



CHAPTER IV

EXPERIMENTS

The experimental procedures for catalytic cracking reaction of n-octane over the various forms of Y-type zeolite catalyst are explained in the following sections.

4.1 Preparation of NaY-type zeolite

The preparation procedures of NaY-type zeolite is shown in Figure 4.1, while reagents used are shown in Table 4.1.

Table 4.1 Reagents used for the preparation of NaY-type zeolite

Reagents	weight
First step:	
<u>Solution S₁</u>	
NaAlO ₂	32.8 g
Distilled water	158 ml
<u>Solution S₂</u>	
Water glass	218.6 g
NaOH	95.9 g
Distilled water	684 - 284 ml
Second step:	
<u>Solution S₃</u>	
Water glass	216.7 g
NaOH	4.5 g
Distilled water	63.5 ml

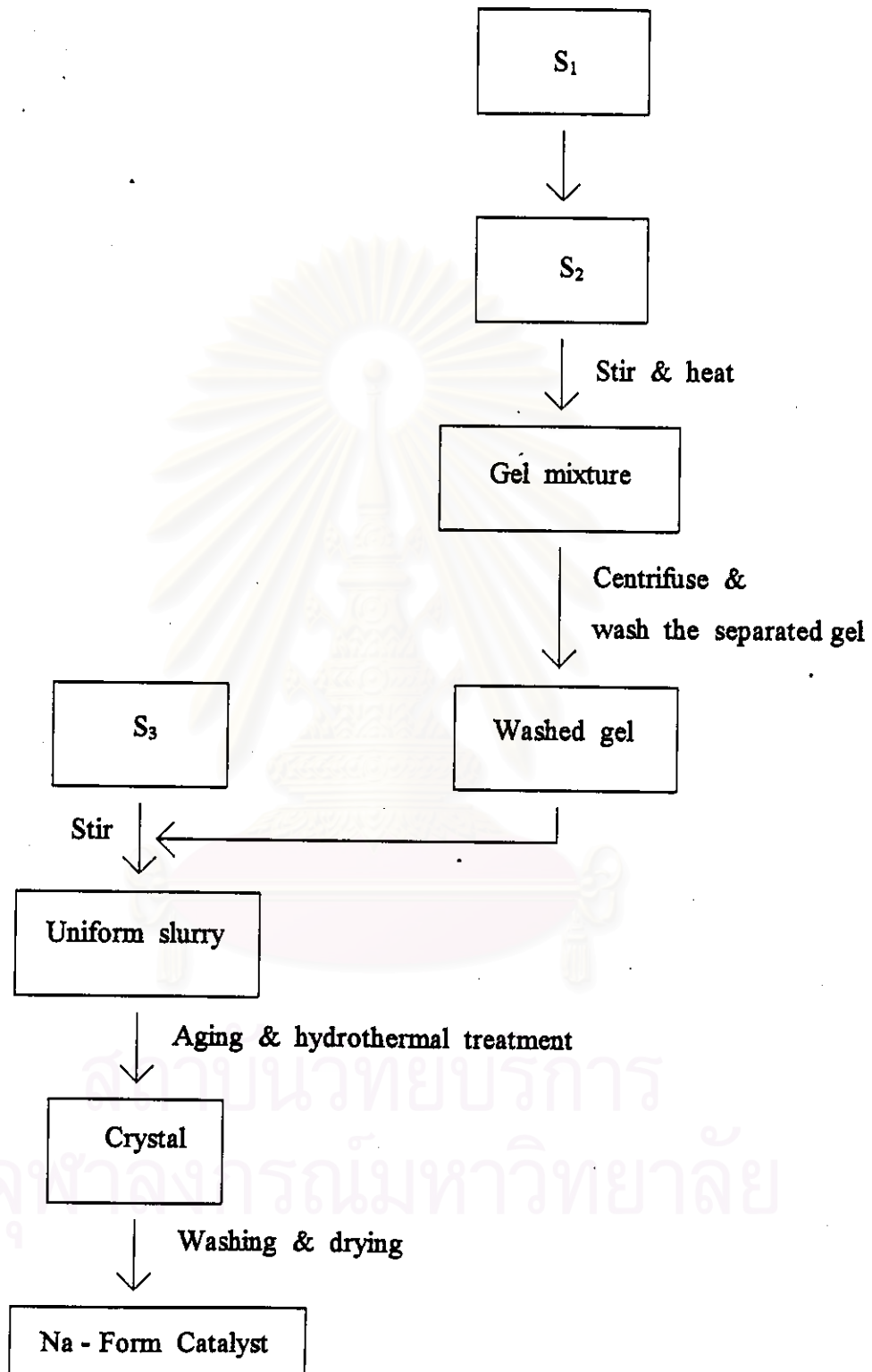


Figure 4.1 Preparation procedure of NaY - zeolite catalyst

4.1.1 Preparation of uniform slurry

The synthesis of NaY-type zeolite was described in patent literature [34]. Sodium aluminate and water glass were used as sources of Al and Si respectively; while Na source was substantially obtained from sodium hydroxide.

The uniform slurry was prepared by the process comprising two main steps. In the first step, S_1 was slowly added into S_2 while vigorous stirring. The mixture was continuously stirred for 2 hr. Then, the mixture was heated to 60 °C and, maintained at that temperature for 1 hr, thereby to form a gel. The gel was washed with water and separated by repeated cycles of centrifugation and decantation. The pH of supernatant solution was also measured.

In the second step, 181 g of the obtained gel from the above step was added into S_3 , and the resultant mixture was stirred to obtain a uniform slurry.

