

CHAPTER III

EXPERIMENTS

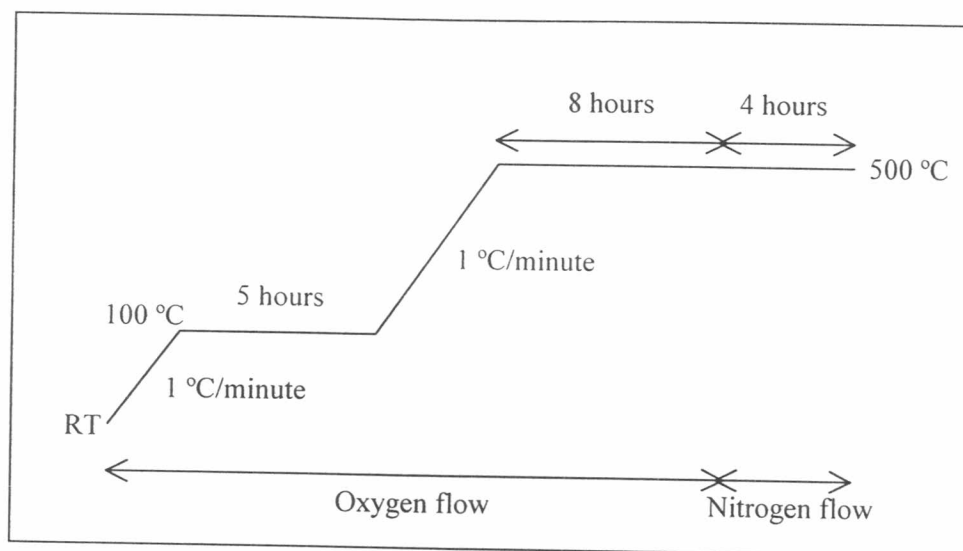
3.1 Instruments and Apparatus

Ovens and Furnaces

All catalysts were crystallized using a Memmert UM-500 oven. The heating of any solid samples at 100-120 °C were also carried out using the same oven. For determination of iron by AAS, calcination of catalysts was performed at 500 °C in a Carbolite RHF 1600 muffle furnace. For catalytic test, calcination of catalysts was performed in a split tube furnace with programmable heating rate of 1°C/minute under oxygen flow for 8 hours followed by nitrogen flow for 4 hours. The heating program is shown in Scheme 3.1

XRD

Synthesized samples were identified for their structure using a Rigaku D/MAX-2200 X-ray diffractometer (XRD) at the Petroleum and Petrochemical College, Chulalongkorn University with nickel filtered Cu K α radiation (30 kV, 30 mA) at an angle of 2 θ range from 1.5° to 10°. The scan speed was 2°/minute and the scan step was 0.02°. The slits for scattering, divergent and receiving were fixed at 0.5, 0.5, and 0.15 nm, respectively.



Scheme 3.1 The heating program for calcination of Fe-MCM-41 catalysts (RT = Room Temperature)

XRF

Iron content in the waste iron oxide was determined using a SISON S X-ray fluorescence spectrometer ARL 8410 at the Department of Science Service, Ministry of Science and Technology.

Atomic Absorption Spectrometer

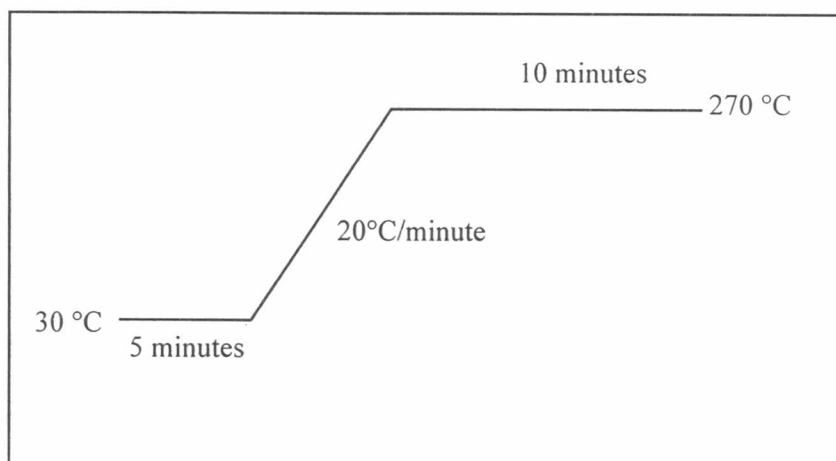
Iron content in the catalysts was performed using a Varian Spectra-AA300 atomic absorption spectrometer with air/acetylene flame, which is located at the Scientific and Technological Research Equipment Center, Chulalongkorn University.

