

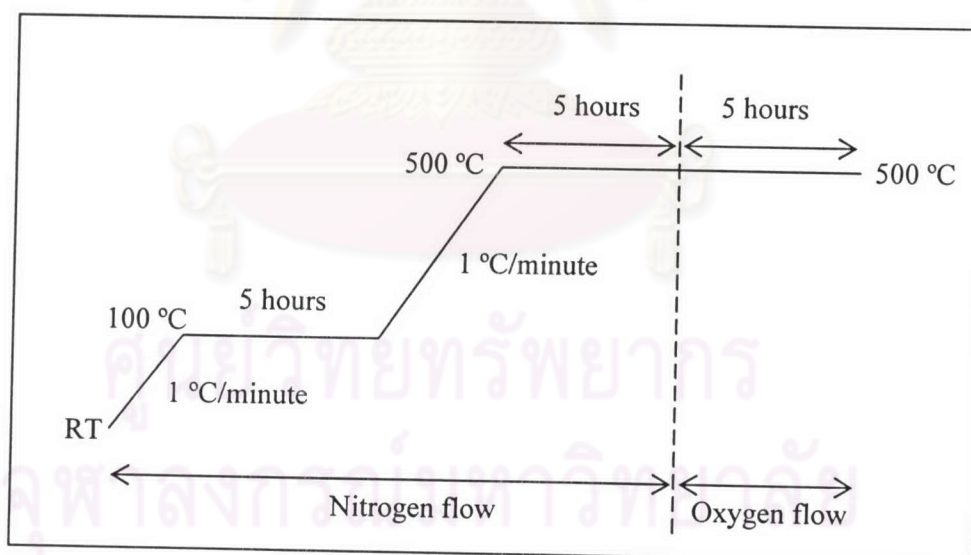
CHAPTER III

EXPERIMENT

3.1 Equipment and Apparatus

Ovens and Furnace

The catalysts were crystallized at 100 °C using a Memmert UM-500 oven. For determination of iron by AAS, calcination of catalysts was performed at 500 °C in a Carbolite RHF 1600 muffle furnace in air. For catalytic test, calcination of catalysts was performed in a split tube furnace with programmable heating rate of 1°C/minute under nitrogen flow from room temperature up to 500 °C and continuously for 5 hours followed by oxygen flow for 5 hours at the same temperature. The heating program is shown in Scheme 3.1.



Scheme 3.1 The heating program for calcination of Fe-SBA-15 catalysts for catalytic reaction (RT = Room Temperature).

X-ray Powder Diffractometer

XRD pattern identifying the SBA-15 structure of the synthesized samples was measured using a Rigaku DMAX 2200 Ultima⁺ X-ray powder diffractometer equipped with a monochromator and a Cu-target X-ray tube (40 kV, 30 mA) at angles of 2θ ranged from 0.6 to 6°.

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.

Electron Spin Resonance Spectrometer

The local sites of iron in the catalysts were investigated on ESR spectra using a JEOL JES-RE2X spectrometer at room temperature calibrated with Manganese maker, which is located at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

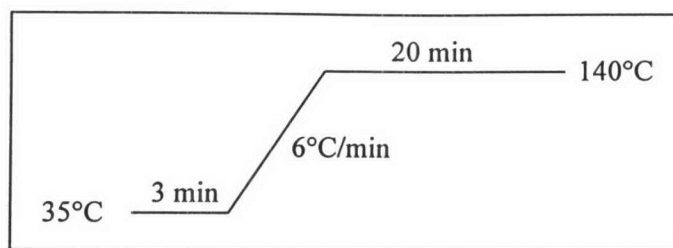
Scanning Electron Microscope

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

Gas Chromatograph

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 was used for determination of the methanol conversion and analysis of the liquid products at constant temperature of 35 °C.

Hydrocarbon gas products were analyzed using a Shimadzu GC-9A gas chromatograph equipped with a 30-m long and 0.53-mm outer diameter Alumina-PLOT column with the GC-oven heating program as shown in Scheme 3.2.



Scheme 3.2 The GC-oven heating program for hydrocarbon gas product analysis.

pH meter

The pH of gel and all solutions were determined using a Metrohm pH meter model 744 which was calibrated by buffer solutions (Merck) with the pH values of 4 and 7 prior to use.

