

Appendix A

THE ACID DIGESTION PROCESS FOR ZEOLITE

1. Grinding the samples into fine powers and drying at 120°C.
2. Weighing 0.2 g of sample treated under step 1, putting it into a Teflon vessel and then adding 5 ml HF, 4 ml HClO₄ and 10 ml HCl (1:1 HCl:H₂O v/v).
3. Heating the Teflon vessel under the low temperature (<180°C), until the fog of HClO₄ vapors was observed.
4. Cooling the vessel and putting 2 ml H₂O₂. After waiting a few minutes, heat the vessel again until see the fog of HClO₄ vapors appears again.
5. Cooling it to the room temperature.
6. Adding 20 %wt. HCl into the vessel to 25 ml.

Appendix B

PREPARATION OF ZEOLITES AND CATALYSTS

1. Preparation of NaY Zeolite

Table B-1 Chemical compositions of working solution for preparation of NaY zeolite.

No	Solution/Composition (g/l)	Na ₂ O	SiO ₂	Al ₂ O ₃	H ₂ O	Density (g/l)
1	Water glass	72.31	267.26	-	933.43	1273
2	High sodium aluminate	290.97	-	48.52	1214.67	1554.16
3	Low sodium aluminate	148.92	-	105.82	1239.40	1494.14
4	Aluminium sulfate	-	-	84.81	1137.37	1222.18
5	Deionized water	-	-	-	1000	1000

Step 1: Preparation of initiating agent (seed)

Basis on 800 ml. seed

Basis ratio : (13-17) Na₂O : (1) Al₂O₃ : (12-16) SiO₂ : (300-400) H₂O.

Input ratio : 14.87 Na₂O : Al₂O₃ : 15 SiO₂ : 316.49 H₂O.

Step 2 : Preparation of aluminosilicate gel (whole gel)

Basis on 8000 ml. whole gel

Basis ratio : (3-5) Na₂O : (1) Al₂O₃ : (8-12) SiO₂ : (120-200) H₂O.

Input ratio : 4.76 Na₂O : Al₂O₃ : 9.55 SiO₂ : 188.32 H₂O.

Table B-2 The quantity of working solution for preparation of NaY zeolite.

Working Solution	Volume (ml.)
<u>Step 1: Preparation of initiating agent</u>	
Water glass	444
High sodium aluminate	277
Deionized water (make up)	79
<u>Step 2: Preparation of whole gel</u>	
Water glass	4720
Initiating agent (from step 1)	800
Aluminium sulfate	1440
Low sodium aluminate	1040

2. Preparation of zeolite catalysts

Table B-3 Distribution of individual rare earth oxide used in experiments.

Type/RE ₂ O ₃ (wt%)	La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Total
RECl ₃ (rich-La)	36.313	1.090	7.935	0.645	0.0004	45.98
RECl ₃ (mixed)	17.568	24.373	2.206	1.222	0.073	45.44

Source: Kritsanaphak, 2001: 85

Table B-4 Solid content of catalyst components.

Material	% Solid*
NaY	76.90
Rich La RECl	50.42
PBA	73.53
Clay RIPP	77.82
REY	91.34
USY	93.77
ZSM-5	93.43

* % Solid was determined at 800°C for 2 hours.

3. Preparation of ZSM-5 Zeolite

Table B-5 Chemical compositions of working solution for preparation ZSM-5 zeolite.

No	Solution/Composition (g/l)	Na ₂ O	SiO ₂	Al ₂ O ₃	H ₂ O	Density (g/l)
1	Water glass	77.7	250	-	937.3	1265
2	Aluminium sulfate	-	-	90	880	970
3	Deionized water	-	-	-	1000	1000
4	Sulfuric acid 25 %wt.	-	-	-	-	-

3.1 Procedure for preparation of ZSM-5

The procedure of NaY zeolite synthesis was transferred from Research Institute of Petroleum Processing (RIPP), China.

Input ratio: 0.084 Na₂O : 0.014 Al₂O₃ : 0.83 SiO₂ : 24.56 H₂O.

1. The solution A was prepared by mixing 200 ml. water glass, 180 ml. deionized water and 0.5 g crystal seed (ZSM-5) and stirred vigorously for 2-3 minutes.

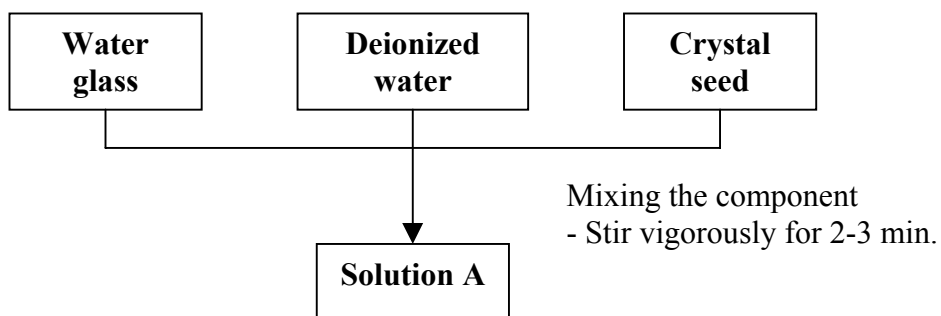
2. The solution B was prepared by mixing 15.7 ml. Al₂(SO₄)₃ solution, 49 g. H₂SO₄ 25 %wt. and 129 ml deionized water and stirred vigorously for 2-3 minutes.

3. The solution B was slowly added into solution A and stirred vigorously, the final stirred for 10 minutes.

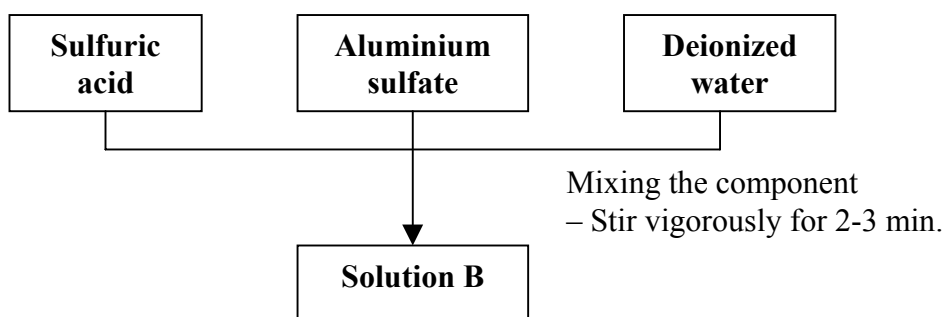
4. Take the slurry into a crystallization vessel, then the slurry was placed into a hot air oven at 180°C for 25 hours.

