

CHAPTER III

EXPERIMENTS

3.1 Instruments and Apparatus

Centrifuge

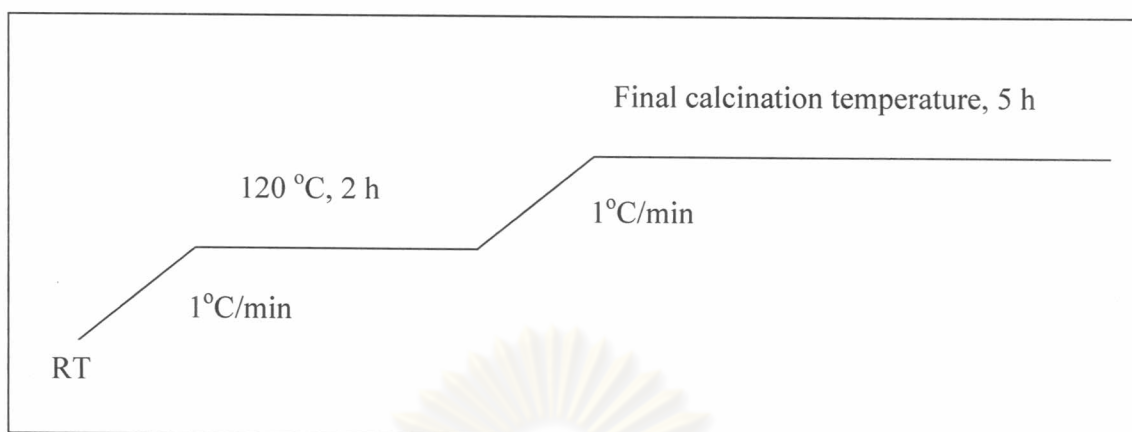
A Centaur 2, Sanyo centrifuge was used to purify clays and collect the synthesized catalysts. The process of purification is aimed for removing quartz and other impurities at various centrifugal speeds.

X-ray Diffractometer (XRD)

The Rigaku, Dmax2200/Ultima⁺ X-ray diffractometer (XRD) with a monochromator and Cu K α radiation (40 kV, 30 mA) was used to determine the basal spacing of clays and the synthetic catalysts. The 2-theta angle was taken from 2 to 30 degree with scan speed of 2 degree/min and scan step of 0.02 degree. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree, 0.15 mm, respectively.

Oven and Furnace

All synthesized samples were dried by a Memmert UM-500 oven at 100°C for 1 day. Metal precursors in the interlayer of clay were converted to metal oxide by calcination using a Carbolite RHF 1600 muffle furnace. The calcination temperature was set between 300 to 600°C for 5 h with the heating rate of 1°C/min. The heating program is shown in Scheme 3.1



Scheme 3.1 The heating program for calcination of Fe-pillared clays (RT = Room Temperature).

Atomic Absorption Spectrometer (AAS)

The iron content in Fe-pillared clays was analyzed using the PE-Analyst 100 (Perkin Elmer)

Inductive Couple Plasma Spectroscopy (ICP)

The amount of gallium in the Ga-doped Fe-pillared clays was analyzed using the Perkin Elmer, ICP-AES, PLASMA1000 located at Scientific and Technological Research Equipment Center, Chulalongkorn University.