The amount of distilled water in S_2 was varied during the range of 284 - 684 ml while the other compositions were fixed as shown in Table 4.1 to find the optimum amount of water addition. (for calculation of various H_2O/SiO_2 ratio by mole see Appendix A-2). Subsequently, parameters were varied such as the pH of gel mixture during 11 - 14, and crystallization time during 24 - 96 hr.

4.1.2 Crystallization

The uniform slurry was charged into a closed glass vessel and placed at room temperature for 16 hr for aging. Thereafter, the glass vessel charged with slurry was heated at temperatures during 85 - 105 °C and

maintained at each temperature for different times during 24 - 26 h. The prepared NaY zeolite was left to cool down to ambient temperature, and then washed with distilled water till pH of washing water became 7 by repeated cycles of centrifugation and decantation. The obtained crystals were then dried overnight at 110 °C.

4.2 Ammonium Ion-Exchange of NaY-Type Zeolite

To 80 ml of 1 N NH_4NO_3 aqueous solution, about 2 g portion of NaY-type zeolite was added. The mixture was heated at 80 °C for 1 h and then washed twice with distilled water to remove nitrate ions by using a centrifugation separator. The above procedure was repeated for 5 times. Finally, the sample was dried overnight in electric oven at 110 °C. The Na-form crystal was thus changed to " NH_4 -form catalyst ".

4.3 Proton-Type Y (HY)

The NH_4Y -type zeolite was calcined in a furnace by heating from room temperature to 500 °C in 1 hr and then kept at that temperature for 2 hr. Therefore, in this step " NH_4Y -type zeolite " was transformed to " HY-type zeolite ".

The catalysts were tableted by a tablet machine. Then, they were crushed and sieved to range of 16 - 20 mesh to provide the reaction.