The Catalytic Apparatus

The catalytic apparatus for methanol conversion test assembled in our laboratory was composed 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 generator. The catalytic apparatus is shown in Figure 3.1.

ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

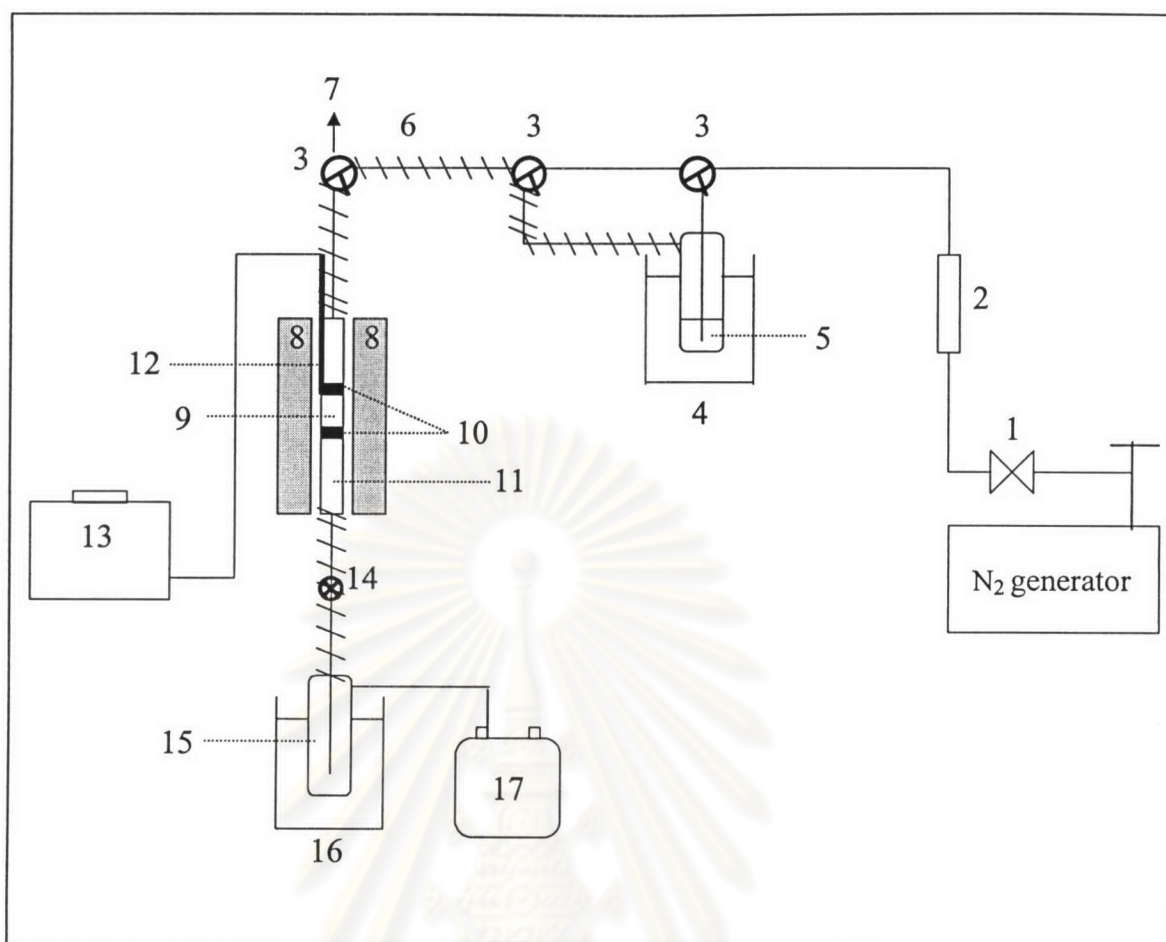


Figure 3.1 Schematic diagrams of the catalytic apparatus for methanol conversion to olefins.