ESR Spectrometer

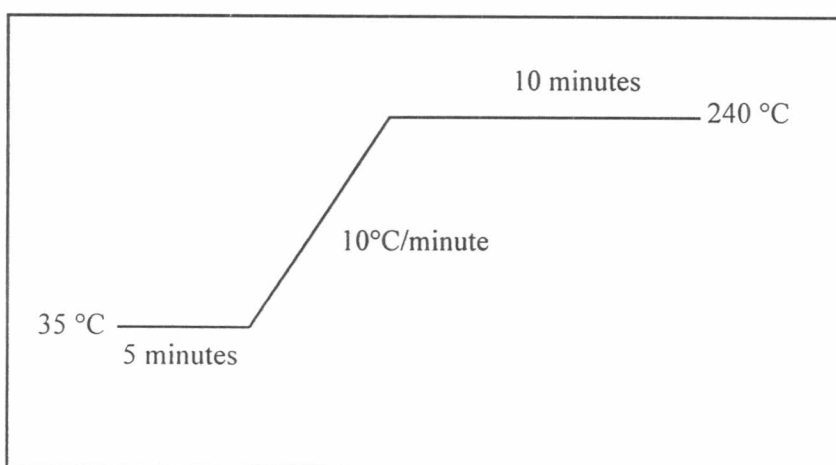
The local sites of iron in catalysts were recorded on ESR spectra using a JEOL JES-RE2X spectrometer at room temperature, which is located at the Scientific and Technological Research Equipment center, Chulalongkorn University.

Gas Chromatography

Liquid products were analyzed using a Shimadzu GC-14B gas chromatograph equipped with a 30-m long, 0.25-mm outside diameter DB-1 column (0.25- μ m film thickness) and the GC detector is a flame ionization detector (FID). The GC heating programs for 0.10 μ L liquid product are shown in Scheme 3.2 and 3.3.



Scheme 3.2 The GC heating program for liquid products from arylation of benzene with benzyl chloride



Scheme 3.3 The GC heating program for liquid products from alkylation of benzene with 2-chlorobutane

Nitrogen Adsorptometer

Characterization of catalyst porosity in terms of nitrogen adsorption-desorption isotherms and BET specific surface area was carried out using a Quantachrome Autosorb-1 nitrogen adsorptometer at the National Metal and Materials Technology Center (MTEC), National Science and Technology Development Agency.

The Catalytic Apparatus

The catalytic apparatus for Friedel-Crafts alkylation of benzene is comprised of a water-cooled condenser, a pair shaped flask, a thermocouple connected with a temperature controller, a silicone oil bath, heating coil, a magnetic stirrer and a UHP-N₂ pipe. The catalytic apparatus is displayed in Figure 3.1.

3.2 Chemical and Gases

Nitrogen gas and oxygen gas with high pure grade were purchased from Thai Industrial Gases (TIG) and were dehydrated by passing through a 40 x 2.5 cm tube of molecular sieve 4A. Ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 98.0 wt.%) was supplied from Carlo Erba. Sodium silicate solution (10.13 wt.% Na₂O, 29.71 wt.% SiO₂, 59.80 wt.% H₂O) was kindly provided from Thai Silicate. Cetyltrimethylammonium bromide (C₁₆TMABr) was from Fluka. Standard liquid mixture for GC analysis was kindly obtained from Thai Olefins Company. Silicone oil (Flash point 350 °C) was from K.H.Co.,Ltd. Other chemicals were from Merck or Fluka, otherwise specifically identified.