Nitrogen Adsorptometer

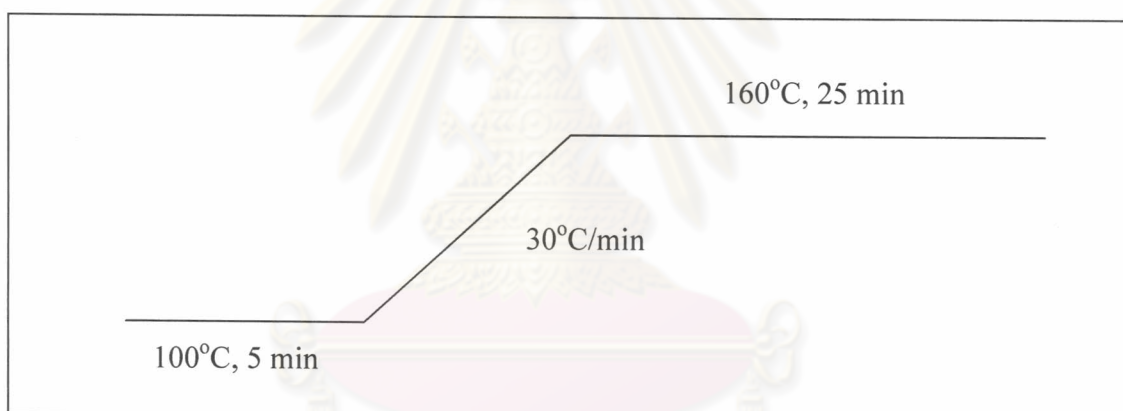
The BET specific surface area of synthesized samples was measured by the Quantachrome Autosorb-1 nitrogen adsorptometer at Department of Chemistry, Faculty of Science, King MongKut's Institute of Technology Ladkrabang Campus.

Scanning Electron Microscope (SEM)

SEM and elemental ion mapping photographs of synthesized samples were analyzed using the JEOL (JSM-5800LV), at Scientific and Technological Research Equipment Center, Chulalongkorn University.

Gas Chromatograph (GC)

Liquid products were analyzed using a Shimadzu GC-14A gas chromatograph equipped with a 30-m long HP-5 column (0.25-mm outer diameter, 0.25 μm film thickness). The detector was flame ionization detector (FID). The GC temperature program was shown in Scheme 3.2



Scheme 3.2 The GC temperature program for liquid products.

Gas Chromatograph and Mass Spectrometer (GC-MS)

Product isomers were identified using the Agilent Technologies 6890N GC system, Agilent 5973 Network Mass Selective Detector and Agilent 7683 Series Injector which was located at Department of Chemistry, Faculty of Science, Mahidol University.

Catalytic Apparatus

The catalytic apparatus for Friedel-Craft alkylation of benzene with 1-dodecene, shown in Figure 3.1, is comprised of:

1. a water-cooled condenser
2. round bottom flask
3. thermocouple
4. temperature controller
5. heating coil
6. silicone oil bath
7. magnetic bar and magnetic stirrer
8. thermometer