- | | | |
|------------------------------|-----------------------------|----------------------|
| 1 = needle valve, | 2 = flow meter, | 3 = three-way valve, |
| 4 = water bath, | 5 = methanol reservoir, | 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

Both Nitrogen gas for catalyst synthesis and oxygen gas for calcination with 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.%), hydrochloric acid (37%), and absolute methanol were supplied from Carlo Erba. Ferrous sulfate heptahydrate (99.5%) was supplied from Merck. Tetraethoxysilane (TEOS, 98%) and standard iron(III) solution for atomic spectroscopy were supplied from Fluka. Triblock copolymer PEO₂₀PPO₇₀PEO₂₀ (Pluronic 123, M.W. 5800) was a product from Aldrich. Standard gas mixture and liquid mixture for GC analysis was kindly obtained from Thai Olefins. Other chemicals were purchased from BDH or Fluka, otherwise specifically identified.

3.3 Direct Synthesis of Fe-SBA-15

3.3.1 Synthesis of Fe-SBA-15

Following the basic synthesis method of ferrisilicate materials³⁰, the prerequisite procedure is the formation of ferrisilicate complexes by adding dropwise the silica source into iron source solution under acidic condition. Therefore tetraethylorthosilicate (TEOS) was added dropwise into acidic solution of iron (Fe²⁺ or Fe³⁺) in HCl aqueous solution. Then this mixture was continuously stirred for 3 h under nitrogen atmosphere. Next step was modified from the synthesis method of Al-SBA-15 invented by Yue *et al.*²⁴. The triblock copolymer PEO₂₀PPO₇₀PEO₂₀ was dissolved in deionized water and then the template solution was transferred into a 500-cm³ 4-neck round bottom flask and was vigorously stirred for 1 h by mechanical stirrer with speed of 350 rounds per minute under nitrogen atmosphere. Next HCl solution was added dropwise into the template solution and continuously stirred for 1 h. After that the ferrisilicate mixture was added dropwise into the template solution at 40 °C and continuously stirred. After continuously stirring for 1 h, the speed of mechanical stirred was reduced to 200 rounds per minute and aging at 40 °C for 24 h. The resulting gel has a molar

composition of $1 \text{ SiO}_2 : x \text{ Fe}_2\text{O}_3 : 0.017 \text{ PEO}_{20} \text{PPO}_{70} \text{PEO}_{20} : 222.16 \text{ H}_2\text{O} : y \text{ HCl}$ where x is 0.00278, 0.00556, and 0.01667 for obtaining the Si/Fe molar ratios in gel of 180, 90, and 30, respectively and y is in range 0.003-6.50 depended on the desired pH that is -0.30, 1.0, 1.5, 2.0, 2.5, and 3.0. Finally the gel was statically crystallized in a Teflon bottle and was heated under its own pressure at $100 \text{ }^\circ\text{C}$ for 2 days. The solid product was separated from the solution by filtration, washed with deionized water until no acid remained, and air-dried. The apparatus for synthesis are presented in Figure 3.2 and the schematic diagram for the gel preparation is demonstrated in Scheme 3.3. To confirm the results, the synthesis conditions were performed twice times.

