Preparation of REY-Zeolite Catalyst

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(1)

Thesis Title   Preparation of REY-Zeolite Catalyst

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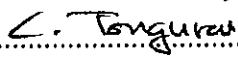**Major Program**   Chemical Engineering

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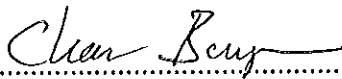
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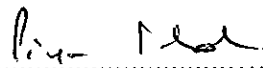
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ชื่อวิทยานิพนธ์	การเตรียมตัวเร่งปฏิกิริยาแรร์เอิร์ทวายซีโอไลต์
ผู้เขียน	นายกฤษณะ กฤษณภักดิ์
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ปีการศึกษา	2543

บทคัดย่อ

แรร์เอิร์ทวายซีโอไลต์เป็นตัวเร่งปฏิกิริยาสำหรับกระบวนการแตกตัวเชิงเร่งปฏิกิริยา โดยงานวิจัยนี้มีจุดประสงค์เพื่อศึกษากระบวนการเตรียมตัวเร่งปฏิกิริยาชนิดแรร์เอิร์ทวายซีโอไลต์ สำหรับการเตรียมตัวเร่งปฏิกิริยานั้นสามารถแบ่งออกเป็นส่วน คือ การสังเคราะห์แรร์เอิร์ทวายซีโอไลต์ และ การเตรียมตัวเร่งปฏิกิริยา โดยการสังเคราะห์แรร์เอิร์ทวายซีโอไลต์ทำได้โดยเริ่มต้นสังเคราะห์โซเดียมวายซีโอไลต์ จากการทำปฏิกิริยาระหว่าง ซิลิกาจากน้ำแก้วและอะลูมินาจากสารละลายอะลูมิเนียมซัลเฟตและโซเดียมอะลูมิเนต แล้วทำการแลกเปลี่ยนไอออนด้วยไอออนของแรร์เอิร์ท สำหรับตัวเร่งปฏิกิริยาได้ถูกเตรียมขึ้น โดยมีปริมาณซีโอไลต์ และเมตริกซ์ชนิด ต่าง ๆ กัน คุณสมบัติทางภาพและทางเคมี สามารถทดสอบได้โดย เครื่อง เอ็กซ์เรย์ดิฟแฟรคโตมิเตอร์ เครื่อง เอ็กซ์เรยฟลูโอเรสเซนต์สเปคโตมิเตอร์ และ เครื่อง สแกนนิ่งอิเลคตรอนไมโครสโคป สำหรับความว่องไวของตัวเร่งปฏิกิริยาจะถูกประเมิน ด้วยการทดสอบค่าจุลกัมมันตภาพ โดยใช้ แก๊สออยล์ ชนิดไลท์ไซเคิลเป็นสารป้อนเข้าทำปฏิกิริยา จากการทดสอบพบว่า ค่าจุลกัมมันตภาพ (microactivity) และปริมาณผลได้ของแก๊สและโค้ก มีแนวโน้มเพิ่มขึ้นเมื่อปริมาณของซีโอไลต์ในตัวเร่งปฏิกิริยาสูงขึ้น ในขณะที่ปริมาณที่เหมาะสมของซีโอไลต์ในตัวเร่งปฏิกิริยาที่ให้ค่าผลได้แก๊สโซลีนสูงสุด มีค่าประมาณ 15 เปอร์เซนต์ สำหรับตัวเร่งปฏิกิริยาที่องค์ประกอบของเมตริกซ์ชนิดต่างกัน จะมีนัยสำคัญเล็กน้อยในการเร่งปฏิกิริยาการแตกตัวของแก๊สออยล์ที่ใช้ในงานวิจัยนี้ และสำหรับตัวเร่งปฏิกิริยาที่มีอะลูมินาเป็นส่วนประกอบในเมตริกซ์จะมีค่าจุลกัมมันตภาพสูงกว่าตัวเร่งปฏิกิริยาที่มีซิลิกาเป็นส่วนประกอบในเมตริกซ์
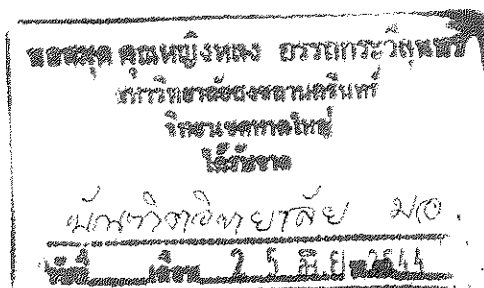
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Thesis Title	Preparation of REY-Zeolite Catalyst
Author	Mr. Kritsana Kritsanaphak
Major Program	Chemical Engineering
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Abstract

REY-zeolite is a catalyst for the fluid catalytic cracking (FCC) process. This work was aimed to study the procedure for preparing REY-zeolite catalyst. The preparation was devided in two parts: preparation of REY-zeolite and preparation of catalyst. NaY zeolite was synthesised by reacting silica source (water glass) with alumina sources (aluminium sulfate and sodium aluminate) and was followed by ion exchanging with rare earth cations to form REY zeolite. The catalysts were prepared by varying matrix types and zeolite contents. The physicochemical properties of catalyst was analyzed using the X-ray diffractometer (XRD), the X-ray fluorescent spectometer (XRF) and the scanning electron microscope (SEM). The activities of catalysts were evaluated using the microactivity test (MAT) for cracking of light cycle oil (LCO, bp. $235\text{-}335^{\circ}C$). From the microactivity test, the yields of gas and coke were found to increase as the zeolite content in the catalyst increased. The zeolite content was optimized at about 15% by maximizing gasoline yield. Different matrix compositions in catalysts have a bit of significance on the cracking of gas oil used in this work. The microactivity of catalyst containing alumina in the matrix is higher than that containing silica in matrix.

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Acknowledgment

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Chapter 1

INTRODUCTION

Introduction

Fluid catalytic cracking (FCC) is one of the most widely used refinery processes for converting heavy oils into more valuable gasoline and higher products. Wherever there is a rapidly growing demand for gasoline, FCC is the cheapest and fastest route to obtain this premium priced product (Houilles et al, 1991). Consequently, much work has been done through the years to improve the yield and/or octane rating of FCC yield and product slate are the cracking catalysts employed. While commercial cracking catalysts include acid-treated natural aluminosilicates, amorphous synthetic silica-alumina combinations and crystalline synthetic silica-alumina (zeolites), the most widely used commercial fluid catalytic cracking catalysts are zeolites. While zeolite for FCC have met with a very high degree of success, they are nevertheless limited by their respective pore sizes as to which hydrocarbon molecular can reach the active acid sites.

When first introduced commercially in the early 1960's, cracking catalysts contained either type X or Y zeolite incorporated in several different matrix compositions. Early zeolite FCC catalysts contained rare earth exchanged zeolite (REX or REY), kaolin clay and binder. The binder was synthetic silica-alumina or alumina, usually peptized pseudoboehmite as was used in many prezeolite FCC catalyst systems (Magee and Mitchell, 1993).

Hydrocarbon conversion catalysts such as fluid cracking catalysts (FCC) which comprise crystalline zeolites dispersed in an inorganic oxide matrix are typically prepared by spray drying an aqueous slurry of zeolite, clay and a suitable binder such as silica sol, alumina sol or silica-alumina hydrogel.

