

## Chapter 3

### Experimental

#### 3.1 Equipment

|  | Model     | Brand              |
|--|-----------|--------------------|
| 1. Magnetic stirrer                      | M21/1     | Framo <sup>®</sup> |
| 2. Mechanical stirrer                    | MDC-NS    | Eyela              |
| 3. Mechanical stirrer                    | RW20DZM   | Janke&Kunkel       |
| 4. Water aspirator                       | A-35      | Eyela              |
| 5. Oven                                  | 500       | Memmert            |
| 6. Programmable temperature control      | PC-600M   | Shinko             |
| 7. Tube reactor/tube furnace             |           |                    |
| 8. Schlenk vacuum/gas line               |           |                    |
| 9. Glove bag                             |           |                    |
| 10. Gas chromatography                   | 9A        | Shimadzu           |
| 11. X-ray diffractometer                 | JTDX-8030 | Jeol               |
| 12. X-ray fluorescence spectrophotometer | ARL8410   | Fison              |
| 13. FTIR spectrophotometer               | Impact400 | Nicolet            |
| 14. UV-VIS spectrophotometer             | Array3000 | Milton Roy         |
| 15. Scanning electron microscope         | 35CF      | Jeol               |
| 16. Atomic absorption spectrophotometer  | AA-680    | Shimadzu           |
| 17. GC-MS                                | QP2000    | Shimadzu           |

### 3.2 Chemicals

|  |               |               |
|--|---------------|---------------|
| 1. Sodium hydroxide  | AR grade      | J.T. Baker    |
| 2. Sodium silicate solution $\text{Na}_2\text{O} : 3.11\text{SiO}_2$ |               | Thai Silicate |
| 3. Alumina trihydrate  | AR grade      | Merck         |
| 4. Aluminium sulfate decaoctahydrate                                 | AR grade      | Merck         |
| 5. Manganese(II)chloride tetrahydrate                                | Reagent grade | Merck         |
| 6. NaY zeolite   | Si/Al = 2.37  | Aldrich       |
| 7. Acetone   | AR grade      | Fluka         |
| 8. 1,2-Dicyanobenzene  | Reagent grade | Merck         |
| 9. Iodobenzenediacetate  | Reagent grade | Aldrich       |
| 10. Tertiary butyl hydroperoxide<br>(t-BuOOH)70% in water            | Reagent grade | Merck         |
| 11. Pyridine   | Reagent grade | Merck         |
| 12. n-Octane   | AR grade      | J.T.Baker     |
| 13. Cyclohexene  | Reagent grade | Fluka         |
| 14. 1-Hexene   | Reagent grade | Fluka         |
| 15. 2-Hexen-1-ol   | Reagent grade | Fluka         |
| 16. Cyclohexene oxide  | Reagent grade | Fluka         |
| 17. Liquid nitrogen  |               | TIG*          |
| 18. Nitrogen gas   |               | TIG*          |
| 19. Oxygen gas   |               | TIG*          |

\* TIG means Thai Industrial Gases, Co., Ltd.

### 3.3 Reagents, Gases and Solvents

**Sodium aluminate solution** (Reagent A; 23.13% Na<sub>2</sub>O, 4% Al<sub>2</sub>O<sub>3</sub> by weight).

An amount of 23.44 g alumina trihydrate was dissolved in 114.75 g boiled solution of sodium hydroxide in 243.75 cm<sup>3</sup> water. The mixture was heated until well uniform and cooled to room temperature before use.

**Sodium aluminate solution** (Reagent B; 22.59% Na<sub>2</sub>O, 20.27% Al<sub>2</sub>O<sub>3</sub> by weight). Like reagent A, an amount of 15.50 g alumina trihydrate was dissolved in a boiled solution of 14.57 g sodium hydroxide in 19.93 cm<sup>3</sup> water.

**Aluminium sulfate solution** (Reagent C; 28.21 % Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 71.79 % H<sub>2</sub>O by weight). Aluminium sulfate decahydrate 54.90 g was dissolved in 45.07 cm<sup>3</sup> water.

**Gases:** All gases were passed through moisture traps containing molecular sieve 4A to remove a trace amount of moisture.

**Solvents:** All solvents were degassed and dehydrated over molecular sieve 4A prior to use.

### 3.4 Preparation of Zeolite Y

#### 3.4.1 Preparation of Nucleation Centers

An amount of 254.63 g sodium aluminate solution (Reagent A) was added dropwise into a mixture of 275.86 g sodium silicate containing 8.99 % Na<sub>2</sub>O and 27.09 % by weight in 135.9 cm<sup>3</sup> deionized water. The mixture was stirred vigorously using

the mechanical stirrer for 2 hours at room temperature. The mixture became a milky gel containing four components of molar ratio as  $13.5 \text{ Na}_2\text{O} : 1.0 \text{ Al}_2\text{O}_3 : 12.5 \text{ SiO}_2 : 266 \text{ H}_2\text{O}$ . After that, an amount of 500 g of the milky gel was diluted with  $178 \text{ cm}^3$  deionized water to contain  $13.5 \text{ Na}_2\text{O} : 1.0 \text{ Al}_2\text{O}_3 : 12.5 \text{ SiO}_2 : 516 \text{ H}_2\text{O}$  and then stirred vigorously for 2 hours. Finally, the diluted milky gels were aged in a capped vessel for 5 days at room temperature to form nucleation centers. Scheme 3.1 illustrates the diagram of preparing nucleation centers.

