

CHAPTER IV

EXPERIMENT

In this chapter, Experimental is divided into three sections. First, Catalyst preparation is presented in section 4.1. Section, characterization of beta zeolite by using XRD, XRF, BET surface area, SEM, and ^{27}Al NMR presented in section 4.2. Third, reaction testing is explained in section 4.3.

4.1 Catalyst Preparation

The synthesis of beta zeolite by dry gel conversion which involves initial preparation of the dry gel powder, and then crystallizing under autogenous pressure of water into the bottom of an autoclave. The preparation procedure of beta zeolite by dry gel conversion is shown in Figure 4.2 and reagents used are shown in Table 4.2, Table 4.3 and Table 4.4 (For calculation see Appendix A-1).

4.1.1 Chemicals

The details of chemicals used in the preparation procedure of beta zeolites are shown in Table 4.1

Table 4.1 The chemicals used in the catalyst preparation

Chemical	Supplier
-Tetraethylammonium hydroxide [TEAOH] (40% by weight aqueous solution)	Fluka
-Cataloid as a source of SiO_2 (30% by weight aqueous solution)	Form Japan
-Sodium hydroxide [NaOH]	Merck
-Aluminium sulfate [$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$]	Univar

In the synthesis of beta zeolite, tetraethylammonium hydroxide, aluminium sulfate and sodium hydroxide were used as organic template, silica, alumina and sodium source, respectively. While water will used as source of steam in the reaction system.

In this study, there were three parameters: 1. Water content as a source of steam, 2. $M_{\text{gel}}/M_{\text{water}}$ ratio, and 3. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio were investigated. Which their effected on formation and characterization of beta zeolite.

4.1.2 Reagents

Table 4.2 Reagents used for the preparation of as-synthesized beta zeolite for the study effect of the water content in the reaction system. The molar ratio of starting materials was $\text{SiO}_2: 0.01\text{Al}_2\text{O}_3: 0.1\text{Na}_2\text{O}: 0.37\text{TEAOH}$.

Reagents	Quantity
TEAOH	13.600 g
NaOH	0.800 g
Cataloid	20.000 g
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	0.668 g
Water as souce of steam	5 ml, 10 ml, 20ml, 30ml, 50ml
Mass of dry gel; For $M_{\text{gel}} / M_{\text{water}}$ ratio of 1.5	15 g



Table 4.3 Reagents used for the preparation of as-synthesized beta zeolite for the study effect of the dry gel mass. The molar ratio of starting materials was SiO_2 : $0.01\text{Al}_2\text{O}_3$: $0.1\text{Na}_2\text{O}$: 0.37TEAOH .

Reagents	Quantity
TEAOH	13.600 g
NaOH	0.800 g
Cataloid	20.000 g
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	0.668 g
Water as souce of steam	10 ml
Mass of dry gel	
For $M_{\text{gel}} / M_{\text{water}}$ ratio of 0.8	8 g
$M_{\text{gel}} / M_{\text{water}}$ ratio of 1.5	15 g
$M_{\text{gel}} / M_{\text{water}}$ ratio of 3.0	30 g

Table 4.4 Reagents used for the preparation of as-synthesized beta zeolite for the study effect of silica to alumina ratios.

Reagents	Quantity
TEAOH	13.600 g
NaOH	0.800 g
Cataloid	20.000 g
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	
For $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$	2.221 g
$\text{SiO}_2/\text{Al}_2\text{O}_3 = 60$	1.111 g
$\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$	0.668 g
$\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$	0.333 g
Water as souce of steam	10 ml
Mass of dry gel; For $M_{\text{gel}} / M_{\text{water}}$ ratio of 1.5	15 g

4.1.3 Preparation of Dry Gel Powder

The preparation of dry gel powder, dry gel having the composition given in Table 4.2, Table 4.3 and Table 4.4 were prepared as follows: The beginning, tetraethylammonium hydroxide (TEAOH) solution and sodium hydroxide (NaOH) granules were mixed and vigorously stirred for 30 minute at room temperature. Cataloid was then added slowly while vigorous stirring. After 2 h, aluminium sulfate dissolved in distilled water was slowly added to the mixture while vigorous stirring and the mixture was continuously stirred for 2 h. Then the mixture was heated to 80°C and dried while stirring. The resultant dry gel was crushed to obtain the white dry gel powder placed in the Teflon beaker located in the stainless steel autoclave of 1000 ml, which contained a small amount of water at the bottom as a source of steam as shown in Figure 4.1.