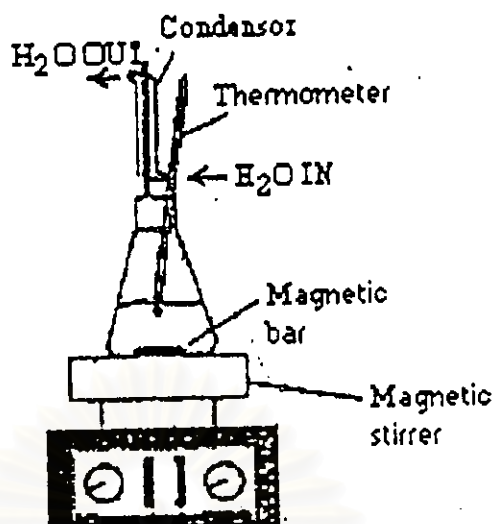


Figure 4.2 A set of apparatus used for preparation of ammonium ion-exchanged on catalyst

4.4 Catalytic Cracking Reaction of n-Octane

4.4.1 Chemical and reagent

n-Octane hydrocarbon purity 99 % was supplied by Carlo erba.

4.4.2 Instruments and apparatus

4.4.2.1 The reactor is a conventional microreactor made from a quartz tube with 0.6 mm inside diameter, so it can be operated at high temperature. The reaction was carried out under ordinary gas flow and atmospheric pressure.

4.4.2.2 In Temperature controller: This consists of a magnetic switch connected to a variable voltage transformer and a RKC temperature controller connected to a thermocouple attached to the catalyst bed in reactor. A dial setting establishes a set point at any temperature within the range between 0 °C to 600 °C.

4.4.2.3 Electrical furnace: This supplies the required heated to the reactor for the reaction. The reactor can be operated from room temperature to 700 °C at maximum voltage.

4.4.2.4 Gas controlling system: nitrogen and air cylinders each equipped with a pressure regulator (0 - 120 psig), an on - off valve and a needle valve were used to adjust flow rate of gas.

4.4.2.5 Gas chromatographs: flame ionization detector - type gas chromatographs, Shimudzu GC - 14 A and GC - 14 B, were used to analyze feed and effluent gas. Operating conditions used are shown in Table 4.2.

Table 4.2 Operating conditions for gas chromatograph

Gas chromatographs	Shimudzu GC - 14 A	Shimudzu GC - 14 B
Detector	FID	FID
Column	Silicon OV-1 ϕ 0.25 \times 50 m	VZ - 10 ϕ 3 \times 3 m
Carrier gas	N ₂ (99.99 %)	N ₂ (99.99 %)
Flow rate of carrier gas	25 ml / min	25 ml / min
Column temperature		
- Initial	35 °C	55 °C
- Final	140 °C	80 °C
Detector temperature	150 °C	150 °C
Injection temperature	45 °C	100 °C
Analyzed gas	gasoline range hydrocarbon	gaseous hydrocarbon
Split ratio	50	-

4.5 Reaction Method

The catalytic cracking reaction of n-octane hydrocarbon was carried out by using a conventional flow apparatus shown in Figure 4.3. A 0.3 g portion of the catalyst was packed in a quartz tubular reactor. Nitrogen gas was supplied from a cylinder to control n-octane partial pressure and flow rate of the system (see Appendix A-4). Catalytic cracking reaction of n-octane was carried out under the following conditions: total pressure 1 atm; n-octane composition 20 % balanced with nitrogen; gas hourly space velocities (GHSV) 1,000 -5,000 h⁻¹; reaction temperatures 300 - 600 °C; times on stream (TOS) 10-60 min.

The procedure used to operate the reactor is as follows:

(1) Adjust the outlet pressure of N₂ gas to 1 kg/cm², and allow the gas to flow through a rotameter.

(2) Adjust 2 three -way valves to allow gas to pass through the upper line through the reactor and measure the outlet gas flow rate by using a bubble flowmeter.

(3) Heat the reactor from room temperature to 450 °C with a heating rate of 20 °C /min and maintain at that temperature for 30 min. Then, the reaction temperatures controlled by the on-off controller were set and wait until the required reaction temperature was reached.

(4) At the same time switch on the heating line, magnetic stirrer and water - bath.

