CHAPTER III

EXPERIMENT

3.1   Equipment and Apparatus

Ovens and Furnace

The catalysts were crystallized at a desired temperature using a Memmert UM-500 oven. Drying of solid samples at the temperature of 100°C was performed using the same oven. The solid samples were calcined at the temperature of 500°C in a split-tube furnace our own made with programmable heating rate of 1°C/min under nitrogen flow for 8 h and followed by oxygen flow for 4 h.

X-ray Powder Diffractrometer

XRD pattern identifying the MFI structure of the synthesized samples was measured using a Rigaku D/Max-2200 X-ray powder diffractrometer at Petroleum and Petrochemical College, Chulalongkorn University, with nickel filtered CuK$_\alpha$ radiation (30kV, 30mA) at an angle of 2θ ranged from 5 to 50°. The scan speed was 5°/min and the scan step was 0.02°. The three slits (scattering, divergent and receiving slits) were fixed at 0.5°, 0.5° and 0.3 mm, respectively.

Atomic Absorption Spectrometer

Iron contents in the catalysts were analyzed using a Varian Spectra-AA300 atomic absorption spectrometer with air/acetylene flame, which is located at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

Nitrogen Adsorptometer

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

Electron Spin Resonance Spectrometer

The local sites of iron in the catalysts were determined at room temperature using a JEOL JES-RE2X spectrometer, which is located at Scientific and Technological Research Equipment Center, Chulalongkorn University.

Scanning Electron Microscope

The morphology and particle size of catalysts were observed using a JEOL JSM-5410LV scanning electron microscope at Scientific and Technological Research Equipment Center, Chulalongkorn University.

The X-ray mapping of iron and silicon in catalysts were recorded using a JEOL JSM-6400 scanning electron microscope at Scientific and Technological Research Equipment Center, Chulalongkorn University.

Particle Size Analyzer

Particle size distributions of the catalysts were measured using Malvern Polydisperse particle size analyzer at Scientific and Technological Research Equipment Center, Chulalongkorn University.

Gas Chromatograph

Hydrocarbon gases were analyzed using a Shimudzu GC-9A gas chromatograph equipped with a 30-m long and 0.53-mm outer diameter Alumina-PLOT column. Liquid samples were analyzed using a Shimadzu GC-14A gas chromatograph equipped with 30-m long and 0.32-mm outer diameter HP-5 (0.25 μm film thickness) column and a 30-m long and 0.25-mm outer diameter Carbowax (0.25 μm film thickness) column. All GC detectors are flame ionization detectors (FID). The GC heating programs for 10-μl of gas, and 1-μl of Volatile Organic Compounds (VOC) analysis are shown in Scheme 3.1 and 3.2, respectively.
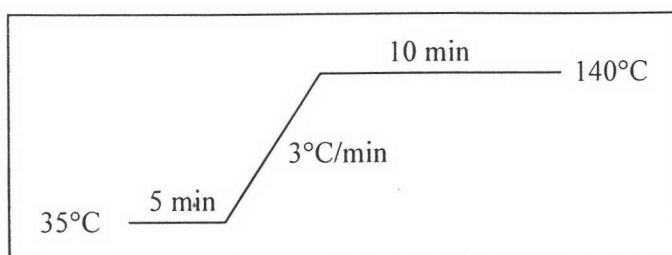
Scheme 3.1 The GC heating program for gas analysis.
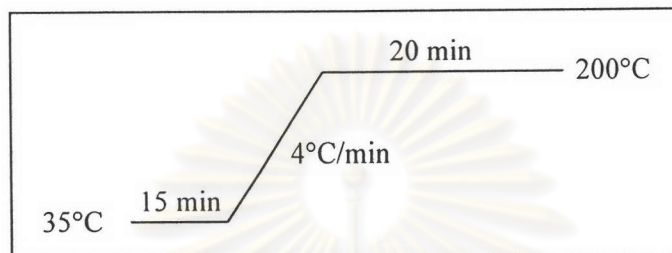
Scheme 3.2 The GC heating program for VOC analysis.

Gas Chromatograph-Mass Spectrometer

VOC were analyzed using a HP-6890N gas chromatograph equipped with a 30-m long and 0.32-mm outer diameter HP-5 (0.25 μm film thickness) column. GC detector is a 5973 Network Mass spectrometer at Center Instrument Facility, Mahidol University. The GC heating programs for 1-μl of VOC are shown in Scheme 3.2.

