

CHAPTER III

EXPERIMENTS

3.1 Equipment and Apparatus

Ovens and Furnaces

The catalysts were preliminary dried at 100°C in a Memmert UM-500 oven and further calcined at 540°C in a Carbolite RHF 1600 muffle furnace with programmable heating rate of 1°C/min.

XRD

The X-ray diffraction was measured using a Rigaku DMAX 2200 X-ray powder diffractometer at College of Petroleum and Petrochemistry, Chulalongkorn University.

Elemental Analyzer

Silicon contents in the catalysts were determined using X-ray fluorescence spectrometer (SISONS Instrument ARL 8410) at Department of Scientific Service, Ministry of Science and Technology. Sodium contents were analyzed using the Shimadzu AA-670 atomic absorption spectrometer with air / acetylene flame, which is located at the Department of Chemistry, Faculty of Science, Chulalongkorn University. Aluminum contents were analyzed using the Varian Spectra AA-300 atomic absorption spectrometer with nitrous oxide / acetylene flame, which is located at Scientific and Technological Research Equipment Center of Chulalongkorn University.

Nitrogen Adsorptometer

The BET specific surface area was measured using the Quantachrome Autosorb-1 nitrogen adsorptometer at National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency.

NMR

Solid State ^{27}Al -NMR spectra were performed using the Bruker Advance DPX 300 MHz NMR at MTEC.

Gas Chromatographs

Hydrocarbon gases were analyzed using a Shimadzu GC-9A gas chromatograph equipped with a 30-m long and 0.53-mm o.d. Alumina-PLOT column. Liquid samples were analyzed using a Shimadzu GC-14B chromatograph equipped with 30-m long and 0.25-mm o.d. DB-1 column and a Shimadzu GC-14A chromatograph equipped with a 30-m long and 0.25-mm o.d. Carbowax column.

The Catalytic Apparatus

The catalytic apparatus assembled in our laboratory comprises a borosilicate tubular reactor of 0.54-mm i.d. or a quartz tubular reactor of 0.60-mm i.d., our-own-made split-tube furnace, a K-type thermocouple connected temperature programming assembly, a gas manifold, a gas-liquid saturator and a gas cylinder. Catalytic apparatus was shown in Figure 3.1.

3.2 Chemicals, Materials and Gases

Zeolites, Na-mordenite with Si/Al = 11 and H-mordenite with Si/Al = 120 were kindly provided by TOSOH Company, Japan with Professor Tatsumi at Yokohama National University as a referee. Nitrogen gas, highly pure grade was purchased from Thai Industrial Gases (TIG) and was dehydrated by passing through a 40 cm x 2.5-cm tubular of the molecular sieve 4A. Absolute methanol was supplied from Carlo Erba. Standard gas mixture and liquid mixture for GC analysis was kindly obtained from Thai Olefins Company. Other chemicals were from Merck or Fluka.