(5) Set the partial vapor pressure of n-octane to the requirement by adjusting the temperature of the water - bath according to the antoine equation,

$$\log p = A - B / (t+C) \quad (4.1)$$

where: p = vapor pressure of n-octane, mmHg

t = temperature, °C

A, B and C = constants

The values of these constants for n-octane are $A = 6.92374$, $B = 1355.126$, $C = 209.517$ and range of temperature that applied ability 19 - 152 °C.

(6) Start to run the reaction by adjusting 2 three-way valves to allow nitrogen gas to pass through n-octane inside the saturator set in the water-bath, and then, carry n-octane into inside of reactor. At that time, the reaction time is taken as zero. The partial pressure of n-octane was controlled by the water-bath temperature.

(7) Take sample to analyze at 30 min on stream. The reaction product were analyzed by gas chromatographs (For calculation see Appendix A-5).

(8) Chromatogram data were changed into weight of reactant and products by calibration curve (in Appendix A-5).

$$\% \text{ n-octane conversion} = \frac{\text{weight of n-octane reacted}}{\text{weight of n-octane in feed}} * 100$$

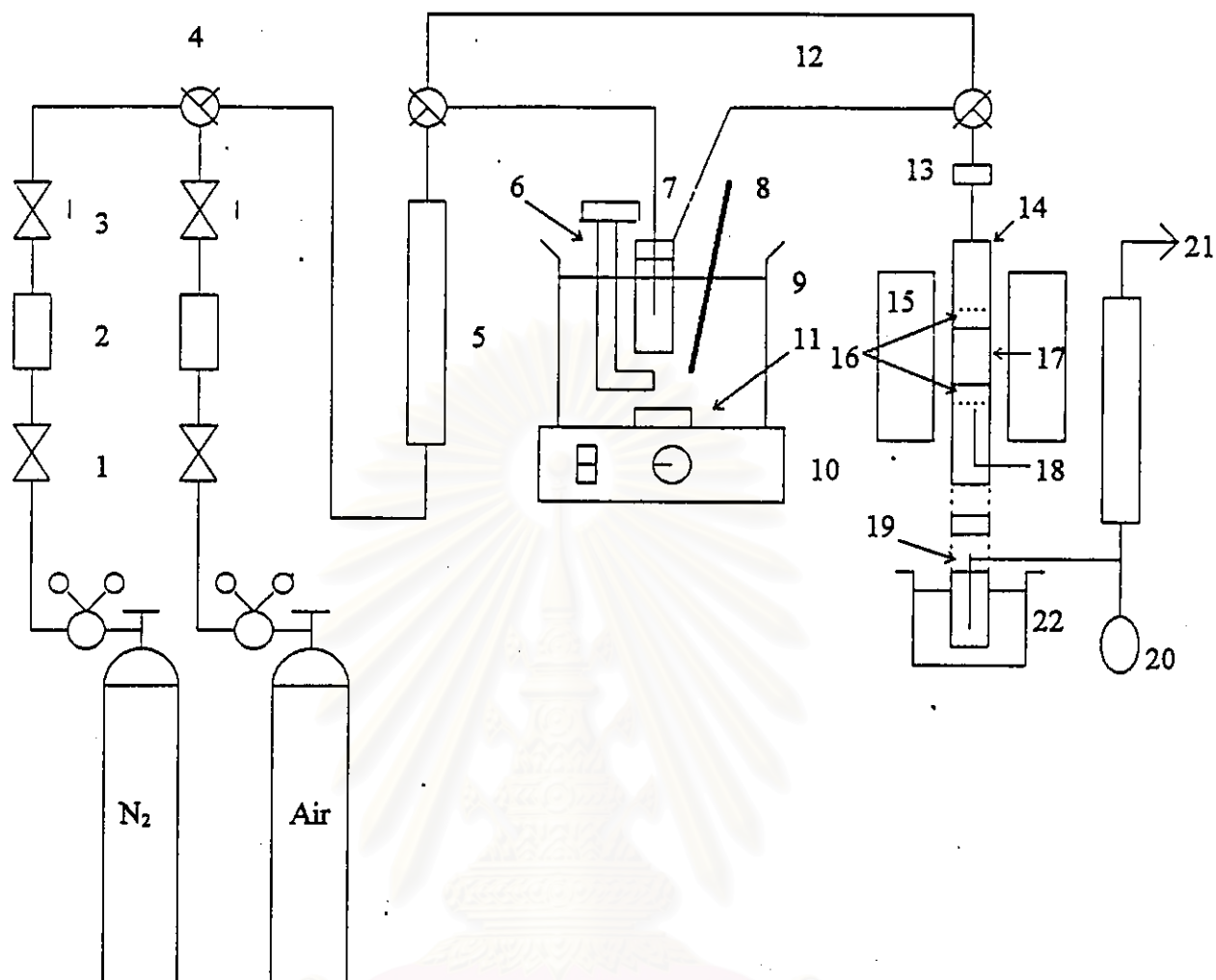
$$\text{selectivity of product } i = \frac{\text{weight of product } i}{\text{weight of n-octane reacted}} * 100$$