The Catalytic Apparatus

The catalytic apparatus for methanol conversion to olefins assembled in our laboratory comprises of a borosilicate tube reactor of 0.54-cm internal diameter our own made split-tube furnace, a K-type thermocouple connected to a temperature programming assemble, a gas manifold, a gas-liquid saturator and a nitrogen gas cylinder. The catalytic apparatus was shown in Figure 3.1.
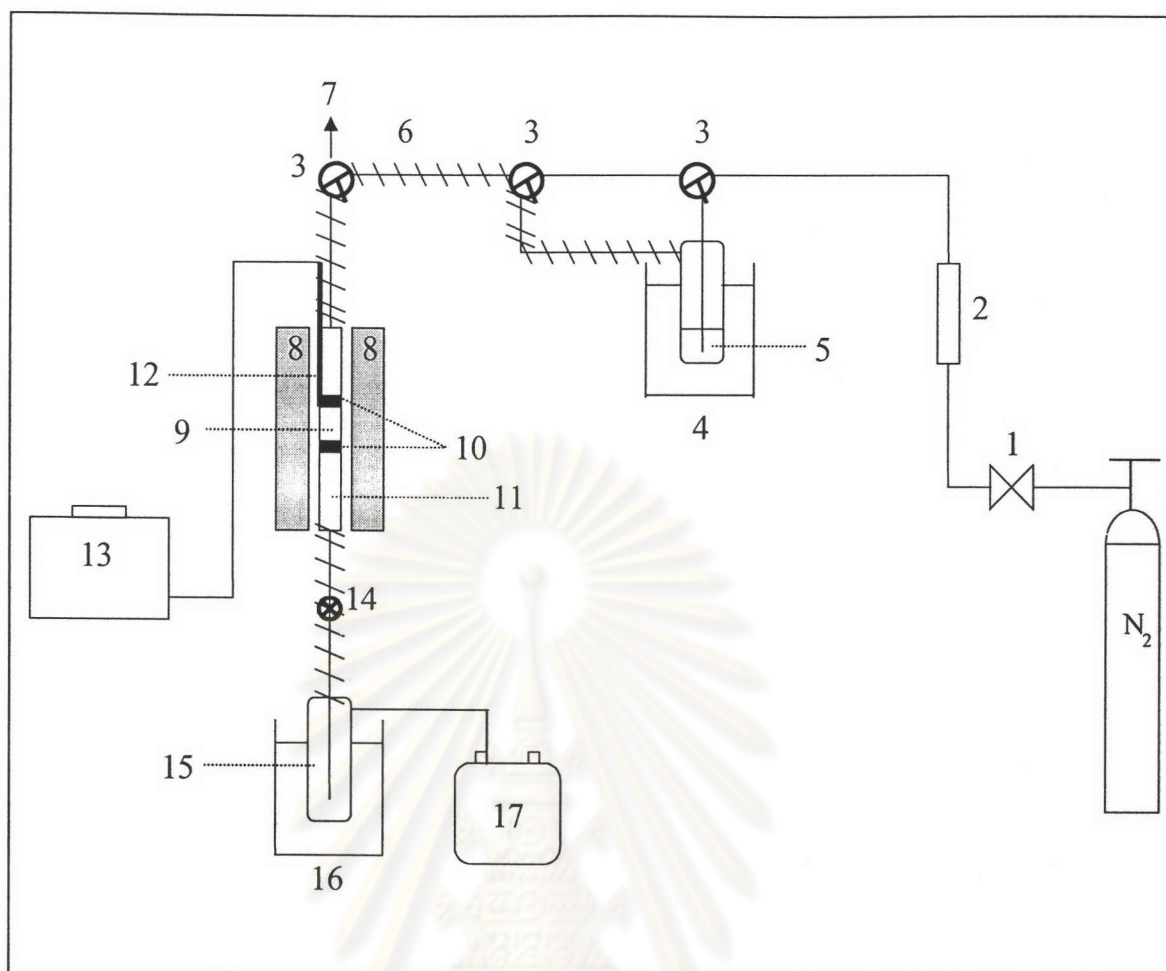
Figure 3.1 Schematic diagrams of the catalytic apparatus for methanol conversion to olefins.