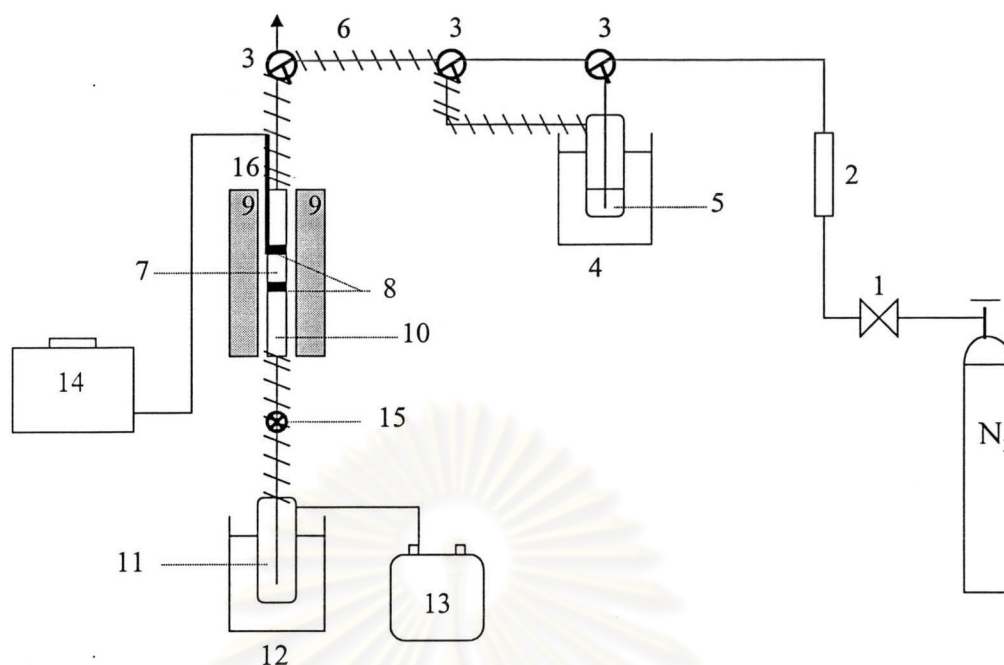


Figure 3.1 Schematic diagram of the reaction apparatus for the methanol conversion

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|----------------------------|---|----------------------------|
| 1 = needle valve, | 2 = flow controller, | 3 = three-way valve, |
| 4 = water bath, | 5 = methanol, | 6 = heating tape, |
| 7 = catalyst, | 8 = quartz wool, | 9 = electric furnace, |
| 10 = tubular reactor, | 11 = cold trap, | 12 = dry ice-acetone bath, |
| 13 = Tedlar bag, | 14 = temperature programmed controller, | |
| 15 = outlet sampling point | 16. Thermocouple | |

3.3 Sample Preparation for AAS

In a 100-cm³ Teflon beaker, 0.0500 g of a calcined catalyst was soaked with 10 cm³ of 6 M HCl and subsequently with 10 cm³ of 48% hydrofluoric acid to get rid off silica in the form of volatile SiF₄ species. The solid was heated but not boiled to dryness on a hot plate. The fluoride treatment were repeated twice more. An amount of 10 cm³ of a mixture of 6 M HCl : 6 M HNO₃ at a ratio 1 : 3 was added and further heated to dryness. An amount of 5 cm³ of 6 M HCl was added to the beaker and warmed for 5 minutes to dissolve the remains. An amount of 10-cm³ deionized water was added to the beaker and warmed for 5 minutes to complete dissolution. The solution was transferred to a 50-cm³ polypropylene volumetric

flask and made to the volume by adding deionized water. The flask was capped and shaken thoroughly. If the sample is not analyzed immediately, the solution was then transferred into a plastic bottle with a treaded cap lined under with a polyethylene seal.

3.4 Preparation of H-MOR

There are three methods to be studied for preparation of H-MOR from Na-MOR via the ammonium ion exchange process. The maximum level of ion exchange or the least amount of non-exchanged sodium ions, along with the unchanged structure is used as the judgement for the best method. Apparatus for the ion exchange of mordenite is shown in Figure 3.2.

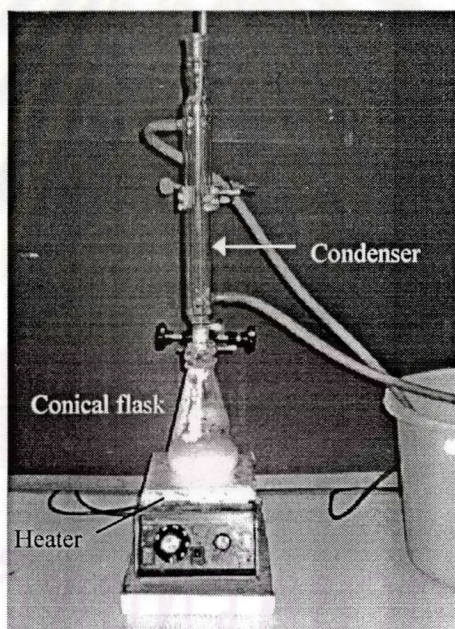


Figure 3.2 Apparatus for the ion exchange of mordenite.

