

CHAPTER IV EXPERIMENT

The synthesis of Beta zeolite for isomerization of n-hexane is explained in the following section.

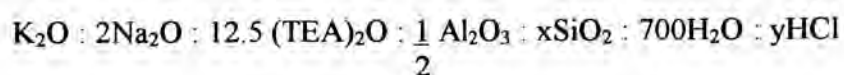
4.1 Preparation of Na, NH₃ and H-Beta Zeolite

The preparation procedures and the reagents used are shown in Figure 4.1 and Table 4.1 (for calculation see Appendix A-1)

4.1.1 Gel composition and reagents

All synthesis mixtures were prepared with the following reagents : tetraethylammonium hydroxide (Fluka, 40% by weight aqueous solution), cataloid as a source of SiO₂ (SiO₂ 30% by weight aqueous solution), sodium aluminate (Wako, Lot LEH 3073, Al/NaOH about 0.81), sodium hydroxide (BDH, 99%), potassium chloride (AJAX CHEMICALS, 99%), sodium chloride (AJAX CHEMICALS, 99.9%).

Gels of the following oxide molar composition were prepared for the synthesis :



x was varied from 30 to 80, and y from 0 to 3, by adding appropriate amounts of NaCl, NaOH and KCl.

Table 4.1 Reagents used for the preparation of Na-Beta

Reagents for the gel preparation		
TEAOH		61.36 g
Cataloid		
for Si/Al = 30		40.00 g
Si/Al = 50		66.66 g
Si/Al = 80		106.67 g
KCl		0.498 g
NaOH		0.458 g
NaAlO ₂		0.702 g
NaCl		0.39 g

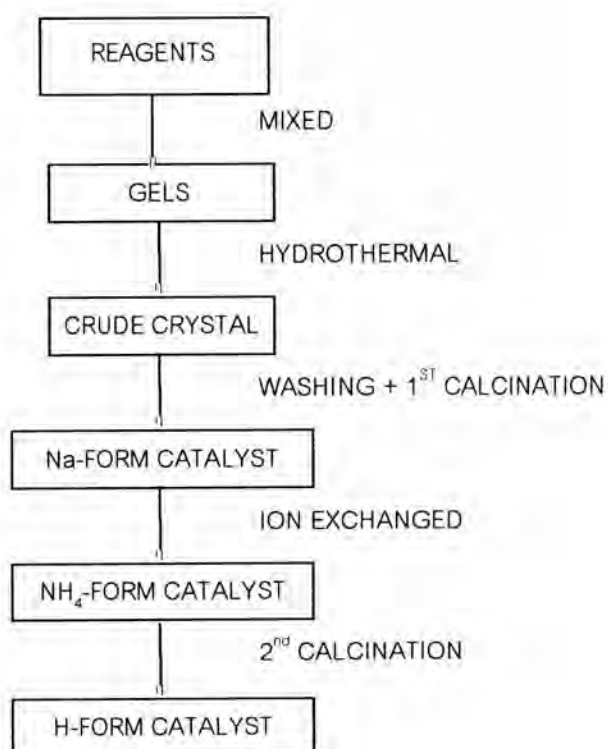


Figure 4.1 Preparation procedure of Beta zeolite

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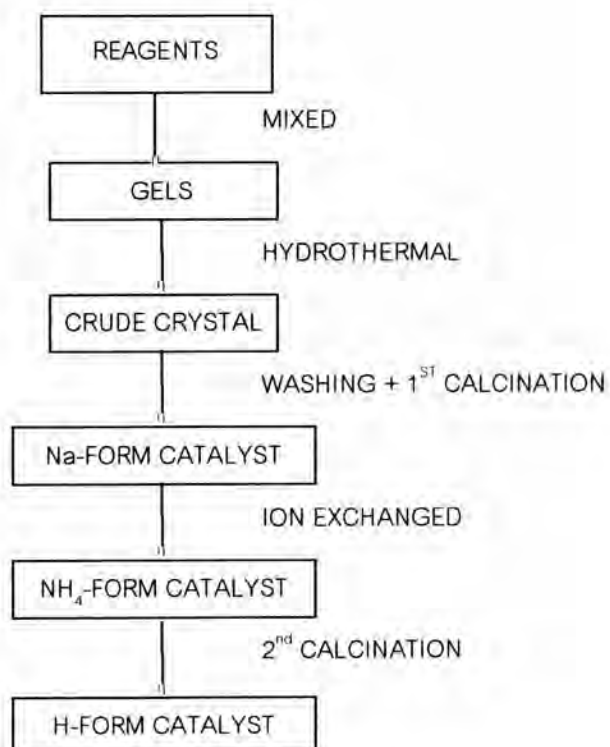