1 = needle valve,	2 = flow meter,	3 = three-way valve,
4 = water bath,	5 = methanol,	6 = heating tape,
7 = inlet sampling point,	8 = electric furnace,	9 = catalyst,
10 = quartz wool,	11 = tubular reactor,	12 = thermocouple,
13 = temperature controller,	14 = outlet sampling point,	15 = cold trap,
16 = dry ice-acetone bath,	17 = Tedlar bag	

3.2   Chemicals and Gases

Nitrogen gas and oxygen gas of high purity grade were purchased from Thai Industrial Gases (TIG) and were additionally dehydrated by passing through a 40 cm x 2.5 tube of molecular sieve 4A. Ferric nitrate nonahydrate (98.0 wt.%) and absolute methanol were supplied from Carlo Erba. Sodium silicate solution (10.13 wt.% Na_2O, 29.71 wt.% SiO_2, 59.80 wt.% H_2O) was kindly provided from Thai Silicate. Tetrapropyl ammonium bromide (98 wt.%, TPABr) was purchased from Aldrich. Standard gas mixture and liquid mixture for GC analysis was kindly obtained from Thai Olefins. Other chemicals were from Merck or Fluka, otherwise specifically identified.

3.3   Direct Synthesis of Fe-MFI

There are three effects to be studied for the synthesis of Fe-MFI. Firstly, the effect of pH of the starting gel mixture on the MFI formation was investigated. The optimal pH was then selected for synthetic condition. Secondly, the effect of the scale for synthesis of Fe-MFI and finally the effect of Si/Fe ratios on the MFI formation were studied.

3.3.1 Synthesis of Fe-MFI at Various pH

Following the procedure reported by Szostak et al.[40] a gel (Si/Fe = 90) with a molar composition of SiO_2 : $0.31Na_2O$: $0.006Fe_2O_3$: $0.10TPABr$: $0.21H_2SO_4$: $59.52H_2O$ was prepared and was further modified by varying the pH of the starting gel as described by Kyu-Wan et al.[73] Three positions of solution were prepared separately. Solution A was prepared by dissolving 0.26 g of ferric nitrate in 21.25 cm^3 of deionized water. Solution B was prepared by dissolving 11.80 g of sodium silicate in 32.42 cm^3 of deionized water. Solution C was prepared by dissolving 1.62 g of TPABr in 2.50 cm^3 of deionized water. Into a 500-cm^3 4-neck round bottom flask containing Solution A, 1.26 g of H_2SO_4 was added dropwise. After that Solution B and C were added dropwise under vigorous stirring for 2 h. Finally, the pH of resulting gel was adjusted to a value of 8.0, 9.0, 9.5, 10.0, 10.5, or 11.0 with 9 M H_2SO_4 or 6 M NaOH. The resulting gel was statically crystallized in a 90-cm^3

Teflon lined stainless-steel autoclaveable vessel and heated under its own pressure at 170°C for 4 days. The solid product was separated from the solution by centrifugation (3000 rpm, 30 min) and washed with deionized water before drying at 100°C overnight. The final product yields 2.84 g. Apparatus for the gel preparation was shown in Figure 3.2.
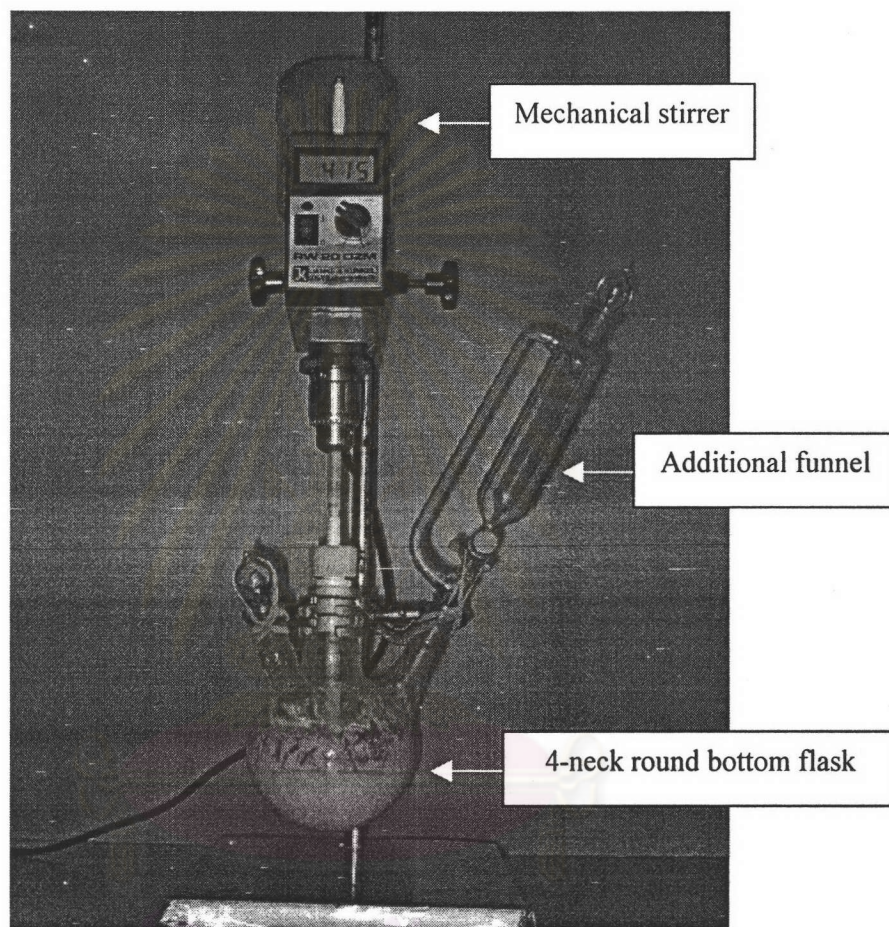