5. The gel was quenched with water and filtered with vacuum pump to remove the solids from mother liquor.

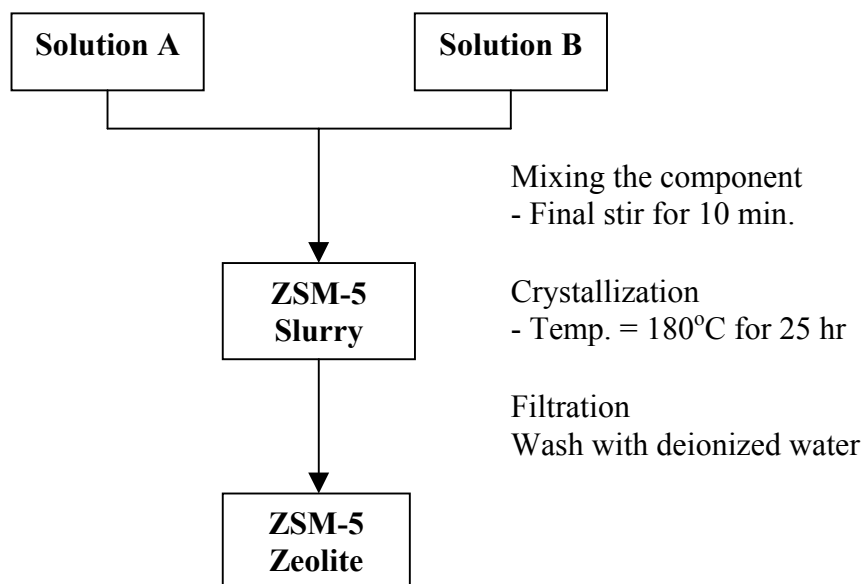
6. Wash with deionized water several time and dried in a hot air oven at 120°C for 4 hours.



(a) Preparation of solution A



(b) Preparation of solution B



(c) Preparation of ZSM-5 zeolite

Figure B-1 Preparation scheme for ZSM-5 zeolite.

Appendix C

HYDROTHERMAL DEACTIVATION (BY HYDROTHERMAL AGING UNIT MODEL CLY-1)

1. Installation and Preparation

1.1 Power Supply

It is better to have a three-phase electrical power. Each L-N voltage is 220 V, AC, 20A, If the lab isn't equipped with three-phase power supply, the three lines should be shorted in the power switch. The water pump and the recorder is lined to AC 220 V.

1.2 Air Supply

There has to be a air supply, its pressure is about 0.4 MPa. It can be from a pipe line or a small air compressor. On the aging unit the air pressure is adjusted to 0.3 MPa, Regulator pressure is adjusted to 0.1 MPa and the air flow is adjusted to 30 ml/min.

1.3 Water

The water used for aging should be demonized water. Before starting aging, the water is to be filled in the water tank to the full scale.

1.4 Temperature Adjustment

The furnace must have a long enough isothermal length (~10 cm). If the isothermal length is not long enough, you can adjust the furnace temperature as following.

Fulfill the aging tube with porcelain rings or sand. Set the three temperature controller of the furnace at nearly 800°C, start heating and air stripping. When the temperature are stable, start water pump at a rate of 25 ml/min. After 40 min gradually adjust the three temperature controllers for the furnace until the isothermal length reaching its maximum at 800°C.

2. Aging Procedure

2.1 Load Catalyst

The catalyst is to be loaded in the middle of the isothermal section of the aging tube as follows.

1. Fill porcelain rings at the bottom of the aging tube up to the isothermal section (about 17 cm. From the bottom). And at its top, put some broken rings, the thickness is about 1-2 cm.
2. Put a quartz cotton layer of about 1-2 cm on its top.
3. Better to fill 40 ml. Catalyst inside the tube.
4. Put a quartz cotton layer of about 1-2 cm. Thick on the top of the catalyst bed.
5. Fill some broken porcelain chips in.
6. Fill the tube with porcelain rings.
7. Put the tube in the furnace and line up.

2.2 Pre Air Stripping and Start Heating

1. Open the air-in valve on the unit panel, adjust the air pressures to 0.3 MPa, regulated pressure be 0.1 MPa, and adjust the air flow to 30 ml/min.
2. Turn the “power” switch on.
3. Set the heating time for 2 hrs.
4. Set the aging time for 4 hrs.
5. Set the alarm time at aging time minus 1 min.
6. Push the button “heat” to start heating.
7. Turn on pump power and set pump rate at 0.41 ml/min.

2.3 Start Hydrothermal Aging

When the aging temperature stays at 800°C for about 10-20 minutes, push the “start” button to start aging. (use water-pump to start pump water, water valve open and the air valve close, and aging time start going on automatically)

2.4 Post Air Stripping

When the aging time has passed, the water-pump stops, water valve closed and the air valve opened automatically by LOGO, the post air stripping begins.

2.5 Finish

After about 10 minutes post air stripping, you can turn off the power and close the air supply, take out the aging tube and cool it down in the air, and then take out the catalyst and separate it from porcelain rings.