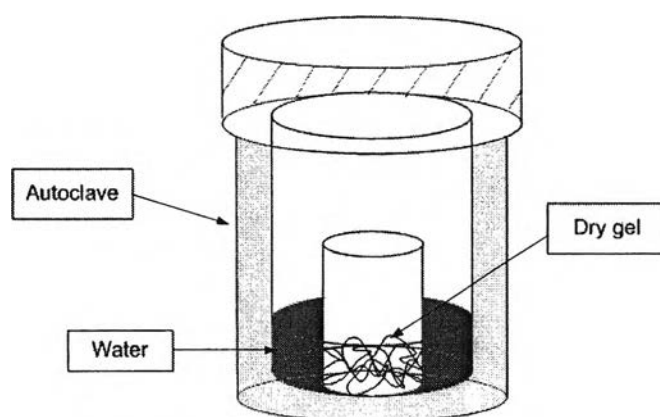


Figure 4.1 Experimental apparatus for the dry gel conversion

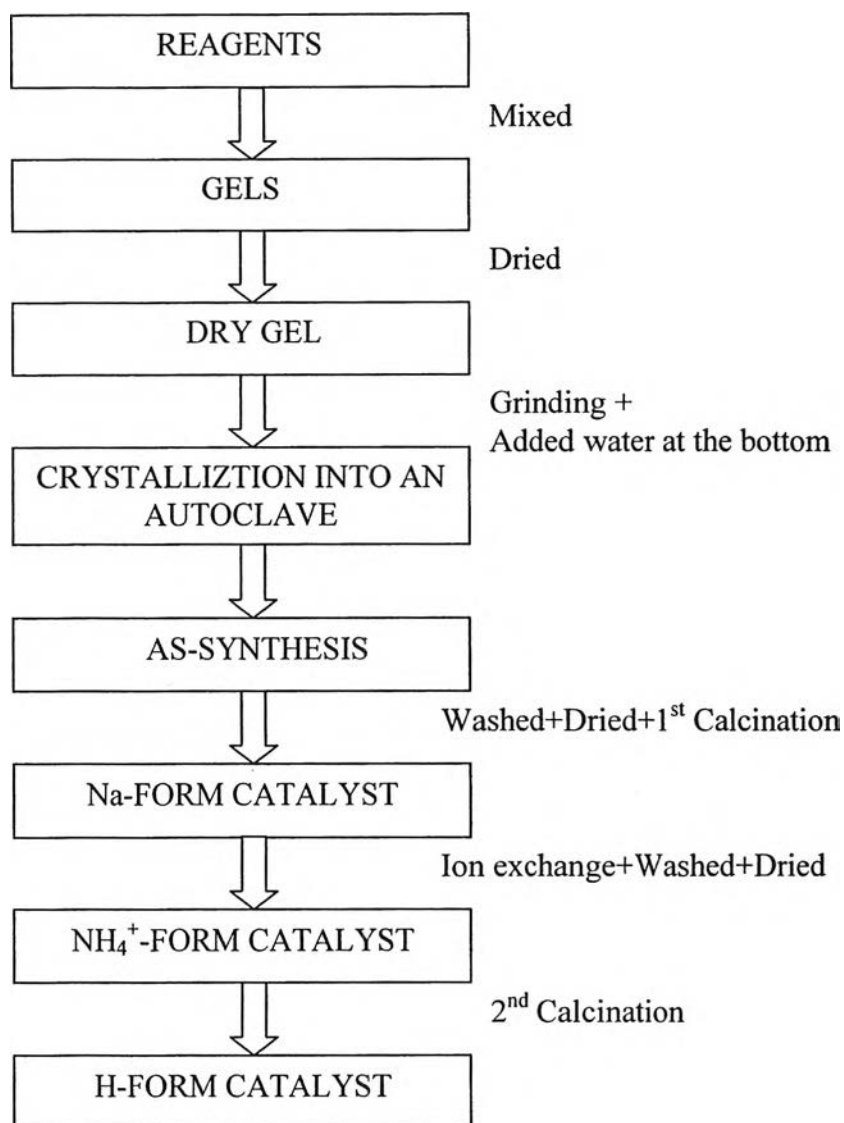


Figure 4.2 Preparation procedure of beta zeolite by dry gel conversion

4.1.4 Crystallization

The white dry gel powder placed in the Teflon beaker located in the stainless-steel autoclave of 1000 ml, which contained a small amount of water at the bottom as a source of steam, as shown in Figure 4.1. The dry gel powder was crystallized in steam at 175°C under autogenous pressure and maintained at this temperature for 24 h. After selected time intervals, the autoclave was immersed in cold water to quench the crystallization process. The obtained solid material was centrifuged at 2,500

r.p.m. (about 15 min for each time) and the recovered solids were washed until $\text{pH} \approx 9$ and dried in an oven at 110°C overnight.

