# CHAPTER III

# EXPERIMENTAL

## 3.1 Starting materials

### 3.1.1 Clays

Bentonite, a raw material was kindly supported by Cernic International Co., Ltd. The compositions of bentonite are summarized in Table 3.1.

**Table 3.1** Bentonite compositions

| **Oxide Components** | **Bentonite*** |
|---|---|
| $SiO_2$ | 63.60 |
| $Al_2O_3$ | 17.60 |
| MgO | - |
| $Fe_2O_3$ | 3.10 |
| CaO | 3.00 |
| $Na_2O$ | 3.40 |
| $K_2O$ | 0.50 |

*information from Cernic International Co., Ltd.

### 3.1.2 Chemicals

1. Sodium hydroxide, NaOH (Merck, reagent grade)
2. Sodium sulfate, $Na_2SO_4$ (Merck, analysis grade)
3. Hydrochloric acid, HCl (Merck, analysis grade)
4. Hydrofluoric acid, HF (Merck, analysis grade)
5. Nitric acid, $HNO_3$ (Merck, analysis grade)
6. Cupric acetate monohydrate, (Fluka Chemika, 99.0%)
7. 3-Chlorobenzaldehyde, (Fluka Chemika, 97.0%)

8. 4-Chlorobenzaldehyde, (Fluka Chemika, 99.0%)
9. 3-Bromobenzaldehyde, (Fluka Chemika, 98.0%)
10. 4-Bromobenzaldehyde, (Fluka Chemika, 98.0%)
11. 4-Cyanobenzaldehyde, (Fluka Chemika, 98.0%)
12. 4-Nitrobenzaldehyde, (Fluka Chemika, 98.0%)
13. Benzaldehyde, (Fluka Chemika, 98.0%)
14. Carbontetrachloride, (Merck, reagent grade)
15. Carbontetrabromide, (Fluka Chemika, 98.0%)
16. Bromotrichloromethane, (Fluka Chemika, 98.0%)
17. Trichlorofluoromethane, (Fluka Chemika, 98.0%)
18. Iodoform, (Fluka Chemika, 98.0%)
19. Iodomethane, (Fluka Chemika, 98.0%)
20. Hexachloro-2-propanone, (Fluka Chemika, 98.0%))
21. Phenylhydrazine, (Fluka Chemika, 95.0%))
22. Hydrazine hydrate, (Carlo Erba, 98.0%))
23. Ethanol, (Merck, analysis grade)
24. Hexane, (Lab-Scan, reagent grade)
25. Dimethylsulfoxide (DMSO), (Mearck-Schuchardt, synthesis grade)
26. Dichloromethane, (Lab-Scan, reagent grade)
27. Acetone, (commercial grade)

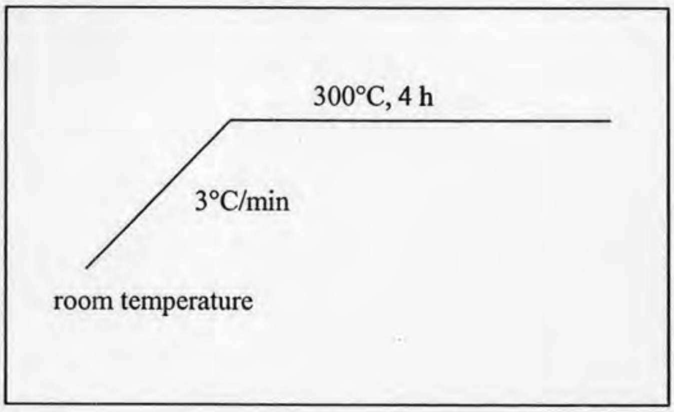
## 3.2 Instrument, apparatus and analytical measurements

### 3.2.1 Centrifuge

The purification of clays and the collection of the synthesized catalysts were processed by centaur 2, Sanyo centrifuge. The purification of clays is aimed for removing quartz and other impurities at various centrifugal speeds.

### 3.2.2 Oven and furnace

Raw clays and all synthesized catalysts were dried in a Memmert UM-500 oven at 100°C for 1 day. The calcination was performed on a Carbolite RHF 1600 muffle furnace in air. Calcination of assynthetic clays catalysts was conducted in order to convert metal precursors in the interlayer of clays into metal oxide. The heating program used for the calcination of Fe-pillared clays is shown in Scheme 3.1.



**Scheme 3.1** The heating program for the calcination of Cu-pillared clays.

### 3.2.3 X-ray diffractometer (XRD)

The XRD patterns and, in consequence, the basal spacings of catalysts (raw clays, are modified clays catalysts) were determined using a Rigaku, Dmax 2200/utima$^+$ X-ray powder diffractometer (XRD) with a monochromater and Cu $K_\alpha$ radiation (40 Kv, 30 mA). The 2-theta angle was ranged from 2 to 30 degree with the scan speed of 3 degree/min and the scan step of 0.02 degree. The scattering slit, divergent slit and receiving slit were fixed at 0.5 degree, 0.5 degree and 0.15 mm, respectively.