Figure 4.1 Preparation procedure of Beta zeolite

4.1.2 Crystallization

The gel obtained was stirred thoroughly before transferring to a stainless-steel autoclave. The gel was heated for crystallization in the autoclave from room temperature to 135 °C in 1 hour under a pressure of 3 kg/cm² (gauge) of nitrogen gas and maintained at this temperature for 40 hours. After selected time intervals, the autoclave were immersed in cold water to quench the crystallization process. The solid material thus obtained was centrifuged at 4,000 r.p.m. (about 15-20 min. for each time) and the recovered solids were washed until pH \approx 9 and dried in an oven at 110 °C overnight.

4.1.3 First Calcination

The dry crystal were calcined in an air stream at 540 °C for 3.5 h by heating them from room temperature to 540 °C in 60 min. This step was to burn off the organic template and to leave the cavities and channels in the crystals. Then, the calcined crystals were cooled to room temperature in a dessicator. After this step the crystals formed were called Na-Beta.

4.1.4 Ammonium ion-exchange

The ion-exchange step was carried out by mixing 3 g of the calcined crystal with 90 ml of 1 M NH₄NO₃ and heated on a stirring hot plate at 80 °C for 1 h. Then, the mixture was cooled down to room temperature. Then, the ion-exchange step was

repeated again. After that, the ion-exchanged crystal was washed twice with deionized water by using centrifugal separator. Then, the ion-exchanged crystal was dried at 100-120°C for at least 3 h in oven. The dried crystals (NH₄-Beta) were then obtained.

4.1.5 Second Calcination

The removable species, i.e. NH₃, NO_x were decomposed by thermal treatment of the ion-exchange crystal in a furnace by heating from room temperature to 500°C in 60 min and maintained at his temperature for 2 hr. After this step the catalysts formed were called H-Beta.

4.2 Platinum Loading

4.2.1 Ion exchange

The ion exchange was conducted by adding 1 g of catalyst in 40 ml of distilled water. The mixture was heated from room temperature to 98°C for 30 min. Then Pt (NH₃)₄Cl₂ solution was added into the mixture and heated at 98°C for an additional 6 hr. The sample was dried overnight at 110°C. Dry crystals were heated in air steam with flow rate 50 ml/min. A constant heating rate of 3°C/min was used to raise from room temperature to 350°C and maintained at that temperature for 10 min (as shown in Figure 4.2). The amount of Pt loading in the catalyst was 0.1, 0.6, and 1.0 wt % (For calculation see Appendix A-2).

The catalysts were tableted by a tablet machine. After tableting the catalysts were crushed and sieved to the range of 8-16 mesh to provide the reaction.

