

## Chapter 3

### EXPERIMENTATION

#### 1. Feedstock

In this research, n-octane was used as a standard feedstock to evaluate the catalytic micro-activity of our synthesized catalysts. The properties of n-octane are listed in Table 3-1.

**Table 3-1** Properties of n-octane.

| Properties       | Values                 |
|------------------|------------------------|
| Purity           | 99.0 %                 |
| Molecular weight | 114.23                 |
| Boiling point    | 125.7 °C               |
| Density at 20 °C | 0.703 g/m <sup>3</sup> |

#### 2. Equipment

1. Balance (Metler Toledo model PB153)
2. Desiccator
3. Electric mixer (Heidolph type RZR 1)
4. Furnace (Carbolite)
5. Hot air oven (Eyela model NDO-600N)
6. Heater (Fisher Scientific)
7. Mortar
8. Thermometer
9. Vacuum pump (Eyela model A-3S)
10. Water bath (Mettmert type W350)

### 3. Instrument

1. Differential Thermal Analysis (Perkin Elmer model DTA 7)
2. Gas Chromatograph (Hewlett Packard model HP 6890 series)
3. Gas Chromatograph (Hewlett Packard model HP 5890)
4. Mass spectrometer (Hewlett Packard model HP 5972 MSD)
5. Integrator (Hewlett Packard model HP 6890 series)
4. Hydrothermal Aging Unit (RIPP model CLY-1)
5. Microactivity Test Unit (RIPP model WFS-1D)
6. X-Ray Diffractometer (Philips model X'Pert-MPD)
7. X-Ray Fluorescence Spectrometer (Philips model PW2400)
8. Thermogravimetric Analysis (Perkin-Elmer model TGA 7)
9. Surface Area and Pore Size Analyzer (COULTER SA3100)
10. Atomic Absorption Spectrophotometer (GBC Scientific Equipment model AA)

### 4. Chemical and Reagents

**Table 3-2** Chemical and reagents used in experiments.

| No. | Chemical and reagents             | Formula  | Grade |
|-----|-----------------------------------|--|-------|
| 1   | Aluminium hydroxide               | $\text{Al}(\text{OH})_3$                               | AR    |
| 2   | Aluminium sulfate                 | $\text{Al}_2(\text{SO}_4)_3$                           | AR    |
| 3   | Aluminium oxide (pseudoboehemite) | $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$      | CR    |
| 4   | Ammonium chloride                 | $\text{NH}_4\text{Cl}$                                 | AR    |
| 5   | Ammonium sulfate                  | $(\text{NH}_4)_2\text{SO}_4$                           | AR    |
| 6   | De-ionized water                  | $\text{H}_2\text{O}$                                   | -     |
| 7   | Hydrochloric acid                 | $\text{HCl}$   | AR    |
| 8   | Hydrofluoric acid                 | $\text{HF}$  | AR    |
| 9   | Kaolin clay                       | $\text{Al}_2(\text{OH})_2 \cdot \text{Si}_2\text{O}_5$ | CR    |
| 10  | Rare earth chloride               | $\text{RECl}_3$  | CR    |
| 11  | Sodium hydroxide                  | $\text{NaOH}$  | AR    |

**Table 3-2** Chemical and reagents used in experiments (continue).

| No. | Chemical and reagents                  | Formula                          | Grade |
|-----|--|----------------------------------|-------|
| 12  | Sodium silicate solution (water glass) | Na <sub>2</sub> SiO <sub>3</sub> | AR    |
| 13  | Hydrogen peroxide                      | H <sub>2</sub> O <sub>2</sub>    | AR    |
| 14  | Zinc chloride                          | ZnCl <sub>2</sub>                | AR    |