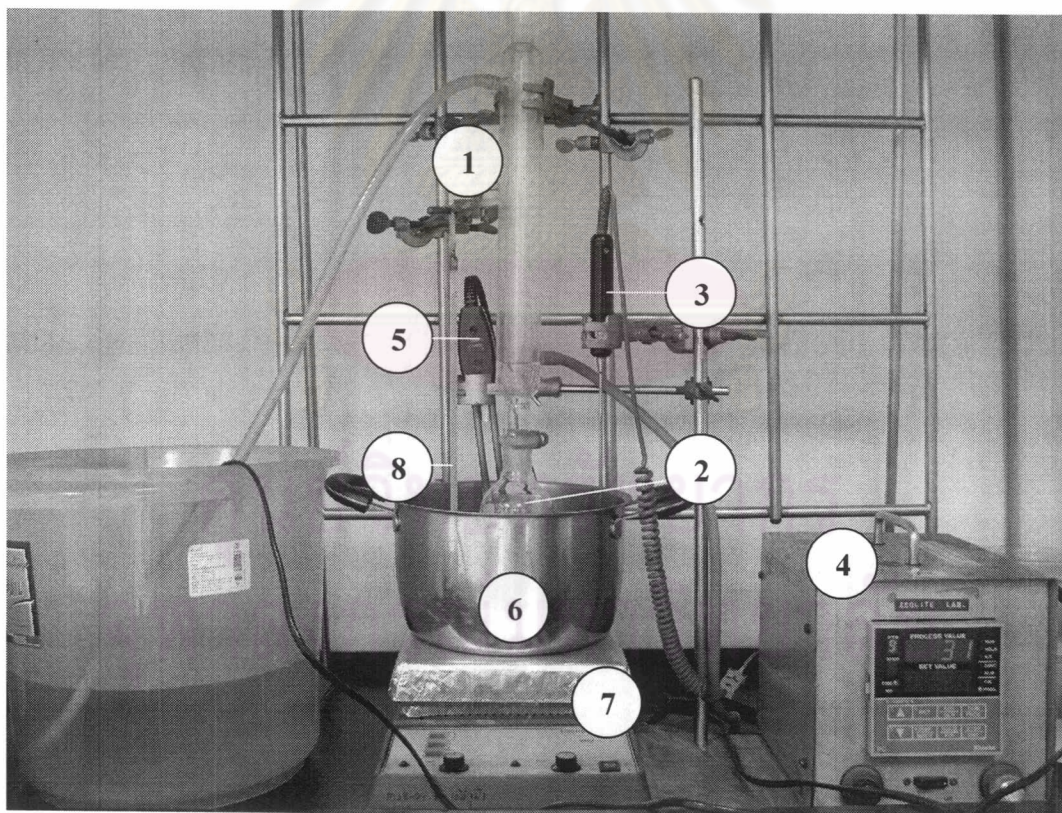


Figure 3.1 Catalytic apparatus.

3.2 Starting Materials

Clays used as the raw material are bentonite and hectorite (Hectabrite DP). Bentonite is kindly supported by CERNIC INTERNATIONAL CO., LTD. Hectorite is also kindly supported by VOLCLAY SIAM LIMITED. The compositions of hectorite and bentonite are summarized in Table 3.1.

Table 3.1 Hectorite and bentonite compositions

	Hectorite ^a	Bentonite ^b
SiO ₂	61.78	63.60
Al ₂ O ₃	1.58	17.60
MgO	20.32	-
Fe ₂ O ₃	1.23	3.10
CaO	10.07	3.00
Na ₂ O	2.80	3.40
K ₂ O	0.33	0.50

^a Data from VOLCLAY SIAM LIMITED

^b Data from CERNIC INTERNATIONAL CO., LTD

Bentonite was purified by fractionated sedimentation. A hundred grams of bentonite was dispersed into 1000 ml of deionized water under vigorous stirring. After sedimentation, the colloid clay was separated out for further centrifuged steps. The sediment is mostly comprised of quartz impurities. Then, the colloid clay was centrifuged at various speed (1000, 2000 and 4000 rpm) and dried at 100°C. The different centrifugal parts of bentonite were characterized by XRD.

3.3 Chemicals

1. Sodium hydroxide, NaOH (Merck, reagent grade).
2. Sodium chloride, NaCl (Scharlau reagent grade).
3. Iron (III) chloride, FeCl₃ anhydrous (Riedel-de Haën).

4. 1-Dodecene, $C_{12}H_{24}$ (Fluka, 95%).
5. Benzene, C_6H_6 (J.T. Baker, reagent grade).
6. n-Pentane, $n-C_5H_{12}$ (Fisher Chemicals, reagent grade).
7. Sodium sulfate anhydrous, Na_2SO_4 (Fluka, 99%).
8. Gallium (III) nitrate hydrate, $Ga(NO_3)_3 \cdot H_2O$ Aldrich, 99.9%).
9. Cumene, C_9H_{12} (Fluka, 98.0%).

3.4 Homoionic Clays

Homoionic clay (Na-ion predominant) was obtained by means of cation exchange. Starting clay was vigorously stirred in 2M NaCl, 5M NaCl and 5M NaOH, with the ratio of clay to Na-solution of 1 g : 50 ml for 1 day at room temperature. The products were washed with deionized water until chloride or hydroxide anions were eliminated by a process of subsequent centrifugation and decantation. The Na-ion exchanged process was repeated for several times in order to investigate the effect of Na-ion exchanged on d-spacing of clay. The product obtained was named Na-clay *e.g.* Na-Bentonite and Na-Hectorite.