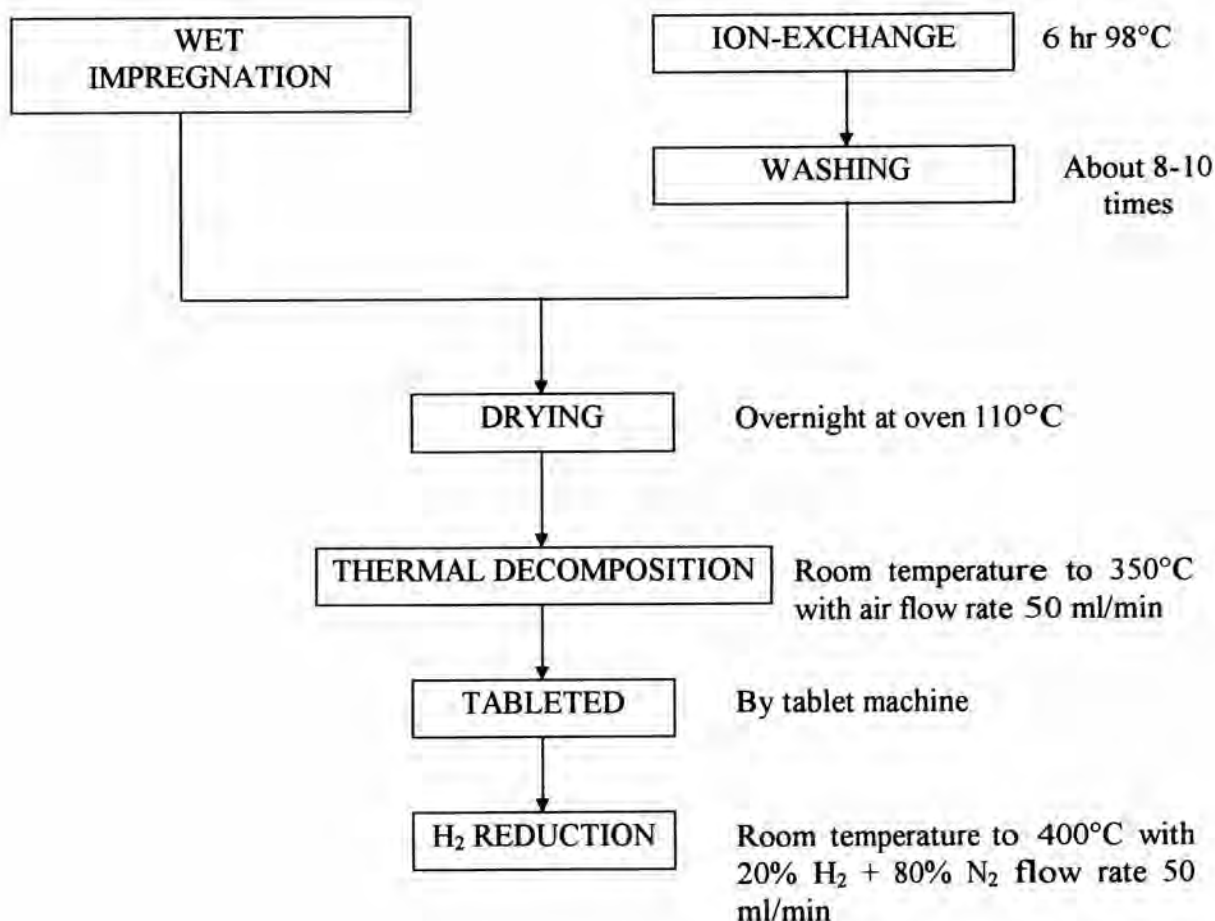


Figure 4.2 Introduction of Pt to Beta zeolite by wet impregnation and ion exchange.

The tableted catalysts were reduced in a microreactor with a stream of 20% H₂-80% N₂ and heated from room temperature to 400°C and kept at 400°C for 30min.

4.2.2 Wet impregnation

The wet impregnation was conducted by adding 1 gram of catalyst was immersed in 20 ml of distilled water. An appropriate amount of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ solution was added to the mixture and then heated from room temperature to 70°C . With stirring, the suspension was evaporated to dryness.

4.3 Isomerization of n-hexane

4.3.1 Chemicals and reagents

n-hexane available from AJAX CHEMICALS, 99.5%

4.3.2 Instruments and Apparatus

4.3.2.1 Reactor : The reactor is a conventional microreactor made from a quartz tube with 6 mm inside diameter, so it can be operated at high temperature. The reaction was carried out under ordinary gas flow and atmospheric pressure.

4.3.2.2 Automatic 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 .

4.3.2.3 Electrical furnace : This supplies the required heated to the reactor for reaction. The reactor can be operated from room temperature up to 700°C at maximum voltage of 220 volt.