This work relates to the preparation of catalysts and matrix components, and in particular to the preparation of rare earth exchanged Y zeolite (REY) containing catalysts, which are highly active for the catalytic conversion of hydrocarbons.

The method for preparing zeolite and catalysts were transferred from Research Institute of Petroleum Processing (RIPP). Some test conditions in this work such as hydrothermal treatment and microactivity test were conducted according to RIPP standard.

Literature Review

Catalytic cracking which came of age as a major refining process in the 1940's was revitalized by the introduction of molecular sieves type catalyst. That resulted in a dramatic improvement in cracking activity and selectivity of the catalyst. The zeolite was found to have intrinsic activity for cracking far greater than the conventional silica-alumina cracking catalysts that were in use at the time of the introduction of the molecular sieve-type catalyst (Baltimore and C.H.E, 1976).

There are several patents describing processes for the preparation of zeolite. U.S. Pat. No. 3,390,958, for example, covers a method of preparing a faujasite type zeolite that is stabilized by action and thermal stabilization. European patent No.

0204236 of Edwards, covers process for preparation of Y type faujasite zeolite having

a smaller than conventional particle size, and the method described for preparation of

cracking catalysts. There are several other patents describing process for preparing the

Y type zeolite containing catalysts with different methods and compositions.

1. Cracking Catalyst

The introduction of the catalytic cracking process in the oil industry at 1920's

was discovered by Eugene Houndry. It was a determinant progress with respect to

prior techniques, by providing for highly improved yields of high-grade motor

gasoline. The various processes operating in fixed bed (e.g. HOUNDRY process)

have been rapidly supplanted by moving bed processes and particularly since the

middle of the 1940's by those of the fluid bed type (Nozemack, et. al. 1985).

The fluid bed (Fluid Catalytic Cracking, FCC) units are now used more

extensively than those of moving bed type. The catalyst circulates there though in a

fluidized state as particles of average diameter ranging from 50 to 70 microns,

granulometry of said powder ranging approximately from 20 to 100 microns.

The catalysts used in the first FCC units were solids of high silica content

obtain by acid treatment of natural clays, either of synthetic silica-aluminas. The main

progress in FCC achieved up to the end of the 1950's was, in particular:

The use of the spray drying technology for preparing catalysts in the form of

spherical particles more easily fluidizable and more resistant to attrition than

the powder obtained by crushing.

The synthesis of silica-aluminas, initially containing a high (about 55% by weight) silica and a low alumina (Lo-Al) proportion and then a high alumina (Hi-Al) content, with about 75% of SiO_2.

And various very substantial improvement concerning metallurgy and equipment design, particularly for regeneration (Houilles, 1991).

It is only at the beginning at 1960's that a major advance took place in the field of catalytic cracking the use of molecular sieves and more particularly of the zeolite of the faujasite structure, first in moving bed process, then, a little later, in FCC process. These zeolites, incorporated with a matrix mainly consisting of amorphous silica-alumina and optionally containing variable proportions of clay, have extended a very high activity for cracking of hydrocarbons. The availability on the market of these new zeolite catalysts has completely changed the cracking process by the very substantial gain of activity and of selectivity to gasoline and also by considerable modifications in the unit technology, particularly: cracking in the riser (tube wherein the catalyst and the charge flow upwardly, see Figure 1-1), decrease of the contact time; modification of the regeneration techniques.

The X zeolite characterized by SiO_2/Al_2O_3 molar ratio from 2 to 3 has been first used. Exchanged to large extent with rare-earth-ions, it is highly active and has a high thermal and hydrothermal stability.
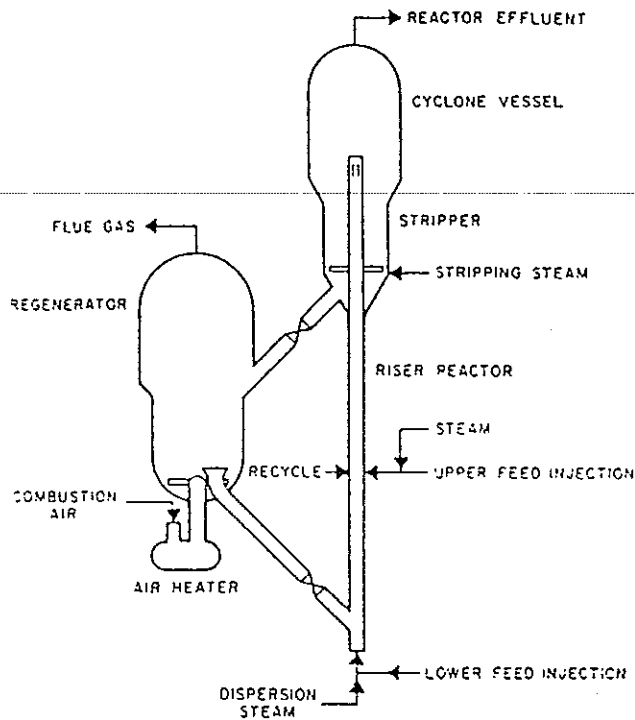
Figure 1-1 Simplified FCC unit diagram.

Source: Von Ballmoos, Harris and Magee, 1997: 1956

Towards the end of 1960's this zeolite has been progressively replaced by Y zeolite which tends to produce slightly less coke and this faujasite Y was exchanged the cations with rare earth and/or ammonium ions to form REY, REHY or HY whose thermal and hydrothermal stability was much improved.

In addition to the type of feedstock and operating conditions of unit, the octane rating of FCC gasoline is also affected by the type of catalyst used in the cracking process. In the mid-1970's, Mobil Oil developed octane-enhancing or octane boosting catalyst which prepared by dealumination of Y zeolite and called ultra-stable Y zeolite (USY) (Sadeghbeigi, 1995).

From the beginning of 1960's the oil industry began to suffer from a shortage of available crude oil, where as the demand for gasoline of high octane number was continuously increasing. Moreover, the available supply was progressively oriented towards heavier and heavier crude oil. The treatment of the latter raised difficult problems for the refiner in view of their high content of catalyst poisons, particularly nitrogenous compounds and metal compounds (mainly nickel and vanadium). In 1975, Phillips Petroleum developed antimony for nickel passivation.

The necessity to treat heavier charges and other more recent problems such as: the progressive but general elimination of lead-containing additives, the slow but substantial evolution in various countries of the demand for middle distillates (kerosene and gas oil), have induced the refiners to make searches for finding improved catalysts whereby the following objects can be met: to obtain thermally hydrothermally more stable catalysts, also more tolerant of metals; to reduce the amount of coke formation at equal conversion rate; to obtain gasoline of higher octane number; to improve the selectivity to middle distillates.

It is mostly desirable to reduce the production of light gas comprising compounds of 1-4 carbon atoms and accordingly the catalysts are so designed as to limit the production of such light gases. But in certain countries, particularly in certain developing countries, the demand for these products or for some of them, particularly propylene, may be high. The catalytic cracking process may meet to a certain extent such a demand, provided that the catalyst be particularly adapted to said production and the process was called "Deep Catalytic Cracking or DCC".