4.1.5 The first calcination

The dry crystal was calcined in an air stream at 540°C for 3.5 h. by heating it 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 desiccator. After this step the crystals formed were called Na-zeolite beta.

4.1.6 Ammonium ion-exchange

The ion exchange step was carried out by mixing the calcined crystal with 2 M NH_4NO_3 (ratio of catalyst and solution is 1 g: 30 ml) 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 exchange crystal was washed twice with deionized water by using a centrifugal separator. Then, the ion exchange crystal was dried at 110°C for at least 3 h. in oven. The dried crystals (NH_4 -zeolite beta) were then obtained.

4.1.7 The second calcination

The removable species, i.e., NH_3 and NO_x , were decomposed by thermal treatment of the ion exchange crystals in a furnace by heating from the room temperature to 540°C in air stream and maintained at this temperature for 3.5 h. After this step, the obtained crystals were H-zeolite beta

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 $\text{CuK}\alpha$ radiation with Ni filter and the operating condition of measurement are shown as follows:

2 θ range of detection : 4 – 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 $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the sample were determined by using XRF analyzer at the Science Service Department, Rama VI Road, Bangkok.

4.2.3 BET surface area measurement

Physical adsorption isotherms are measured near the boiling point of a gas (e.g., nitrogen, at -196°C). From these isotherms the amount of gas needed to form a monolayer can be determined. If the area occupied by each adsorbed gas molecule is known, the surface area can be determined for all finely divided solids, regardless of their chemical composition.

The specific surface area of samples was calculated using the Brunauer-Emmett-Teller single point method on the basis of nitrogen uptake measured at liquid-nitrogen boiling point temperature equipped with a gas chromatograph.

4.2.3.1 BET apparatus

The reaction apparatus of BET surface area measurement consisted of two feed lines of helium and nitrogen. The flow rate of the gases was adjusted by means

of fine-metering valve on the gas chromatograph. The sample cell made from pyrex glass. The operation condition of gas chromatograph (GOW-MAC) is shown in Table 4.5.

Table 4.5 Operating condition of gas chromatograph (GOW-MAC)

Model	GOW-MAC
Detector	TCD
Helium flow rate	30 ml/min
Detector temperature	80 ° C
Detector current	80 mA

4.2.3.2 Procedure

The mixture gas of helium and nitrogen was flown through the system at the nitrogen relative pressure of 0.3. The catalyst sample was placed in the sample cell, ca. 0.3-0.5 g, which was then heated up to 160°C and held at that temperature for 2 h. Then the catalyst sample was cooled down to room temperature and the specific surface area was measured. There were three steps to measure the specific surface area.

Adsorption step: The catalyst that set in the sample cell was dipped into the liquid nitrogen. Nitrogen gas that was introduced into the system was adsorbed on the surface of the catalyst sample until equilibrium was reached.

Desorption step: The sample cell with nitrogen gas-adsorbed catalyst sample was dipped into a water bath at room temperature. The adsorbed nitrogen gas was desorbed from the surface of the catalyst sample. This step was completed when the integrator line was back in the position of the base line.

Calibration step: 1 ml of nitrogen gas at atmospheric pressure was injected through the calibration port of the gas chromatograph and the area was measured. The area was the calibration peak. The calculation method is explained in Appendix A-3.

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 ^{27}Al Magnetic Angle Spinning Nuclear Magnetic Resonance (^{27}Al MAS NMR)

Quantitative analysis of aluminum tetrahedral in zeolite was conformed by ^{27}Al -magnetic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR, BRUKER DPX-300 spectroscopy operating at 78.2 MHz) at National Metal and Materials Technology Center (MTEC) Bangkok.

4.3 Reaction Testing

4.3.1 Chemicals and Reagents

Methanol is available from MERCK, 99.9 % for methanol conversion.