4.3.2.4 Gas Controlling System : hydrogen and nitrogen are equipped with a pressure regular (0-120 psig), an on-off valve and a needle valve were used to adjust flow rate of gas.

4.3.2.5 Gas Chromatographs : flame ionization detector-type

Gas chromatograph, Shimadzu GC-14A. Operating conditions used are shown in Table 4.2

4.3.3 Reaction Method

The isomerization of n-hexane was carried out by using a conventional flow apparatus shown in Figure 4.5. A 0.3 g portion of the catalyst was packed in the quartz tubular reactor. The reaction was carried out under the following conditions : atmospheric pressure, gas hourly space velocities (GHSV), 380-3200 h⁻¹, reaction temperatures, 150-350°C.

Table 4.2 Operating conditions for gas chromatograph

Gas chromatographs	Shimadzu GC-14A
Detector	FID
Column	Chemical C18 80/100 8 ft
Carrier gas	N ₂ (99.99%)
Flow rate of carrier gas	25 cc/min
Column temperature	50°C
Detector temperature	200°C
Injector temperature	200°C

The procedure used to operate this reactor is as follows :

(1) Adjust the outlet pressure of nitrogen and hydrogen to 1 kg/cm², and allow the gas to flow through a rotameter (See Appendix A-4), measure the outlet gas flow rate by using a bubble flowmeter.

(2) Heat up the reactor (under N₂ flow) by raising the temperature from room temperature to 150°C in 30 min and then hold at that temperature for 10 min. Then the temperature was raised from 150°C to the required temperature and wait until the required reaction temperature becomes constant.

(3) Set the partial vapour pressure of n-hexane to the requirement by adjust the temperature of water bath following this equation[51](see Appendix A-6).

$$\ln(P_{vp}/P_c) = (1-x)^{-1} [(VP A)x + (VP B)x^{1.5} + (VP C)x^3 + (VP D)x^6] \quad (4.1)$$

$$\text{Where } x = 1 - T/T_c$$

(4) Start to run the reaction by adjusting 2 three way valves to allow hydrogen gas to pass through n-hexane inside the saturator set in the water-bath. The partial pressure of n-hexane was controlled by the water-bath temperature.

(5) Take sample for analyzed at 20 min on stream (see Appendix A-5). The reaction products were analyzed by FID-type gas chromatograph.