Table 1-1 Technological Progresses of FCC and Cracking Catalyst

Year	Type	Process (Equipment)	Catalyst
1936	Static	Houndry (Houndry Process Co./Socony Vacuum)	Natural activated clay, 1936
1942	FCC	Model I (Standard Oil Co., New Jersey)	Si-Al, tablet, 1942
1943	Moving	Thermofor Catalytic Cracking	Si-Al, bead, 1944
1944	FCC	Model II (Standar Oil Co., New Jersey)	Si-Al, powder, 1942
1947	FCC	Model III (ESSO)	Si-AL, microsphere, 1946
	FCC	Folded type unit (UOP)	
	Moving	Houndriflow (Houndry Process Co.)	
1950	Moving	Air lift (Socony Vacuum)	
1951	FCC	Orthoflow (Kellogg)	
1952	FCC	Model IV (ESSO)	Si-Al (Hi), microsphere, 1954
1953	FCC	Orthoflow B (Kellogg)	
1956	FCC	Riser-bed, 2-stage cracking (Shell)	Semi-synthetic Si-Al, microsphere, 1959
1960	FCC	Orthoflow C (Kellogg)	REX, bead, 1964
1961	FCC	HOC Process (Phillips)	REY, microsphere, 1966
1967	FCC	Dual-riser, Hi-Lo side-by-side (Texaco)	
1971	FCC	Full-riser, Hi-Lo side-by-side (Gulf)	
1972	FCC	High temp. full regeneration (Amoco)	High density, REY, microsphere, 1972
1974	FCC	High efficiency regeneration (UOP), with coke burning vessel	

Table 1-1 Technological Progresses of FCC and Cracking Catalyst (continuation)

Year	Type	Process (Equipment)	Catalyst
1976	FCC	Orthoflow F (Kellogg)	USY, microsphere,
1979	FCC	Ultracracking (Kellogg-Amoco)	1978
1981	FCC	RFCC (SW-Total)	
		R2R (IFP)	
		RCC (UOP-Ashland)	
1994	FCC	Resid Unit RFCC	
1995	FCC	RFG 1 Simple Model	
1997	FCC	RFG 2 Complex Model	

Source: Adapted from Shi-Ying, 1998: 8-2, Sadeghbeigi, 1995: 2, Magee and

Letzsch, 1994: 352

1.1 Catalyst Component (Grace Davidson, 1993)

FCC catalysts consist of a range of extremely small spherical particles and are usually available in fine, medium and coarse grades. These grades have average particle size (APS) of about 58, 64 and 72 microns.

Fluid cracking catalysts are comprised of a number of components, each of which is designed to enhance the overall performance of catalyst.

Components contained in most catalysts are zeolite, clay, matrix and binder. State-of-the-art catalysts are multicomponent materials. Each component improves one or more aspects of catalyst performance. Catalysts can have all components incorporated into a single particle or be comprised of blends of individual particle with different functions.
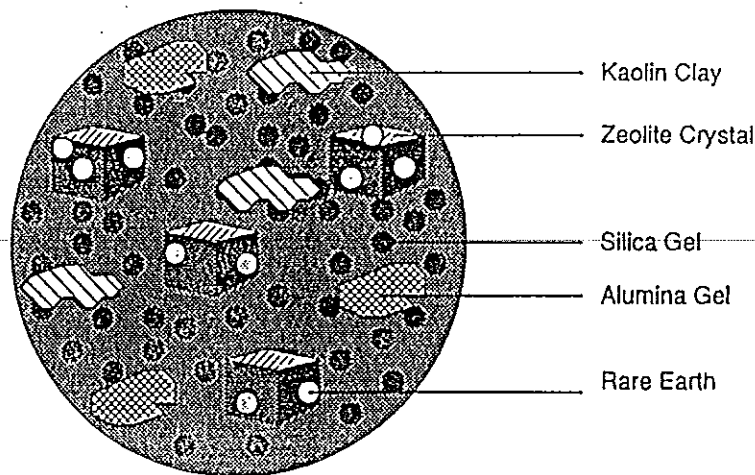
Figure 1-2 FCC Catalyst Particle

Source: Avidan (Eds.: Magee and Mitchell Jr.), 1993: 3

1.1.1 Zeolite

The primary source of activity of cracking catalyst is zeolite. Zeolite actually refers to a large mineral group of crystalline materials. Nevertheless, the word "zeolite" is commonly used to indicate the crystalline component added to fluid cracking catalyst to provide its activity and selectivity. Specifically, the zeolite used in cracking catalyst is faujasite. Faujasite is a crystalline three-dimensional aluminosilicate of the zeolite mineral group with ion exchange capacity has a pore opening of 8-9 Å.

To be technically correct, the crystalline component added to fluid cracking catalyst to provide activity and selectivity is called faujasite but faujasite is also commonly referred to as molecular sieve, zeolite or just plain sieve.

Another zeolite used in cracking catalyst, called ZSM-5, is discussed in the "Additive" section. Mobil Oil Corporation first added zeolite to catalysts in the

early 1960's. Zeolite was incorporated in bead catalysts used in several of their TCC units and proved to be very successful. In 1964 Mobil successfully tested a zeolite-containing fluid cracking catalyst in a commercial unit. Today all fluid cracking catalysts contain zeolites.

1.1.1.1 Zeolite Structure

Faujasite occurs naturally in nature but due to its scarcity it is synthesized in commercial facilities. Faujasite is manufactured in the sodium form (standard-Y) by crystallization of sodium aluminate and sodium silicate. Primary structure units of faujasite are tetrahedra, made up of one silicon and four oxygen atoms and one aluminum and four oxygen atoms. Tetrahedral from truncated octrahedra (sodalite) that unite by means of hexagonal prisms, forming faujasite.
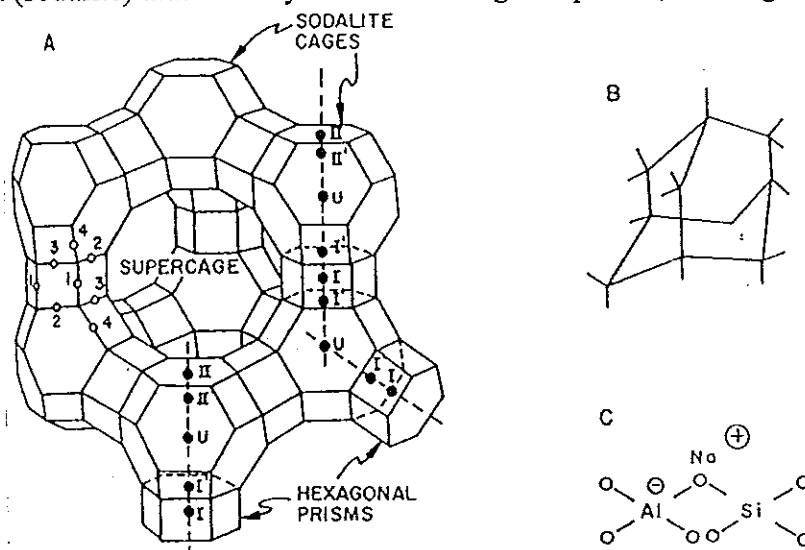
Figure 1-3 Representation of the zeolite Y (Faujasite), (A) framework showing oxygen types (o), possible cation locations (●), and secondary building units; (B) adamantanoid pore structure in faujasite; (C) basic unit of cation exchange/functionality.