Appendix D

INTRUMENTAL METHODS OF CRACKING CATALYST (BY MICROACTIVITY TESTING UNIT MODEL WFS-1D)

1. MAT Unit (Angkasuwan, 1999)

In this work we used MAT unit model WFS-1D produced by Research Institute of Petroleum Processing (RIPP), SINOPEC. WFS-1D is designed according to the standard method developed by RIPP and mainly used to test the activity index of cracking catalyst. The standard test method of cracking catalyst microactivity index in China is RIPP 92-90, the conditions are:

Standard feed gas oil: Straight-run light oil, boiling range of 235-337 °C

Reaction temperature	: 460 ±1°C
Feed oil weight	: 1.56 ±0.01 g
Feeding time	: 70 sec
Post stripping time	: 10 min
Stripping nitrogen flow-rate	: 20-30 ml/min

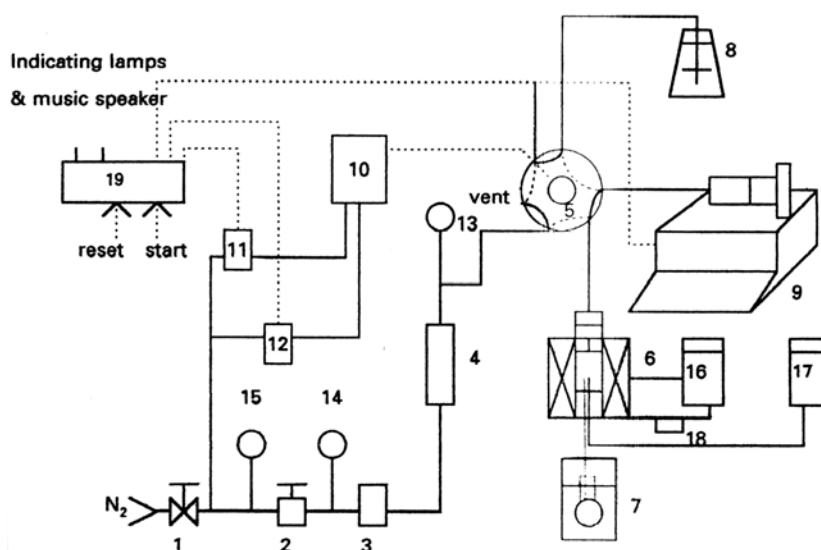


Figure D-1 The process diagram of MAT unit.

1 : valve	8 : feed oil bottle	15 : inlet pressure gauge 0-
2 : pressure	9 : injection pump	0.16 MPa
3 : flow regulator	10 : six-port valve driver	16 : temperature controller
4 : rotary flow meter	11 : solenoid valve	(furnace)
5 : six-port valve	12 : solenoid valve	17 : temperature monitor
6 : reactor & heater	13 : reaction pressure	(reactor)
7 : ice bath & collect bottle	gauge 0-0.16 MPa	18 : solid relay
	14 : regulated pressure	19 : programmable logic
	gauge 0-0.4 MPa	controller

1.1 Reaction and Collection System

The system includes the reactor, the heating furnace, the condenser well and the collecting bottle. The reactor is the heart of the reaction system where the reaction takes place. The screw bar is at the reactor's upper section, around which the feed oil is vaporized. Under the bar there is an isothermal section, the length is about 7 cm. Where the catalyst is to be loaded. At the bottom, liquid product is collected in receiver bottle by pass through a long needle that is joined with the receiver bottle by rubber tube, the bottle is immersed in the condense well filled with ice and water. A medical syringe needle sticks into the rubber tube, through it the cracking gas exits.

1.2 Feed Oil Injection System

This includes the injection pump, the six-ways valve and the feed oil bottle. It is used to smoothly inject 1.56 ± 0.01 g. feed oil into the reactor within 79 sec.

1.3 Stripping System

It includes the pressure regulator, the gas-flow regulator, pressure gauge and rotary flow-meter. The functions of this system are:

1. Pre-stripping : The nitrogen stripping before oil injection can ensure the catalyst is in the nitrogen atmosphere and water-free
2. Post-stripping: After oil injection the nitrogen stripping can get residual oil in the tuber into reactor and strip out all reaction production from reactor.

1.4 Measurement and Control System

The system includes the temperature controllers, the solenoid valves and the programmable logic controller (PLC). The two temperature controllers are the same, one indicates the catalyst bed temperature, the other one a controls temperature of the furnace. They are intelligent controllers produced by Shimandan (Shimadzu), Japan, with PID self tuning, automatic cold conjunction temperature compensation, thermocouple linearisation and deviant correction. Due to unique of the furnace manufacture technology, the reactor has more than 7 cm. Long isothermal catalyst bed with only one heater.

The PLC controls the injection pump and the six-port valve. The operating procedures are as follows (refer to Figure B-1) :

1. Preparation step: If the nitrogen source is supplied, when the power switch turns on the PLC will draw the six-port valve to the position shown by the dotted lines. That is the pre-stripping.
2. Oil injection step: After the reactor bed temperature has stabled, push the “start” button, then the six-ways valve will turn to the position shown by the solid lines, the syringe plug goes forward, the feed is injected into the reactor through the six-ways valve.
3. Oil suction step: After 70 seconds of oil injection, the six-ways valve turns back to the dotted lines position. Then post-stripping begins and syringe

plug goes backward, the feed oil is sucked into the syringe from the feed oil bottle.

4. Squeezing step: When the oil-suction has lasted for 70 seconds the syringe plug goes forward again for 20 seconds to squeezing out gas bubbles.
5. Post-stripping: When post-stripping lasts about 10 min. the speaker song music, the system goes back to the preparation step again. In order to keep the syringe plug always stay at a certain position, only in this period the reset button is enable.

2. PC Work Station (Optional)

2.1 Functions

PC workstation is designed to work with WFS-1D to change and save test parameters, remote control, print report, display the history or real time trace of process variables. It is linked to the test unit through a serial communication card, but the test unit can work independently.

2.2 Operations

2.2.1 Start up

1. Enter Window 3.11
2. Double click Group WFS-1D
3. Double click the icon WFS-1D of the group
4. Input the operator's name and click "OK" then go into the working window

2.2.2 Operations in the main working window:

1. To change the temperature controller's parameter: There are two temperature controllers. The upper one is used to indicate the reaction temperature, The lower one is used to control the furnace's temperature. The set value can be changed on its window, click "SV" to send it to the controller. The PID parameters can be changed by click the "PID", click the PID diagram blank place can close the PID window.

2. To change the operation time parameters: There is operation timetable on the right of the main working window. The feeding time (T1), sucking time (T2), preparing time (T3) and purging time (T4) all can be changed. The ranges are :

$$0 \leq T1 \leq 150s$$

$$T1 \leq T2 \leq T1 + 30s$$

$$T3 = T2 - T1 (s)$$

$$T4 \leq 991 - T1 (s)$$

After they are set or changed, click “OK” then click “SEND”, these parameters can be send to PLC of the test unit.