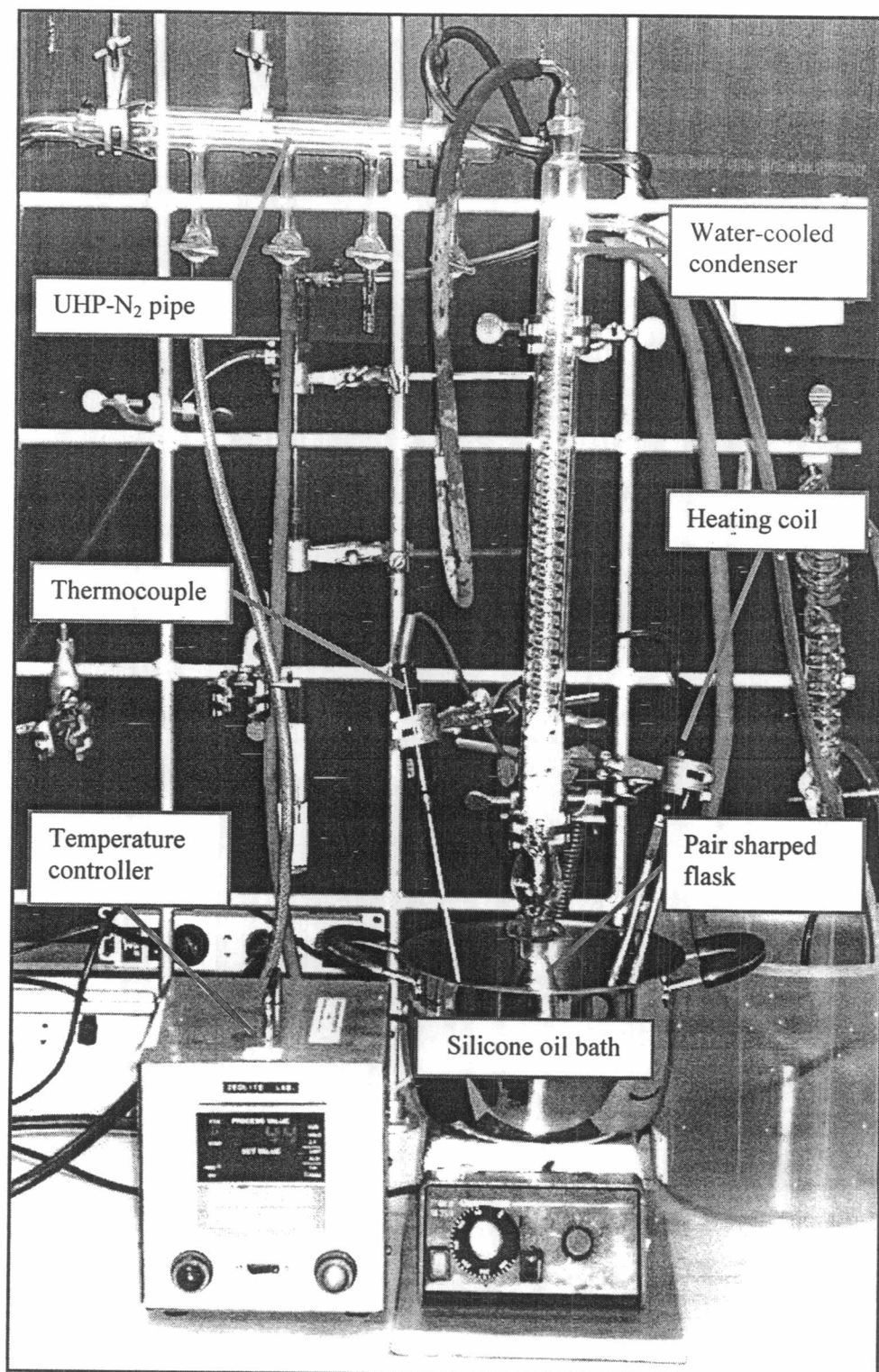


Figure 3.1 Catalytic apparatus for Friedel-Crafts alkylation of benzene

3.3 Sample Preparation for AAS

In a 100-cm³ Teflon beaker, 0.0400 g of a calcined catalyst was soaked with 10 cm³ of concentrated hydrochloric acid (conc. HCl) and subsequently with 10 cm³ of 48% hydrofluoric acid (HF) to remove the silica in a form of volatile SiF₄ species. The solid was heated but not boiled to dryness on a hot plate. The removal of silica was repeated three times. 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. 5 cm³ of 6 M HCl was added to the beaker and warmed for 5 minutes to dissolve the remains. 10 cm³ of 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 up the volume by adding deionized water. The flask was capped and shaken thoroughly. If the sample was 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 Iron Oxide from Industrial Iron Waste⁽⁶⁸⁾

The iron oxide was prepared by pipetting 50 cm³ of the iron waste solution to a 500-cm³ beaker and heated but not boiled on the hot plate for 30 minutes. After filtration, the iron waste solution was boiled while a 6 M ammonia solution (NH₃) was added drop by drop from a buret to the solution. The precipitated iron oxide was filtered and washed several times with 0.5% ammonium nitrate solution (NH₄NO₃) to remove chloride. The precipitate was dry overnight in the oven at 120 °C. After drying, the brown solid was obtained. The solid was purified again by digesting in 25 cm³ of 6 M HCl, boiled under vigorous stirring for 30 minutes and filtered. While the orange solution was boiled, a 6 M NH₃ was added drop by drop again. The precipitate was filtered, washed with 0.5% NH₄NO₃ and dried overnight in the oven at 120 °C. The brown solid product named iron oxide waste (Waste-Fe₂O₃) was obtained at a yield of 15.53 g.