Method A: In a typical ion exchange, 6.0 g of Na-MOR was mixed with 900 cm³ of 0.05 M ammonium chloride solution and boiled with stirring overnight. The ammonium-form mordenite obtained was separated from the solution by centrifugation (4000 rpm, 30 min) and washed with deionized water until no chloride left on the solids. If chloride still existed, it should be leached to the washing water and be precipitated with 0.1

M silver nitrate solution. The sample was dried at 100°C overnight in an oven. The dried sample was coded as H-MOR(A).

Method B: The treatment was performed as described in Method A but it was repeated twice more before drying in an oven at 100°C overnight and was subsequently calcined in a muffle furnace at 540°C for 10 h. The sample was coded as H-MOR(B).

Method C : This method comprised of two-step treatment, ammonium exchange and residual sodium activation at 540°C for 10 h. The treatment was repeated twice more and the final product was noted as H-MOR(C).

The samples treated by these three different methods were analyzed for the sodium amounts left in the zeolite samples using atomic absorption spectrophotometer. The structures of the zeolite samples were investigated using XRD to ensure the mordenite structure.

3.5 Factors Involved in Dealumination of Mordenite

The catalysts with different Si/Al ratios were prepared by modifying the aluminum-rich sodium-form mordenite-type zeolite, so called Na-MOR, Si/Al = 11, obtained from TOSOH, Japan. To remove a certain amount of aluminum from Na-MOR, the zeolite was converted to hydrogen form with a notation of H-MOR, by the ion-exchange process prior to the acid treatment with hydrochloric acid at an elevated temperature. To obtain the catalysts with required Si/Al ratios, those factors influencing the dealumination process via acid leaching of the hydrogen-form mordenite were studied. Apparatus for dealumination of the zeolite is shown in Figure 3.3.

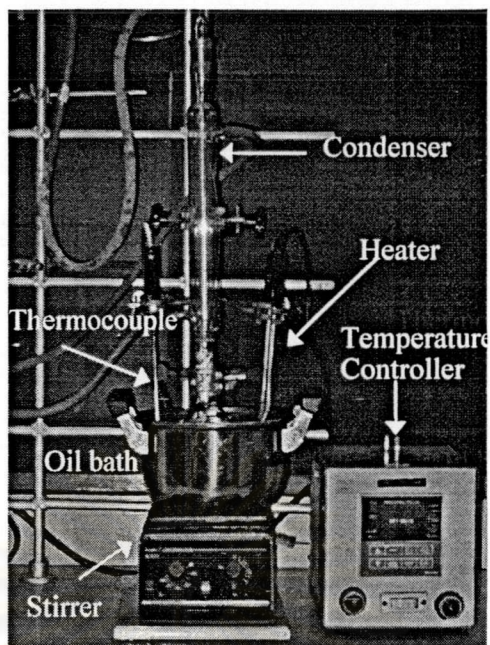


Figure 3.2 Apparatus for dealumination of H-MOR.

3.5.1 Study on Effect of Temperature on the Extent to Dealumination

Into a 50-cm³ round bottom flask 1.0 g of H-MOR (Si/Al = 11) and 25 cm³ of 1.0 M HCl solution were added. The reflux distillation of the mixture was conducted using an oil bath at 90, 100, 110 or 120°C for 3 h. The acid treated solids were separated by centrifugation (4000 rpm, 30 min) and washed several times with deionized water until no chloride. The dealuminated mordenite samples were dried in an oven at 100°C overnight and subsequently calcined in a muffle furnace at 540°C for 10 h. The calcined samples were characterized using NH₃-TPD and AAS techniques.

3.5.2 Study on Effect of Acid Concentration on the Extent to Dealumination

In a 50-cm³ round bottom flask 1.0 g of H-MOR was mixed with 25 cm³ of a hydrochloric acid solution with various concentration: 0.1, 0.5, 1.0, 2.0, 4.0 and 6.0 M. Then, the reflux distillation of the slurry was operated using an oil bath at 100°C for 3 h. The acid treated solids were separated by centrifugation (4000 rpm, 30 min) and washed several times with deionized water until no chloride. The dealuminated mordenite samples were dried in an oven at 100°C overnight and subsequently calcined in a muffle furnace at

540°C for 10 h. The calcined samples were characterized using XRD, NH₃-TPD and AAS techniques.