Figure 3.2   Apparatus for the gel preparation.

3.3.2 Synthesis of Fe-MFI with Various Si/Fe Ratios at pH of 9.0

To obtain the variation of iron contents in the catalysts, Fe-MFI samples with the Si/Fe ratios in gel of 90, 30 and 10 were synthesized in a similar way as described in Section 3.3.1. The pH of gel was fixed at 9.0. For the small-scale preparation, the amount of iron nitrate required for each preparation was shown in Table 3.1. For a large-scale preparation, the amounts of reactants were shown in Table 3.2, and statically crystallizing in a 250-cm^3 Teflon lined stainless-steel autoclaveable vessel.

Table 3.1   Amounts of ferric nitrate with various Si/Fe ratios for the synthesis of Fe-MFI in the small-scale preparation

Si/Fe ratio in gel	Weight of $Fe(NO_3)_3$ (g)	Fe Amount (mmol)
90	0.2650	0.325
30	0.7975	0.987
10	2.3975	2.975

**Table 3.2**   Amount of reactants for Fe-MFI synthesis in the large-scale preparation

Reactants	Weight (g)
$Fe(NO_3)_3.9H_2O$	0.6625 (Si/Fe ratio in gel of 90)
	1.9938 (Si/Fe ratio in gel of 30)
	5.9938 (Si/Fe ratio in gel of 10)
Sodium silicate	29.50
TPABr	4.06
H_2SO_4	3.16
H_2O	140

3.3.3 Synthesis of Fe-MFI with Various Si/Fe Ratios at pH of 10.5

To obtain the maximum loading of iron in the catalyst, Fe-MFI samples with the Si/Fe ratios in gel of 90, 30 and 10 were synthesized in a similar way as described in Section 3.3.1 without adjusting the pH of gel in the final step. Consequently, the pH rose to a value of 10.3-10.5. However, at higher iron content, the pH of the final gel was lower, so the gel was adjusted with 6 M NaOH to the pH necessary for crystallization. The schematic diagram for the gel preparation with various Si/Fe ratios was illustrated in Scheme 3.3.

