pore volume of catalyst.
2. ZSM-5 catalyst was impregnated with aqueous solution of cobalt by the incipient wetness technique. The cobalt solution was dropped slowly to the ZSM-5 catalyst.
3. The impregnated support was left to stand at room temperature for 6 hours to assure adequate distribution of metal complex. After that the catalyst was dried in the oven at 110 °C overnight.
4. The catalyst was calcined in air at 540°C for 3.5 h.

4.2 Characterization

4.2.1 X- Ray Diffraction analysis (XRD)

Crystallinity and X-ray diffraction (XRD) patterns of the catalysts were performed by a X-ray diffractometer SEIMENS D500 connected with a personal computer with Diffract AT version 3.3 program for fully control of the XRD analyzer. The experiments were carried out by using $\text{CuK}\alpha$ radiations with Ni filter and the operating condition of measurement are shown as below:

2 θ range of detection : 6 – 40 °

Resolution : 0.04 °

Number of Scan : 10

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

4.2.2 X-Ray Fluorescence analysis (XRF)

Quantities of SiO₂/Al₂O₃ in the sample were determined by atomic absorption spectroscopy using Varian, Spectra A8000 at the Department of Science Service, Ministry of Science Technology and Environment.

4.2.3 BET surface area measurement

The surface area (A_{BET}) of the samples was calculated using BET technique, Micromeritics ASAP 2020.

4.2.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was employed for including the shape and size of the prepared zeolite crystal. The JEOL JSM-35 CF model at the Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC) was used for this purpose.

4.2.5 Temperature Programmed Adsorptions of Ammonia (NH₃-TPD)

The acid properties were observed by Temperature programmed desorption (TPD) equipment by using micromeritics chemisorb 2750 Pulse Chemisorption System.

4.2.6 X-ray Photoelectron Spectroscopy (XPS)

The XPS spectra, the binding energy and the composition on the surface layer of the catalysts were determined by using a Kratos Amicus X-ray photoelectron spectroscopy. The analyses were carried out with these following conditions: Mg Ka X-ray source at current of 20 mA and 12 kV, 0.1 eV/step of resolution, and pass energy 75 eV and the operating pressure was approximately 1×10^{-6} Pa

4.3 Reaction Testing

4.3.1 Chemicals and Reagents

Methanol was available from MERCK, 98.9 % for methanol conversion.

4.3.2 Instruments and Apparatus

(a) Reactor: The reactor was a conventional micro reactor made from a quartz tube with 6 mm inside diameter. The reaction was carried out under N_2 gas flow and atmospheric pressure.

(b) Automatic Temperature Controller: This unit consists of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller connected to a thermocouple attached to the catalyst bed in reactor. A dial setting established a set point at any temperatures within the range between $0^\circ C$ to $500^\circ C$.

(c) Electric Furnace: This supply the required heated to the reactor for reaction. The reactor could be operated from room temperature up to $200-500^\circ C$.

(d) Gas Controlling Systems: Nitrogen was equipped with pressure regulator (0-120 psig), an on-off valve and a needle valve were used to adjust flow rate of gas.

(e) Gas Chromatographs: Operating conditions were shown in Table 4.3.

Table 4.3 Operating condition gas chromatograph for methanol to hydrocarbons

Gas chromatograph	Shimadzu GC8A	Shimadzu GC14B	Shimadzu GC14B
Detector	TCD	FID	FID
Column	Porapack-Q	VZ-10	Bentone 34
Carrier gas	He (99.999%)	N ₂ (99.999%)	N ₂ (99.999%)
Carrier gas flow	30 ml./min.	30 ml./min.	30 ml./min
Column temperature			
- Initial	90°C	30°C	50°C
- Final	90°C	140°C	50°C
Detector temperature	100°C	150°C	80°C
Injector temperature	100°C	40°C	80°C
Analyzed gas	Methanol	Hydrocarbon C ₁ -C ₄	Hydrocarbon

4.3.3 Reaction Method

The methanol conversion was carried out by using a conventional flow as shown in Figure 4.2. A 0.05 portion of the catalyst was packed in the quartz tubular reactor of 6 mm inner diameter. Nitrogen gas was supplied from a cylinder to control methanol partial pressure and flow rate of the system. Methanol conversion reaction was carried out under the following conditions:

Total pressure, 1 atm; methanol composition 20%; balance gas, nitrogen; GHSV, 25000 h⁻¹ ; reaction temperature 200-500 °C

The procedure used to operate this reactor was follows;

- 1) Adjust the pressure of nitrogen gas to 1 kg/cm², and allow the gas to flow through a Rota meter, measure the outlet gas flow rate by using a bubble flow meter.
- 2) Heat up the reactor (under N₂ flow) by raising the temperature from room temperature to 200-500° C and then hold at this temperature about 30 min for preheating catalyst.
- 3) Put methanol 20 ml in saturator and set the temperature of water bath at 29° C at this temperature. The concentrations of methanol in saturator were 20% mol.
- 4) Start to run the reaction by adjusting 2 three way valves to allow nitrogen gas to pass through reactants inside saturator in water bath.
- 5) Take sample for analyzed by gas chromatograph after the reaction ran for 30 minutes.

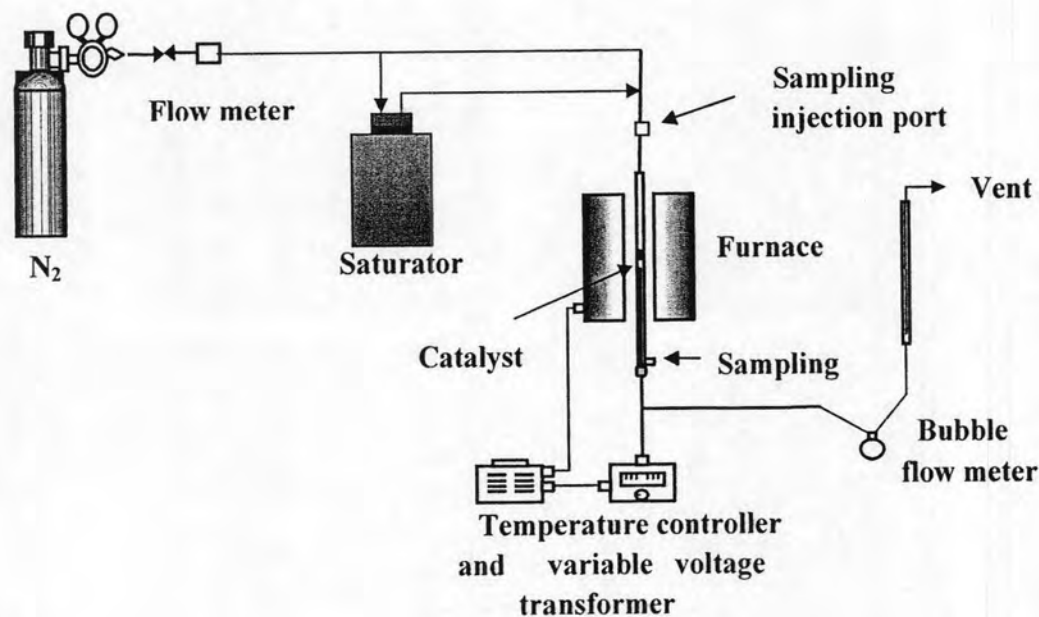


Figure 4.2 Schematic diagram of the reaction apparatus for reaction.