2.3 Commands

There are several command blocks at the main working window button:

1. “RUN” : begin to run
2. “RESET” : to reset the system
3. “EXIT” : to quit from the main working window
4. “SAVE” : to save the parameters onto the system’s hard disk
5. “LOAD” : to load the parameter from the system’s hard disk
6. “QUIT” : to quit from the WINDOWS
7. “CALCULATOR” : to use system’s calculator
8. “REPORT” : to print test report. Each report can contain two test

reports. According to the prompt input parameters, and then click “OK”, the computer can calculate out the needed parameters, and then click “PRINT” and then click “PRINT” and the report can be print out Click “EXIT” to quit from the window.

9. “TRACE” : to display the temperature’s trace. In this window there are several command blocks.

- “HISTORY” : to display history traces, the test number can be selected by click “SELECT” and “TIME”

- “SET SCALE”: to set the temperature’s scale by input the minimum/maximum temperature.

- “EXIT” : to quit from this window

3. Preparation before Operation

3.1 Reactor's Temperature

In order to have reactor's catalyst bed temperature correctly indicated, its thermocouple should be calibrated regularly (half or one year) with standard or recently calibrated thermocouple and standard differential potential meter. The deviation value should input into the temperature controller.

The catalyst bed temperature of the reactor should be controlled at $460 \pm 1\text{C}$. It can be obtain by adjusting the furnace temperature controller's set value.

3.2 Tested Catalyst

In order to have the test catalyst correctly weight, before load it into reactor it should be dried in oven for an hour at $110\text{-}120^\circ\text{C}$.

3.3 Feed Oil

Heavy oil isn't suitable for this apparatus

3.4 Feed Oil Weight Calibration

In order to have a correct injected oil weight, it is suggested to calibrate the weigh every day before experiment. The method is to insert the joint to a small bottle, then push the "start" button, when the squeezing step finished, push the "reset" button and weigh the bottle. If the oil weight is not $1.56 \pm 0.01\text{ g}$, adjust the pump's speed and calibrate again.

Example Calibration of the syringe pump.

Feed oil: gas oil (Light Cycle Oil, LCO) obtained from RIPP

Flow rate ml/min	1.52	1.52	1.52	1.52	1.52	1.52	1.52
Measured Value (g)	1.569	1.571	1.563	1.557	1.556	1.556	1.559
average = 1.562 g							

3.5 Material Balance Test :

In this test the cracking gas is not collected and the coke deposit is not detected either, so in practice test the material balance is not done. The material balance test here is like this: Instead of using catalyst, use quartz sand to do the same process as with catalyst, weight the collected oil, it should be more than 98% of the injected feed.

Example Blank test for checking liquid recovery.

Feeding amount (g)	1.562	1.562	1.562	1.562
Liquid Recovery (g)	1.547	1.567	1.558	1.537
Balance (loss, g)	0.015	-0.005	0.004	0.025
% recovery	99.0	100.32	99.7	98.4

4. Operation Steps

1. Adjust the gas tank pressure to 0.30-0.35 MPa and then turn on the power switch, WFS-1D goes stripping status automatically.

2. Put some quartz fiber, at the reactor's bottom, weight 5 g. of catalyst and load it into the reactor. Put the reactor into the furnace and link it to the six-port valve.

3. Link the collect bottle to the reactor with rubber tube and then put the bottle into the ice bath well.

4. When the reactor's temperature has stabled for 5 min, push the "start" button then the unit work in automatic for injection, suction, squeezing and post-stripping.

After 10 minutes stripping, the speaker sings music indicating that the test has finished.

5. Take off the collect bottle and wipe out the water on the bottle, weigh the bottle and note down the collected oil weight, put it in a refrigerator for G.C. analysis.

6. Take out the reactor from the furnace and take out the catalyst.

5. Analyses of Reacted Product and Data Disposal

The liquid product and gas product analyzed with G.C. and then calculated the MAT with program WFS-1D.

Appendix E

DIFFRACTION ANALYSIS BY X-RAY DIFFRACTOMETER (XRD)

1. Determination of Relative Zeolite Diffraction Intensities of Faujasite-Type Zeolite-Containing Materials (ASTM D 3906)

1.1 Apparatus and Reagents

1. X-ray diffractometer equipped with a strip chart recorder and using Copper K-alpha radiation.
2. Drying oven set at 110°C.
3. Hydrator maintained at 35% relative humidity by a saturated solution of salt, such as CaCl₂.H₂O.
4. Planimeter.
5. NaY powder and RE exchanged Y powder.

1.2 Procedure

1. Divide the sample finely to permit packing of sample into an XRD sample holder as a self-supporting window.
1. Place about 1.5 g of the sample in the drying oven at 110°C for 1 hr. Cool the sample in the hydrator and hold at room temperature for at least 16 hr.
3. Obtain a first XRD pattern by scanning over the angle range from 14 to 35 deg 2θ at 1 deg/min. Figure B-10 shows such a patterns for the reference NaY zeolite.
4. If this first pattern of the sample contains XRD peaks of some nonfaujasite components, it must be established whether this may cause interference in the following steps.
5. Obtain a second XRD pattern by scanning over a small angle range at 0.25 deg/min. The preferred angle range is from 22.5 to 25.0 deg 2θ, the (533) peak.

1.3 Calculation

1. Measure the width of the (533) or alternative peaks obtained from step 5. The width is measured at half the peak height, that is, half way between the background and the peak maximum.
2. The objective of the method, a value for “XRD intensity/NaY,” is obtained in this step. This involves a comparison of the sum of peak heights from the patterns obtained in Step 3.
3. The equation used is the following:

$$\% \text{ XRD intensity/NaY} = C_X/C_R$$
 where: C_X = peak for the sample
 C_R = reference NaY
4. Under certain conditions it may be desirable to base the comparison of zeolite XRD intensity on a single peak rather than on eight peaks. This is the case when the pattern from the sample is very weak so that on the (533) peak, for example, can be measured.
5. Values frequently obtained in Step 2 for the “pure” zeolites listed are given as follows for general guidance:

	%XRD, Intensity/NaY
NaY, NaX	90 to 105
NH ₄ Y	100 to 115
REY	25 to 50
USY	80 to 95

