

CHAPTER IV

EXPERIMENT

The synthesis of Beta zeolite for the alkylation of benzene with isopropanol is explained in the following section.

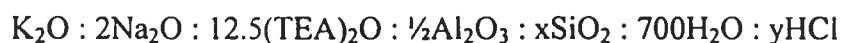
4.1 Preparation of Na, NH₄ and H-Beta Zeolite

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 3.73, Al/NaOH about 0.81), sodium hydroxide (MERCK, analytical grade), potassium chloride (AJAX CHEMICALS, analytical grade), sodium chloride (MERCK, analytical grade).

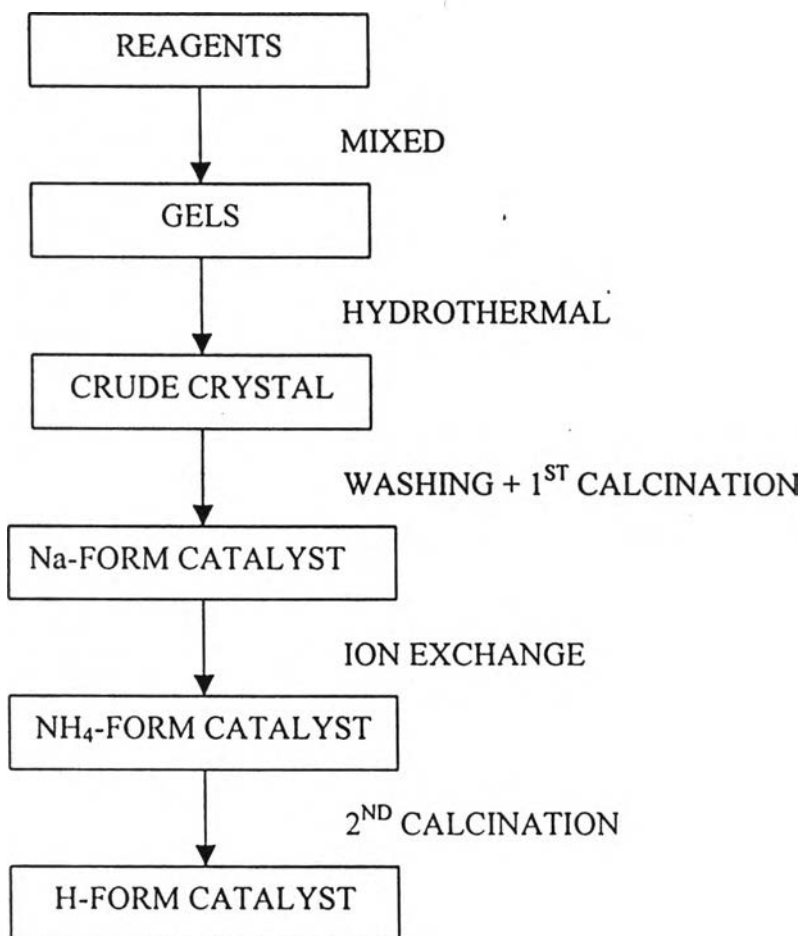
Gels of the following oxide molar composition were prepared for the synthesis:



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 zeolite

Name	wt
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 procedures 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 was immersed in cold water to quench the crystallization process. The solid material thus obtained was centrifuged at 2,500 r.p.m. (about 15 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 calcinations

The dry crystal was calcined in an air stream at 540°C for 3.5 hr. 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 desiccator. After this step the crystals formed were called Na-Beta zeolite.

4.1.4 Ammonium ion-exchange

The ion-exchange step was carried out by mixing the calcined crystal 2 M NH₄NO₃ (ratio of catalyst and solution is 1 g : 30 ml) and heated on a stirring hot plate at 80°C for 1 hr. Then, the mixture was cooled down to room temperature. Then, the ion-exchange step was repeated again. After that, the ion-exchange crystal was washed twice with deionized water by using centrifugal separator. Then, the ion-exchanged crystal was dried at 110°C for at least 3 hr. in oven. The dried crystals (NH₄-Beta zeolite) were then obtained.

4.1.5 Second calcinations

The removable species, i.e. NH_3 , 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. in air stream and maintained at his temperature for 2 hr. After this step the catalysts formed were called H-Beta zeolite.