Source: Venuto and Habib Jr., 1979: 34

Figure 1-3 represents the basic repeating unit of faujasite often referred to as the "unit cell" (UC). A truncated octahedron and hexagonal prism are indicated in the figure. The 8-9 Å opening into the unit cell is seen in the center of the structure. There are four such openings in each unit cell.

Junctures between sodalite and hexagonal prisms, surrounding the opening, are oxygen atoms at the vertices of either silica or alumina tetrahedral. Twelve oxygen atoms surround each opening.

1.1.1.2 Zeolite Chemistry (Sadeghbeigi, R., 1995)

As stated above, a typical zeolite consists of silicon and aluminum atoms that are tetrahedrally joined by four oxygen atoms. Silicon is in a +4 oxidation state, therefore, a tetrahedron containing silicon is neutral in charge. In contrast, aluminum is in a +3 oxidation state. This indicates that each tetrahedron containing aluminum has a net charge of −1, which must be balanced by a positive ion.
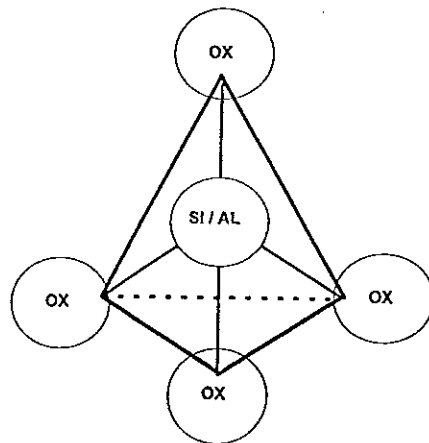
Figure 1-4 Silicon/aluminum-oxygen tetrahedron.

Source: Sadeghbeigi, 1995: 81

Solution containing sodium hydroxide is commonly used in synthesizing the zeolite. The sodium serves as the positive ion to balance the negative charge of aluminum tetrahedron. This zeolite is called soda Y or NaY. The NaY zeolite is not hydrothermally stable because of the high sodium content. Ammonium ion is frequently used to displace sodium. Upon drying the zeolite, ammonia is vaporized. The resulting acid sites are both the Brønsted and Lewis types. The Brønsted acid sites can be further exchanged with rare earth cation such as cerium and lanthanum to enhance their strengths.

The multi cations, e.g., the rare earth La^{3+}, can also be used to remove sodium ions generate acid sites. Commercially and aqueous mixture of rare earth salts, with lanthanum salts as the major component, is used to minimize costs (see Table 1-2 for the distribution of individual rare earth oxides as a function of source). Typically these ions are hydrated in aqueous solution and after calcination they partially dehydrate. This allows the cations to migrate throughout the zeolite framework, even into the smaller sodalite cages and hexagonal prisms, where they can exchange with the previously inaccessible Na ions. As the calcination temperature increases dehydroxylation occurs, generating protons and hydroxyl groups which are associated with the metal cations reducing their charge by +1 (e.g., $La(H_2O)_x^{3+} \rightarrow La(H_2O)_{x-1}(OH)^{2+} + H^+$). The protons are available for acid catalysis and other reactions. The hydroxy rare earth cations become "fixed", possibly through the framework oxygens, in the smaller cages and increase both thermal and hydrothermal stability of the zeolitic framework.

Although the generation of sites capable of donating protons gives rise to acidity, the overall acid properties of zeolite are influenced by many factors. The above discussion has focused on how Brønsted acidity is generated in zeolites. However, Brønsted acidity is not only type of acidity that can occurs in zeolites. Dehydration during zeolite calcination can cause two Brønsted acid sites to convert into a new type of acid site, an electron pair acceptor called a Lewis site (Fig 1-6).

Na⁺ ... Na⁺

O O O O O O O
Si Al⁻ Si Si Al⁻ Si
O O O O O O O O O O O

↓ NH₄⁺

NH₄⁺ ... NH₄⁺

O O O O O O O
Si Al⁻ Si Si Al⁻ Si
O O O O O O O O O O O

↓ −NH₃

H⁺ ... H⁺

O O O O O O O
Si Al⁻ Si Si Al⁻ Si
O O O O O O O O O O O

↓

H⁺ ... H⁺

O O O O O O O
Si Al⁻ Si Si Al⁻ Si
O O O O O O O O O O O
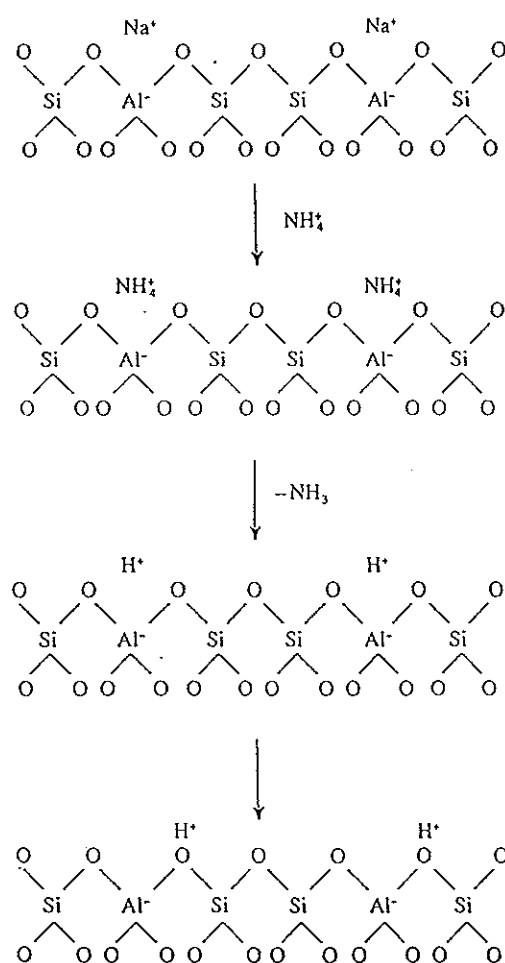
Figure 1-5 Formation of Brønsted sites in four-coordinate silica-alumina species.

Source: Humphries, Harris and O'Connor (Eds.: Magee and Mitchell), 1993: 46

$$\text{O} \quad \text{O} \quad \overset{H^{\bullet}}{\text{O}} \quad \text{O} \quad \overset{H^{\bullet}}{\text{O}} \quad \text{O}$$
$$\text{Si} \quad \text{Al}^{-} \quad \text{Si} \quad \text{Al}^{-} \quad \text{Si}$$
$$\text{O} \quad \text{O O} \quad \text{O O} \quad \text{O O} \quad \text{O O} \quad \text{O}$$

$$\downarrow \;\; -H_2O$$

$$\text{O} \quad \text{O} \qquad \text{O} \quad \text{O} \quad \text{O}$$
$$\text{Si} \quad \text{Al}^{-} \quad \text{Si}^{\bullet} \quad \text{Al} \quad \text{Si}$$
$$\text{O} \quad \text{O O} \quad \text{O O} \quad \text{O O} \quad \text{O O} \quad \text{O}$$
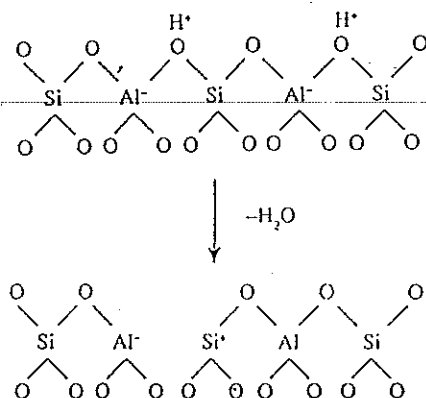
Figure 1-6 Formation of a Lewis acid site from dehydroxylation or two Brønsted

acid sites.