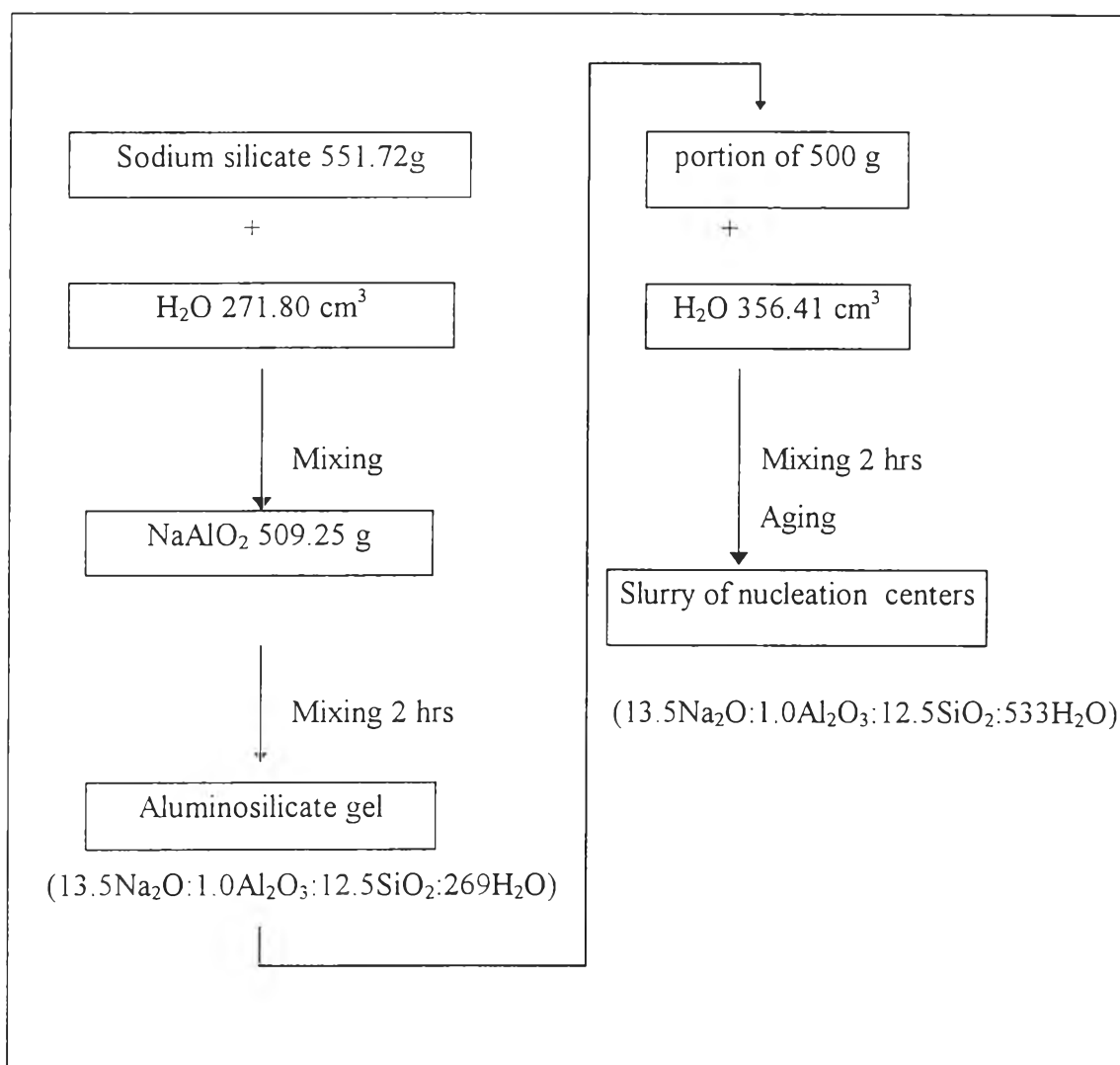
### 3.4.2 Preparation of Zeolite NaY Crystals

A reaction mixture having molar ratio  $1.9 \text{ Na}_2\text{O} : 1.0 \text{ Al}_2\text{O}_3 : 6.0 \text{ SiO}_2 : 100 \text{ H}_2\text{O}$  was prepared by adding 91.31 g of nucleation centers into the solution of 210.41 g sodium silicate and  $19.05 \text{ cm}^3$  deionized water. The mixture was stirred vigorously using the mechanical stirrer. An amount of 43.78 g of sodium aluminate solution (Reagent B) was added slowly while stirred continuously. Then 97 g of aluminium sulfate solution (Reagent C) was dropwise added. The mixture was further agitated vigorously for 2.5 hours to obtain a homogeneous mixture. The gels were transferred to a  $500 \text{ cm}^3$  glass jar and tightly closed, and the jar was heated in an oven at  $100 \text{ }^\circ\text{C}$ . Various periods of crystallization times were studied. After the desired crystallization time, the solids were filtered from the mother liquor and washed with deionized water until the filtrate was free of hydroxide. The solids were dried at  $105 \text{ }^\circ\text{C}$  and ground finely. The powders were characterized by X-ray powder diffraction technique. Scheme 3.2 illustrates the diagram of preparing zeolite Y crystals.