$$\text{yield} = \frac{\text{selectivity of desired products} * \text{conversion}}{100}$$

4.6 Characterization of Catalysts

4.6.1 BET surface area measurement

This method was a physical adsorption of nitrogen gas on the surface of catalyst to find the total surface area. BET surface areas of these catalyst were measured by Micromeritics ASAP 2000 of Chemical Laboratory of Department of Chemical Engineering, Chulalongkorn University.



1. On - off valve; 2. Gas filter; 3. Needle valve; 4. Three - way valve
 5. Flow meter; 6. Water bath heater; 7. Saturator set containing n-Octane;
 6. Thermocouple; 9. Water bath; 10. Stirring controller; 11. Magnetic bar;
 12. Heating line; 13. Sampling port; 14. Tubular reactor; 15. Electric furnace;
 16. Quartz wool; 17. Catalyst; 18. Thermocouple; 19. Ribbon heater;
 20. Soap - film flowmeter; 21. Purge; 22. Trap;

Figure 4.3 Schematic diagram of the reaction apparatus for the catalytic cracking reaction of n-octane

4.6.2 X - ray diffraction patterns

X-ray Diffraction pattern of these catalysts were measured by the D 5000 diffractometer of Siemens at Petrochemical Engineering Research Laboratory, Chulalongkorn University.

4.6.3 Morphology

The size and shape of the catalysts was observed by using JEOL LSM - 35CF at the Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC).

4.6.4 Acidity measurement

The acidity measurement was assessed by using the technique of temperature programmed desorption (TPD) of NH_3 with a Shimadzu thermal analyzer TGA-50 at Petrochemical Engineering Research Laboratory, Chulalongkorn University.

The temperature program of the NH_3 - TPD measurement is shown in figure 4.5. Catalyst (15 mg) was heated from room temperature to $450\text{ }^\circ\text{C}$ with a constant heating rate of $20\text{ }^\circ\text{C}/\text{min}$ with N_2 gas flowing at $50\text{ ml}/\text{min}$. The temperature was kept at $450\text{ }^\circ\text{C}$ for 5 min. After the catalyst was dried, the temperature was lowered to $50\text{ }^\circ\text{C}$ in N_2 gas stream. N_2 gas was then replaced with 5 % NH_3 (95 % N_2). When the amount of adsorbed - NH_3 attained its maximum, NH_3/N_2 gas was replaced with N_2 gas again. The catalyst was heated to $80\text{ }^\circ\text{C}$ and kept at that temperature until physically adsorbed NH_3 was desorbed. The temperature was then raised from $80\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ ($10\text{ }^\circ\text{C}/\text{min}$) to desorb the chemically adsorbed NH_3 (For calculation see Appendix A-3).