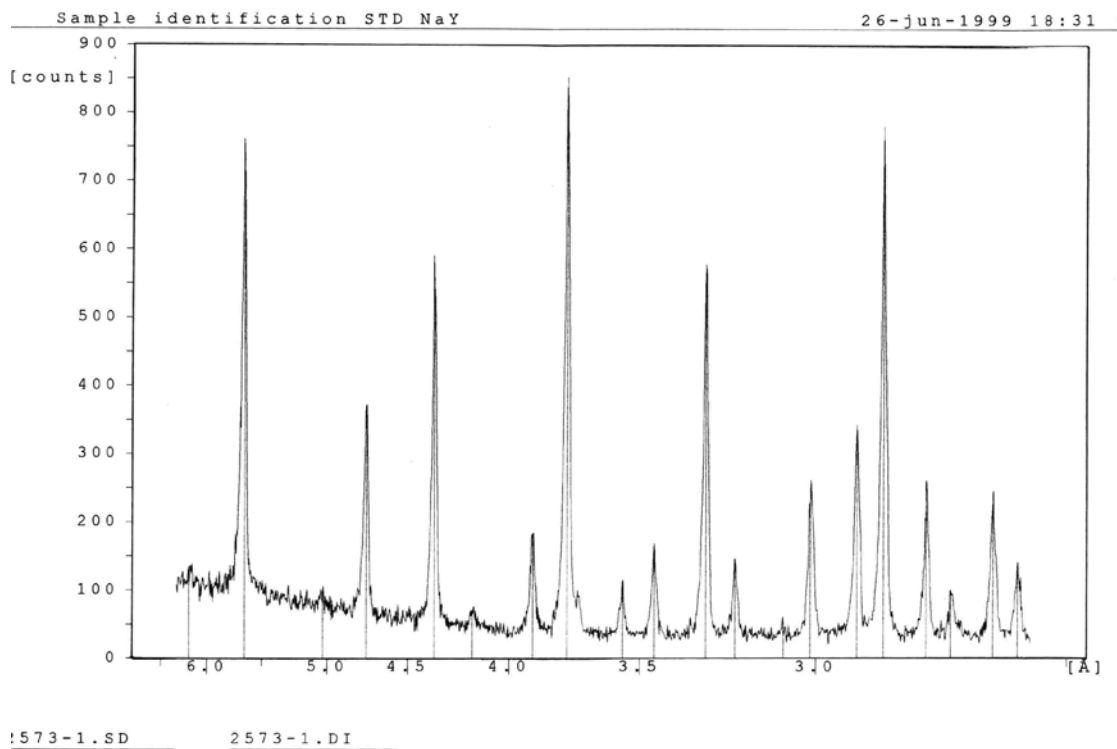


Figure E-1 X-ray Diffraction of reference (standard) NaY zeolite.

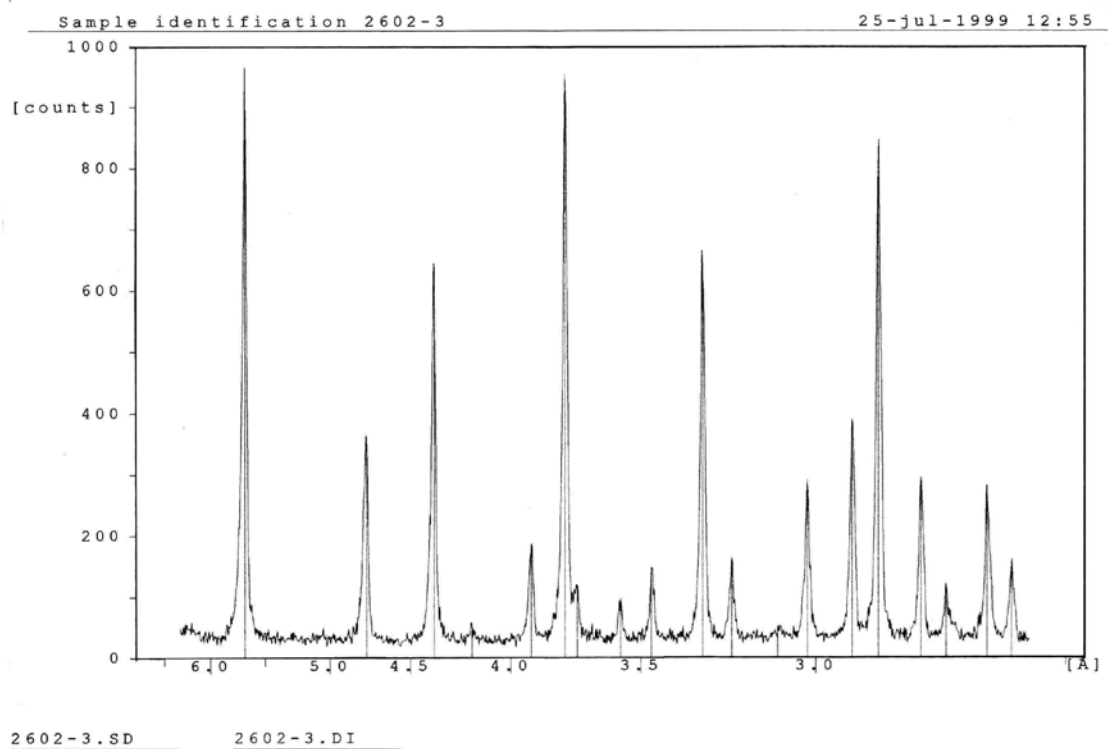


Figure E-2 X-ray Diffraction pattern of NaY zeolite from this work.

An example of the relative crystallinity calculation (the peak 533 method)

Use the following equation:

$$\% \text{ XRD intensity/NaY (533)} = 100 \times (C_X/C_R)$$

Where: C_X = peak for the sample

C_R = reference NaY

At peak 533,

$$C_X = (0.12) \times (924) = 110.88$$

$$C_R = (0.14) \times (812) = 113.68$$

$$\begin{aligned} \% \text{ XRD intensity/NaY (533)} &= 100 \times (110.88/113.68) \\ &= 97.54\% \end{aligned}$$

2. Determination of Relative Crystallinity of Zeolite ZSM-5 by X-Ray Diffraction (ASTM D 5758)

2.1 Apparatus and Reagents

1. X-ray diffractometer equipped with a strip chart recorder and using Copper K-alpha radiation.
2. Drying oven set at 110°C.
3. Hydrator (Laboratory Desiccator) maintained at 35% relative humidity by a saturated solution of salt, such as $\text{CaCl}_2 \cdot \text{H}_2\text{O}$.
4. Planimeter.
5. ZSM-5 powder.