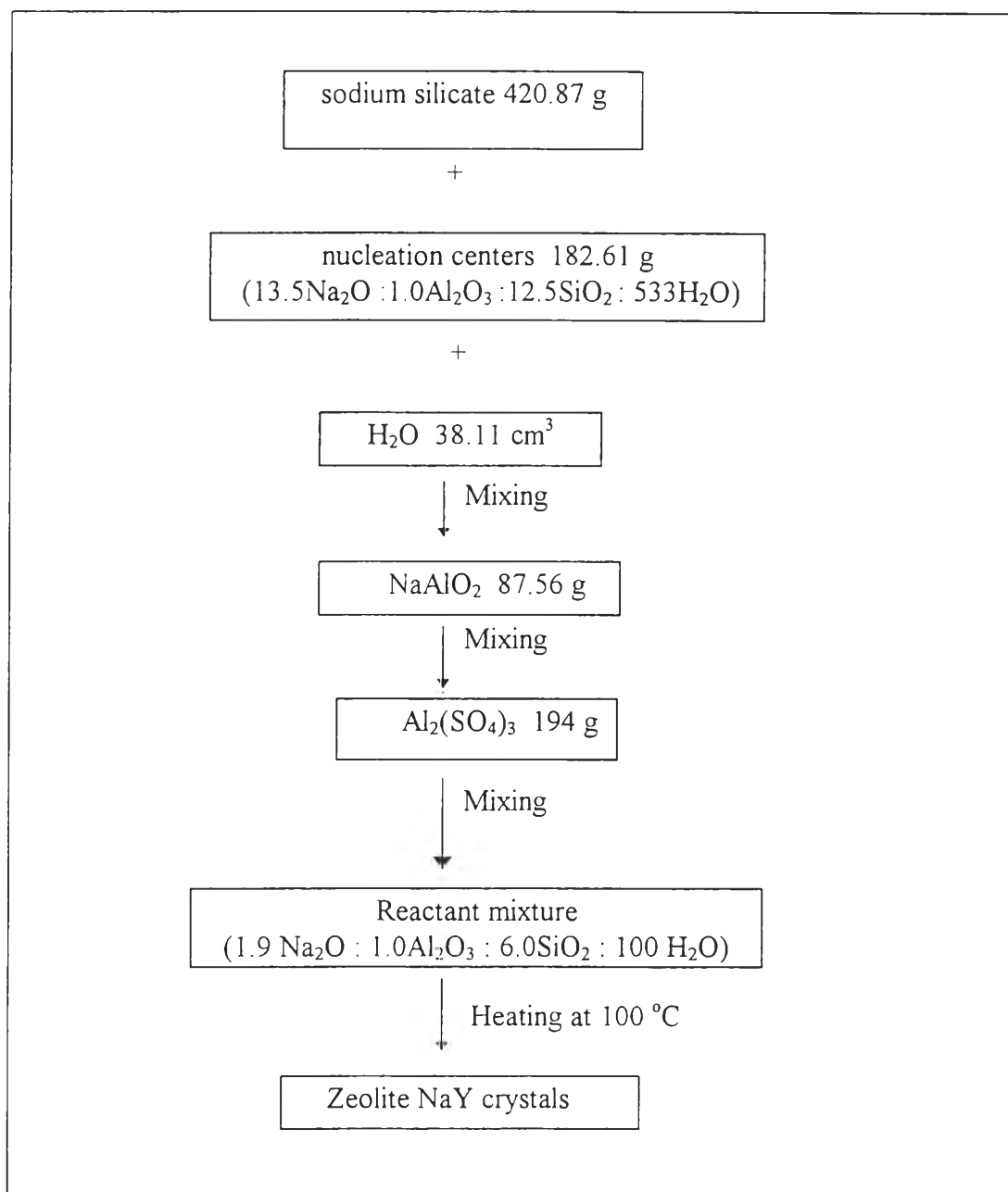
### 3.4.3 Calculation for Preparation of the Nucleation Centers and Reaction Mixture

#### Mixture

Tables 3.1 - 3.3 show how to calculate amounts of materials used to prepare the nucleation centers and the reaction mixture.



**Scheme 3.1** Preparation of the nucleation centers having the composition of  
 $13.5\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 12.5\text{SiO}_2 : 533\text{H}_2\text{O}$ .



**Scheme 3.2** The diagram of preparing zeolite Y crystals from the nucleation centers and a reactant slurry having composition of 1.9 Na<sub>2</sub>O : 1.0 Al<sub>2</sub>O<sub>3</sub> : 6.0 SiO<sub>2</sub> : 100 H<sub>2</sub>O.

**Table 3.1** Components in preparation of the nucleation centers having the oxide ratio of  $13.3\text{Na}_2\text{O}_2 : 1.0\text{Al}_2\text{O}_3 : 12.5\text{SiO}_2 : 266\text{H}_2\text{O}$ .

| Material  | Weight<br>(g) | M.W. | Na <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | H <sub>2</sub> O |
|---|---------------|------|-------------------|--------------------------------|------------------|------------------|
| M.W.  |               |      | 62                | 102                            | 60               | 18               |
| Al <sub>2</sub> O <sub>3</sub> 3 H <sub>2</sub> O   | 31.25         | 156  | -                 | 0.2                            | -                | 0.6              |
| NaOH  | 153           | 40   | 1.9               | -                              | -                | 1.9              |
| H <sub>2</sub> O  | 325           | 18   | -                 | -                              | -                | 18.1             |
| Sodium silicate<br>(Na <sub>2</sub> O : 3.11 SiO <sub>2</sub> )<br>8.99 % Na <sub>2</sub> O<br>27.09% SiO <sub>2</sub><br>59.15% H <sub>2</sub> O | 551.72        |      | 0.8               | -                              | 2.5              | 18.2             |
| H <sub>2</sub> O  | 271.8         | 18   | -                 | -                              | -                | 15.1             |
| Sum   | 1332.77       |      | 2.7               | 0.2                            | 2.5              | 53.9             |
| Molar ratio required  |               |      | 13.5              | 1.0                            | 12.5             | 269.             |

**Table 3.2** Components in preparation of the nucleation centers having  
the composition  $13.3\text{Na}_2\text{O}:1.0\text{Al}_2\text{O}_3:12.5\text{SiO}_2:533\text{H}_2\text{O}$ .