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

4.2 Alkylation of benzene with isopropanol

4.2.1 Chemicals and reagents

Benzene and isopropanol available from MERCK, 99.5%

4.2.2 Instruments and Apparatus

4.2.2.1 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.

4.2.2.2 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 .

4.2.2.3 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.

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

4.2.2.5 Gas Chromatographs: Operating conditions used are shown in Table 4.2.

Table 4.2 Operating condition for gas chromatograph

Gas chromatographs	Shimadzu GC-14B
Detector	Flame ionization detector-type (FID)
Capillary Column	DB-1 (30 m × 0.248 mm)
Carrier gas	N ₂ (99.999%)
Split ratio	1:50
Detector temperature	250°C
Injector temperature	200°C
Column temperature	
- Initial temperature	40°C
- Initial time	5 min
- Program rate 1	5°C/min
- Program rate 2	10°C/min
- Final time 1	25 min
- Final time 2	100 min
- Final temperature 1	80°C
- Final temperature 2	200°C

4.2.3 Reaction Method

The alkylation of benzene with isopropanol was carried out by using a conventional flow shown in Figure 4.2. A 0.3 g portion of the catalyst was packed in the quartz tubular reactor. The reaction was carried out under the following condition

atmospheric pressure, gas hourly space velocities (GHSV) 1000-5000 h⁻¹, reaction temperature 100-300°C.

The procedure used to operate this reactor is as follows:

1) Adjust the outlet pressure of nitrogen to 1 kg/cm², and allow the gas to flow through a rotameter (See Appendix A-2), measure the outlet gas flow rate by using a bubble flowmeter. For example, gas flow rate was 30 ml/min at GHSV 3000 h⁻¹.

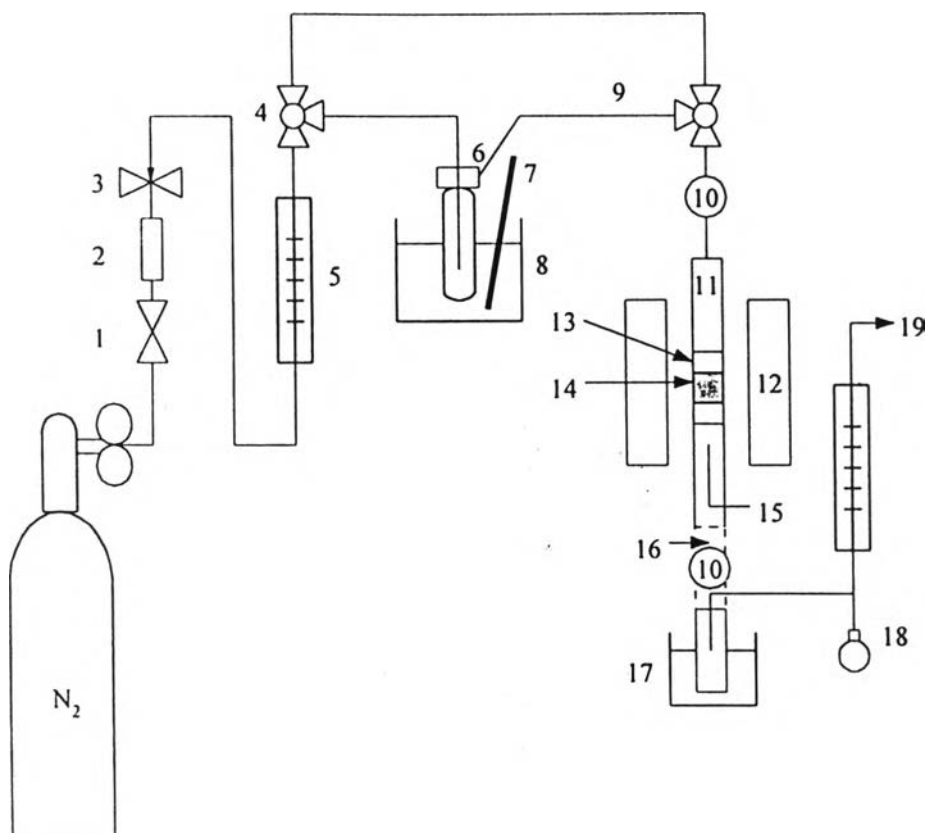
2) Heat up the reactor (under N₂ flow) by raising the temperature from room temperature to 300°C in 30 min and then hold at this temperature about 30 minute for preheat catalyst. Then the temperature was cooled down from 300°C to the required temperature and wait until the required reaction temperature becomes constant.