### 3.2.4 Inductively coupled plasma spectroscope (ICP)

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

### 3.2.5 Nitrogen adsorption/desorption (Brunauer-Emmett-Teller Method, BET)

The BET specific surface area of raw clays and synthesized Fe-pillared clays were measured by the Quantachrome Autosorb-1 nitrogen adsorptometer.

### 3.2.6 Nuclear magnetic resonance spectroscopy (NMR)

The $^1$H NMR spectra were obtained in $CDCl_3$ and determined by model Mercury plus 400 NMR spectrometer which operated at 399.84 MHz.

### 3.2.7 Chromatography

- Thin layer chromatography (TLC) was carried on aluminium sheets precoated with silica gel (Merck's, kieselgel 60 PF254).

- Column chromatography was performed on silica gel (Merck's, Kieselgel 60 G).

### 3.3 Homoionic clays

Homoionic clays were prepared by purification and then ion exchanged following the previous work by Josept *et al.* [39].

#### 3.3.1 Purification of Bentonite

According to Kanjanaboonmalert [40], bentonite was purified by fractionated sedimentation. Thirty grams of bentonite were dispersed in 1,000 mL of deinoized water under vigorous stirring for 3 h at RT. Then, the colloid bentonite was collected and separated from quartz sediments by centrifugation. The colloid clay was centrifuged at 4,000 rpm and dried at 100°C. The purified bentonite was characterized by XRD technique.

#### 3.3.2 Na-ion exchange

Na-bentonite was prepared by cation exchange. The purified bentonite was suspended in 5 M NaOH with the ratio of clay to Na-solution as 1 g: 50 mL for 1 day at RT. The hydroxide ions and the excess Na ions were removed from Na-bentonite by dialysis. Then the products were dried at 100°C. The above process was repeated three times. The Na-exchanged bentonite was characterized using XRD technique.

### 3.4 Synthesis of Cu-pillared clays

Cu-pillared clays were synthesized according to the protocol reported by Josept [38] by intercalation of copper precursors, following by calcinations at high temperature. Cu-bentonite was prepared by slurring Na-bentonite (10 g), previously dried at 100°C overnight, with 0.5 M aqueous solution of $Cu(OAc)_2$ (50 mL) at 90°C for 4 h and then cooled to RT. The colloid Cu-bentonite was centrifuged at 4,000 rpm and then the solid obtained was washed many times with water and dried at 100°C for 12 h, and followed by calcined at 300°C for 4 h in a muffle furnance. The obtained products were characterized using XRD technique and ICP-AES, respectively.

### 3.5 Sample preparation for ICP

The calcined catalyst (0.0400 g) in a 100 mL teflon beaker was soaked with 10 mL of conc HCl and subsequently with 10 mL of 48%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 for three times. The solution of 6M HCl: 6M $HNO_3$ at a ratio of 1:3 was added to 10 mL of a mixture and further heated to dryness. 5 mL of 6M HCl was added to the beaker, and the mixture was warmed for 5 min to complete dissolution. The solution was transferred to 50 mL polypropylene volumetric flask and made up the volume by adding deionized water. 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.

## 3.6 Optimum conditions study on olefination of aldehydes

### 3.6.1 General procedure

**Step 1:** An aromatic aldehyde (10 mmol) was added to the solution of hydrazine (10 mmol) connected with a condenser for refluxing. The solution was continuously stirred for 3 h and cooled. After the specific time or the reaction was finished, the reaction mixture was monitored by TLC.

**Step 2:** 25% Aqueous solution of ammonia (3.33 mL) and selected halogenated reagent 5 eq (50 mmol) were added to the mixture of hydrazone with 30 wt% of catalyst. The reaction was continued stirring for the desired time and temperature and followed by TLC. When the reaction was completed, the catalyst was simply filtered out. The solvent was evaporated to dryness under reduced pressure to afford the product. The mixture was separated with silica gel column and the obtained product was analyzed by NMR.

### 3.6.2 Effect of the amount of catalyst

The olefination reaction was carried out according to the general procedure, but the amount of Cu-pillared bentonite to aldehyde was changed to 3, 5, 20, 30, 50 and 70 wt%.

### 3.6.3 Effect of reaction temperature

The olefination of carbonyl compounds was performed according to the general procedure, but varied reaction temperature as RT and reflux temperature.

### 3.6.4 Effect of type of halogenated reagent

The olefination of carbonyl compounds was carried out according to the general procedure, but using different halogenated reagents: $CBr_4$, $CCl_3Br$, $CHI_3$, $CH_3I$ and $CCl_3F$.