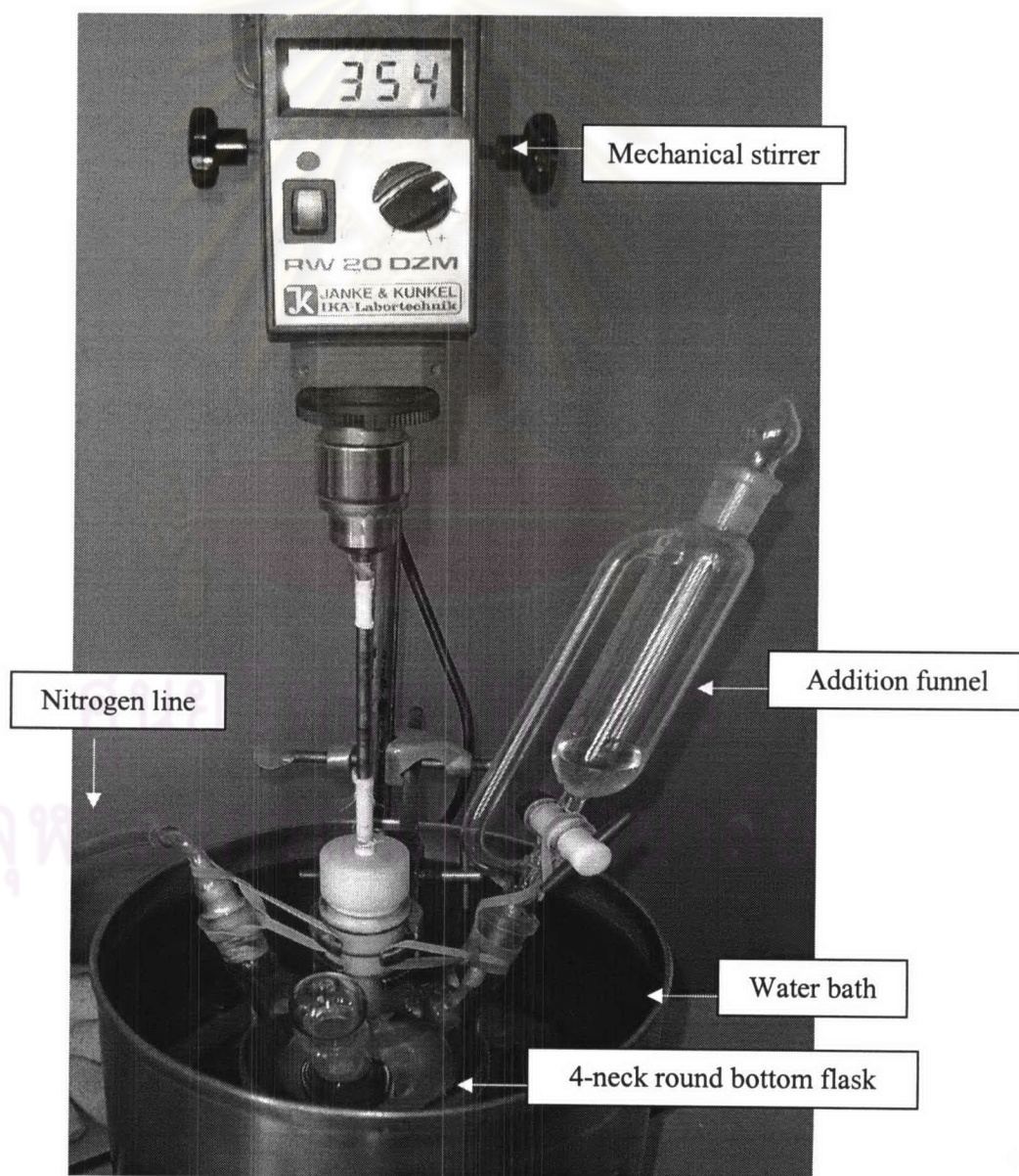