AR: Analytical Reagent Grade

CR: Commercial Reagent Grade

## 5. Procedure and Experiments

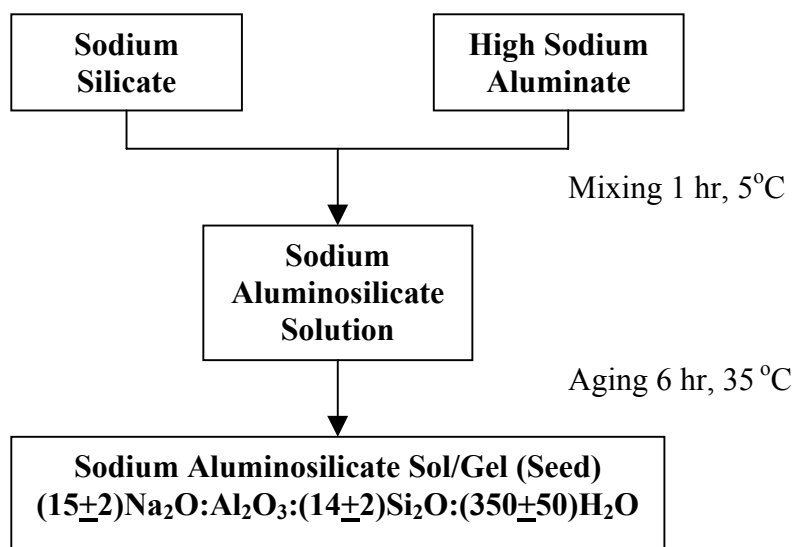
### 5.1 Preparation of zeolite

#### 5.1.1 Preparation of NaY zeolite

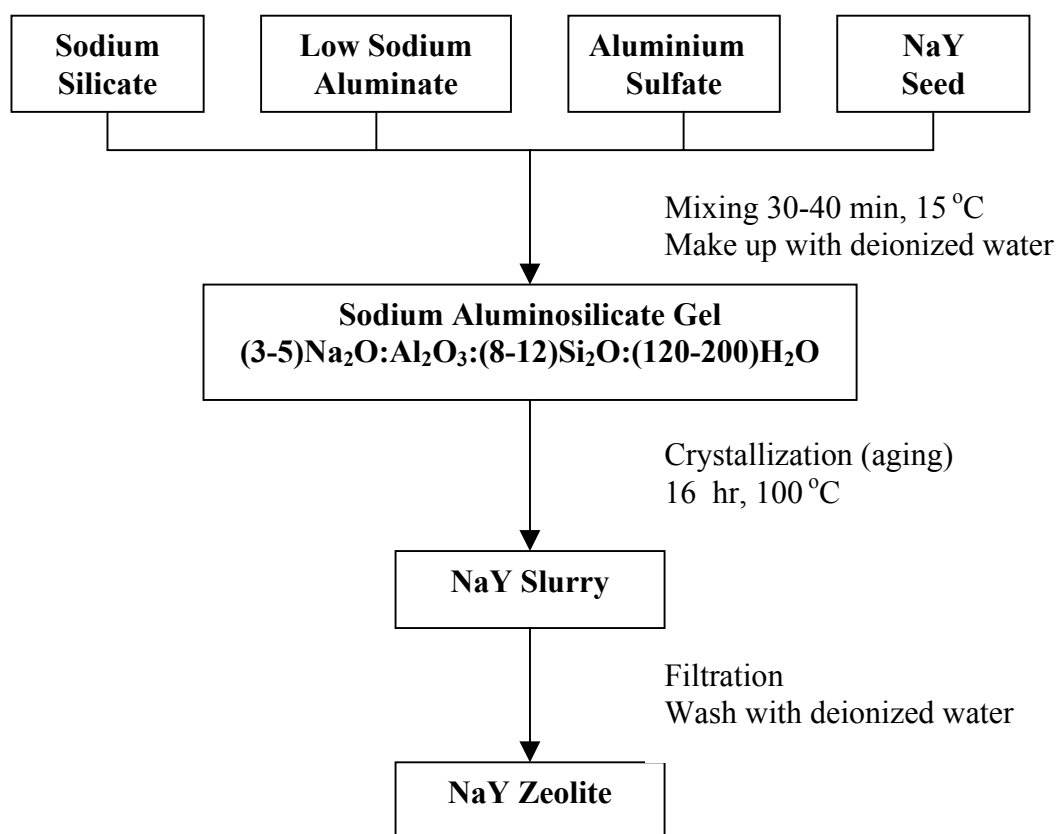
The procedure of NaY zeolite synthesis was transferred from Research Institute of Petroleum Processing (RIPP), China. This procedure was also reviewed and developed in the master thesis of a graduate student from the Department of Chemical Engineering, PSU (Jakkrit, 2000).

The seed (initial agent) prepared by cooling all working solution are listed in Table B-1 of Appendix B to 5°C. The procedures are as followed: (1) place water-glass in a plastic container, (2) slowly add high sodium aluminate, (3) add deionized water and keep stirring at 5°C for 1 hour, and (4) statically age the obtained solution at 35°C for 6 hours. The gel obtained from this step is called "seed or activated waterglass".

The gel were prepared by mixing seed (from above) in water-glass and stirring at room temperature for 5 minutes. Aluminium sulfate was slowly added and stirred vigorously for 10 minutes. Sodium aluminate was continuously added into the slurry and stirred vigorously for 2 minutes. The gel was placed into a hot air oven, temperature was increased to 100°C and aged for 16 hours. The gel was quenched with water and filtered with vacuum pump to remove the solids from mother liquor. The product was washed several times and dried in a hot air oven at 110°C overnight (Figure 3-1).