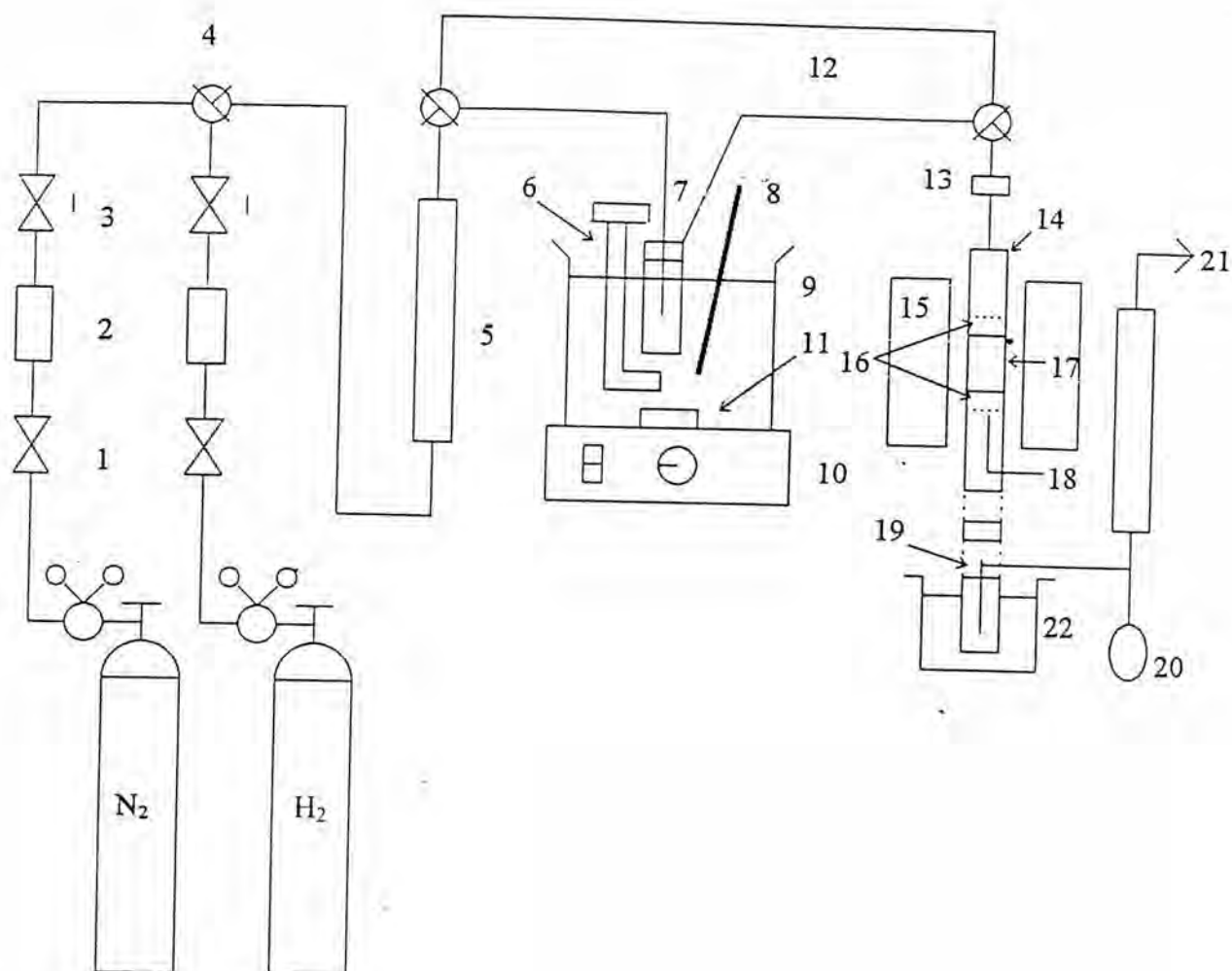
4.4 Characterization of the Catalysts

4.4.1 X-ray Diffraction Patterns

X-ray diffraction (XRD) patterns of the catalysts were performed with SIEMENS XRD D5000 at Petrochemical Engineering Research Laboratory, Chulalongkorn University.

4.4.2 BET Surface Area Measurement

Surface areas of the catalysts were measured by the BET method, with nitrogen as the adsorbate using a micromeritics model ASAP 2000 at liquid-nitrogen boiling point temperature at the Analysis Center of Department of Chemical Engineering, Faculty of 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 n-hexane isomerization.

4.4.3 Morphology

The shape and the distribution of the size of the crystals were observed by JEOL Scanning Electron Microscope (SEM) at the Scientific and Technological Research Equipment Center, Chulalongkorn University (STREC).

4.4.4 Chemical Analysis

Percentage of metals was analyzed by X-ray fluorescence spectrometer (XRF) technique. The silicon and aluminum content of the prepared catalyst was analyzed by X-ray fluorescence spectrometer (XRF) at the department of science service, Ministry of Science, Technology and Environment.

4.4.5 Acidity Measurement

The acidity measurement was assessed by using the technique of temperature-programmed-desorption (TPD) of NH_3 with a Shimadzu thermal analyzer TA-51 at Petrochemical Engineering Research Laboratory, Chulalongkorn University.

The temperature program for the NH_3 -TPD measurement is shown in Figure 4.6. A portion of catalyst (15 mg) was heated from room temperature to 450°C with a constant heating rate of $20^\circ\text{C}/\text{min}$ with N_2 gas flow at 50 ml/min. The temperature was kept at 450°C for 5 min. After the catalyst was dried, the temperature was lowered to 50°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 was desorbed. The temperature was then raised from 80°C to 600°C ($10^\circ\text{C}/\text{min}$) to desorb the chemically absorbed NH_3 (For calculation see Appendix A-3).