3.5 Direct Synthesis of Fe-MCM-41 with a Si/Fe Ratio in Gel of 50 Using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as Iron Source and One-step Crystallization

The gel with a molar composition of $\text{SiO}_2 : 0.01 \text{Fe}_2\text{O}_3 : 0.23 \text{Na}_2\text{O} : 0.51 \text{C}_{16}\text{TMABr} : 72.70 \text{H}_2\text{O}$ was prepared. The iron solution (solution A) was prepared by dissolving 0.6250 g of ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and 0.67 g of concentrated sulfuric acid (conc. H_2SO_4) in 9.00 g of deionized water. The template solution (solution B) was prepared by dissolving 14.40 g of cetyltrimethylammonium bromide ($\text{C}_{16}\text{TMABr}$) in 83.34 g of deionized water. In a 500-cm³ 4-neck round bottom flask containing solution A, 15.45 g of sodium silicate solution and solution B were added dropwise under vigorous stirring, respectively. The apparatus for the gel preparation is displayed in Figure 3.2. The resulting gel was crystallized in Teflon bottle at 100 °C for 10 days. The solid product was filtered, washed several times with deionized water and dried overnight in air at room temperature. The white solid product named Fe-MCM-41-OS was obtained at a yield of 5.05 g. The schematic diagram for the gel preparation using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is shown in Scheme 3.4.

3.6 Direct Synthesis of Fe-MCM-41 with a Si/Fe Ratio in Gel of 50 Using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as Iron Source and Two-step Crystallization

The gel with a molar composition of $\text{SiO}_2 : 0.01 \text{Fe}_2\text{O}_3 : 0.23 \text{Na}_2\text{O} : 0.51 \text{C}_{16}\text{TMABr} : 72.70 \text{H}_2\text{O}$ was prepared. The iron solution (solution A) was prepared by dissolving 0.6250 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.67 g of conc. H_2SO_4 in 9.00 g of deionized water. The template solution (solution B) was prepared by dissolving 14.40 g of $\text{C}_{16}\text{TMABr}$ in 83.34 g of deionized water. In a 500-cm³ 4-neck round bottom flask containing solution A, 15.45 g of sodium silicate solution and solution B were added dropwise under vigorous stirring, respectively. The resulting gel was

crystallized in Teflon bottle at 100 °C for 2 days. The gel was adjusted pH to 9.50 with 50% acetic acid (CH_3COOH) and then recrystallized again at 125 °C for 6 days. The solid product was filtered, washed several times with deionized water and dried overnight in air at room temperature. The white solid product named Fe-MCM-41-N3 was obtained at a yield of 8.32 g. The schematic diagram for the gel preparation using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is shown in Scheme 3.5.