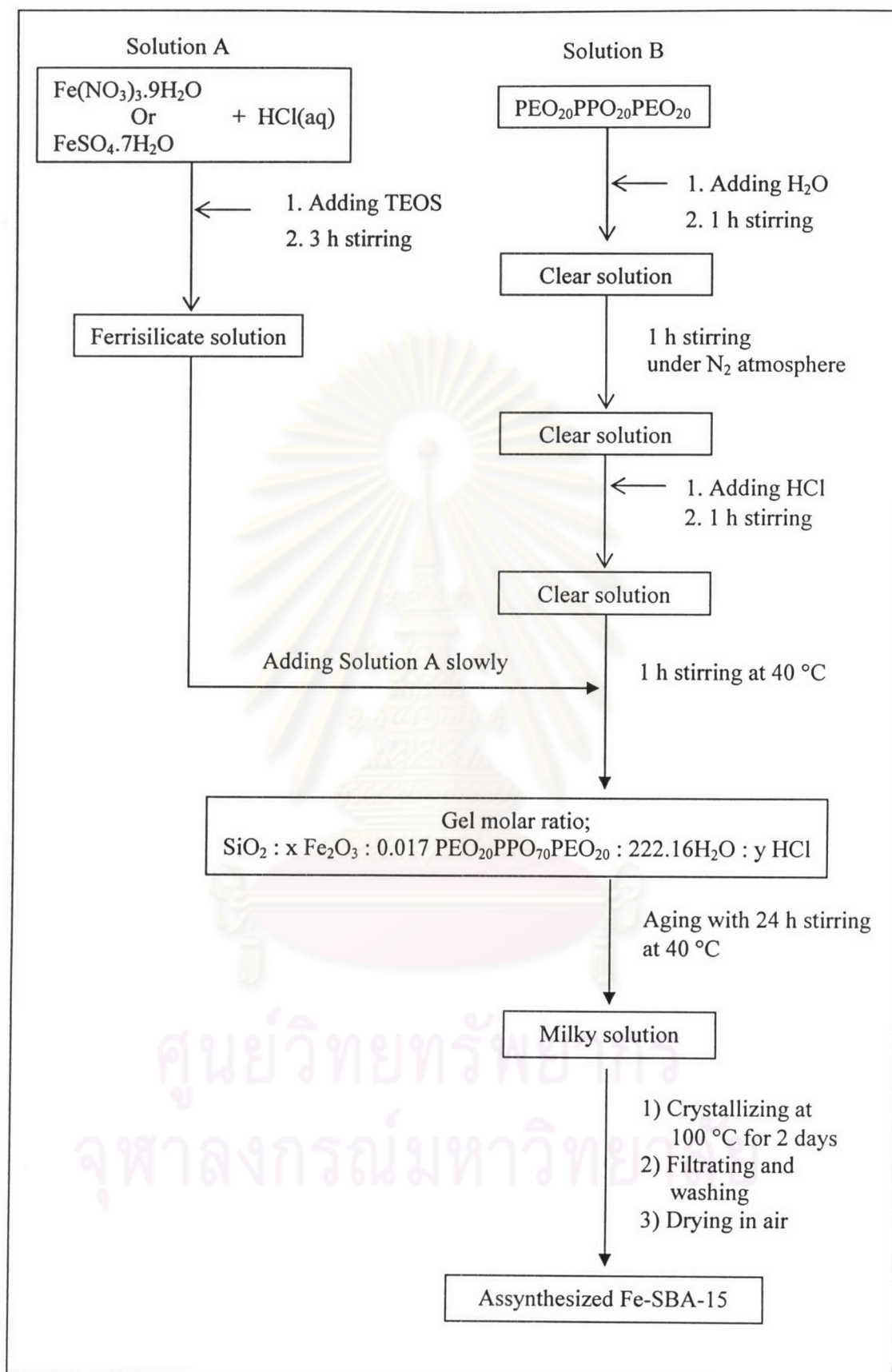