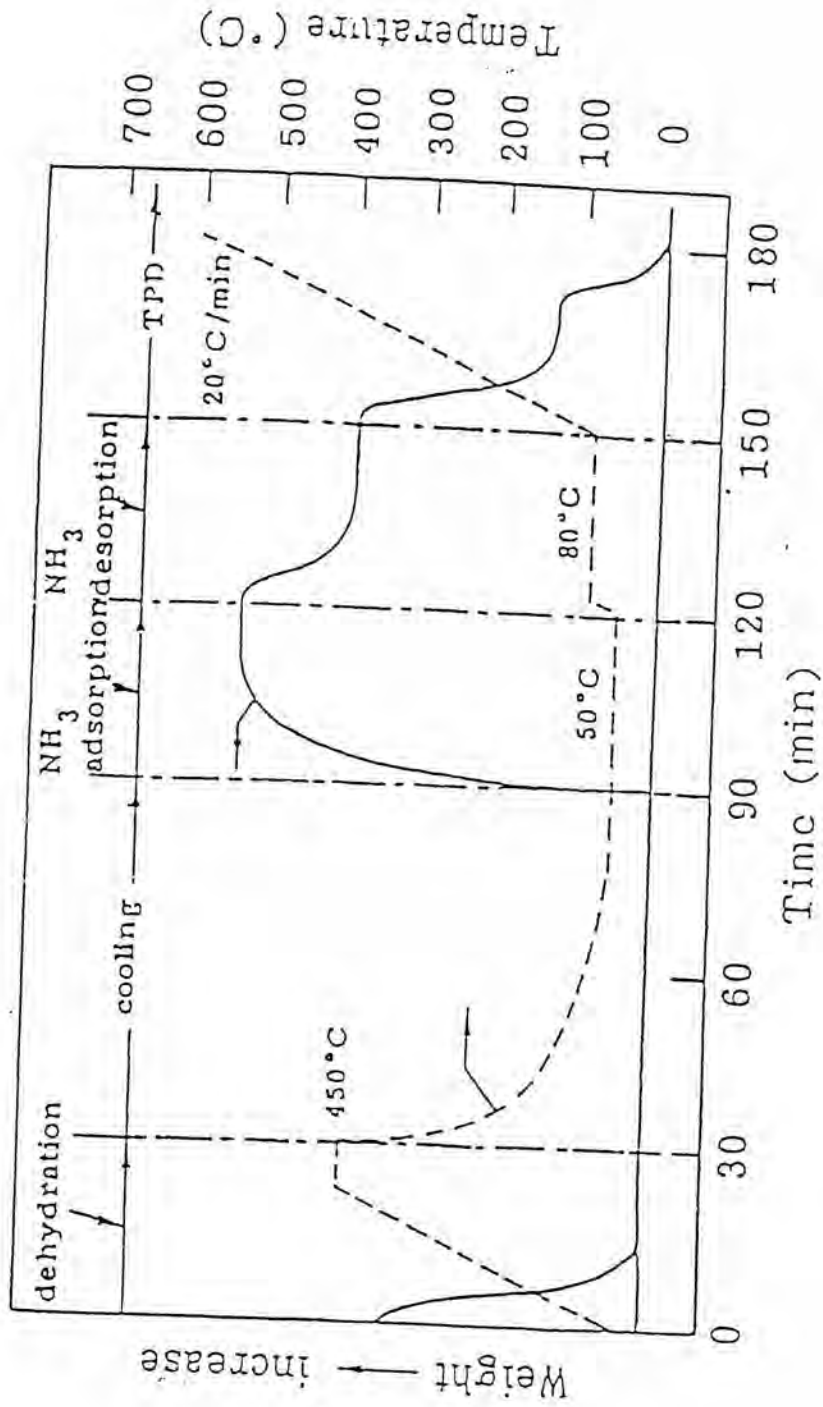


Figure 4.4 Temperature program for NH_3 -TPD measurement [45]