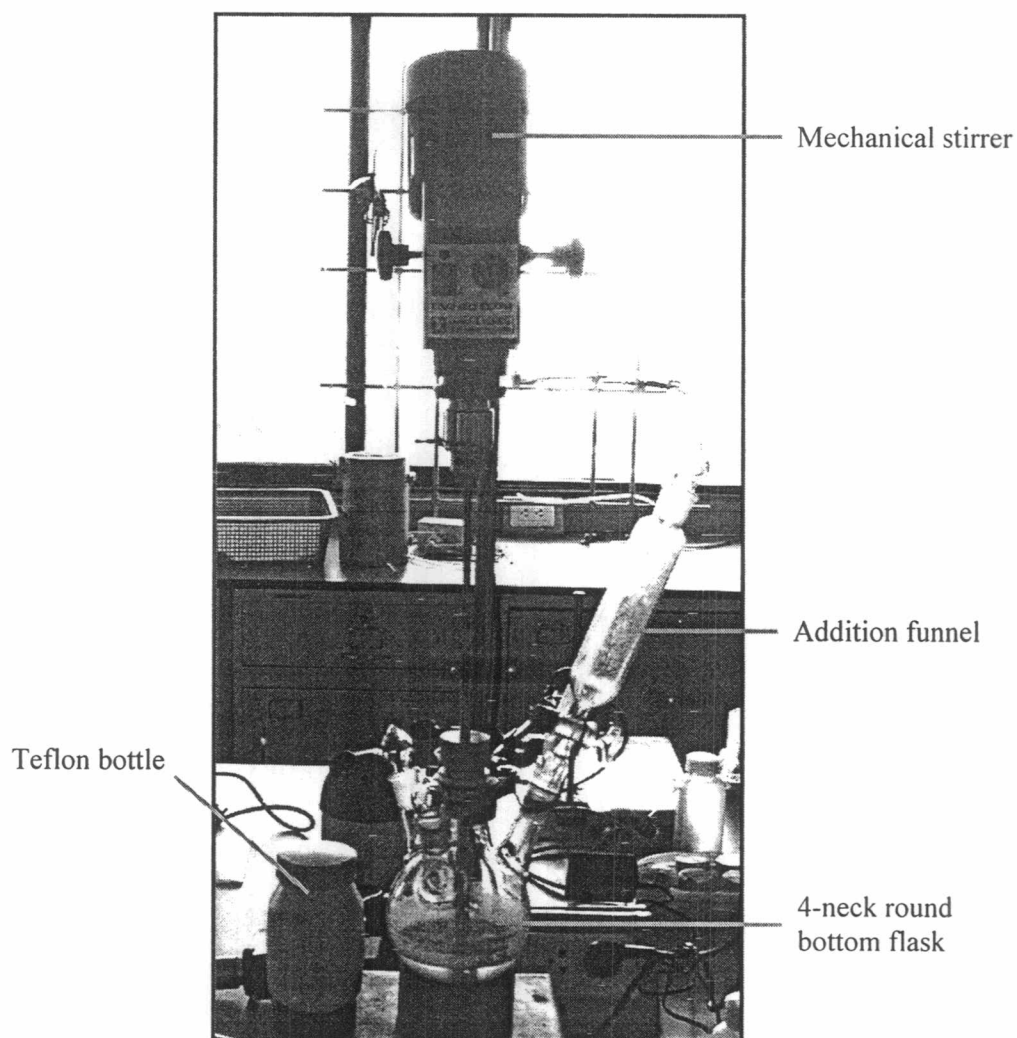
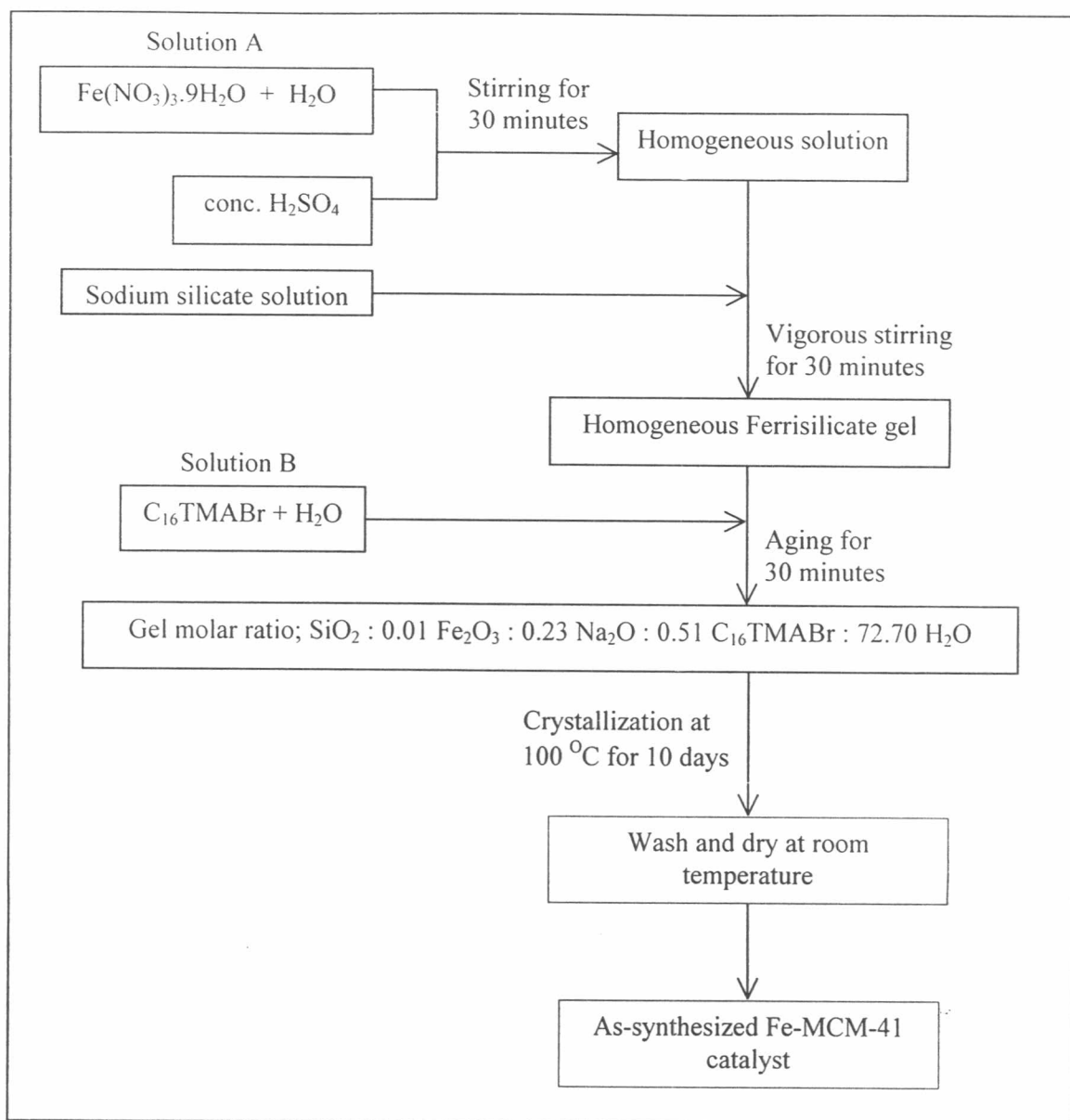