(a) Step 1: Preparation of seed



b) Step 2: Preparation of NaY zeolite

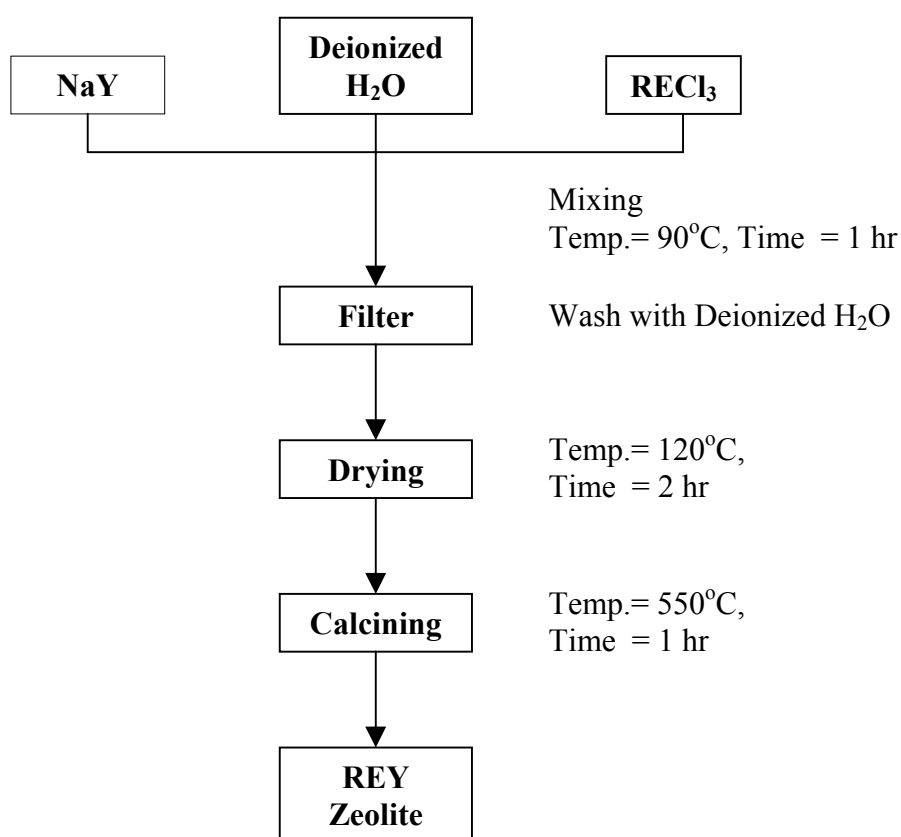
**Figure 3-1** Preparation scheme for NaY zeolite.

### 5.1.2 Preparation of Rare Earth Exchanged Y Zeolite (REY)

This procedure was also reviewed and developed in the master thesis of graduate students from the Department of Chemical Engineering, PSU (Kritsana, 2001 ; Sutha, 2001).

The procedure for preparation of REY zeolite was performed by using NaY zeolite and exchanging it with 0.36 M Rich-lanthanum chloride. First, NaY zeolite was mixed to hot deionized water. Then, Rich-lanthanum chloride was added continuously while stirring at 90°C for 1 hour. Next, the slurry was filtered by a vacuum pump and was washed with warm deionized water (60°C) to remove free chloride ion. After that, the filter cake was dried at 120°C in an oven for 2 hours. Then, the sample was calcined at 550°C for 1 hour in a furnace.

The calcined sample was ion-exchanged again using the same procedure above (2<sup>nd</sup> ion exchange). In this step, the REY zeolite was calcined at 550 °C for 1 hours as shown in Figure 3-2.



**Figure 3-2** Preparation scheme for REY zeolite.

### 5.1.3 Preparation of Ultrastable Y Zeolite (USY) from NaY

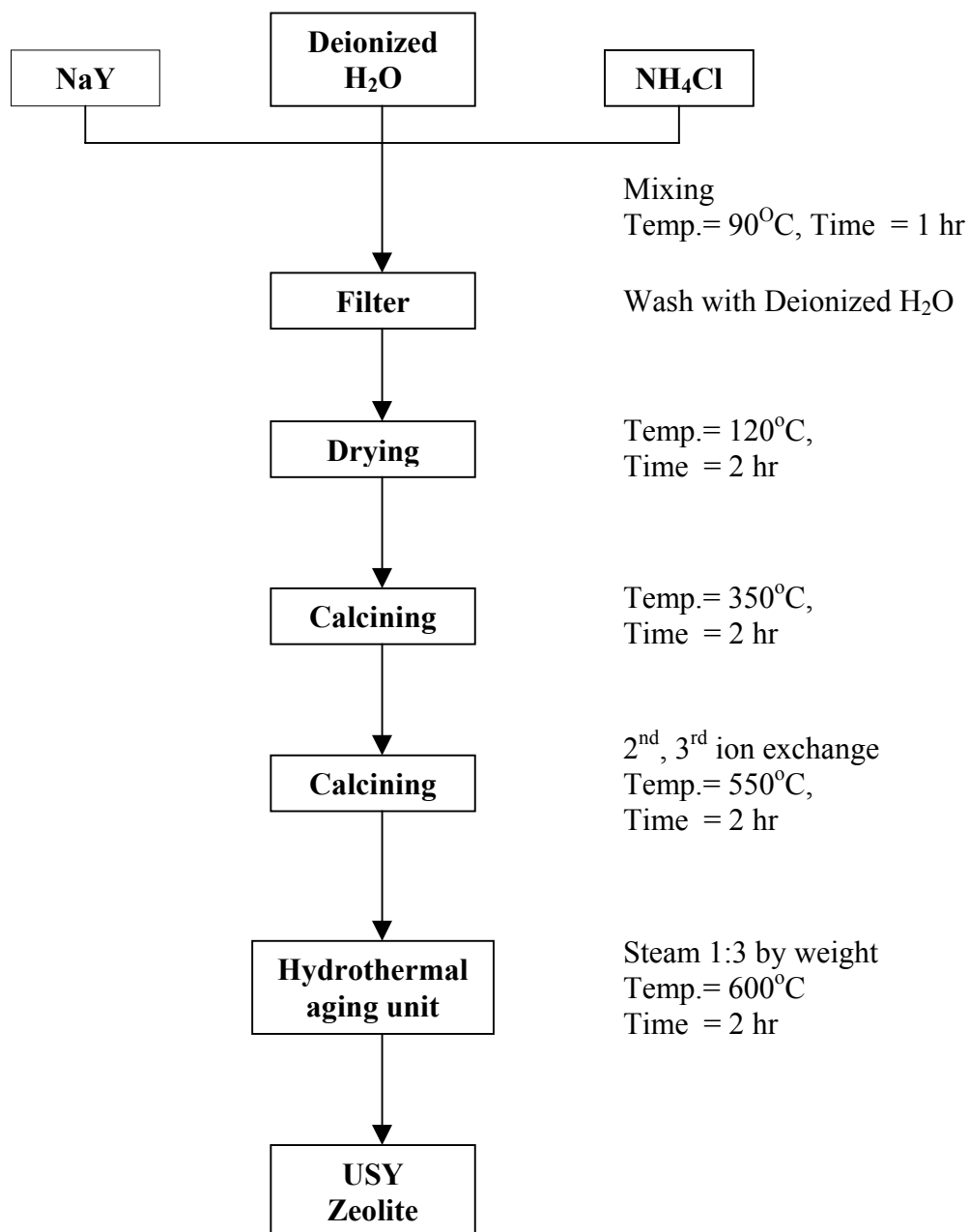
This procedure was also reviewed and developed in the master thesis of a graduate student from the Department of Chemical Engineering, PSU (Wachira, 2001).