## 3.7 Variation of aldehyde

The general procedure using $CCl_4$, DMSO and Cu-pillared bentonite as halogenated reagent, solvent and catalyst respectively at room temperature for 4 h was carried out. Different aldehyde: 3-chlorobenzaldehyde, 4-bromobenzaldehyde, 3-bromobenzaldehyde, 4-cyanobenzaldehyde, 3-nitrobenzaldehyde and benzaldehyde were employed instead of 4-chlorobenzaldehyde.

All products could be characterized their identity by $^1$H NMR

**1-(2,2-Dichlorovinyl)-4-chlorobenzene:** [2] yellow liquid (72%), $R_f$ 0.58 (hexane). $^1$H-NMR ($CDCl_3$) δ (ppm): 6.81 (1H, s, $Cl_2$=C$\underline{H}$), 7.34 (2H, d, $J$ = 8.65 Hz, Ar$\underline{H}$), and 7.47 (2H, d, $J$ = 8.65 Hz, Ar$\underline{H}$).

**1-(2,2-Dichlorovinyl)-3-chlorobenzene:** [2] yellow liquid (53%), $R_f$ 0.60 (hexane). $^1$H-NMR ($CDCl_3$) δ (ppm): 6.72 (1H, s, $Cl_2$=C$\underline{H}$), 7.17 (1H, t, $J$ = 7.17 Hz, Ar$\underline{H}$), 7.37 (1H, D, $J$ = 6.54 Hz, Ar$\underline{H}$), and 7.61 (1H, s, Ar$\underline{H}$).

**1-(2,2-Dichlorovinyl)-4-bromobenzene:** [2] colorless crystals (69%), $R_f$ 0.53 (hexane). $^1$H-NMR ($CDCl_3$) δ (ppm): 6.79 (1H, s, $Cl_2$=C$\underline{H}$), 7.39 (2H, d, $J$ = 8.42 Hz, Ar$\underline{H}$), and 7.50 (2H, d, $J$ = 8.50 Hz, Ar$\underline{H}$).

**1-(2,2-Dichlorovinyl)-3-bromobenzene:** [2] colorless liquid (60%), $R_f$ 0.60 (hexane). $^1$H-NMR ($CDCl_3$) δ (ppm): 6.79 (1H, s, $Cl_2$=C$\underline{H}$), 7.24 (1H, t, $J$ = 7.67 Hz, Ar$\underline{H}$), 7.40 (1H, D, $J$ = 7.93 Hz, Ar$\underline{H}$), and 7.69 (1H, s, Ar$\underline{H}$).

**4-(2,2-Dichlorovinyl)-benzonitrile:** [2] yellow liquid (68%), $R_f$ 0.50 (hexane). $^1$H-NMR ($CDCl_3$) δ (ppm): 6.81 (1H, s, $Cl_2$=C$\underline{H}$), 7.34 (2H, d, $J$ = 8.62 Hz, Ar$\underline{H}$), and 7.47 (2H, d, $J$ = 8.57 Hz, Ar$\underline{H}$).

**1-(2,2-Dichlorovinyl)-3-nitrobenzene:** [2] yellow liquid (61%), $R_f$ 0.48 (hexane). $^1$H-NMR ($CDCl_3$) δ (ppm): 6.93 (1H, s, $Cl_2$=C$\underline{H}$), 7.57 (1H, t, $J$ = 8.50 Hz, Ar$\underline{H}$), 7.83 (1H, d, $J$ = 7.79 Hz, Ar$\underline{H}$), 8.17 (1H, d, $J$ = 8.26 Hz, Ar$\underline{H}$) and 8.43 (1H, s, Ar$\underline{H}$).

**1-(2,2-Dichlorovinyl)-benzene:** [2] yellow liquid (25%), $R_f$ 0.56 (hexane). 1H-NMR (CDCl3) δ (ppm): 6.87 (1H, s, $Cl_2$=C$\underline{H}$), 7.36 (3H, m, Ar$\underline{H}$), and 7.54 (2H, d, $J$ = 7.36 Hz, Ar$\underline{H}$).

### 3.8 Variation of halogenated reagent

According to general procedure of olefination, the reaction was carried out using 4-chlorobenzaldehyde and DMSO at RT for 24 h. Different halogenated reagents: $CCl_3Br$, $CBr_4$, $CCl_3F$, $CHI_3$ and $CH_3I$ were employed instead of $CCl_4$.

### 3.9 Reuse of catalyst

The catalytic efficiency in a reaction cycle for industrial economy was investigated by reusing the catalyst. The used Cu-clays catalyst was regenerated by calcined at 300°C for 4 h. The structural characterization of the used Cu-clays catalyst was tested using XRD and $N_2$-adsorption desorption techniques. Then, the regenerated Cu-clays catalyst was reused in the olefination reaction.