3.4 Sample Preparation for AAS

In a 100-cm^3 Teflon beaker, 0.0400 g of a calcined catalyst was soaked with 10 cm^3 of 37% HCl and subsequently with 10 cm^3 of 48% hydrofluoric acid to get rid off silica in the form of volatile SiF$_4$ species. The solid was heated not boiled to dryness on a hot plate. The fluoride treatment were repeated twice more. An amount of 10 cm^3 of mixture of 6 M HCl : 6M HNO$_3$ at a ratio 1 : 3 was added and further heated to dryness. An amount of 10 cm^3 deionized water was added to the beaker and warmed for 5 minutes to complete dissolution. The solution was transferred to a 50-cm^3 polypropylene volumetric flask and made to the volume by adding deionized water. The flask was capped and shook thoroughly. If the sample is not analyzed immediately, the solution was then transferred into a plastic bottle with a treaded cap lined with a polyethylene seal.
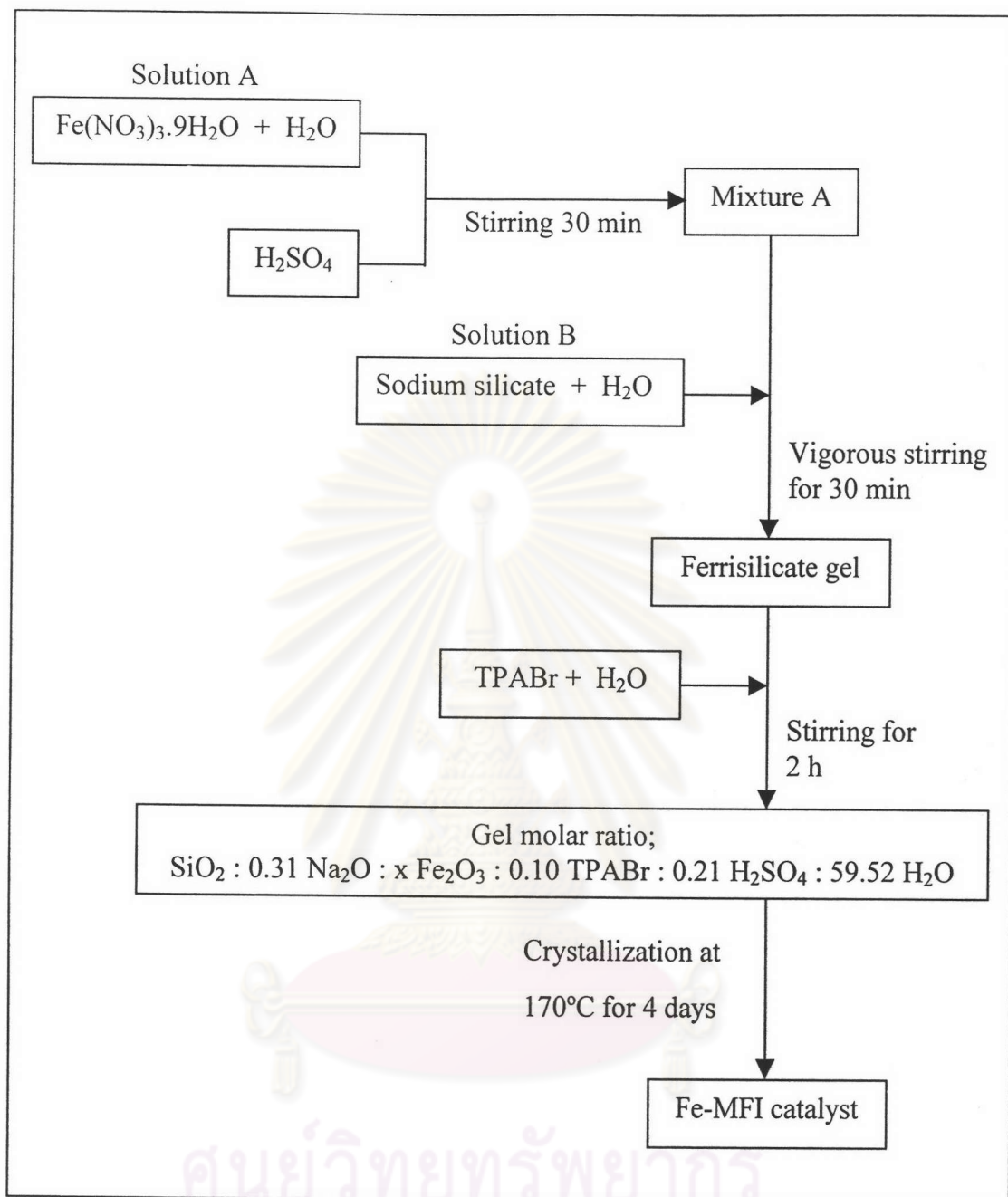
Scheme 3.3 Preparation diagram of the gel mixture with various Si/Fe ratios in the synthesis of Fe-MFI.