The procedure for preparation of HY zeolite was performed by using NaY zeolite (dry basis),  $\text{NH}_4\text{Cl}$  and deionized water at ratio of 1: 1: 20 by weight. First, NaY zeolite was added in warm ( $60^\circ\text{C}$ ) deionized water. Then  $\text{NH}_4\text{Cl}$  was added and continuously stirred at  $90^\circ\text{C}$  for 1 hour. Next, the slurry was filtered by a vacuum pump and washed with warm deionized water to remove free chloride ion. After that, the filter cake was dried at  $120^\circ\text{C}$  in an oven for 2 hours. Then, the sample was calcined at  $350^\circ\text{C}$  for 2 hours in a furnace.

The calcined sample was ion-exchanged again using the same procedure from above (2<sup>nd</sup> ion exchange). In this step, the HY zeolite was calcined at  $550^\circ\text{C}$  for 2 hours.

The fully  $\text{NH}_4$ -exchanged zeolite (3<sup>rd</sup> ion exchange) was processed and calcined at  $550^\circ\text{C}$  for 2 hours.

In the steam calcination of USY zeolite, HY zeolites (3<sup>rd</sup> ion exchange) were taken for steam calcination. First, the samples were put into a micro reactor and placed in the furnace of hydrothermal aging unit model CLY-1 (see Appendix C). The ratio of samples to steam was 1:3 by weight. The inert gas ( $\text{N}_2$ ) was passed through the micro reactor and the furnace was heated to  $600^\circ\text{C}$ . When the temperature was reached, steam was passed through the micro reactor for 2 hours. Finally, the inert gas was passed to expel the volatile matters for 15 minutes as shown in Figure 3-3.



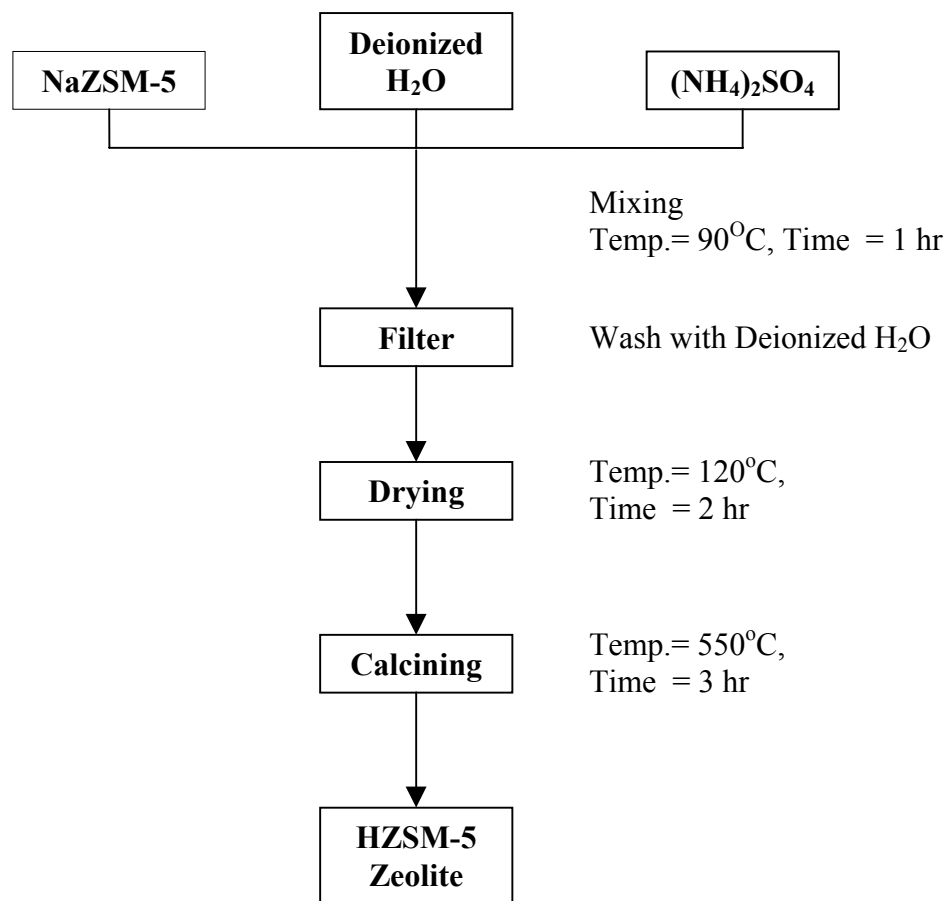
**Figure 3-3** Preparation scheme for USY zeolite.