Figure 3.2 Apparatus for the gel preparation.



Scheme 3.3 Preparation diagram of the gel mixture in the synthesis of Fe-SBA-15, namely Method I.

3.3.2 The study of effect for synthesis of Fe-SBA-15

3.3.2.1 The effect of aging step

To investigate the importance of the aging step during synthesis, two methods of gel preparation were performed with and without aging step at 40 °C for 24 h before crystallization. The synthesis recipe was similar to that reported in Section 3.3.1, except the pH was maintained near 1.5 and Fe^{3+} was used as iron source at Si/Fe = 90.

3.3.2.2 The effect of reagent-addition order

In addition to the recipe in Scheme 3.2 (Method I), analogous method was performed by simultaneous addition of the iron source in acid solution and TEOS contemporaneously dropped into the solution B without previously mixed (namely Method II). The schematic diagram for the Method II is demonstrated in Scheme 3.4. The optimal method was selected to prepare the rest Fe-SBA-15.

3.3.2.3 The effect of pH gel

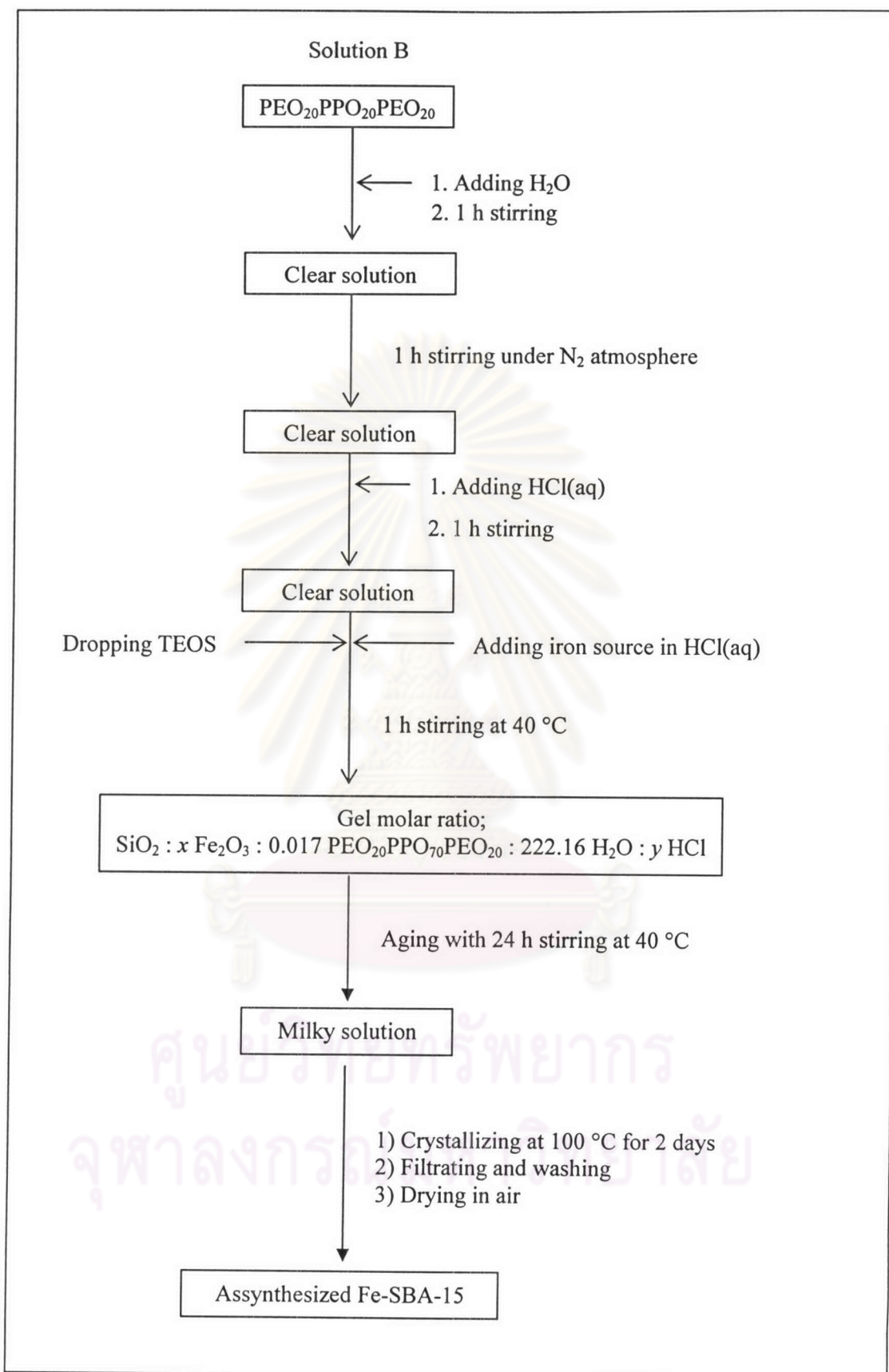
The pH of gel was controlled by the concentration of HCl solution in gel that was represented in term of gel molar ratio (Si/HCl). The pH of -0.30, 1.00, 1.50, 2.00, 2.50, and 3.00 which were corresponded to the y in gel ratio in range of 0.003-6.50 was studied in the Fe-SBA-15 synthesis.

3.3.2.4 The effect of iron source

The iron sources used were ferrous sulfate (FeSO_4) as Fe^{2+} source and ferric chloride (FeCl_3) as Fe^{3+} source. Fe-SBA-15 using both of iron sources was synthesized under nitrogen atmosphere to prevent the oxidation of Fe^{2+} to Fe^{3+} .

3.3.2.5 The effect of amounts of iron in gel

Fe-SBA-15 samples synthesized at Si/Fe molar ratios of 30, 90, and 180, including pure silica SBA-15 (no iron) were investigated.



Scheme 3.4 Preparation diagram of the gel mixture in the synthesis of Fe-SBA-15 for study the effect of reagent-addition order, namely Method II.

3.4 Sample Preparation for AAS

The as-synthesized Fe-SBA-15 materials were calcined in air to remove the triblock copolymer template. Then 0.0400 g of a calcined catalyst is soaked with 10 cm³ of 37% HCl in a 100-cm³ Teflon beaker and subsequently with 10 cm³ of 48% hydrofluoric acid to get rid off silica in the form of volatile SiF₄ species. The solid is heated not boiled to dryness on a hot plate. The fluoride treatment were repeated twice more. An amount of 10 cm³ of mixture of 6 M HCl: 6M HNO₃ at a ratio 1: 3 is added and further heated to dryness. An amount of 10 cm³ deionized water is added to the beaker and warmed for 5 minutes to complete dissolution. The solution is transferred to a 50-cm³ polypropylene volumetric flask and made to the volume by adding deionized water. The flask is capped and shaken thoroughly and the solution is then transferred into a plastic bottle with a treaded cap lined with a polyethylene seal.

