

Chapter 2

Experimentation

The scope of experiment in this study was divided into two parts. The first part was concerned with the preparation of USY, REHY, REY and composite zeolite catalyst. The second part was the evaluation of the prepared catalysts by using Micro Activity Testing unit (MAT) at standard conditions using Fang gas oil as a standard feedstock.

Equipment

1. Electric mixer (Heidolph type RZR 1 made in Germany)
2. Hot air oven (Eyela model NDO-600N made in Japan)
3. Vacuum pump (Eyela model A-3S made in Japan)
4. Water bath (Mettler type W350 made in Germany)
5. Furnace

Instruments

1. Gas Chromatograph (SHIMADZU model GC-14BPF)
2. Integrator (Hewlett Packard model HP3295)
3. Hydrothermal Aging Unit (RIPP model CLY-1)
4. Microactivity Testing Unit (RIPP model WFS-1D)
5. X-Ray Diffractometer (Philips model X'Pert-MPD)
6. X-Ray Fluorescence Spectrometer (Philips model PW2400)
7. Thermogravimetric Analysis (Perkin-Elmer model TGA 7)
8. Surface Area and Pore Size Analyzer (COULTER SA3100)
9. Atomic Absorption Spectrophotometer (AAS) model AA (GBC Scientific Equipment Pty. Ltd.901)

Chemical and Reagents

Table 2-1 Chemical and reagents used in experiment

No.	Chemical and reagents	Formula	Grade
1	Aluminium	$Al(OH)_3$	AR
2	Aluminium sulfate	$Al_2(SO_4)_3$	AR
3	Sodium hydroxide	NaOH	AR
4	Sodium silicate solution (water glass)	Na_2SiO_3	CR
5	De-ionized water	H_2O	-
6	Rare earth chloride (rich-La)	$RECl_3$	CR
7	Ammonium chloride	NH_4Cl	AR
8	Hydrochloric acid	HCl	AR
9	Aluminium oxide (pseudoboehmite)	$Al_2O_3 \cdot 3H_2O$	CR
10	Kaolin Clay	$Al_2(OH)_2 \cdot Si_2O_5$	CR

AR: Analytical Reagent Grade

CR: Commercial Reagent Grade

Experimental Procedure

1. Preparation of zeolite

1.1 Synthesis of NaY zeolite

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

Step 1: The seed (initial agent) prepared by cooling all working solution listed in Table A-1 of Appendix A to 5°C. Place water-glass in a plastic container. Slowly add high sodium aluminate, add deionized water and keep stirring at 5°C for 1 hour. Statically age the obtained solution at 35°C for 6 hours. The gel obtained from this step was called "seed or activated waterglass".

Step 2: The gel prepared by mixing seed (from step 1) in water-glass and keep stirring at room temperature for 5 minutes. Aluminium sulfate was slowly added and stirred vigorously for 10 minutes. Continuously add sodium aluminate into the slurry and stirred vigorously for 2 minutes. Put gel into hot air oven, then increase temperature to 100°C, and age for 16 hours. Quench with water, and filter with vacuum pump to remove the solids from mother liquor. Wash with deionized water several times and dry in hot air oven at 110°C for overnight.

1.2 Preparation of Ultrastable Y Zeolite (USY) from NaY

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

Step1: Preparation of NH₄Y zeolite. The procedure for preparation of NH₄Cl zeolite was performed by using NaY zeolite (dry basis), NH₄Cl and deionized water ratio 1: 1: 20 by weight. First, NaY zeolite was added in hot deionized water, then added NH₄Cl and continuous stirring at 90°C for 1 hour. Next, the slurry was filtered by a vacuum pump and washed with hot 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 350°C for 2 hours in the furnace.

The calcined sample was ion-exchanged again by the same procedure of above preparation of NH₄Y zeolite (2nd ion exchange). In this step, the NH₄Y zeolite was calcined at 550 °C for 2 hours.

The fully NH_4 -exchanged zeolite (3rd ion exchange) was processed and calcined at 550°C for 2 hours.

Step 2: The steam calcination of USY zeolite. NH_4Y zeolites (3rd ion exchange) were taken to 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 D). The amount of samples to steam is 1:3 by weight. The inert gas (N_2) was passed through the micro reactor and the furnace was heated to 600°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.

1.3 Preparation of Rare Earth Hydrogen Y Zeolite (REHY)

This procedure was also reviewed and developed in the master thesis of the graduated student of Department of Chemical Engineering, PSU (Rattana, 2001).