3.5 Synthesis of Fe-Pillared Clays

Na-clay was dispersed in deionized water (10% w/w) by vigorous stirring for 1 day. A 1M iron (III) chloride solution was slowly added into the suspended clay. The ratio of Fe^{3+} to clay was varied from 0.5 to 240 meq per gram of clay. The mixture was stirred continuously for 24 h at room temperature. Then, the product was washed with deionized water until chloride ions were removed by a process of centrifugation and decantation. The as-synthesized samples were finely grounded and dried at room temperature for 1 day. Afterwards, they were calcined at $300^\circ C$ for 5 h in a muffle furnace. The calcined products obtained were named HFe_x and BFe_x , where x is the amount of iron loading in meq per gram of clay. H and B stand for hectorite and bentonite, respectively.

3.6 Synthesis of Ga-doped Fe-Pillared Hectorite

The Ga-doped Fe-Pillared Hectorite was synthesized by two methods. For method A or direct intercalation, Na-clay was dispersed in deionized water (10% w/w) with vigorous stirring for 1 day. The aqueous mixture of iron (III) chloride (FeCl_3) and gallium (III) nitrate hydrate ($\text{GaNO}_3 \cdot \text{H}_2\text{O}$) was slowly added into the suspended clay. The $\text{Fe}^{3+}:\text{Ga}^{3+}$ to clay ratio was 10:1 meq per gram of clay. The mixture was stirred continuously for 24 h at room temperature. Then, it was washed with deionized water until chloride and nitrate ions were eliminated by a process of centrifugation and decantation. On the other hand, the method B is impregnation of gallium (III) nitrate hydrate ($\text{GaNO}_3 \cdot \text{H}_2\text{O}$) on the HFe_{10} with the $\text{Fe}^{3+}:\text{Ga}^{3+}$ ratio fixed at 10:1 meq. However, the as-synthesized samples from two methods were finely grounded and dried at room temperature. Afterthat, the as-synthesized samples were calcined at 300°C for 5 h in a muffle furnace. The calcined products obtained from method A and B were named $\text{HFe}_{10}\text{Ga}_1$ and $\text{HFe}_{10}\text{Ga}_1\text{I}$, where I stands for impregnation, respectively.

3.7 Sample Preparation for AAS and ICP

The calcined catalyst (0.0400 g) in a 100 cm^3 teflon beaker was soaked with 10 cm^3 of concentrated hydrochloric acid (conc. HCl) and subsequently with 10 cm^3 of 48% hydrofluoric acid (HF) to remove silica out in form of volatile SiF_4 species. The mixture was heated, but not boiled to dryness, on a hot plate. The removal of silica was repeated three times. 10 cm^3 of a mixture, 6M HCl : 6M HNO_3 at a ratio 1 : 3, was added and further heated to dryness. 5 cm^3 of 6M HCl was added to the beaker, and the mixture was warmed for 5 min to complete dissolution. The solution was transferred to a 50 cm^3 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 treated cap lined under with a polypropylene seal.

3.8 Calcination of Fe-Pillared Clays

All as-synthesized Fe-pillared clays were calcined before using as catalysts. To obtain the optimal temperature for calcination, the as-synthesized Fe₁₀-pillared hectorite (as-HFe₁₀) was calcined between 300 to 600°C for 5 h. The obtained products were characterized using XRD technique.

3.9 Alkylation of Benzene with 1-Dodecene

The Friedel-Crafts alkylation of benzene with 1-dodecene was performed in batch mode. A 0.2785 g catalyst was added to the mixture of benzene and 1-dodecene (0.05 : 5 x 10⁻³ mol) in a round bottom flask connected with a cooling condenser for refluxing. The mixture was continuously stirred and the reaction was performed at 60 to 150°C and 15 to 600 min in a silicone oil bath. After that, the reaction was quenched with deionized water and the catalyst was filtered from the mixture. The organic layer, mixture products, was separated and dried with sodium sulfate (Na₂SO₄). The mixture products were diluted with n-pentane and analyzed by GC using cumene as an internal standard. The isomer products were identified by GC-MS.

3.10 Reuse of Catalyst

The catalytic efficiency of catalyst in reaction cycle for industrial economy was investigated by reusing the catalyst. The used HFe₁₀ catalyst was calcined at 300°C for 5h. The structural characterization of the used HFe₁₀ catalyst was tested using XRD and N₂-adsorption-desorption techniques, respectively. Then, the used HFe₁₀ catalyst was performed in the reaction again.