#### 5.1.4 Preparation of HZSM-5 (ZSM-5)

The procedure for preparation of HZSM-5 zeolite was transferred from Research Institute of Petroleum Processing (RIPP), China.

The procedure for preparation of HZSM-5 zeolite was performed by using NaZSM-5 zeolite (dry basis),  $(\text{NH}_4)_2\text{SO}_4$  and deionized water at a ratio of

1: 2: 10 by weight. First, NaZSM-5 zeolite was added in warm (90°C) deionized water, then (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added and continuously stirred at 90°C for 1 hour. Next, the slurry was filtered by a vacuum pump and washed with warm deionized water to remove free chloride ion (1<sup>st</sup> ion exchange). The HZSM-5 zeolite was ion-exchanged again using the same procedure above (2<sup>nd</sup> ion exchange). After that the filter cake was dried at 120°C in an oven for 2 hours. Then, the HZSM-5 zeolite was calcined at 550°C for 3 hours in a furnace. Finally, the HZSM-5 zeolite was obtained. Na<sub>2</sub>O content should not be more than 1% (If the Na<sub>2</sub>O content was more than 1%, the procedure must be repeated) as shown in Figure 3-4.



**Figure 3-4** Preparation scheme for HZSM-5 zeolite.



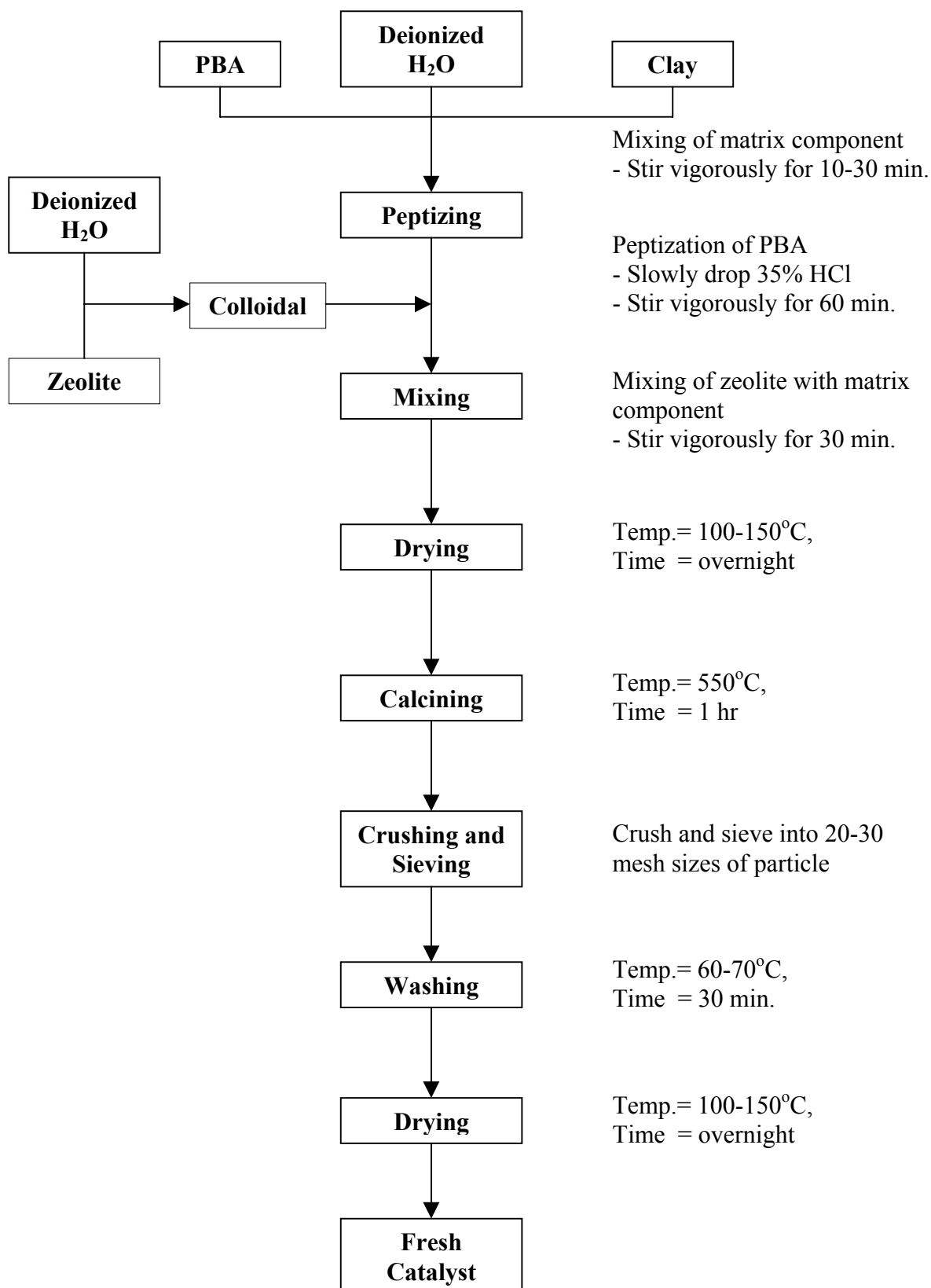
## 6. Preparation of Catalysts

The procedure for preparation of cracking catalyst zeolite was transferred from Research Institute of Petroleum Processing (RIPP), China. This procedure was also reviewed and developed in the master thesis of a graduate student from the Department of Chemical Engineering, PSU (Kritsana, 2001).

First, deionized water was poured into a stainless steel vessel then was slowly added with RIPP clay and PBA. After stirring for 15 minutes, 35% HCl was slowly dropped into the slurry keeping stir for 1 hour. Then, zeolite (well dispersed in water) was added and was stirred vigorously for 30 minutes. After that, deionized water was filled to keep the slurry solid content at 20-25 %. The slurry was placed in a hot air oven and was dried at 100-150°C overnight. Finally, the sample was calcined in air at 500°C for 1 hour.