3.5 Organic Template Removal

An organic template, TPABr, used in the preparation step of the catalysts was removed from the catalysts pores by converting to carbon dioxide at high temperature. The as-synthesized Fe-MFI samples were calcined in a quartz boat from room temperature to 500°C in a tube furnace with programmable heating rate of 1°C/min under dry nitrogen flow for 8 h followed by heating under dry oxygen flow for 4 h.[73] The heating program was shown in Scheme 3.4.
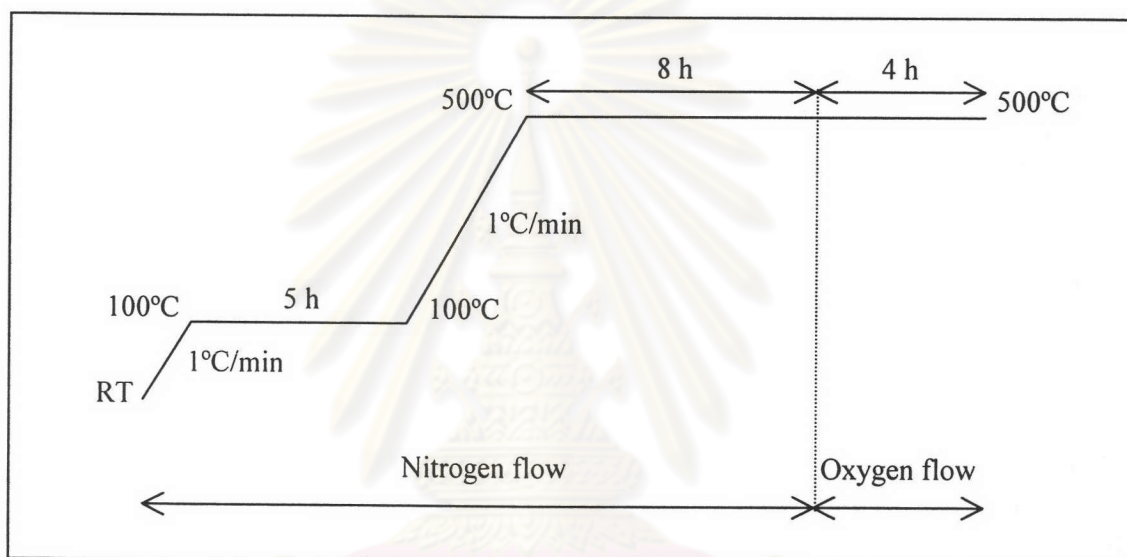
Scheme 3.4 The heating program for calcination of the Fe-MFI catalysts (RT = Room Temperature).[73]

3.6 Preparation of H-Fe-MFI

There are two methods to be studied for preparation of H-Fe-MFI from parent NaH-Fe-MFI *via* the ammonium ion exchange process. The catalytic activity test for methanol conversion to olefins was used as the judgment for the best method. Apparatus for the ammonium ion exchange of Fe-MFI was shown in Figure 3.3.

Method A: An amount of 2.0 g NaH-Fe-MFI (Si/Fe = 87) prepared at the pH value of 9.0 in the small-scale preparation was ion exchanged with 76-cm³ of 0.05 M ammonium chloride solution at boiling temperature with stirring 3 h. The ammonium-form iron-

containing MFI was separated from the solution by centrifugation (3000 rpm, 30 min) and washed with deionized water until no chloride left. The sample was dried at the temperature of 100°C overnight in an oven. The dried sample was eventually calcined in a split-tube furnace at the temperature of 500°C for 12 h as described in Section 3.5. The catalyst obtained by this method was denoted as H-Fe-MFI(A).
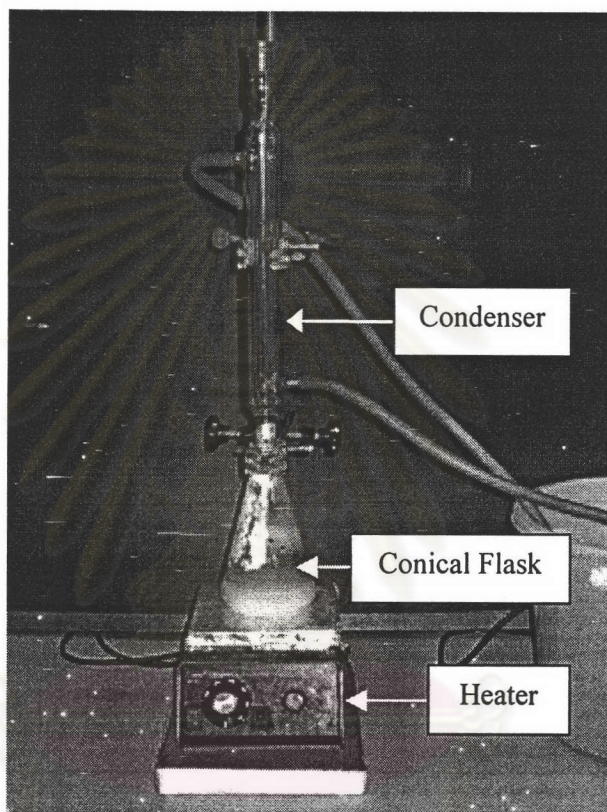

Figure 3.3   Apparatus for the ammonium ion exchange of Fe-MFI.

Method B: The treatment was performed as explained in the method A, but increasing time of reflux to overnight and the treatment was repeated once more. The catalyst prepared by this method was denoted as H-Fe-MFI(B).