| Material                                       | Weight<br>(g) | M.W. | $\text{Na}_2\text{O}$ | $\text{Al}_2\text{O}_3$ | $\text{SiO}_2$ | $\text{H}_2\text{O}$ |
|--|---------------|------|-----------------------|-------------------------|----------------|----------------------|
| M.W.   |               |      | 62                    | 102                     | 60             | 18                   |
| Nucleation centers<br>(13.5: 1.0 : 12.5 : 269) | 500           |      | 1.01                  | 0.08                    | 0.94           | 20.22                |
| $\text{H}_2\text{O}$                           | 356.41        | 18   | -                     | -                       | -              | 19.80                |
| Sum  | 856.41        |      | 1.01                  | 0.08                    | 0.94           | 40.02                |
| Molar ratio required                           |               |      | 13.3                  | 1.0                     | 12.5           | 533                  |



**Table 3.3** Components in preparation of the reaction mixture having the composition  $1.9\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 6.0\text{SiO}_2 : 100\text{H}_2\text{O}$

| Material   | Weight<br>(g) | M.W. | Na <sub>2</sub> O | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | H <sub>2</sub> O |
|--|---------------|------|-------------------|--------------------------------|------------------|------------------|
| <b>M.W.</b>  |               |      | 62                | 102                            | 60               | 18               |
| <b>Nucleation centers<br/>(13.3 : 1.0 : 12.5 : 533)</b>  | 182.61        |      | 0.22              | 0.02                           | 0.20             | 8.53             |
| <b>Sodium silicate<br/>(Na<sub>2</sub>O : 3.11 SiO<sub>2</sub>)</b>  | 420.87        |      | 0.61              | -                              | 1.9              | 13.83            |
| <b>NaAlO<sub>2</sub> solution<br/>22.59% Na<sub>2</sub>O<br/>20.27% Al<sub>2</sub>O<sub>3</sub><br/>57.15% H<sub>2</sub>O</b>              | 87.56         |      | 0.32              | 0.17                           | -                | 2.78             |
| <b>H<sub>2</sub>O</b>  | 38.11         | 18   | -                 | -                              | -                | 2.12             |
| <b>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution<br/>28.21% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub><br/>71.79% H<sub>2</sub>O</b> | 194           |      | - 0.48            | 0.16                           | -                | 7.74             |
| <b>Sum</b>   | 923.10        |      | 0.67              | 0.35                           | 2.1              | 35               |
| <b>Molar ratio required</b>  |               |      | 1.9               | 1.0                            | 6.0              | 100              |

From Table 3.3, the initial reactants were prepared in excess basicity, so acidic salt, aluminum sulfate was used to reduce the basicity. The addition of the aluminum sulfate also increases the alumina content. Therefore, the amount of  $\text{Al}_2\text{O}_3$  must be considered in the final amount while  $\text{Na}_2\text{SO}_4$  has no effect on synthesis of the zeolite.

The neutralization process is described as follows:



#### 3.4.4 Preparation of Manganese Zeolite (MnY)

The fully hydrated zeolite NaY was prepared by storing zeolite NaY in a desiccator containing a beaker of saturated solution of ammonium chloride for at least 3 days. The fully hydrated zeolite NaY was ion exchanged with  $\text{Mn}^{2+}$  aqueous solution. An amount of 0.465 g of manganese(II) chloride tetrahydrate was dissolved in 1,000  $\text{cm}^3$  of deionized water, then 5 g of fully hydrated zeolite NaY was poured into  $\text{Mn}^{2+}$  aqueous solution to form MnY zeolite that contains 8 moles of  $\text{Mn}^{2+}$  per unit cell that means 1 mole of  $\text{Mn}^{2+}$  per supercage. The slurry was heated to 70-80 °C and stirred with a magnetic stirrer for 24 hours. Zeolite MnY was filtered and washed with deionized water to removed chloride and then dried in an oven at 105 °C for 1 hour. The filtrate was kept for analysis of manganese content by AAS. Similarly, 2 and 3 moles  $\text{Mn}^{2+}$  per supercage were prepared using 0.93 and 1.395 g of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , respectively. The manganese exchanged zeolite powders were characterized for structure stability using XRD and elemental analysis using XRF.

### 3.5 Preparation of Zeolite Y Phthalocyanine Encapsulated

#### 3.5.1 Dehydration of Zeolite MnY

Each manganese exchanged zeolite was dehydrated at 100 °C under vacuum for 2 hours and at 450 °C for 10 hours (heating rate of 2 °C / min). Dehydration apparatus is shown in Figure 3.1 and the heating diagram for the dehydration of the zeolite was shown in Scheme 3.3. After cooling to room temperature under vacuum, the dehydrated manganese exchanged zeolite was then transferred to a Schlenk flask and kept under nitrogen prior to use.