Source: Humphries, Harris and O'Connor (Eds.: Magee and Mitchell),

1993: 47

1.1.1.3 Zeolite Types (Sadeghbeigi, 1995; Grace Davison, 1993)

Zeolites employed in the manufacture of the FCC catalyst are

synthetic versions of naturally occurring zeolites called faujasites. There are about 40

known natural zeolites and over 150 zeolites which have been synthesized. Of this

number, only a few have found commercial applications. Table 1-2 shows properties

of major synthetic zeolites.

The zeolites with applications to FCC are Type X, Type Y, and

ZSM-5. Both X and Y zeolites have essentially the same crystalline structure. The

major difference is that the X zeolite has a lower silica/alumina ration than the Y

zeolite.

ZSM-5 is a versatile zeolite that some refiners add to the unit to increase olefin yields and octane of the FCC gasoline. Its application is further discussed in Section 1.1.4

Table 1-2 Properties of Major Synthetic Zeolites

Source: Sadeghbeigi, 1995: 82

Zeolite Type	Pore, Size Dimensions (Å)	Silica-to-Alumina Ratio	Processes
Zeolite A	4.1	2-5	detergent manufacturing
Faujasite (X, Y)	7.4	3-6	catalytic cracking and hydrocracking
ZSM-5	5.2 x 5.8	30-200	xylene isomerization, benzene alkylation, catalytic cracking, catalyst dewaxing and methanol conversion
Mordenite	6.7 x 7.0	10-12	Hydro-isomerization, dewaxing

Until the late 1970's, the NaY zeolite was mostly used because of a higher activity and better thermal and hydrothermal stability than X zeolite. Performance of Y zeolite is influenced by its method of manufacture and treatment. There are two basic zeolites used in cracking catalysts that have distinctive performances:

Standard – Y (REY, REHY, HY)

Ultrastable – Y (USY, REUSY)

Type	UCS (Å)	Wt% Na$_2$O
NaY	24.68	13.0
NH$_4$Y	24.73	2.5
REY	24.68	2.5
CREY	24.65	0.3
RENH$_4$Y	24.70	2.5
CREHY	24.54 - 24.60	0.3
HY	24.50	2.5
NH$_4$Y	24.53	0.3
USY	24.35	0.03
RENH$_4$Y	24.50 - 24.56	0.3

Sodalite Cage

Supercage

Unit Cell Size (UCS)

Has a Total of 4 Complete, 6 Half and 8 One-Eighth Cages. It Contains 192 Si and Al Atoms
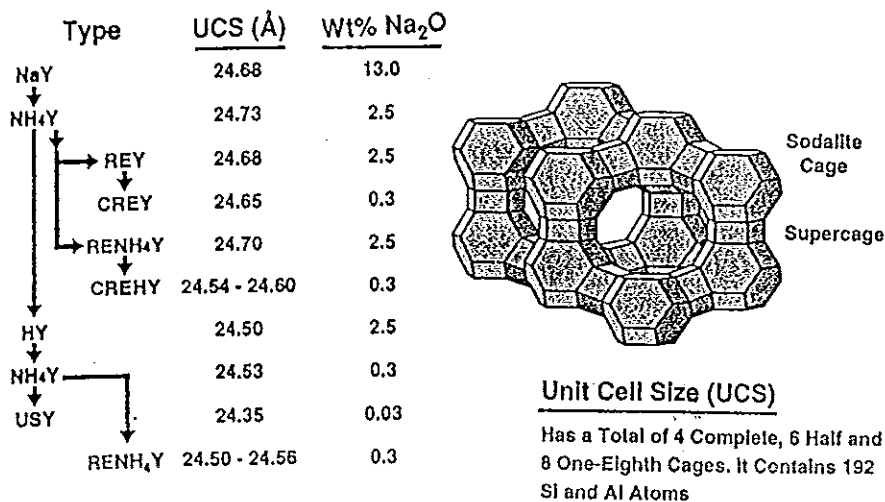
Figure 1-7 Y Zeolite derivatives

Source: Avidan (Eds.: Magee and Mitchell Jr.), 1993: 4

A. Rare Earth Exchanged Y Zeolite

The NaY zeolite is mostly ion exchanged with rare earth components. Rare earth components such as lanthanum and cerium were used to replace sodium in the structure. Principal sources of rare earth are monazite and bastnaesite sands, both of which give mixed rare earth chloride solution containing predominately cerium, lanthanum and neodymium. The actual breakdown of the oxides is given in Table 1-3.

Table 1-3 Distribution of Individual Rare Earth Oxide or a Function of Source

Source: Magee and Blazek (Ed.: Rabo), 1976: 621

Element/Source	Monazite (%)	Bastnaesite (%)
Cerium, Ce	46	50
Lanthanum, La	24	24
Neodymium, Nd	17	10
Praseodymium, Pr	6	4
Samarium, Sm	3	1
Gadolinium, Gd	2	0.5
Others	2	0.5

Table 1-4 Reactions in REY and REHY Zeolites

Source: Scherzer, 1989: 248

Thermal Treatment

a. Framework dehydration/dehydroxylation
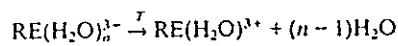
b. Cation dehydration $\quad RE(H_2O)_n^{3-} \xrightarrow{T} RE(H_2O)^{3+} + (n-1)H_2O$

c. Hydrolysis $\quad RE(H_2O)^{3+} \xrightarrow{T} REOH^{2+} + H^+$

d. Ionic migration $\quad [RE(OH)^{2+}]_{\alpha\text{-cage}} \xrightarrow{T} [RE(OH)^{2+}]_{\beta\text{-cage}}$

e. Oxidation of Ce $\quad 2Ce(OH)^{2+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2Ce(OH)^{3+} + H_2O$

f. Hydroxy complex formation $\quad 2RE(OH)^{2+} \xrightarrow{T} [RE\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{O}{\underset{O}{<\,>}}}}RE]^{4+}$
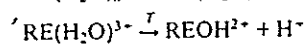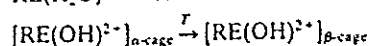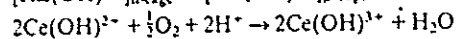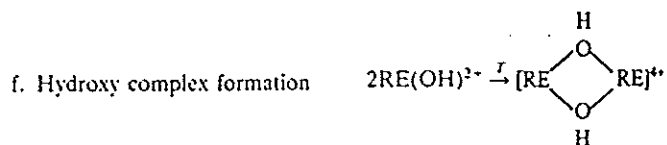
Hydrothermal Treatment