The procedure for preparation of REHY zeolite was performed by using NaY zeolite exchange with 0.36 M Rich-lanthnum chloride and 0.5 M NH_4Cl . The ratio of NaY zeolite (dry basis) to water is about 1:10 by weight. First, NaY zeolite was mixed to 0.36 M Rich-lanthnum chloride, then NH_4Cl was added continuously while stir at $95\text{-}100^\circ\text{C}$ for 1.5 hour. The slurry was filtered by a vacuum pump and was washed with hot 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 2 hours in a furnace.

The calcined sample was ion-exchanged again by the same procedure of above preparation of REHY zeolite (2nd ion exchange). In this step, the REHY zeolite was calcined at 550°C for 2 hours.

1.4 Preparation of Rare Earth Exchanged Y Zeolite (REY)

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

The procedure for preparation of REY zeolite was performed by using NaY zeolite exchange with 0.36 M Rich-lanthnum chloride. First, NaY zeolite was mixed to hot deionized water, then Rich-lanthanum chloride was added continuously while stir at 90°C for 1 hour. Next, the slurry was filtered by a vacuum pump and was washed with hot deionized water (60°C) to remove free chloride ion. After that the filter cake dried at 120°C in an oven for 2 hours. Then, the sample was calcined at 350°C for 2 hours in a furnace.

The calcined sample was ion-exchanged again by the same procedure of above preparation of REY zeolite (2nd ion exchange). In this step, the REY zeolite was calcined at 550 °C for 2 hours.

2. 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 the graduated student of Department of Chemical Engineering, PSU (Kritsana, 2001).

First, deionized water was poured into a stainless steel vessel then was slowly added RIPP clay and PBA. After stirring 15 minutes, was slowly dropped 35% HCl into the slurry and keep stirring 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 of 20-25 %. The slurry was put in hot air oven and was dried at 100-150°C for 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 off isolated-Na by NH₄Cl solution (CAT:H₂O:NH₄Cl = 1:15:0.03)

at 60-70°C for 30 minutes. Finally, the catalyst was dried again in hot air oven at 100-150°C for overnight.

The catalysts were prepared with varying matrix and zeolite content and their activities were measured by using microactivity test. All of catalysts and matrices were listed in Table 2-2 and Table 2-3

Table 2-2 Composition of USY, REY and REHY-zeolite catalysts.

Batch no.	Zeolites (%)	PBA Binder (%)	RIPP Kaolin clay (%)
1	0	20	80
	REY		
2	5	20	75
3	10	20	70
4	15	20	65
5	20	20	60
6	25	20	55
7	30	20	50
8	35	20	45
9	40	20	40
	REHY		
10	5	20	75
11	10	20	70
12	15	20	65
13	20	20	60
14	25	20	55
15	30	20	50
16	35	20	45
17	40	20	40
	USY		
18	10	20	70
19	20	20	60
20	30	20	50
21	40	20	40
22	50	20	30
23	60	20	20

Table 2-3 Composition for preparation mixed-zeolite catalysts.

Batch no.	Zeolites, (%)		PBA Binder (%)	RIPP Kaolin clay (%)
	REY	USY		
24	30	10	20	40
25	20	20	20	40
26	10	30	20	40
27	22.5	7.5	20	50
28	15	15	20	50
29	7.5	22.5	20	50
	REHY	USY		
30	30	10	20	40
31	20	20	20	40
32	10	30	20	40
33	22.5	7.5	20	50
34	15	15	20	50
35	7.5	22.5	20	50

3. Test procedure and Test Conditions

3.1 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 was shown in Figure 2-1.