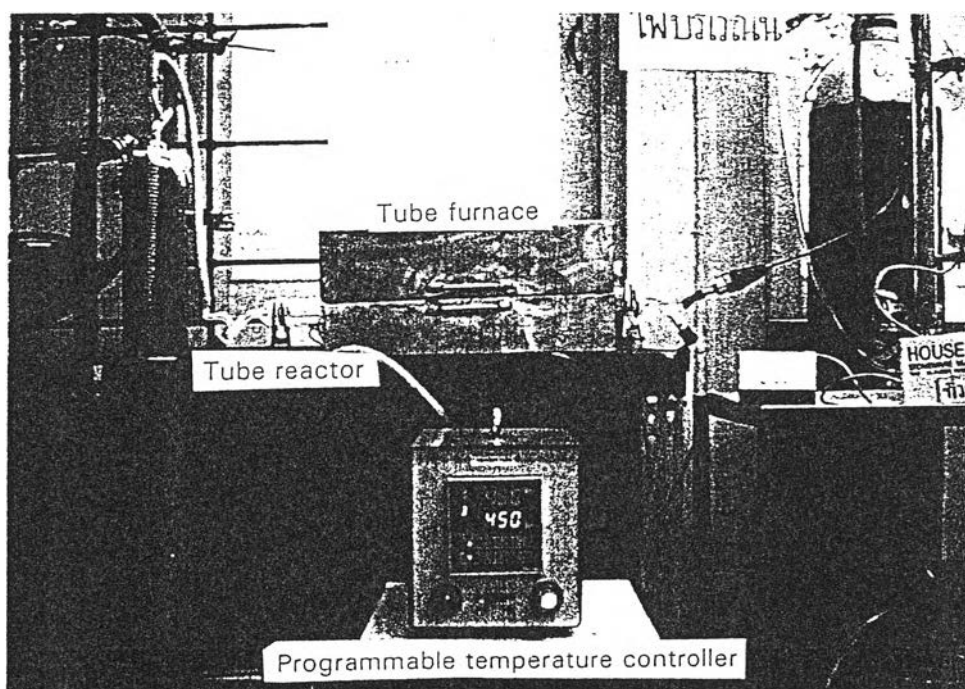
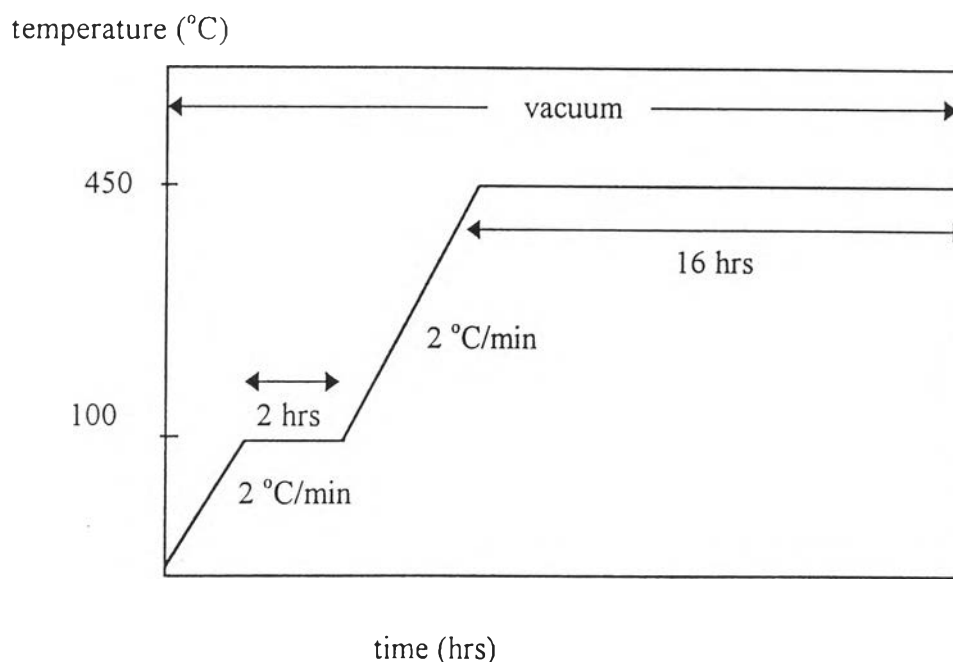


Figure 3.1 Apparatus for zeolite dehydration.