3.5 Organic Template Removal

An organic template, PEO₂₀PPO₇₀PEO₂₀, 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-SBA-15 samples were calcined in a quartz boat from room temperature to 100°C for 5 h in a tube furnace under N₂ atmosphere with programmable heating rate of 1°C/min to remove the moisture in materials, then the materials were heated up to 500 °C with heating rate of 1 °C/min and dwelled at the same temperature for 5 h followed by heating under dry oxygen flow for 5 h. The heating program is shown in Scheme 3.1.

3.6 Test of the Fe-SBA-15 Catalysts for Methanol Conversion

The selected Fe-SBA-15 catalysts were freshly calcined at 500 °C before catalytic test was performed. An amount of 0.05 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 1 ton was held on the catalyst wafer for 3 min and then it was crushed into tiny pellets of a size 2 x 2 x 0.7 mm³ approximately. Then a 0.25 g portion of the tiny pellets Fe-SBA-15 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 20 mm resulting in a catalyst volume of 0.46 cm³. The catalyst was then activated in the tubular reactor at the temperature of 500°C for 1 h under the nitrogen flow at 60 cm³/min. After that the catalyst was cooled to the desired temperature. 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 17.23 cm³/min. Before the reaction was performed, the 10-μl portion of methanol vapor was withdrawn from the catalytic line at the septum point above the catalyst (number 7 in Figure 3.1) and after the time on stream of 30 min, a 10-μl portion of gas products was withdrawn from the catalytic line at the septum point below the catalyst location (number 14 in Figure 3.1) by a gas tight syringe and was analyzed for methanol fed and remained, respectively, using a GC equipped with a HP-5 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 3.3. The volatile liquid was analyzed using a GC equipped with the HP-5 coated capillary column.