3.6 Preparation of Dealuminated H-MOR

3.6.1 H-MOR with Si/Al Molar Ratio = 40

Into a typical reflux distillation set-up, 1.0 g of H-MOR and 25 cm³ of 2.32 M HCl solution was added. The mixture was heated using an oil bath at 100°C for 3 h. The acid treated solids were separated by centrifugation (4000 rpm, 30 min) and washed several times with deionized water until no chloride observed by precipitation with silver nitrate solution. The product of H-MOR(40) was dried in an oven at 100°C overnight and subsequently calcined in a muffle furnace at 540°C for 10 h. The calcined H-MOR(40) was characterized using XRD, AAS and ²⁷Al-NMR techniques.

3.6.2 H-MOR with Si/Al Molar Ratio = 80

Similarly to describe above, 1.0 g of H-MOR was reflux heated in 25 cm³ of 5.46 M HCl solution using an oil bath at 100°C for 3 h. The acid treated solids were separated by centrifugation (4000 rpm, 30 min) and washed several times with deionized water until no chloride left. The product of H-MOR(80) was dried in an oven at 100°C overnight and subsequently calcined in a muffle furnace at 540°C for 10 h. The calcined H-MOR (80) was characterized using XRD and AAS techniques.

3.7 Catalytic Activity Tests of the Mordenite Catalysts

The catalysis was carried out using apparatus shown in Figure 3.1. The feed of 20% methanol in nitrogen was introduced to the tubular reactor at a constant gas-hourly space velocity (GSHV) of 2000 h⁻¹ which is correspondent to a gas flow of 11 cm³/min for 0.2 g of catalyst or 22 cm³/min for 0.4 g of catalyst.

3.7.1 Preparation of Tiny Pellet Catalysts

The catalysts under the examination on the methanol conversion to olefins have different Si/Al ratios: 11, 39, 73 and 120. An amount of 0.1 g of each ground catalyst was pressed toward a 0.7-mm thick self-supporting wafer using a stainless steel die of a 13-mm inner diameter, in the similar manner to making KBr samples for IR measurement. The hydraulic press with pressing force of 3 tons was held on the catalyst wafer for 5 min. In an agate mortar, the catalyst wafer was crushed into tiny pellets of a size $2 \times 2 \times 0.7 \text{ mm}^3$, approximately.

3.7.2 Study on Effect of Time on Stream on Methanol Conversion

An amount of 0.20 g of the tiny pellet H-MOR catalyst having the Si/Al ratio of 11 was loaded into a middle part of a borosilicate tubular reactor, 5.4-mm inner diameter and was held in place by a plug of quartz wool. The catalyst portion was also covered with small amount of quartz wool. The height of the catalyst portion was 13 mm resulted in the catalyst volume of 0.30 cm^3 . For activation of the catalyst, the catalyst in the tubular reactor was then heated at 500°C for 1 h, at the pure nitrogen flow of $40 \text{ cm}^3/\text{min}$. The feed of 20% methanol in nitrogen was passed from the top through the catalyst at a GHSV of 2000 h^{-1} or $11 \text{ cm}^3/\text{min}$ measured at the tube outlet while the catalyst was still heated at 500°C . The outlet gas was sampled out from the catalytic line every 20 min (20, 40 and 60 min) and collected into a Tedlar bag for 3 min before closing the stopper on the bag. The gas products were analyzed for hydrocarbon components using the GC equipped with the Alumina-PLOT column.