3) Put benzene 10 ml and isopropanol 10 ml in saturator and set the temperature of water bath at 25°C. At this temperature, the concentration of benzene and isopropanol in saturator were 15.7% mol and 5.6%mol respectively. The saturator should to be changed every 1 hour to maintain concentration of reactants.

4) Start to run the reaction by adjusting 2 three way valves to allow nitrogen gas to pass through benzene and isopropanol inside the saturator set in the water bath.

5) Take sample for analyzed at 40 min on stream (See Appendix A-3). The reaction products were analyzed by FID-type gas chromatograph.

6) The spent catalyst was regenerated by heat it up with rate 10°C/ min under air flow (10 ml/min) until the temperature reaches 550°C and holds it about 1 hour.



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| 1. On-off valve | 2. Gas filter | 3. Needle valve | 4. Three-way valve |
| 5. Flow meter | 6. Saturator | 7. Thermocouple | 8. Water bath |
| 9. Heating line | 10. Sampling port | 11. Tubular reactor | 12. Electric furnace |
| 13. Quartz wool | 14. Catalyst | 15. Thermocouple | 16. Heating tape |
| 17. Trap | 18. Soap-film flowmeter | | 19. Purge |

Figure 4.2 Schematic diagram of the reaction apparatus for the alkylation of benzene with isopropanol

4.3 Characterization of the catalysts

4.3.1 X-ray Diffraction Patterns

X-ray diffraction (XRD) patterns of the catalysts were performed with SIEMENS XRD D5000, accurately measured in the $4-44^\circ 2\theta$ angular region, at petrochemical Engineering Research Laboratory, Chulalongkorn University.

4.3.2 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.

4.3.3 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).

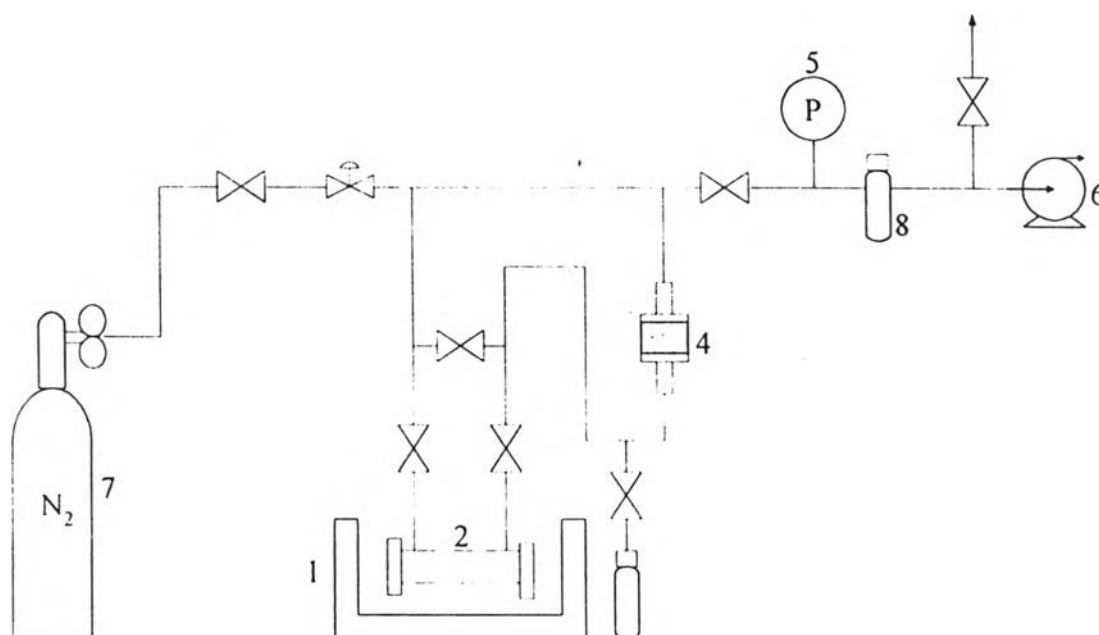
4.3.4 Chemical Analysis

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.