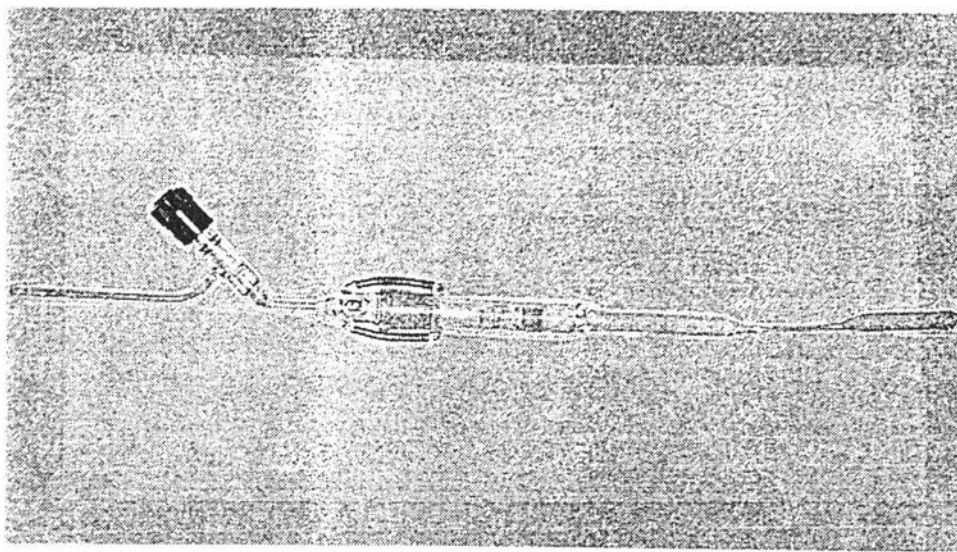


**Scheme 3.3** The heating diagram for dehydration of zeolite MnY.

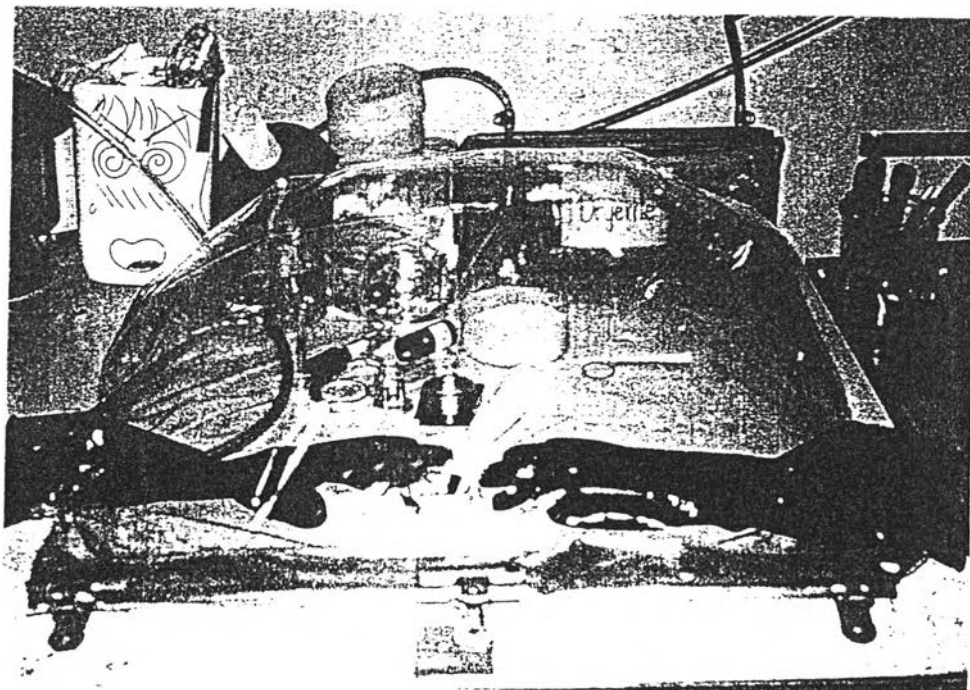
### 3.5.2 Encapsulation of Phthalocyanine in the Zeolite MnY

An amount of 1 g of the dehydrated exchanged zeolite was mixed with 1 g ( $7.8 \times 10^{-3}$  mol) of 1,2-Dicyanobenzene (sixfold excess) in a glove bag which was filled with dry nitrogen. In the glove bag, the solid mixture was then introduced into a glass tube which is capped with a vacuum valve at one end, (shown in Figure 3.2). The glass tube was taken out from the glove bag and evacuated at  $10^{-3}$  mmHg for 2 hours and subsequently sealed by a flame tip to make an ampule before heating in the furnace at 270 °C for 40 hours. After heating, the solids changed from white to grayish green. The product was purified by soxhlet extraction, using solvents: acetone, pyridine, and finally acetone. Each extraction was performed until the colorless solvent was obtained. The apparatus for soxhlet extraction was shown in Figure 3.4. The resulting

powders were vacuum dried in the tube furnace at 200 °C for 8 hours, and characterized using FTIR, UV-VIS spectrometers, and the elemental analyzer. The final product, manganese phthalocyanine (MnPcY) was stored in a Schlenk flask under nitrogen.