The local sites of iron in Fe-MFI treated by Method B were recorded using ESR spectrometer to compare with those in the parent NaH-Fe-MFI.

3.7 Test of the Fe-MFI Catalysts for Methanol Conversion to Olefins

The Fe-MFI catalysts were freshly calcined at 500°C before catalytic test was performed. An amount of 0.1 g of each ground catalyst was pressed into a 0.7-mm thick self-supporting wafer using a stainless steel die of a 13-mm inner diameter, in the same manner as making KBr samples for IR measurement. The pressing force of 3 tons was held on the catalyst wafer for 2 min and then it was crushed into tiny pellets of a size 2 x 2 x 0.7 mm^3 approximately. A 0.30-g portion of the tiny pellets Fe-MFI catalyst was loaded into the middle of a borosilicate tubular reactor, 0.54 cm and hold in place by a plug of quartz wool. The catalyst portion was also covered with small amount of quartz wool. The height of the loaded catalyst was 16 mm resulting in a catalyst volume of 0.37 cm^3. The catalyst was then activated in the tubular reactor at the temperature of 500°C for 1 h under the nitrogen flow at 60 cm^3/min. Feed of 20% methanol in nitrogen was passed from the top through the catalyst at a gas-hourly space velocity (GHSV) of 2000 h^{-1} or 13.56 cm^3/min. After the time on stream of 40 min, a 10-μl portion of gas products was withdrawn from the catalytic line at the septum point below the catalyst location by a gas tight syringe and was analyzed for methanol remained using a GC equipped with a Carbowax capillary coated column. At the same time liquid products were collected in a cold trap sunk in a dry ice/acetone bath, while gas products were collected in a Tedlar bag. The gas products were analyzed using a GC equipped with the Alumina-PLOT column. Subsequently, liquid products in the cold trap were evacuated. Apparatus for evacuation of the volatile liquid from the liquid products was shown in Figure 3.4. The volatile liquid was analyzed using a GC equipped with the HP-5 coated capillary column.
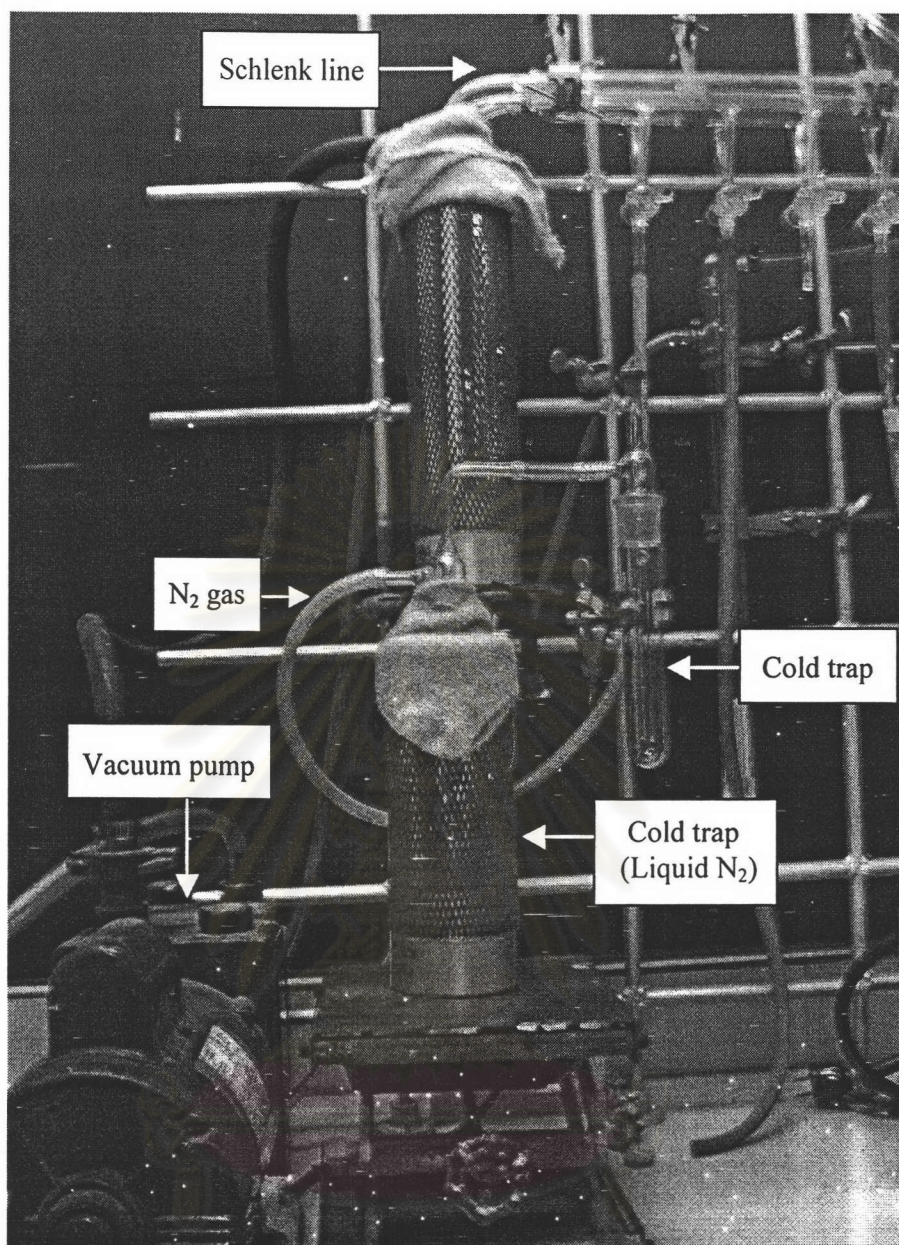
Figure 3.4 Apparatus for evacuation of the volatile organic compounds from the liquid products.