The calcined sample was crushed and sieved to 20-40 mesh particle sizes. After that, the catalyst was washed to remove the isolated-Na. The catalyst, NH<sub>4</sub>Cl and deionized water in a ratio of 1: 0.03: 15 was stirred at 60-70°C for 30 minutes. Finally, the catalyst was dried again in a hot air oven at 100-150°C overnight (Figure 3-5).

The catalysts were prepared with varying matrix and zeolite content and their activities were measured using the microactivity test unit. All of catalysts and matrices are listed in Table 3-3, Table 3-4 and Table 3-5.



**Figure 3-5** Preparation scheme for catalyst.

**Table 3-3** Composition of REY catalysts.

| <b>Batch No.</b> | <b>REY (%)</b> | <b>PBA binder (%)</b> | <b>Kaolin clay (%)</b> |
|------------------|----------------|-----------------------|------------------------|
| 1                | 0              | 20                    | 80                     |
| 2                | 20             | 20                    | 60                     |
| 3                | 25             | 20                    | 55                     |
| 4                | 30             | 20                    | 50                     |
| 5                | 35             | 20                    | 45                     |

**Table 3-4** Composition of USY catalysts.

| <b>Batch No.</b> | <b>USY (%)</b> | <b>PBA binder (%)</b> | <b>Kaolin clay (%)</b> |
|------------------|----------------|-----------------------|------------------------|
| 1                | 0              | 20                    | 80                     |
| 2                | 20             | 20                    | 60                     |
| 3                | 30             | 20                    | 50                     |
| 4                | 40             | 20                    | 40                     |
| 5                | 50             | 20                    | 30                     |

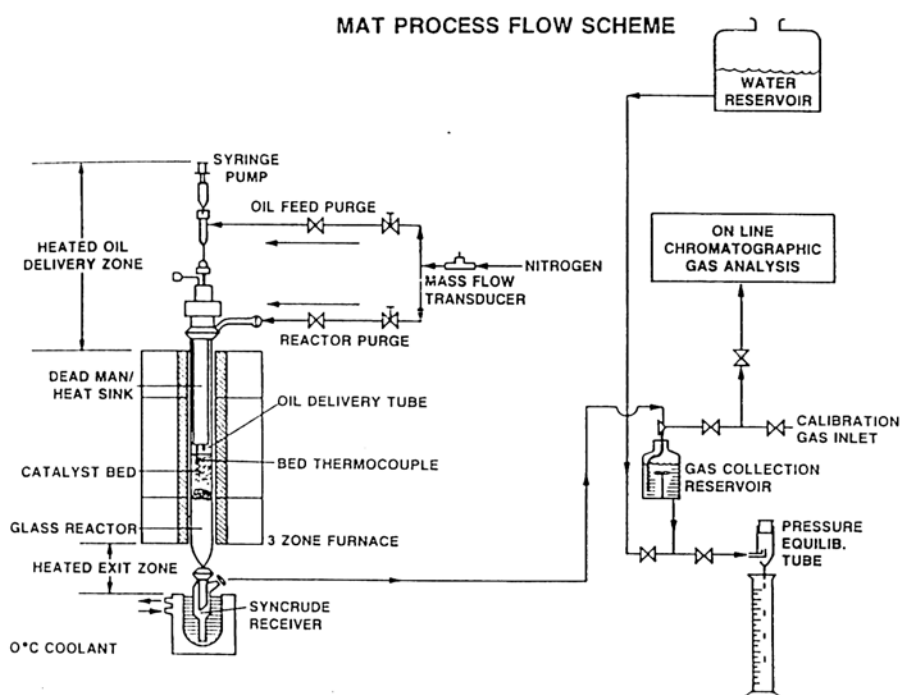
**Table 3-5** Composition of REY-ZSM-5 catalysts.