a. Hydrolysis
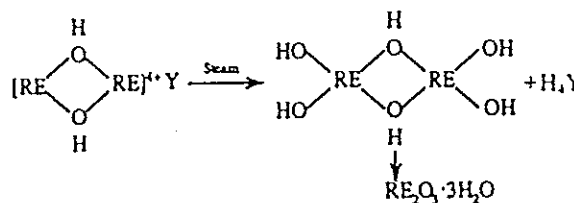
b. Dealumination
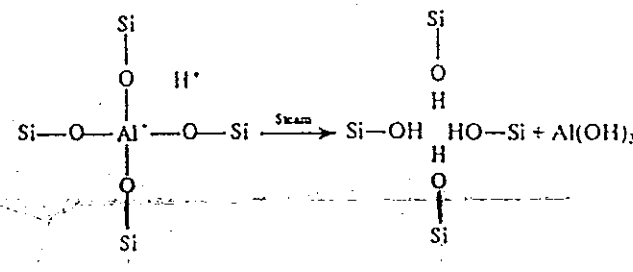
Rare Earth exchange uncrosses the activity of the zeolite and retards crystal destruction and dealumination in the steam-calcining environment of regenerator. The reactions that take place in REY and REHY zeolite upon thermal and hydrothermal treatment are summarized in Table 1-4.

Thermal treatment of REY and REHY results in the formation of additional acid sites, due to the hydrolysis of partially hydrated rare earth ions (Scherzer, 1989). REY and REHY calcined at 480°C has only Brønsted acidity, while calcination at higher temperatures results in a decrease in Brønsted acidity (dehydroxylation) and the formation of Lewis acidity. Hydrothermal treatment results in partial hydrolysis of the rare earth zeolite bond and in partial framework dealumination, with corresponding decrease in total acidity and unit cell size (UCS). The higher degree of rare earth exchange of zeolite, the higher the UCS of the equilibrated zeolite in the equilibrium catalyst. While fresh REY and REHY has a UCS in the range of 24.60 to 24.65 Å (depending upon Si/Al ratio and rare earth content), in equilibrium catalysts the UCS of the zeolite is usually in the range of 24.50 to 24.55 Å.

Figure 1-8 is a comparison of the equilibrium unit cells of a REY and a USY zeolite.

Equilibrium USY
7 Al Atoms / UC
UCS = 24.25 Å
SiO_2/Al_2O_3 = 54

Equilibrium REY
23 Al Atoms / UC
UCS = 24.39 Å
SiO_2/Al_2O_3 = 15
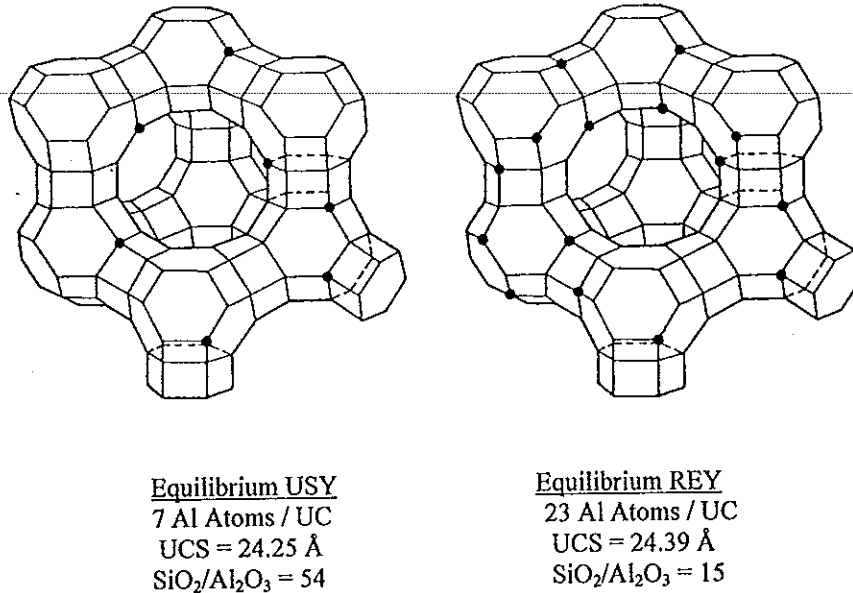
Figure 1-8 Equilibrium Representations of REY and USY Zeolites.

Source: Grace Davison, 1993: 120

B. Dealuminated Y-Zeolite

NaY is produced by crystallization of sodium aluminate and sodium silicate. It can serve as a raw material for catalyst after washing or it can be converted to USY.

USY is by for the most widely used zeolite in fluid cracking catalysts. USY is made by special manufacturing techniques that increase the silicon/aluminum atomic ratio of the parent standard Y zeolite structure, a process called dealumination. Zeolite dealumination is achieved by steam calcination or chemical treatment.

Table 1-5 Preparation of Dealuminated Y Zeolites

Source: Scherzer, 1989: 233

I. Hydrothermal treatment of NH₄Y zeolites (formation of Ultrastable Y zeolites)

I. Hydrothermal treatment of NH$_4$Y zeolites (formation of Ultrastable Y zeolites)

II. Chemical treatment
   A. Dealumination with silicon enrichment
      1. Reaction with (NH$_4$)$_2$SiF$_6$ in solution
      2. Reaction with SiCl$_4$ vapors
   B. Dealumination without silicon enrichment
      1. Reaction with chelating agents (e.g., EDTA)
      2. Reaction with F$_2$ gas
      3. Reaction with volatile, nonsiliceous halide (e.g., COCl$_2$, BCl$_3$)

III. Hydrothermal and chemical treatment. Reaction of Ultrastable Y zeolite with:
   A. Acid (e.g., HCl, HNO$_3$)
   B. Base (e.g., NaOH)
   C. Salts (e.g., KF)
   D. Chelating agents (e.g., EDTA)
   E. Volatile halides (e.g., COCl$_2$)

The dealumination process extracts aluminum from the framework and heals the site with silicon, without collapsing the framework structure. The resulting USY zeolite is more resistant to deactivation in the FCC unit (more stable) than its parent stand-Y for two basic reason:

(1) its lower framework aluminum content reduces the thermodynamic driving force for expelling additional aluminum and collapsing the structure at FCC regenerator conditions and

(2) its sodium levels is generally lower due to additional processing.