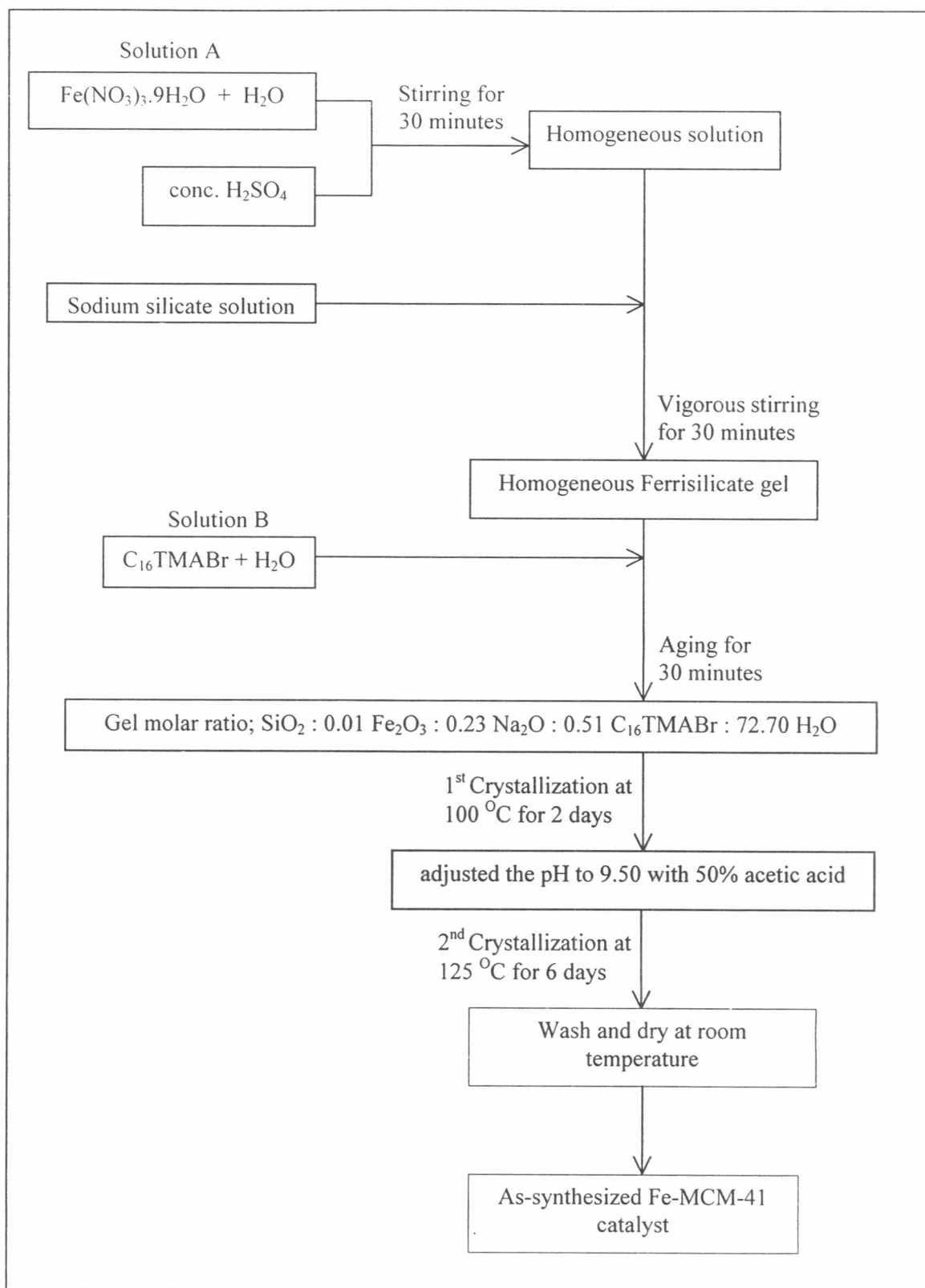