4.3.5 Acidity Measurement

Infrared spectroscopy and temperature programmed desorption of pyridine was used to investigate the acidic properties of Beta zeolite. The flow diagram of in-situ FT-IR apparatus is depicted in figure 4.3. All gas lines, valves and fitting in this apparatus are made of pyrex glass except for IR gas cell and sample disk holder which are of quartz glass in order to avoid the adsorption of any gas species which may remain on the inner surface of glass tube while the system was evacuated. A Nicolet model impact 400 FT-IR equipped with deuterated triglycine sulfate (DTGS) detector and connected to a personal computer with Omnic version 1.2a on Windows software (to fully control the functions of the IR analyzer) were applied to this study. The analyzer was placed on a movable table for conveniently adjustment.

About 0.06 g. of catalyst powder was pressed into self-supporting disk form with about 1 cm diameter by using a stainless steel press apparatus. The sample dish was placed into quartz in situ IR gas cell. The cell was attached with two KBr windows at both ends. Prior to adsorption, the sample was heated at 300°C and evacuated to about 10^{-4} torr for 1 hr. After that the sample was cooled down to room temperature and pyridine was introduced into the IR cell by self-vaporizing in vacuum condition and was circulated through the system by electromagnetic pump. After 2 hr of adsorption, the excess, weakly adsorbed and physisorbed pyridine was removed by evacuating at 150°C for 30 min. Desorption was then carried out by evacuation at progressively higher temperature, every 50°C, and IR spectra were recorded at the various stages of desorption. Each spectrum was completed by 500 scan at a resolution of 4 cm^{-1} . Background spectrums, i.e. prior to adsorption, were subtracted from all spectra so that the effects of adsorption and thermal treatments could be more clearly seen.



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|-------------------------------------|--------------------------|-------------------------------|
| 1. FT-IR Analyzer | 2. IR quartz gas cell | 3. Pyridine tube |
| 4. Electromagnetic circulating pump | | 5. Digital pressure indicator |
| 6. Vacuum pump | 7. Nitrogen gas cylinder | 8. Solvent trap |