Hydrothermal pretreatment to stabilize the zeolite has advantages over chemical treatments. During hydrothermal manufacture, pores 30 to

60 Å, called mesopores, are formed in the zeolite. Such pores are not found in chemically dealuminated USY. These pores, or channels, are created when a small portion of the aluminum is not replaced by silicon during hydrothermal dealumination.
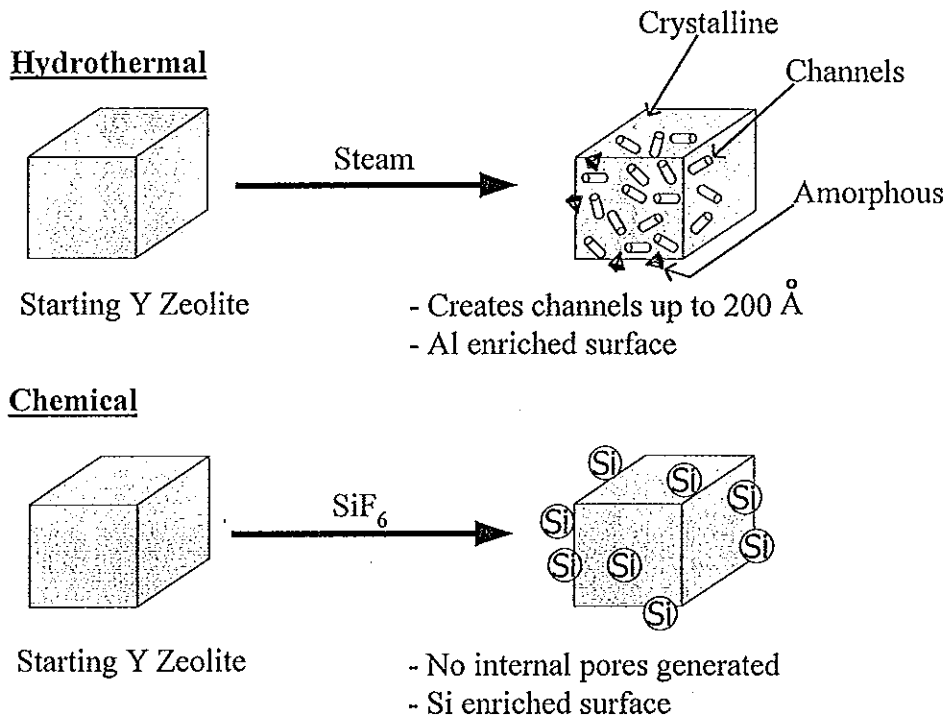
Figure 1-9 Zeolite dealumination.

Source: Adapted from Grace Davison, 1993: 118

Figure 1-9 shows a schematic of the process. The increased porosity enhances diffusion within the zeolite. USY zeolite have significantly fewer exchange sites, since the number of exchange sites in the zeolite is equivalent to the number of framework aluminum atom. Therefore a partially rare earth exchanged can be done to form REUSY zeolite. Further more, the number of Brønsted acid sites in

USY zeolites is also smaller than in conventional REY zeolites. Such differences in

acidity have impact on the catalytic activity and selectivity of USY zeolites.

Table1-6 Cracking selectivity of different Y zeolites and of active matrix.

Source: Scherzer (Eds.: Magee and Mitchell Jr.), 1993: 162

	USY	REUSY	REHY	REY	
Unit cell size	← decrease →				Matrix
Framework Si/Al	← increase →				Activity
RE content	← decrease →				
Dry yield	Low	Low	Low	Low	High
C3/C4 yield	High	Moder.	Moder.	Low	High
C3/C4 olefins	High	Moder.	Moder.	Low	High
Coke/conversion	V. Low	V. Low	Low	Moder.	High
Gasoline selectivity	Moder.	High	High	High	Low
Octane potential	High	Moder.	Low	Low	High
LCO selectivity	Moder.	Moder.	Low	Low	High
DO selectivity	Moder.	Moder.	High	High	Low

1.1.2 Filler and Binder

1.1.2.1 Filler

The filler is clay incorporated into the catalyst to dilute its

activity. Clay is an important component that fulfills the remaining catalyst particle

performance requirements (density, attrition resistance, particle size distribution, etc.).

Clay serves as a heat sink and transfer medium. It can also serve as a sink of sodium,

improving the catalyst's resistance to sodium poisoning. Clay provides a little or no

activity to catalyst, but it does provide mechanical strength and density to the particle

for optimum fluidization properties (Grace Davison, 1993).

In all known FCC catalysts, the clay of choice is kaolin [Al_2

$(OH)_2 Si_2O_5$]. Its ability to form high solid pumpable slurries, low surface area, and

ease of packing a result of its platelet structure make kaolin particularly suitable. Most manufacturers purchase the kaolin as a 60-65 wt% slurry (usually dispersed with sodium silicate or tetrasodiumpyrophosphate) and use it without further processing.

Some parameters of the kaolin are critical for FCC manufacturing. Specifically, the kaolin particle size must be small to ensure that the resulting FCC catalyst processes good apparent bulk density (ABD) and attrition resistance. Average particle size (by sedigraph) of 0.3 to 0.4 micron with a 90% point of approximately 1 micron are normal for FCC use. The iron and titania content of the clay can also be important. High iron or titania levels can lead to undesirable secondary reactions, such as gas and coke formation and increased CO combustion in the regenerator, when such clays are used in the manufacture of cracking catalysts. Titania levels below 3.0 wt% and an iron content of 0.4 to 0.8 wt% are considered acceptable. Because of environmental concerns, the crystalline silica content of the clay has also become an important parameter (Woltermann, Magee and Griffith, 1993).

1.2.2.2 Binder

Binder is "glue" that holds all catalyst components together. Zeolite clay and matrix must be held together. Binder may or may not have catalytic activity (Sadeghbeigi, R., 1995). The binder was synthetic silica-alumina or alumina, usually peptized pseudoboehmite. These binders were active themselves, although with different selectivity in the catalytic cracking of oil molecules. At present, four binder systems are used in the commercial production of FCC catalyst, an

extraordinary number have been examined in laboratory preparations. Table 1-7 shows the four binder types and their main characteristics.

Table 1-7 Commercial FCC Binders

Source: Woltermann, Magee and Griffith (Eds.: Magee and Mitchell Jr.), 1993: 117

Type	Surface	Activity
Silica Sol	20 m²/g	Very low
Aluminum Chlorhydrol (ACH)	60-80 m²/g	Moderate
Peptized Alumina	300 m²/g	High
Self-Binding (In situ)	-	High

A. Silica Sol

The acidified silica sol binder was introduced commercially in the mid-1970's. The binder was attractive for its low activity, ease of manufacture, and dispersibility. The sol is produced by intimate mixture of sodium silicate and acidified aluminum sulfate solution (Ostermaier and Elliot, 1976). A clear, low viscosity silica sol results. Because silicate gels rapidly in the pH range from 11.0 to 3.5, the silicate and acid-alum must be mixed rapidly to prevent local pH excursions and micro gelatin of the sol. Thus extremely effective local mixing is required.

Furthermore, gel time is also strongly affected by reactant concentrations and solution temperature. Consequently, the sols are made at relatively low silica solids (10 wt%) and cooling of the components is required. Mediocre

mixing, elevated temperatures (> 100°F), or high silicate concentrations cause the formation of turbid sol or gel particles with poor binding characteristics. Once formed, the sol is in a metastable state. Particle growth is dependent on temperature, pH, and silica concentration. Even sol formed under conditions known to impart good binding can form microgel within one hour of synthesis and form a clear silica gel within several hours at a pH equal to 2.5 to 2.7. Although producing the sol from the interaction of silicate with sulfuric acid is possible, the sol product is unstable with respect to changes in pH and rapidly gel when mixed other FCC catalyst components. The presence of aluminum (Al^{3+}) offers some buffering capacity to the sol and prevent rapid gelation of the spray dryer feed slurry. When the sol is mixed with the other components, it rapidly disperses throughout the slurry. When spray dried, the sol rapidly gels, binding the components together.