Figure 3.2 Gel preparation apparatus



Scheme 3.4 Fe-MCM-41 synthesis diagram for one-step crystallization



Scheme 3.5 Fe-MCM-41 synthesis diagram for two-step crystallization

3.7 Direct Synthesis of Fe-MCM-41 with Various Si/Fe Ratios

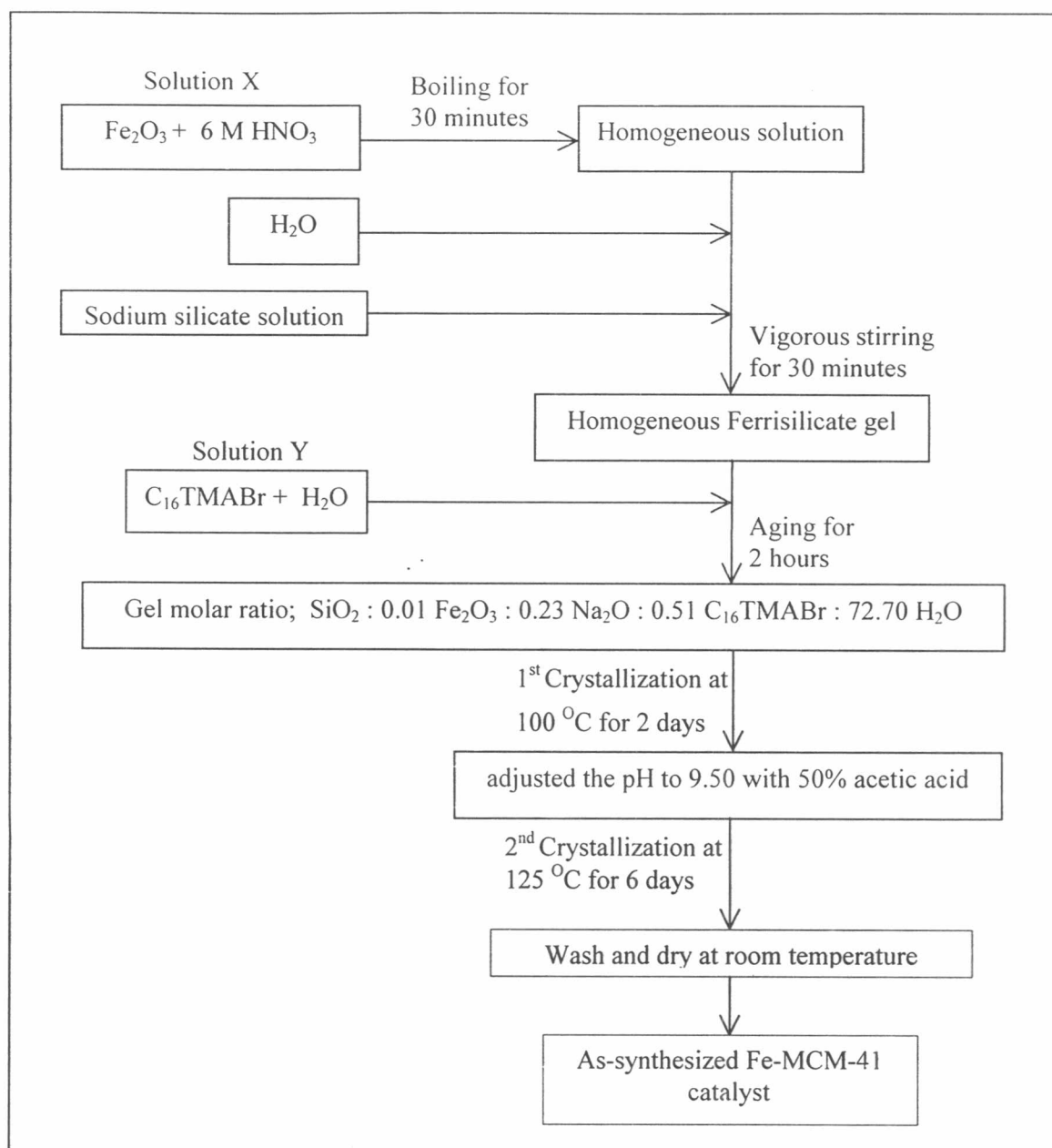
The gel with a molar composition of $\text{SiO}_2 : x \text{Fe}_2\text{O}_3 : 0.23 \text{Na}_2\text{O} : 0.51 \text{C}_{16}\text{TMABr} : 72.70 \text{H}_2\text{O}$ was prepared ($x = 0.0050 - 0.0167$). The iron solution (solution A) was prepared by dissolving y g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($y = 1.0482, 0.7862, 0.6250, \text{ and } 0.3144$ g for sample with Si/Fe ratio of 30, 40, 50, and 100, respectively) and 0.67 g of conc. H_2SO_4 in 9.00 g of deionized water. The template solution (solution B) was prepared by dissolving 14.40 g of $\text{C}_{16}\text{TMABr}$ in 83.34 g of deionized water. In a 500-cm^3 4-neck round bottom flask containing solution A, 15.45 g of sodium silicate solution and solution B were added dropwise under vigorous stirring, respectively. The resulting gel was crystallized in Teflon bottle at 100°C for 2 days. The gel was adjusted pH to 9.50 with 50% CH_3COOH and then recrystallized again at 125°C for 6 days. The solid product was filtered, washed several times with deionized water and dried overnight in air at room temperature. The experimental data of as-synthesized samples prepared by two-step crystallization are summarized in Table 3.1