3.7.3 Study on Effect of Temperature on Methanol Conversion

An amount of 0.40 g of the tiny H-MOR pellets with the Si/Al ratio of 11 was loaded into the middle part of the borosilicate tubular reactor and held in place by a plug of quartz wool. The catalyst portion was also covered with small amount of quartz wool. The height of the catalyst portion was 26 mm resulted in the catalyst volume of 0.60 cm^3 . The catalyst in the tubular reactor was then heated at 500°C for 1 h, at the pure nitrogen flow of $40 \text{ cm}^3/\text{min}$. The feed of 20% methanol in nitrogen was introduced from the top through the

catalyst at a GHSV of 2000 h^{-1} at the tube outlet while the catalyst was still heated at a required temperature. The tests were performed at different temperatures: 300, 350, 400, 450, and 500°C . After 40 min of the time on stream, a $10\text{-}\mu\text{l}$ volume of the gas sample was withdrawn from the line at the septum point below the catalyst location for methanol analysis using the GC equipped with the Carbowax column. At the same time the gas products were collected into a Tedlar bag and analyzed for hydrocarbon components using the GC equipped with the Alumina-PLOT column.

3.7.4 Study on Effect of Si/Al ratio on Methanol Conversion

3.7.4.1 Effect of Si/Al Ratio at High Temperature

An amount of 0.40 g of the tiny pellet H-MOR catalysts having different Si/Al ratios: 11, 39, 73 and 120, was loaded into the borosilicate tubular reactor and held in place by a plug of quartz wool. The catalyst portion was also covered with small amount of quartz wool. The catalyst-portion height was 26 mm resulted in the catalyst volume of 0.60 cm^3 . The catalyst in the tubular reactor was then heated at 500°C for 1 h, at the pure nitrogen flow of $40 \text{ cm}^3/\text{min}$. The feed of 20% methanol in nitrogen was passed from the top through the catalyst at a GHSV of 2000 h^{-1} at the tube outlet while the catalyst was still heated at 500°C . After 40 min of the time on stream, a $10\text{-}\mu\text{l}$ volume of the gas sample was withdrawn from the line at the septum point below the catalyst location for methanol analysis using the GC equipped with the Carbowax Column. At the same time the gas products were collected into a Tedlar bag and analyzed for hydrocarbon components using the GC equipped with the Alumina-PLOT column

3.7.4.2 Effect of Si/Al Ratio at Low Temperature

The experiment was performed in similar manner to what was described in Section 3.7.4.1 except the reaction temperature was lowered to 300°C .

3.7.5 Determination of Catalyst Life Time

An amount of 0.20 g of the tiny pellet H-MOR catalyst with the Si/Al ratios 11 and 120, was loaded into the borosilicate tubular reactor and held in place by a plug of quartz wool. The catalyst portion was also covered with small amount of quartz wool. The height of the catalyst was 13 mm resulted in the catalyst volume of 0.30 cm³. The catalyst in the tubular reactor was then heated at 500°C for 1 h, at the pure nitrogen flow of 40 cm³/min. The feed of 20% methanol in nitrogen was passed from the top through the catalyst at a GHSV of 2000 h⁻¹ at the tube outlet while the catalyst was still heated at 500°C. A 10-μl portion of the gas sample was withdrawn every 20 min from the line at the septum point below the catalyst location for methanol analysis using the GC equipped with the Carbowax column.

3.8 Determination of Coke Deposited on the Catalysts

The coke deposited on the catalysts was determined by the difference in mass before and after calcination as followed in Equation 3.1.

$$\% \text{ wt. Coke} = \frac{(W_{\text{cal}} - W_{\text{un-cal}}) \times 100}{W_{\text{cal}}} \quad (3.1)$$

When, W_{cal} = Weight of the used catalyst after calcination at 540°C

$W_{\text{un-cal}}$ = Weight of the used catalyst before calcination

3.8.1 Study on Effect of Temperature on Coke Formation on Catalyst

The used catalysts with Si/Al ratio of 11 at various temperatures were dried in an oven at 200°C for 2 h. The dehydrated catalysts were calcined in a muffle furnace at 550°C for 10 h. The extents to coke formation were determined using the weight loss upon calcination and Equation 3.1.

3.8.2 Study on Effect of Si/Al Ratio on Coke Formation on Catalyst

The catalysts with various Si/Al ratios used at 300 and 500°C were determined for the coke content in the same way as described in Section 3.8.1.



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