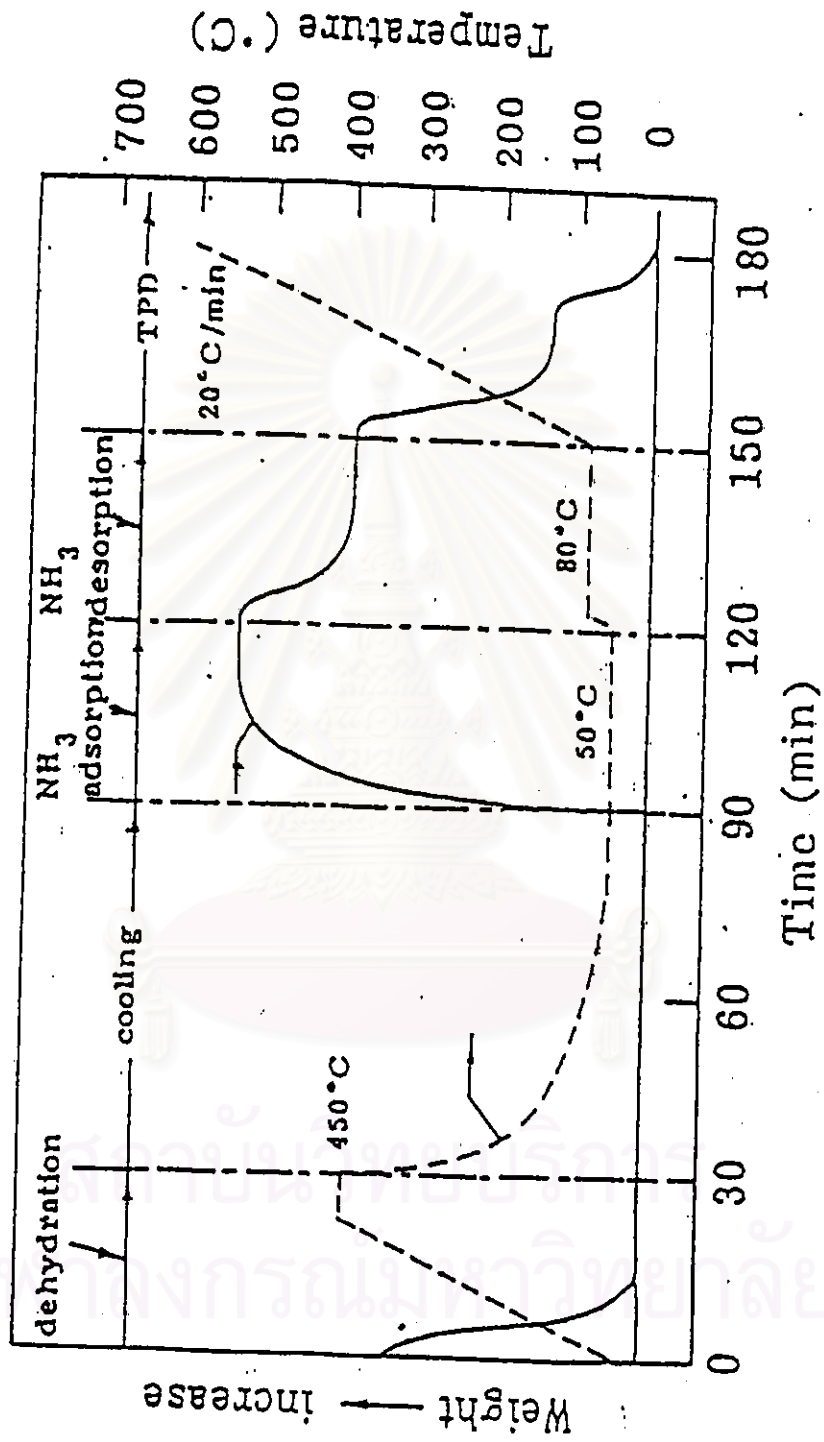


Figure 4.4 Temperature program for the NH_3 -TPD measurement