2.2 Procedure

1. Carry out steps 2 through 4, in an identical manner, for both the sample ZSM-5 and the reference ZSM-5.
2. Place about 1.5 g of fine divided ZSM-5 in the drying oven at 105°C for 2 hr. Cool the sample in the hydrator and hold at room temperature for at least 16 hr.
3. Pack the humidity-conditioned sample in to an XRD sample holder.
4. Obtain a first XRD pattern of the reference ZSM-5 (in the same day) scanning over the angle range from 11 to 32 deg 2θ using instrument

parameter best suited to the X-ray diffractometer. The scan rate should be no larger than 1.0 °/min. The scan range includes the diffraction peaks that are to be used in the calculation for relative crystallinity. The XRD pattern of the sample can be also used to check for crystalline phase other than ZSM-5 that might be present and might interface with utility of the calculation of Procedure A. Figure D-3 shows a pattern for the reference pattern for the reference ZSM-5 used in the testing of this test method.

4. If a strip chart recorder is used, set the chart drive at 20 mm/min. Select the scale factor (amplification) for the reference ZSM-5 pattern so that the strongest peaks at 23.1° 2θ is between 15% and 100% of full scale. The same scale factor should be used for the sample ZSM-5 pattern. However, if the sample gives considerably lower peak intensities, the scale factor may be reduced (amplification increased) in order to provide reasonable peak heights.

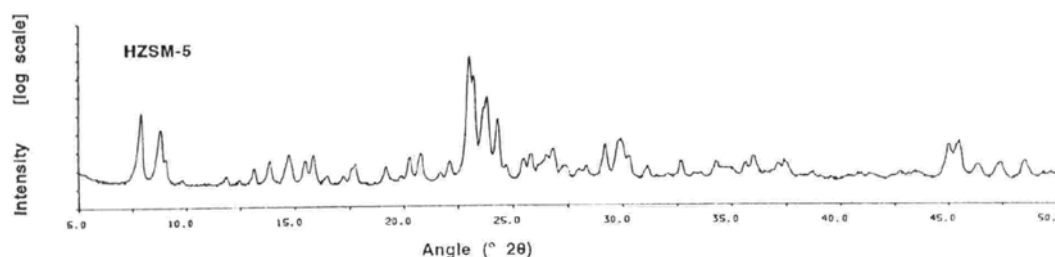


Figure E-3 X-ray Diffraction wide scan pattern of ZSM-5 zeolite.

2.3 Calculation

2.3.1 Procedure A (Integrated Peak Area Method)

This calculation involves a comparison of the integrated peak areas in the range of 22.5 to 25.0° 2θ (measured above background).

1. Obtained an integrated peak area encompassing the three to five strong peaks in the 22.5 to 25.0° 2θ range for both the sample ZSM-5 and the reference ZSM-5. The area is generally determined in one of two ways:

- 1.1 From the counts recorded by a digital integrating system that is used while obtaining the pattern.
- 1.2 By measuring the area under the peaks with a planimeter.
2. Calculate the relative crystallinity using the equation:
$$\% \text{ XRD relative crystallinity/ZSM-5} = (S_X/S_R) \times 100$$
Where: S_X = integrated peak area for the sample ZSM-5
 S_R = integrated peak area for the reference ZSM-5

1.3.2 Procedure B (Peak Height Method)

This calculation involves a comparison of the integrated peak areas in the range of 22.5 to 25.0° 2 θ (measured above background).

1. Construct a base line from the center of the background scatter at 21.2 ° 2 θ to the center of the background scatter at 25.0° 2 θ on the XRD patterns of the sample ZSM-5 and reference ZSM-5. Determine the absolute heights of the respective peaks centered at 24.3° 2 θ ; that is measure the height, in millimeters, from the baseline to the apex of the peak. Figure D-4 shows an example of the peak height determination.
2. Calculate the relative crystallinity using the equation:
$$\% \text{ XRD relative crystallinity/ZSM-5} = (H_X/H_R) \times 100$$
Where: H_X = peak height for the sample ZSM-5
 H_R = peak height for the reference ZSM-5

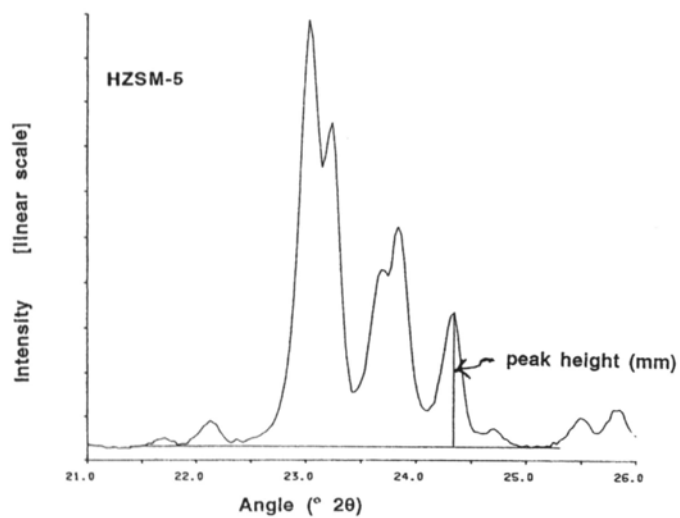


Figure E-4 X-ray Diffraction short scan pattern of zeolite ZSM-5.