Table 3.1 Experimental data of as-synthesized samples prepared by two-step crystallization

Sample name	Si/Fe	Aging time of synthesis gel (hours)	Yield of as-synthesized product (g)
Fe-MCM-41-N1	30	2	5.90
Fe-MCM-41-OV24H	30	24	5.59
Fe-MCM-41-N2	40	2	5.67
Fe-MCM-41-N3	50	0.5	8.32
Fe-MCM-41-N4	50	2	7.25
Fe-MCM-41-N5	50	2	5.71
Fe-MCM-41-N6	100	2	6.03

3.8 Direct Synthesis of Fe-MCM-41 with a Si/Fe Ratio in a Gel of 50 Using Waste-Fe₂O₃ as Iron Source

The iron solution (solution X) was prepared by digesting 0.1305 g of Waste-Fe₂O₃ in 2.55 g of 6 M nitric acid (HNO₃). The solution was boiled on the hot plate for 30 minutes, cooled to room temperature and then 7.28 g of deionized water was added to the solution before it was transferred to a 500-cm³ 4-neck round bottom flask. The template solution (solution Y) was prepared by dissolving 14.40 g of C₁₆TMABr in 83.34 g of deionized water. In the 500-cm³ 4-neck round bottom flask containing solution X, 15.45 g of sodium silicate solution and solution Y were added dropwise under vigorous stirring, respectively. The resulting gel was crystallized in a Teflon bottle at 100 °C for 2 days. The gel was adjusted pH to 9.50 with 50% CH₃COOH and then recrystallized again at 125 °C for 6 days. The solid product was filtered, washed several times with deionized water and dried overnight in air at room temperature. The white solid product named Fe-MCM-41-NW4 was obtained at a yield of 6.06 g. The schematic diagram for the gel preparation using Waste-Fe₂O₃ is demonstrated in Scheme 3.6.



Scheme 3.6 Fe-MCM-41 synthesis diagram for Waste-Fe₂O₃

3.9 Catalytic Experiment of Fe-MCM-41 Catalysts

3.9.1 Arylation of Benzene with Benzyl Chloride

In the pair shaped flask containing 5.50 cm³ of benzene and a magnetic bar, 0.36 cm³ of benzyl chloride (benzene/benzyl chloride mole ratio = 20) and 0.0600 g of calcined Fe-MCM-41 catalyst was added. The flask was connected with the water-cooled condenser as shown in Figure 3.1. The reaction was performed in a silicone oil bath at various temperature (40, 50, 60, and 100 °C) and time (1, 2, and 4 hours). The liquid product was filtered, rinsed several times with acetone, and transferred to a 25-cm³ volumetric flask. 0.1 cm³ of cumene was added as the internal standard and the solution was made up the volume by adding acetone. The product was identified by GC and GC-MS, respectively.

3.7.2 Alkylation of Benzene with 2-chlorobutane

As describe above, 5.50 cm³ of benzene, 0.33 cm³ of 2-chlorobutane (benzene/2-chlorobutane mole ratio = 20), and 0.06 g of Fe-MCM-41 catalyst were added to the reaction flask. The reaction was performed in the silicone oil bath at various temperature (50, 60, 80, and 100 °C) and time (2 and 4 hours). The liquid product was filtered, rinsed several times with acetone, transferred to a 10-cm³ volumetric flask in which 0.1 cm³ of cumene was added as the internal standard and made up the volume by adding acetone. The product was identified by GC and GC-MS, respectively.