**Figure 3.2** Glass tube to make an ampule



**Figure 3.3** Glove bag

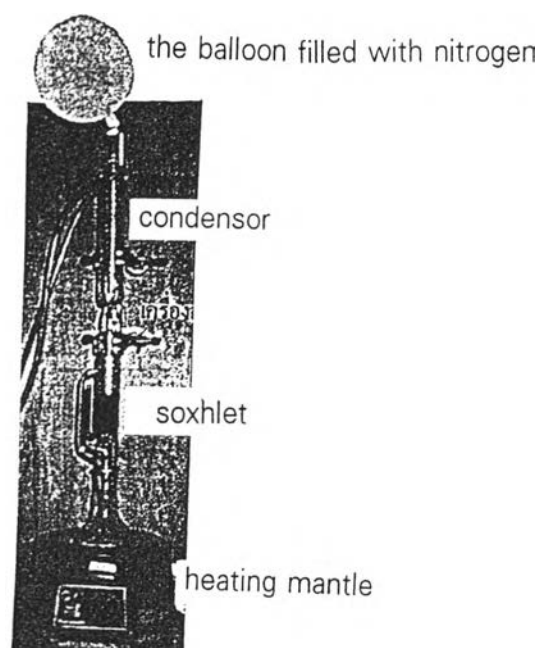


Figure 3.4 The soxhlet extraction apparatus

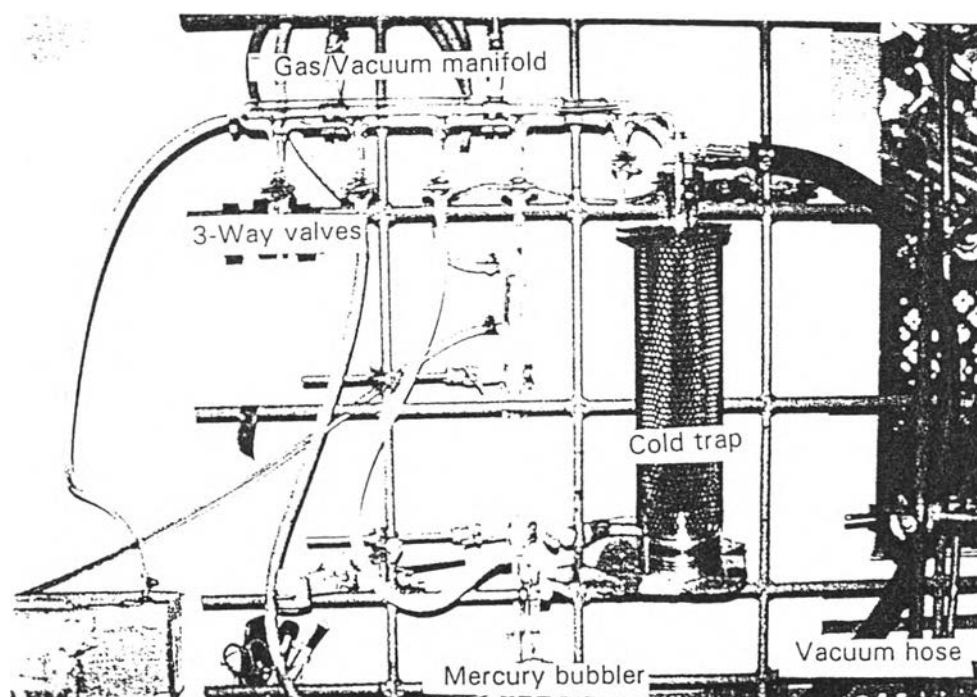
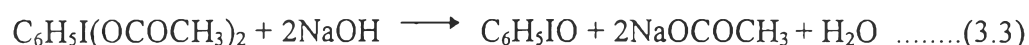


Figure 3.5 Schlenk line

### 3.6 Catalytic Activity Test for Oxidation of Olefins

#### 3.6.1 Preparation of Iodosobenzene

The process for preparing an oxidant, iodosobenzene was modified from the method reported by J.G. Sharefkin and H. Saltzman<sup>57</sup>. The starting material iodobenzene diacetate was hydrolyzed in base to form iodosobenzene as shown in Equation 3.3



Finely ground iodobenzene diacetate 32.2 g. (0.10 mole) was placed in a 250 cm<sup>3</sup> beaker, and 150 cm<sup>3</sup> of 3 M sodium hydroxide solution was added over a 5 minute period with vigorous stirring. The lumps of solid that formed were macerated with a stirring rod or spatular for 15 minutes, and the reaction mixture stood for additional 45 minutes to complete the reaction. A 100 cm<sup>3</sup> of water was added, the mixture was stirred vigorously, and the crude solid iodosobenzene was collected on a Buchner funnel. The wet solid was returned to the beaker and macerated in 200 cm<sup>3</sup> of water, and dried by continuous suction. Final purification was affected by macerating the dried solid in 75 cm<sup>3</sup> of chloroform. The iodosobenzene was separated by filtration and air dried. The weight of the compound was 18.7-20.5 g (85-93 % yield); m.p. 210 °C (caution! Explosive).

### 3.6.2 Catalysis on Oxidation of Cyclohexene Using Iodosobenzene as Oxidant

#### 3.6.2.1 Tendency of Oxidation Products in the Presence of Solvent

An amount of 0.375 g ( $1.7 \times 10^{-2}$  mmol, or 0.015 % Mn by weight of the substrate) of the zeolite Y loaded manganese phthalocyanine (MnPcY) and 1.10 g (5 mmol) of iodosobenzene were transferred into a 250 cm<sup>3</sup> Schlenk flask. An amount of 50 cm<sup>3</sup> of n-octane was added as solvent to the Schlenk flask. An amount of 7.5 cm<sup>3</sup> (75 mmol) of cyclohexene was finally added to the system. The mixture was continuously stirred. The products at a portion of 0.5 cm<sup>3</sup> were collected for gas chromatographic analysis every 5 hours until 40 hours. Sampling of product was carried out using a gas tight syringe with the millipore filter on the tip, penetrating through the septum capped on the Schlenk flask.

#### 3.6.2.2 Effect of the Amount of Iodosobenzene

An amount of 0.075 g ( $3.4 \times 10^{-3}$  mmol, or 0.015 % Mn by weight of the substrate) of the catalyst MnPcY, 1.5 cm<sup>3</sup> (15 mmol) of cyclohexene, and 10 cm<sup>3</sup> of n-octane were added into each of four 250 cm<sup>3</sup> Schlenk flasks. Different amounts of iodosobenzene: 0.220, 0.440, 1.100 and 1.540 g (1, 2, 5, and 7 mmol, respectively) were added into each flask. After stirring for 24 hours, the solid phase was filtered off and washed thoroughly with diethyl ether. To the collected filtrate, 8  $\mu$ l (0.08 mmol) of



cyclohexanol as internal standard was added and shaken thoroughly. The liquid was analyzed using gas chromatography.

### **3.6.2.3 Correction Factor for Vaporization of Products in the Filtration Step**

Into a 250 cm<sup>3</sup> Schlenk flask, 0.05 g (0.5 mmol) of cyclohexene oxide, 0.1 g (1.0 mmol) of cyclohexanone, and 3.0 g (30 mmol) of cyclohexene were added. After 6 hours, the solid phase was filtered off and washed thoroughly with diethyl ether. To the collected filtrate, 8  $\mu$ l (0.08 mmol) of cyclohexanol internal standard was added. The liquid was analyzed using gas chromatography.

### **3.6.2.4 Oxidation of Cyclohexene Without Solvent**

To improve the yield of products, oxidation of cyclohexene without solvent was performed to concentrate the substrate. The amounts of 0.075 g ( $3.4 \times 10^{-3}$  mmol, or 0.0076 % Mn by weight of the substrate) of MnPcY, 0.440 g (2 mmol) of iodosobenzene and 3.0 cm<sup>3</sup> (30 mmol) of cyclohexene were put into a 250 cm<sup>3</sup> Schlenk flask. The reaction mixture was stirred using a magnetic stirrer. After required periods of stirring for 1, 2, 3, 4, 5, 6, 8, 24 and 48 hours, the solid phase was filtered off and washed thoroughly with diethyl ether. To the collected filtrate, 8  $\mu$ l (0.08 mmol) of cyclohexanol internal standard was added. The liquid was analyzed using gas chromatography.