Figure 4.3 Flow diagram of instrument used for pyridine adsorption experiment

4.3.6 Temperature programmed oxidation (TPO)

a) Materials

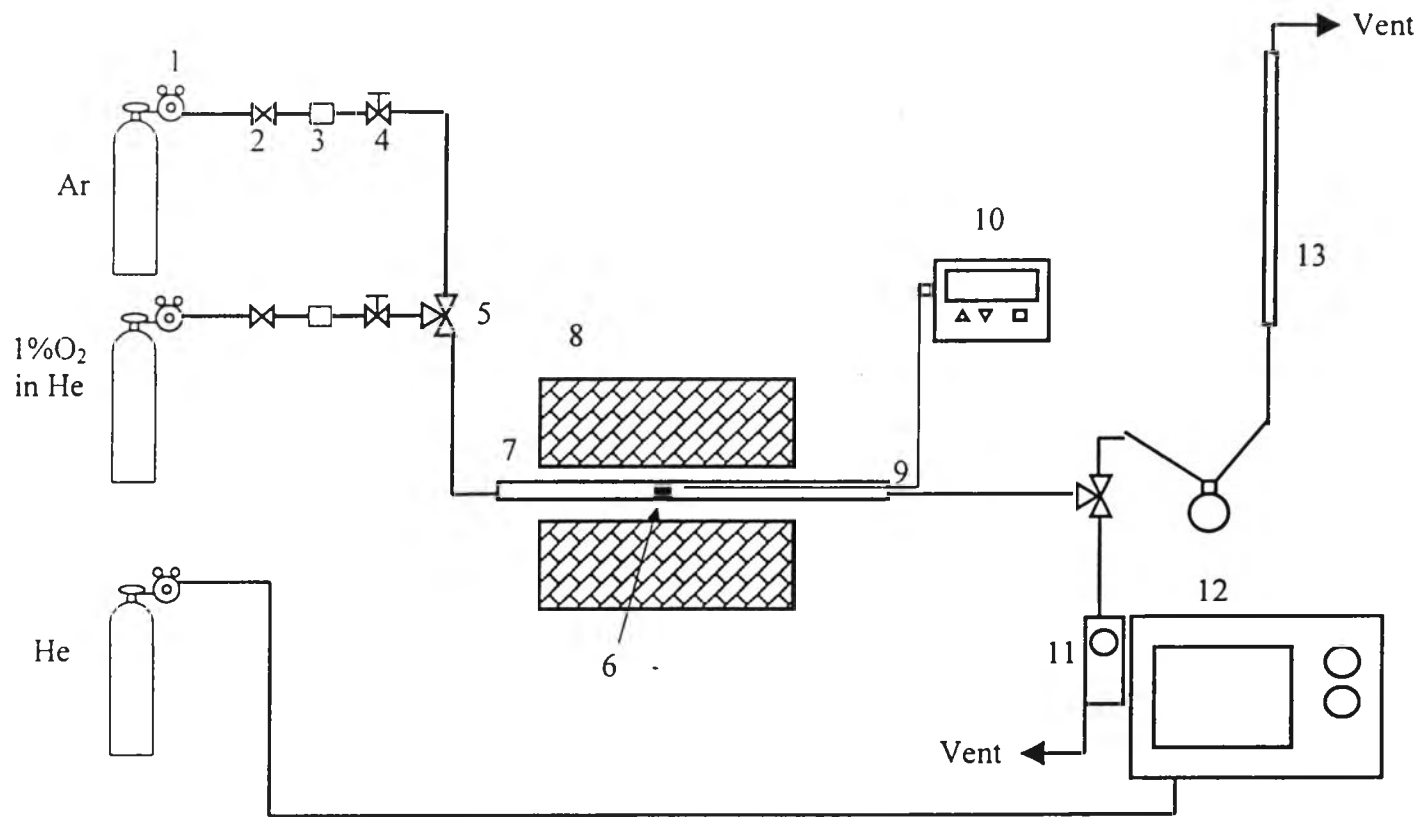
The 1% vol oxygen in helium gas mixture supplied by Thai Industrial Gas was used as an oxidizing agent. The ultra high purity helium was used for purging the system before starting the experiment.

b) Apparatus

Temperature Programmed Oxidation of catalyst was carried out in a quartz tube reactor (8 mm. OD) placed inside an electrical furnace. The furnace temperature was controlled by a temperature controller (PC 600, Shinko). During the oxidation the effluent gas was analyzed using a gas chromatograph (SHIMADZU 8 AIT) equipped with a gas sampling valve (1.5 ml. Sampling loop) and a thermal conductivity detector. Figure 4.4 shows the flow diagram of this system.

Table 4.3 Operating condition of gas chromatograph (SHIMADZU 8 AIT)

Model	SHIMADZU 8 AIT
Detector	TCD
Packed column	Porapack QS (200x0.32cm)
Helium flow rate	60 ml/min
Column temperature	90°C
Detector/injector temperature	110°C
Detector current	90 mA



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|-----------------------|----------------------------|-------------------|-----------------------|
| 1. Pressure regulator | 2. On - off valve | 3. Gas filter | 4. Metering valve |
| 5. 3-way valve | 6. Catalyst bed | 7. Reactor | 8. Furnace |
| 9. Thermocouple | 10. Temperature controller | 11. Sampling port | 12. Gas chromatograph |
| 13. Bubble flow meter | | | |

Figure 4.4 Flow diagram of temperature programmed oxidation system

c) TPO procedure

1. The coke catalyst was packed in the middle of a quartz microreactor before placing the reactor inside the furnace.
2. The 1% vol oxygen in helium gas was flowed through the catalyst at the flow rate of 30 ml/min.
3. The temperature programmed oxidation of coke was started. The temperature was raised to 900°C with the heating rate of 5°C/min. When the temperature reached 50°C, the effluent was sampled and analyzed every 5 min by the on-line gas sample.
4. The amounts of carbon dioxide produced and oxygen consumed were measured.
5. After the catalyst temperature reached 900°C, the 1% vol oxygen in helium gas was changed to ultra high purity helium and the reactor was cooled down.