4.3.2 Instruments and Apparatus

(a) Reactor: The reactor is 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 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 establishes a set point at any temperatures within the range between 0°C to 600°C .

(c) Electric Furnace: This supply the required heated to the reactor for reaction. The reactor can be operated from room temperature up to 700°C at maximum voltage of 220 volt.

(d) Gas Controlling Systems: Nitrogen is 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 are shown in Table 4.6.

Table 4.6 Operating condition for gas chromatograph

Gas chromatograph	Shimadzu GC8A	Shimadzu GC14A	Shimadzu GC14B
Detector	TCD	FID	FID
Column	Porapack-Q	OV-1	VZ10
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	40°C	70°C
- Final	90°C	150°C	70°C
Detector temperature	100°C	120°C	100°C
Injector temperature	100°C	120°C	150°C
Analyzed gas	CH ₃ OH	Hydrocarbon	Hydrocarbon C ₁ -C ₄

4.3.3 Reaction Method

The methanol conversion was carried out by using a conventional flow as shown in Figure 4.3. A 0.1 portion of the catalyst was packed in the quartz tubular reactor. The reaction was carried out under the following procedure:

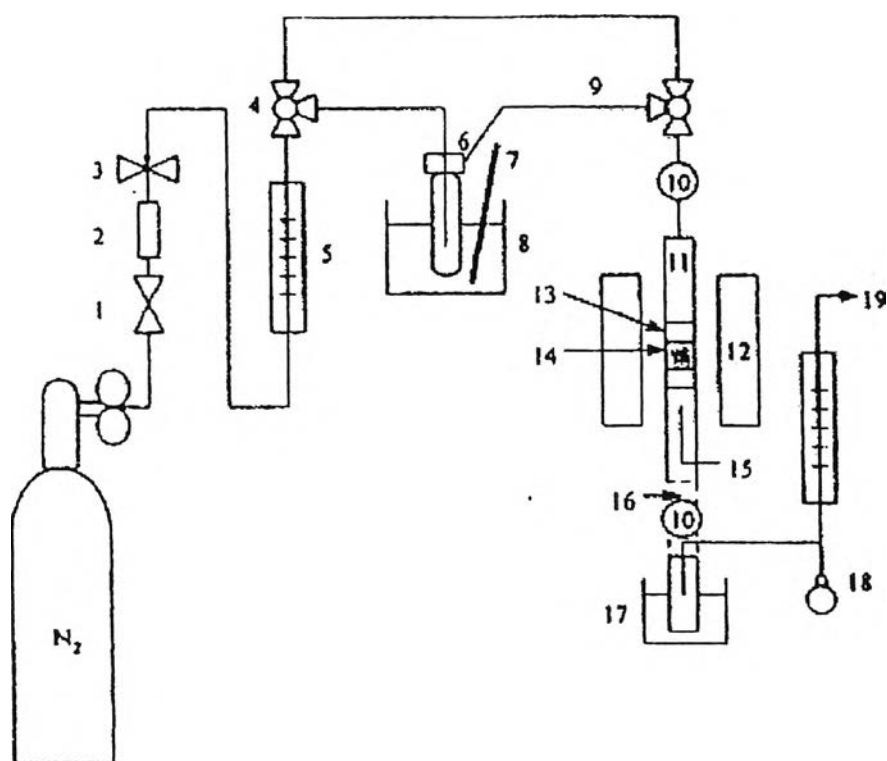
1) Adjust the pressure of nitrogen to 1 kg/cm^2 , and allow the gas to flow through a rotameter (See Appendix A-6), measure the outlet gas flow rate by using a bubble flowmeter. Gas flow rate was about 11.31 ml/min at GHSV about 4000 h^{-1} .

2) Heat up the reactor (under N_2 flow) by raising the temperature from room temperature to 450°C in 45 min 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 25°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 1 h.



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|-----------------|-------------------------|---------------------|----------------------|
| 1. On-off valve | 2. Gas filter | 3. Needle valve | 4. Three-way valve |
| 5. Flow meter | 6. Saturator | 7. Thermocouple | 8. Water bath |
| 9. Heating line | 10. Sampling port | 11. Tubular reactor | 12. Electric furnace |
| 13. Quartz wool | 14. Catalyst | 15. Thermocouple | 16. Heating tape |
| 17. Trap | 18. Soap-film flowmeter | 19. Purge | |

Figure 4.3 Schematic diagram of the reaction apparatus for reaction