### 3.6.2.5 Effect of the Amount of MnPcY

Into each of five 250 cm<sup>3</sup> Schlenk flask, 3.0 cm<sup>3</sup> (30 mmol) of cyclohexene and 0.440 g (2 mmol) of iodosobenzene were transferred. Different amount of MnPcY was added into each Schlenk flask, *i.e.* 0.075 g ( $3.4 \times 10^{-3}$  mmol, or 0.0076 % Mn by weight of substrate), 0.100 g ( $4.5 \times 10^{-3}$  mmol, or 0.010 % Mn by weight of substrate), 0.150 g ( $6.8 \times 10^{-3}$  mmol, or 0.015 % Mn by weight of substrate), 0.200 g ( $9.1 \times 10^{-3}$  mmol, or 0.020 % Mn by weight of substrate), and 0.250 g ( $1.14 \times 10^{-2}$  mmol, or 0.025 % Mn by weight of substrate). The reaction mixtures were stirred for 24 hours. The solid phase was filtered off and washed thoroughly with diethyl ether. To the collected filtrate, 8  $\mu$ l (0.08 mmol) of cyclohexanol internal standard was added. The liquid was analyzed using gas chromatography.

## 3.6.3 Catalysis on Oxidation of Cyclohexene Using Oxygen as Oxidant

### 3.6.3.1 Effect of Time

Into each of seven 250 cm<sup>3</sup> Schlenk flasks, 0.075 g ( $3.4 \times 10^{-3}$  mmol, or 0.0076 % Mn by weight of substrate) of MnPcY and 3.00 cm<sup>3</sup> (30 mmol) of cyclohexene were transferred. Oxygen gas was passed into each flask until approximately 1 atm pressure was obtained by slowly turning off the gas cylinder and the flask was then closed. The mixtures were stirred continuously for a required

period. The reaction time was varied as 2, 4, 5, 6, 8, 24, and 48 hours. After that, the solid phase was filtered off and washed thoroughly with diethyl ether. To the collected filtrate, 8  $\mu\text{l}$  (0.08 mmol) of cyclohexanol internal standard was added. The liquid was analyzed using gas chromatography.

### 3.6.3.2 Effect of the Amount of MnPcY

Into each of five 250  $\text{cm}^3$  Schlenk flasks, 3.0  $\text{cm}^3$  (30 mmol) of cyclohexene was added. Different amount of MnPcY was added into each Schlenk flask *i.e.*: 0.075 g ( $3.4 \times 10^{-3}$  mmol, or 0.0076 % Mn by weight of substrate), 0.100 g ( $4.5 \times 10^{-3}$  mmol, or 0.010 % Mn by weight of substrate), 0.150 g ( $6.8 \times 10^{-3}$  mmol, or 0.015 % Mn by weight of substrate), 0.200 g ( $9.1 \times 10^{-3}$  mmol, or 0.020 % Mn by weight of substrate) and 0.250 g ( $1.14 \times 10^{-2}$  mmol, or 0.025 % Mn by weight of substrate). Oxygen gas was passed into each flask until approximately 1 atm pressure was obtained by slowly turning off the gas cylinder and the flask was then closed. The reaction mixtures were stirred for 6 hours. The solid phase was filtered off and washed thoroughly with diethyl ether. To the collected filtrate, 8  $\mu\text{l}$  (0.08 mmol) of cyclohexanol internal standard was added. The liquid was analyzed using gas chromatography.

### 3.6.4 Oxidation of 1-Hexene

#### 3.6.4.1 Oxidation of 1-Hexene with Iodosobenzene in Solvent

An amount of 0.375 g ( $1.7 \times 10^{-2}$  mmol, or 0.015 % Mn by weight of substrate) of the zeolite Y loaded manganese phthalocyanine (MnPcY), and 1.10 g (5 mmol) of iodosobenzene were transferred into a 250 cm<sup>3</sup> Schlenk flask. A 50 cm<sup>3</sup> of n-octane was added as solvent to the Schlenk flask. An amount of 6.25 cm<sup>3</sup> (75 mmol) of 1-hexene was finally added to the system. The mixture was continuously stirred for a required period. The products at a portion of 0.1 cm<sup>3</sup> were collected for gas chromatographic analysis every 5 hours until 72 hours. Sampling of product was carried out using a gas tight syringe with the millipore filter on the tip, penetrating through the septum capped on the Schlenk flask.

#### 3.6.4.2 Oxidation of 1-Hexene with Oxygen Gas in the Absence of Solvent

Into a 250 cm<sup>3</sup> Schlenk flask, 0.375 g ( $1.7 \times 10^{-2}$  mmol, or 0.015 % Mn by weight of substrate) of MnPcY and 6.25 cm<sup>3</sup> (75 mmol) of 1-hexene were transferred. Oxygen gas was passed into the flask until approximately 1 atm pressure was obtained by slowly turning off the gas cylinder and the flask was then closed. The mixtures were stirred continuously for required periods. The products at a portion of

0.1 cm<sup>3</sup> were collected for gas chromatographic analysis every 5 hours until 72 hours. Sampling of product was carried out using a gas tight syringe with the millipore filter on the tip, penetrating through the septum capped on the Schlenk flask. To the collected sample, 6.7 μl (0.08 mmol) of 2-hexanol internal standard was added. The liquid was analyzed using gas chromatography.