| <b>Batch No.</b> | <b>REY (%)</b> | <b>ZSM-5 (%)</b> | <b>PBA binder (%)</b> | <b>Kaolin clay (%)</b> |
|------------------|----------------|------------------|-----------------------|------------------------|
| 1                | 25             | 0                | 20                    | 55                     |
| 2                | 25             | 4                | 20                    | 51                     |
| 3                | 25             | 8                | 20                    | 47                     |
| 4                | 25             | 12               | 20                    | 43                     |
| 5                | 35             | 0                | 20                    | 55                     |
| 6                | 35             | 4                | 20                    | 41                     |
| 7                | 35             | 8                | 20                    | 37                     |
| 8                | 35             | 12               | 20                    | 33                     |

## 7. Test procedure and Test Conditions

### 7.1 Evaluation

The laboratory evaluation of cracking catalysts has evolved into a very common method for measuring performance characteristics of commercial or experimental catalyst samples. The Microactivity Test (MAT) is the primary tool in accessing the performance of catalyst samples. The schematic for MAT is shown in Figure 3-6.



**Figure 3-6** Schematic for typical MAT unit.

Source: Moorehead, McLean and Cronkright; 1993: 226

### 7.1.1 A Microactivity Test Method and Test Condition of MAT

(see MAT set up and operation in Appendix D)

|                                      |                           |   |
|--------------------------------------|---------------------------|---|
| Catalyst loading:                    | 5                         | g |
| Oil weight:                          | $1.56 \pm 0.01$           | g |
| Catalyst/Oil ratio:                  | 3.2                       |   |
| Feedstock:                           | n-octane                  |   |
| Weight hourly space velocity (WHSV): | $16 \text{ hr}^{-1}$      |   |
| Feeding rate:                        | 1.337 g/min.              |   |
| Feeding time:                        | 70 sec                    |   |
| Temperature:                         | $460 \pm 1^\circ\text{C}$ |   |
| Purging time:                        | 600 sec                   |   |

Liquid produced from MAT was then analyzed using the Gas Chromatograph.

$$\text{Microactivity (MA, \%)} = 100 - \left[ \left( \frac{100 - A}{C} \right) \times B \right]$$

where

A = Gasoline yield (%wt.), analyzed by GC

B = Liquid produced from MAT, (g)

C = Feed oil, (g)



**Figure 3-7** Microactivity Test Unit (MAT) model WFS-1D.

### **Gas Chromatograph condition for analysis of liquid products**

Gas Chromatograph model: HP 6890

Column: Rtx-1 PONA (crossbond 100% dimethyl polysiloxane  
100m×0.25 mm ID×0.25 μm)

Detector: Flame Ionization Detector (FID)

Carrier gas: Ultra high purity helium, flow rate 1 ml/min.

|                          |   |
|--------------------------|---|
| Combustion gas:          | High purity hydrogen, flow rate 30 ml/min.<br>Air zero grade, flow rate 400 ml/min.               |
| Make up gas:             | High purity nitrogen, flow rate 29 ml/min.  |
| Split ratio:             | 100: 1  |
| Sample injection volume: | 1 $\mu$ l   |
| Injector temperature:    | 250°C   |
| Detector temperature:    | 250°C   |
| Column temperature:      | 50°C to 110°C with a rate of 2°C/min., then raise<br>from 110°C to 220°C with a rate of 20°C/min. |

#### **Gas Chromatograph condition for analysis of gas products**

|                          |  |
|--------------------------|--|
| Gas Chromatograph model: | HP 5890  |
| Column:                  | HP-PLOTQ (polystyrene-divinylbenzene based PLOT<br>30 m $\times$ 0.32 mm ID $\times$ 0.25 $\mu$ m) |
| Detector:                | Mass spectrometer HP-5972 MSD  |
| Carrier gas:             | Ultra high purity helium, flow rate 1 ml/min.  |
| Split ratio:             | 12: 1  |
| Sample injection volume: | 0.25 $\mu$ l   |
| Injector temperature:    | 250°C  |
| Detector temperature:    | 260°C  |
| Column temperature:      | 80°C to 240°C with a rate of 10°C/min.,<br>hold at 240°C for 5 min.                                |

#### **Gas Chromatograph condition for analysis of research octane number**

|                          |  |
|--------------------------|--|
| Gas Chromatograph model: | HP 5890  |
| Column:                  | Rtx-1 PONA (crossbond 100% dimethyl polysiloxane<br>100 m $\times$ 0.25 mm ID $\times$ 0.25 $\mu$ m) |
| Detector:                | Mass spectrometer HP 5972 MSD  |
| Carrier gas:             | Ultra high purity helium, flow rate 1 ml/min.  |
| Split ratio:             | 30: 1  |
| Sample injection volume: | 1 $\mu$ l  |

Injector temperature: 250°C  
Detector temperature: 250°C  
Column temperature: 50°C hold 2 min. to 110°C with a rate of 2°C/min., then raise from 110°C to 220°C with a rate of 20°C/min., hold at 220°C for 10 min.