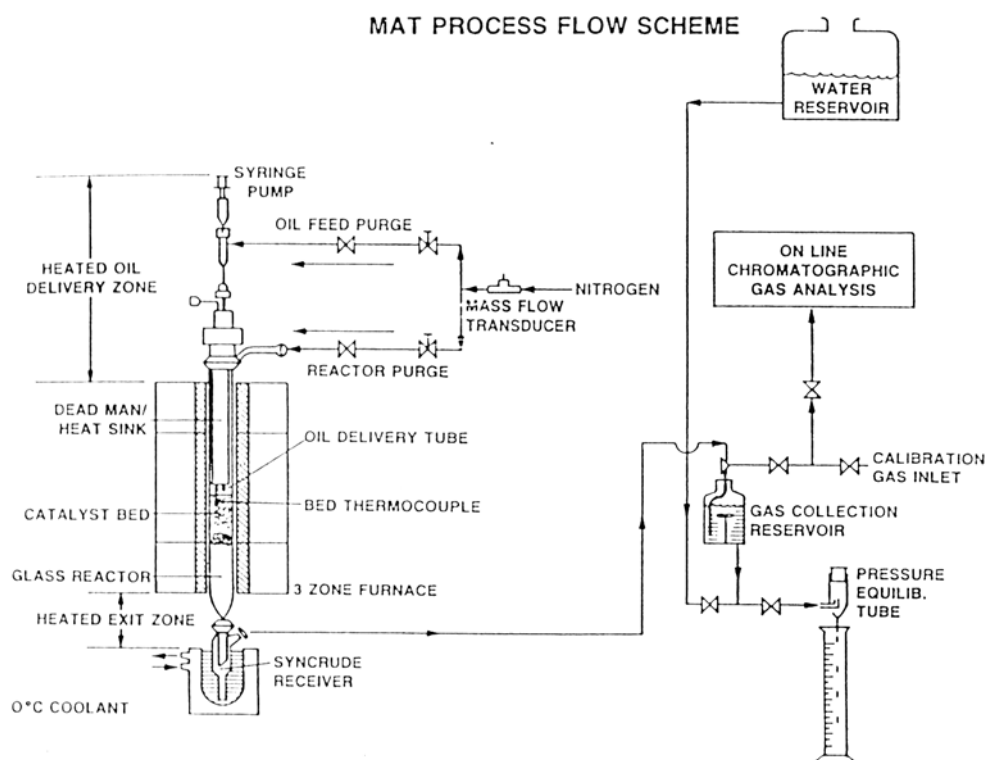


Figure 2-1 Schematic for typical MAT unit

Source: Moorehead, McLean and Cronkright; 1993: 226

3.1.1 A Microactivity Test Method and Test Condition of MAT

(see MAT set up and operation in Appendix B)

Catalyst loading:	5	g
Oil weight:	1.56 ± 0.01	g
Catalyst/Oil:	3.2	
Feedstock:	Fang Gas Oil (LCO, bp. 260-340 °C)	
Weight hourly space velocity (WHSV):	16	hr ⁻¹
Feeding rate:	1.337	g/min
Feeding time:	70	sec
Temperature:	460 ± 1	°C
Purging time:	600	sec

Liquid produced from MAT was then analyzed by 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)

Condition for Gas Chromatograph (GC)

Column:	Pack Column (OVI, methylsilocane)
Detector:	Frame Ionization Detector (FID)
Carrier gas:	Nitrogen (Purity 99.99%, OFN),
Flow rate	35-40 ml/min
Combustion gas:	Hydrogen, flow rate 40 ml/min
Auxiliary gas:	Air, flow rate 400 ml/min

Sample injection volume: 1 μ l

Temperature of vaporization chamber (injector): 280 $^{\circ}$ C

Temperature of detector chamber: 280 $^{\circ}$ C

Temperature of column chamber: 35 $^{\circ}$ C to 80 $^{\circ}$ C with a rate of 15 $^{\circ}$ C/min, then raise
from 80 $^{\circ}$ C to 235 $^{\circ}$ C with a rate of 8 $^{\circ}$ C/min
hold at 235 $^{\circ}$ C for 10 min.

3.1.2 Hydrothermal Treatment Procedure and Test Condition

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

Condition for hydrothermal aging

Catalyst loading: 15-30 g

Aging temperature: 800 $^{\circ}$ C

Aging time: 4 hr

H₂O/Cat: 3.0 gH₂O/gCat-hr

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

3.2 Characterization

Physicoproperties of zeolite and catalyst composition have been performed by using several instruments according to ASTM standard. The instruments for characterization of catalysts and standard method used were listed in Table 2-4.

Table 2-4 Characterization listed for zeolite and catalyst components

No.	Characteristic	Instrument	Method
1	Relative crystallinity	X-ray diffractometer (XRD)	ASTM D3906-80
2	Unit Cell Size (UCS)	X-ray diffractometer (XRD)	ASTM D3942-80
3	RE ₂ O ₃ content	X-ray fluorescent spectrometer (XRF)	Typical standard
4	Na ₂ 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