3.7.1 Effect of Na ions on MTO

The NaH-Fe-MFI, H-Fe-MFI(A), and H-Fe-MFI(B), catalysts having the same Si/Fe ratio of 87 and prepared at the pH of 9.0 in the small-scale preparation were loaded separately into the tubular reactor. The catalyst was activated under nitrogen flow at the temperature of 500°C for 1 h. Subsequently, the feed of 20% methanol in nitrogen was passed from the top through the catalyst at a GHSV of 2000 h^{-1} or 13.56 cm^3/min at the tube outlet,

while the catalyst was still heated at the reaction temperature of 500°C. After 40 min of the time on stream, gas and volatile liquid products were collected and analyzed by GC. The catalytic activity test for methanol conversion was used as the judgment for the best method for the preparation of H-Fe-MFI catalyst.

3.7.2 Effect of Temperature on MTO

The tiny pellet H-Fe-MFI catalyst with the Si/Fe ratio of 87 at the pH value of 9.0 in the small-scale preparation was loaded into a tubular reactor. Catalytic test was performed as described in the previous section at different temperatures: 300, 350, 400, 450, and 500°C. After 40 min of time on stream, gas and volatile liquid products were collected and analyzed by GC.

3.7.3 Blank Test on MTO

To study effect of thermal cracking of methanol on MTO the blank test for methanol conversion to olefins was performed using only quartz wool instead of catalyst at a GHSV of 2000 h^{-1}, at the reaction temperature of 300 and 450°C and the time on stream of 40 min. The gas and volatile liquid products were collected and analyzed by GC.

3.7.4 Effect of Si/Fe Ratio on MTO

H-Fe-MFI with the Si/Fe ratios of 80, 25, and 9.9 at the pH of 10.5 in the small-scale preparation were used as catalysts. The catalytic activities of methanol conversion were tested at a GHSV of 2000 h^{-1}, at the reaction temperature of 450°C, and time on stream of 40 min. Gas and volatile liquid products were collected and analyzed by GC.

3.7.5 Effect of Catalyst Morphology on MTO

To study the effect of catalyst morphology on methanol conversion, H-Fe-MFI with different pH and different preparation scale were used as catalysts. Using the H-Fe-MFI catalyst with the Si/Fe ratio in gel of 90 prepared at the pH value of 9.0 and 10.5 in the small-

scale preparation and the pH value of 9.0 in the large-scale preparation as catalysts. Similarly, the methanol conversion to olefins was tested at a GHSV of 2000 h^{-1}, at the reaction temperature of 450°C and the time on stream of 40 min. Gas and volatile liquid products were collected and analyzed by GC.

3.8   Determination of Coke Deposited on the Catalysts

Each catalyst from Section 3.7.1 to 3.7.5 was dried in an oven at the temperature of 200°C for 3 h. Coke was removed from the catalyst by calcination the used catalyst in a muffle furnace at 600°C for 8 h. The amount of coke deposited on the catalyst was determined by the difference in mass before and after calcination according to equation (3.1):

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

When, W_{cal} = Weight of the used catalyst after calcination at 600°C

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