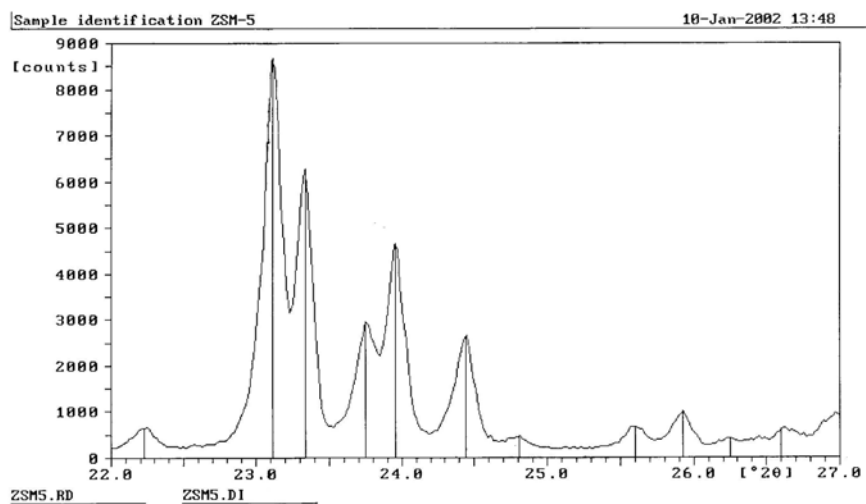


Figure E-5 X-ray Diffraction pattern of ZSM-5 zeolite of this work.

3. Determination of the Unit Cell Dimension of a Faujasite-type Zeolite (ASTM D 3942)

2.1 Apparatus and Reagents

1. X-ray diffractometer
 - Model X' Pert-MPD
 - Scan at $0.25^\circ 2\theta/\text{min}$
 - Anode material : copper tube
2. Drying Oven, set at 110°C
3. Hydrator, maintain at 35% relative humidity by a saturated solution of anhydrous calcium chloride (CaCl_2) maintain at $23\pm 3^\circ\text{C}$
4. Silicon powder

2.2 Procedure

1. Place 1 g. of powdered catalyst sample the drying oven at 110°C for 1 hr.
2. Blend 1 g. of powdered catalyst sample with about 0.05 g. of silicon in a mortar and grind until intimately mixed. Place a thin bed of the mixed sample in the hydrator for at least 16 hr. Some samples may be require a longer equilibration time. Pack the hydrated sample in the diffractometer mount
3. Determine the X-ray diffractometer pattern across range from 62 to $71^\circ 2\theta$
4. Measure the angle of the zeolite reflections at about 62.898° and $68.274^\circ 2\theta$ and that of the 66.218° silicon reflection to at least two decimal places.

Note: when low intensity prevents use of these high-angle reflections, as for example with equilibrium catalysts containing rare earth elements, measure the strong zeolite reflection near 27.356 , 31.338 and 36.391 and the silicon reflection at $33.150^\circ 2\theta$

2.3 Calculation

1. Correct the measured reflection angles for the zeolite by adding the

correction factor to each the quantity (Calculated minus measured angle of the silicon reflection). When the silicon reflection of CoK α_1 radiation is measured, the calculated angle is 66.128°.

Note: The corresponding calculated angles when lower angle reflections must be used is 33.150° 2 θ (CoK α_1)

- Convert the corrected angles of reflection to d-spacing values using the Equation :

$$d_{hkl} = \lambda/2 \sin\theta$$

Where:

d_{hkl} = distance between reflecting planes having the Miller indices hkl (nm x 10), and

λ = wave length of X-ray radiation which is 1.7889 Å for CoK α_1 Note that the angle used in this calculation is only θ .

- Calculated the unit cell dimension, of the zeolite in catalyst using the equation

$$\alpha = \{(d_{hkl})^2 (h^2 + k^2 + l^2)\}^{1/2}$$

Where the sum ($h^2 + k^2 + l^2$) of respective zeolite reflections has the following values

Reflection	($h^2 + k^2 + l^2$)
68.274°2 θ	243
62.898°	211
36.391°	75
31.338°	56
27.356°	43

Note: Certain component of a catalyst matrix can interfere with individual peaks. For example, quartz may interfere with the reflection at 31.338° when interference occurs, other reflections should be used in the calculation.

- Average the valued of α calculated from more than one reflection.

An Example of Unit Cell Size Determination (a sample of NaY)

Calculation

<u>Degrees 2θ</u>			
<i>Measured</i>	<i>Corrected</i>	$(h^2 + k^2 + l^2)$	$(a, \text{Å})$
63.125	63.143	211	24.82
66.205	66.218	silicon	-
68.165	68.178	243	<u>24.84</u>
		Average	<u>24.83</u>

Note: the correction factor in the above calculation is {66.218 (standard diffraction angle of Si) – 66.205 (measured diffraction angle of Si) = 0.013°} and is simply added to the measured angle of the two zeolite reflections.

Table F-1 Definitions of the 31 hydrocarbon groups.

Group number	Components
1	Components eluting before n-butane
2	n-Butane
3	Components eluting between n-butane and isopentane
4	Isopentane
5	Components eluting between isopentane and n-pentane
6	n-Pentane
7	Components eluting between n-pentane and 2-methylpentane
8	2-and 3- methylpentane and components eluting between 2-and 3- methylpentane
9	Components eluting between 3- methylpentane and n-hexane
10	n-Hexane
11	Components eluting between n-hexane and benzene
12	Benzene
13	Components eluting between benzene and 2-methylhexane
14	2-and 3- methylhexane and components eluting between 2-and 3- methylhexane
15	Components eluting between 3- methylhexane and n-heptane
16	n-Heptane
17	Components eluting between n-heptane and toluene
18	Toluene
19	Components eluting between toluene and 2-methylheptane
20	2-and 3- methylheptane and components eluting between 2-and 3- methylheptane
21	Components eluting between toluene and 3-methylheptane and n-octane
22	n-Octane
23	Components eluting between n-octane and ethylbenzene
24	Ethylbenzene
25	Components eluting between ethylbenzene and p-xylene
26	p-Xylene plus m-xylene
27	Components eluting between m-xylene and o-xylene
28	o-Xylene
29	Components eluting after m-xylene up to and include n-nonane
30	Components eluting between n-nonane and n-decane
31	n-Decane and Components eluting after n-decane

1. Calculation

The multiple regression analysis was used to establish values effective octane number and also lead response terms in the following types of equation:

$$\text{RON} = \Sigma (b_r W_r) + \text{lead response terms}$$

Where

b_r = weight effective octane number of group r

W_r = weight fraction of group r

This equation was derived because it allowed the G.C. data, which is usually in terms of percent weight, to be employed without conversion to percent volume.

Table F-2 The mean and standard deviations of the concentration of each group in the data, their regression coefficients.