**Figure 3-8** Gas Chromatograph model 6890 series equipped with Integrator model HP 6890 series.



**Figure 3-9** Gas Chromatograph model HP 5890 equipped with Mass Spectrometer model HP 5972 MSD.



### 7.1.2 Hydrothermal Treatment Procedure and Test Condition

(see hydrothermal aging unit set up and operation in Appendix C)

The freshly prepared catalysts were deactivated using hydrothermal aging unit. The primary objective is to deactivate a fresh catalyst so that its performance in the MAT is representative of what is observed when testing a commercially deactivated sample of the same catalyst. In this way, prediction of commercial performance for new catalysts can be made.

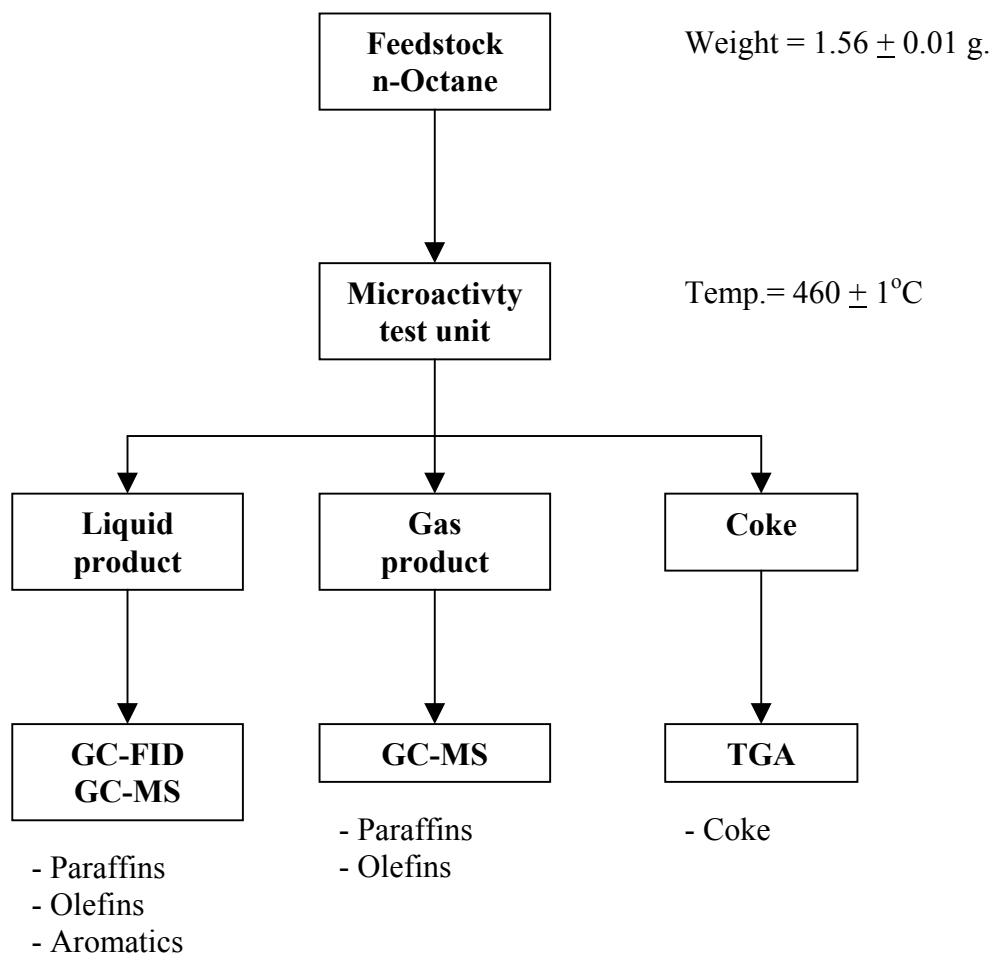
#### Hydrothermal aging condition

|                       |                                 |
|-----------------------|---------------------------------|
| Catalyst loading:     | 15-30 g                         |
| Aging temperature:    | 800°C                           |
| Aging time:           | 4 hr                            |
| H <sub>2</sub> O/Cat: | 3.0 g H <sub>2</sub> O/g Cat-hr |

Catalysts are usually loaded at ambient temperature and the steaming of catalysts is generally done in the presence of 100 percent steam.



**Figure 3-10** Hydrothermal Aging Unit model CLY-1.



**Figure 3-11** Schematic for test condition.

### 7.1.3 Characterization

Physicoproperties of zeolite and catalyst composition have been performed using several instruments according to ASTM standard. The instruments for characterization of catalysts and standard method used are listed in Table 3-6.

**Table 3-6** Characterization list for zeolite and catalyst components.

| No. | Characteristic                         | Instrument                                | Method           |
|-----|--|---|------------------|
| 1   | Relative crystallinity                 | X-ray Diffractometer (XRD)                | ASTM D3906-97    |
| 2   | Unit Cell Size (UCS)                   | X-ray Diffractometer (XRD)                | ASTM D3942-97    |
| 3   | RE <sub>2</sub> O <sub>3</sub> content | X-ray Fluorescent Spectrometer (XRF)      | Typical standard |
| 4   | Na <sub>2</sub> O content              | Atomic Absorption Spectrophotometer (AAS) | Typical standard |
| 5   | Specific surface area                  | Surface Area and Pore Size analyzer (BET) | ASTM D3663-78    |
| 6   | Coke content                           | Thermogravimetric Analysis                | Typical standard |