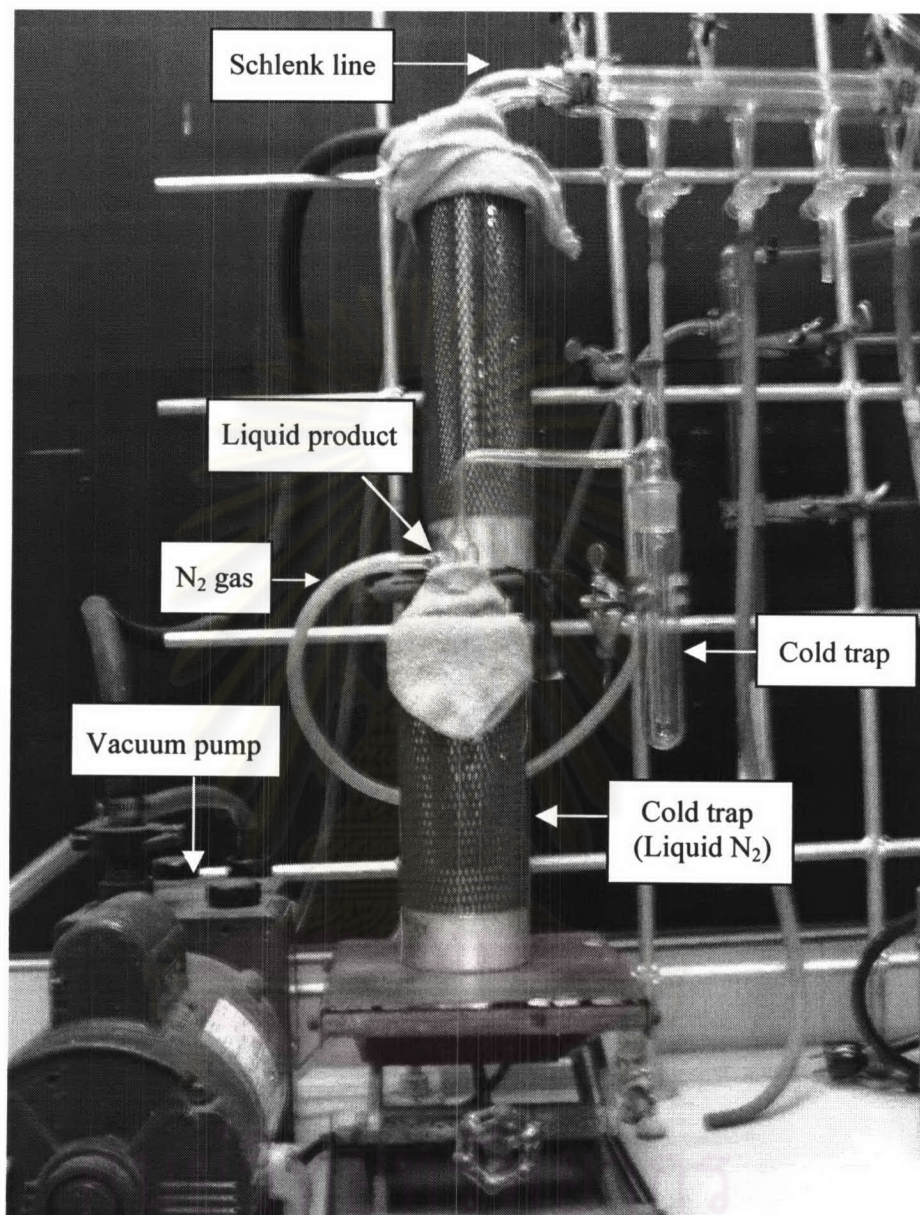


Figure 3.3 Apparatus for evacuation of the volatile organic compounds from the liquid products.

3.6.1 Effect of temperature on methanol conversion

The temperatures of 300, 400, and 500 °C were varied in order to study the influence of temperature on the methanol conversion and selectivity to products. The optimal temperature was chosen for testing the rest effect.

3.6.1.1 Blank test on methanol conversion

To study the methanol conversion due to pyrolysis at high temperature, the blank test for methanol conversion was performed using only quartz wool in tube reactor instead of catalyst at a GHSV of 2000 h⁻¹, at various temperatures of 300, 400 and 500°C and time on stream (TOS) of 30 minute. The gas and volatile liquid products were collected and analyzed by GC.

3.6.1.2 Catalyst test on methanol conversion

The Fe-SBA-15 sample which was synthesized under the following condition: Fe³⁺ as iron source, pH of 2.5, and Si/Fe in gel of 90, was selected for the test at various temperatures of 300, 400, and 500 °C under the same condition as for the blank test.

3.6.2 Effect of Fe sources on methanol conversion

The Fe-SBA-15 materials chosen to study the effect of Fe²⁺ and Fe³⁺ sources were prepared under the following condition: pH of 2.5 in gel and Si/Fe ratio in gel of 180. The catalytic test was performed at the optimal temperature from topic 3.6.1 under following condition: 0.25 g of catalyst, GHSV = 2000 h⁻¹, temperature of methanol in reservoir of 35 °C, and TOS of 30 minute. The gas and volatile liquid products were collected and analyzed by GC.

3.6.3 Calculation for Conversion of Methanol in methanol conversion

Methanol conversion activity was evaluated in term of conversion of methanol into other hydrocarbons.

$$\text{Methanol conversion (\%)} = \frac{(A_{\text{in}} - A_{\text{out}})}{A_{\text{in}}} \times 100 \quad (3.1)$$

Where A_{in} = GC peak area of methanol from inlet sampling (number 7 in Figure 3.1)

and A_{out} = GC peak area of methanol from outlet sampling (number 14 in Figure 3.1)

The high value of conversion means the high activity in converting of methanol to products.

3.6.4 Determination of Coke Deposited on the Catalysts

When the reaction finished, nitrogen gas was flow through each catalyst from Section 3.6.1.2 and 3.6.2 for 15 minute at the reaction temperature to remove other remained substance. Then coke was removed from the catalyst by calcination of the used catalyst in a muffle furnace at 600°C for 10 h. The amount of coke deposited on the catalyst was determined by the difference in mass before and after calcination according to Equation (3.2):

$$\% \text{ wt. Coke} = \frac{|W_{\text{cal}} - W_{\text{un-cal}}| \times 100}{W_{\text{cal}}} \quad (3.2)$$

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

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