Chromatographic group r	Regression coefficient b_r
1	103.9
2	88.1
3	144.3
4	84
5	198.2
6	67.9
7	95.2
8	86.6
9	95.9
10	20.9
11	94.9
12	105.2
13	113.6
14	80
15	97.8
16	-47.8
17	62.3
18	113.9

Table F-2 The mean and standard deviations of the concentration of each group in the data, their regression coefficients (continue).

Chromatographic group	Regression coefficient
r	b_r
19	115.1
20	81.7
21	109.7
22	10.5
23	96.1
24	122.6
25	45.4
26	102
27	73.3
28	123.6
29	35
30	112
31	85.6

Appendix G

EXPERIMENTAL DATA

Table G-1 N-octane catalytic cracking on REY zeolite in liquid product.

	REY (% wt.)				
	0	20	25	30	35
% Conversion	1.04	1.56	4.07	5.29	7.80
Liquid selectivity	91.99	79.55	33.45	25.71	17.79
Gas & Coke selectivity	8.01	20.45	66.55	74.29	82.21
% Liquid yield	0.96	1.24	1.36	1.36	1.39
% Gas & Coke yield	0.08	0.32	2.71	3.93	6.41
% Paraffins	88.75	76.03	78.60	79.41	80.27
% Olefins	9.32	19.75	15.32	12.19	10.34
% Aromatics	1.93	4.22	6.08	8.40	9.39
Paraffins/Olefins	9.52	3.85	5.13	6.51	7.76
Paraffins/Aromatics	45.98	18.02	12.93	9.45	8.55
Research Octane Number	81.38	92.42	97.52	87.62	85.42

Table G-2 N-octane catalytic cracking on REY zeolite in gas product.

	REY (% wt.)				
	0	20	25	30	35
% Paraffins	95.7	89.4	89.91	90.86	94.31
% Olefins	4.27	10.60	10.09	5.69	5.69

Table G-3 N-octane catalytic cracking on USY zeolite in liquid product.

	USY (% wt.)				
	0	20	30	40	50
% Conversion	1.04	3.22	2.63	1.32	1.06
Liquid selectivity	91.99	38.04	43.97	75.70	86.14
Gas & Coke selectivity	8.01	61.96	56.03	24.30	13.86
% Liquid yield	0.96	1.22	1.16	1.00	0.91
% Gas & Coke yield	0.08	1.99	1.48	0.32	0.15
% Paraffins	88.75	78.34	76.67	73.44	70.98
% Olefins	9.32	20.03	21.24	22.08	21.48
% Aromatics	1.93	1.63	2.09	4.48	7.54
Paraffins/Olefins	9.52	3.91	3.61	3.33	3.30
Paraffins/Aromatics	45.98	48.06	36.68	16.39	9.41
Research Octane Number	81.38	83.77	83.95	75.1	88.91

Table G-4 N-octane catalytic cracking on REY zeolite in gas product.

	USY (% wt.)				
	0	20	30	40	50
% Paraffins	95.70	95.84	78.71	58.16	57.57
% Olefins	4.27	4.16	21.29	41.84	42.43

Table G-5 N-octane catalytic cracking on ZSM-5 and 35% REY zeolite in liquid product.

ZSM-5 (% wt.)	35% REY			
	0	4	8	12
% Conversion	7.80	7.95	8.34	9.56
Liquid selectivity	17.79	28.14	33.5	47.16
Gas & Coke selectivity	82.21	71.85	66.49	52.83
% Liquid yield	1.39	2.24	2.79	4.51
% Gas & Coke yield	6.41	5.71	5.55	5.05
% Paraffins	80.27	74.77	67.94	46.05
% Olefins	10.34	14.89	20.32	35.10
% Aromatics	9.39	10.33	11.75	18.83
Paraffins/Olefins	7.76	5.02	3.34	1.31
Paraffins/Aromatics	8.55	7.24	5.78	2.45
Research Octane Number	85.42	88.56	91.12	96.87

Table G-6 N-octane catalytic cracking on ZSM-5 and 35 % REY zeolite in gas product

ZSM-5 (% wt.)	35% REY			
	0	4	8	12
% Paraffins	94.31	76.14	74.96	69.44
% Olefins	5.69	23.85	25.03	30.55

Table G-7 N-octane catalytic cracking on ZSM-5 and 25% REY zeolite in liquid product.

ZSM-5 (% wt.)	25% REY			
	0	4	8	12
% Conversion	4.07	7.56	7.73	7.85
Liquid selectivity	33.45	33.45	43.91	48.30
Gas & Coke selectivity	66.55	56.09	51.70	49.97
% Liquid yield	1.36	3.32	3.73	3.93
% Gas & Coke yield	2.71	4.24	3.99	3.93
% Paraffins	78.60	67.96	64.81	56.85
% Olefins	15.32	24.66	27.23	34.86
% Aromatics	6.08	7.38	7.96	8.29
Paraffins/Olefins	5.13	2.76	2.38	1.63
Paraffins/Aromatics	12.93	9.21	8.14	6.86
Research Octane Number	97.52	98.43	99.40	104.87

Table G-8 N-octane catalytic cracking on ZSM-5 and 25% REY zeolite in gas product.

ZSM-5 (% wt.)	25% REY			
	0	4	8	12
% Paraffins	89.91	68.90	63.37	59.55
% Olefins	10.09	31.09	36.62	40.44

Table G-9 N-hexadecene catalytic cracking on ZSM-5 and REY zeolite in liquid product.

ZSM-5 (% wt.)	25% REY		35% REY	
	0	12	0	12
% Conversion	45.72	26.48	50.71	47.08
% Liquid yield	27.55	12.01	27.62	24.90
% Gas yield	16.11	13.50	21.21	20.37
% Coke yield	2.08	0.98	1.82	1.81
% Paraffins	72.23	66.68	72.15	62.05
% Olefins	16.90	22.27	16.77	26.72
% Aromatics	10.86	11.05	11.06	11.21
Research Octane Number	78.06	80.75	82.64	84.12

Table G-10 N-hexadecane catalytic cracking on ZSM-5 and REY zeolite in gas product.

ZSM-5 (% wt.)	25% REY		35% REY	
	0	12	0	12
% Paraffins	60.75	55.73	65.78	54.86
% Olefins	39.25	44.27	34.22	45.14