Several patents described the process for preparing silica sol with different techniques. For example:

Elliott has prepared silica sol by adding a strong mineral acid to sodium silicate and adjusted the pH of the sol to form gel (Elliott Jr., 1975).

Hoffman described the process for preparing a silica sol by passing sodium silicate through an ion exchange resin column to form a silica sol containing about 5% silica (Hoffman et al., 1976).

B. Aluminum Chlorhydrol

The aluminum chlorhydrol (ACH) binder was introduced commercially in the late 1970's. The binder is a hydroxylated aluminum based sol containing chloride as the counter ion. Aluminum Chlorhydrol can be produced by reacting aluminum metal with hydrochloric acid to get clear solution at pH 3.0 to 4.0. The aluminum-chloride ratio can be varied and determines the amount of various molecular weight alumina oligomers in the sol. Likewise, the material can be produced by the slow hydrolysis of $AlCl_3$ solution with base. Addition rate of the base to the $AlCl_3$ solution is critical as is mixing to prevent the formation of $Al(OH)_3$ gel.

Unlike silica sol, the solution structure of ACH is not particularly sensitive to time or temperature but is sensitive to pH. Because of its high chloride content (12%), ACH is also considerably more corrosive, especially at elevated temperature, to stainless steel catalyst preparation equipment than is silica sol. The ACH remains stable indefinitely at constant pH and can be refluxed without gelling and without any other noticeable change in sol properties.

C. Peptized Alumina

Another commonly used alumina based binder is prepared by peptizing pseudoboehmite alumina (PBA), usually with formic acid. The action of the acid on the reactive alumina produces an alumina sol with particle size in the range of several hundred nanometers. The opaque, milky-white color of the sol testifies to its significantly larger particle size compared with silica sol or ACH. Other monobasic acids such as HCl and HNO_3 can also be used to peptize the alumina but formic seems to be the commercial choice, because of fewer problems in terms of

stack emissions or corrosion. Pseudoboehmite alumina cannot be peptized with di- or tri-basic acids, such as sulfuric acid. After acidification, the peptized alumina is mixed with the other FCC components and spray dried. Like ACH, the spray dried microspheres have little green strength and cannot be slurried in water without significant damage. The sol itself is somewhat unstable with respect to pH, time and temperature. Depending on alumina concentration and pH, the sol will gel within ten minutes to several hours. Unlike silica sol, the gel particles seem to be only weakly bound, and whether gelation affects the binding properties of the sol is unclear.

Pseudoboehmite possesses surface areas of more than 300 m^2/g and undergoes a phase change to gamma alumina at FCC unit regenerator temperatures. The acidity of gamma alumina is well documented. Hence, this binder is active for gas oil cracking and serves a dual purpose as an active bottoms cracking component and binder. Bottoms are large high molecular weight components in the FCC feed. Usually their size makes them too large for diffusion into the zeolite pore (diameter = 7.4 Å).

D. In Situ Binding

The in situ type of FCC catalyst preparation introduced by Engelhard contains no added binder (Haden et al., 1972). The first preparative step calls for forming kaolin microspheres. However, clay-to-clay particle binding after spray drying is quite weak, and the particles cannot be slurried in water without complete breakdown. After high temperature calcination (approximately 1800°F) the particles develop significant attrition resistance and maintain their microspherical shape during the second step of the in situ crystallization process in caustic solution at

180°F.

The crystallization step imparts even more hardness to the microsphere and forms intrastructural NaY. Hydroxyl on the surface of the clay platelets react with one another at high temperature to eliminate water and from oxygen-bridged bonds between the particles.

During crystallization, significant silica is removed from the particle to leave micropores which are filled by the intrastructural zeolite particle growth. Significant porosity in the 30 to 100 Å range results. The remaining matrix is higher in alumina than the starting kaolin because of the silica removal and possesses significant acidity. The combination of acidity and high surface area make this material an active matrix for bottom cracking. The large matrix surface area and exposure of contaminant metal present in the clay can lead to high coke and gas make. Retaining some of the silica reduces some of this undesirable matrix activity by reducing overall surface area. Recent technology using combinations of metakaolin and seed technology seems to reduce the porosity and surface area to an even greater extent.

1.1.3 Matrix (von Ballmoos, Harris and Magee, 1997)

Generally speaking, the portion of cracking catalyst which is not the primary active component (invariable type-Y zeolite one of its hydrothermally altered low U.C.S. modifications) may be referred to as matrix. The component parts of the matrix may by categorized as follows:

- A catalytically active portion containing larger pores than the primary zeolite active component. This large pore system, while substantially

less active than zeolite portion, function to partially crack molecules which are larger than the zeolite entry pores. Catalytic activity of the matrix may also be directed at mitigating the deleterious effects of nickel, vanadium, iron and sodium which are present in the gas oil feed to greater or lesser extents;

- A binder which also may be catalytically active but functions primarily to bind the components of the catalyst into an attrition resistant 60-micrometer microspheres; and

- A kaolinite filler which functions to densify the microsphere and introduces a large-pore macrosystem which is believed to facilitate access of large alphaltene composites (2-5 nm and larger) to active portions of the matrix or active sites associated with the exterior structure of the zeolite component.

Catalytically Active Matrix Component

Control of matrix activity in catalyst systems is accomplished by regulating the amount of a specific matrix active component (such as alumina phases which transform into either high surface area gamma or etc. alumina at high temperature) to achieve a desired level of matrix surface are in the finished catalyst. Since at least 50% of all gaseous feed molecules are larger than the 0.74 nm opening of the principle active component of the catalyst (type-Y molecular sieve) it is essential to have a catalytically active matrix component with a relatively large pore diameter. Furthermore, since some asphaltenes in heavy feedstock can reach 2-5 nm in size, the presence of a large pore active matrix becomes critical. Diffusional data of

large molecules suggests that several pore size ranges in active matrix should be present a microporous range from < 2.0 to 5.0 nm, a mesoporous range from 5.0 to 15.0 nm and a macroporous range above 15.0 nm to perhaps 500 to 1000 nm. Various residual feed cracking processes are said to profit from this type matrix porosity. Basically, the object of matrix cracking activity is to provide some initial molecular weight reduction in molecules too large to access the 0.74 nm type-Y pores so that the resulting molecular fragments will then fit and be selectively cracked to desirable products. Table 1-8 shows the different in activities and selectivitites of cracking products from catalyst containing active and inactive matrix.

Table 1-8 Effect of Matrix Activity on Product Selectivity (MAT data)

Source: Scherzer, 1989: 310

	REY zeolite in amorphous active matrix	REY zeolite in low-SA inactive matrix
SA matrix, m^2/g	130.0	30.0
Conversion, wt%	65.0	65.0
C_3, wt%	1.4	1.3
$C_3^=$, wt%	3.2	2.8
C_4, wt%	6.0	5.7
$C_4^=$, wt%	3.5	2.9
$C_3^=$/tot. C_3	0.70	0.68
$C_4^=$/tot. C_3	0.37	0.34
Gasoline, wt%	43.5	46.5
Coke, wt%	6.2	4.5

In addition, matrix components can also provide metals tolerance to sodium, nickel and vanadium, as well as density control of the composite catalyst and

increased stability to steam deactivation during use. There is evidence that separate catalyst particles containing active matrix ingredients will perform many of the functions of active matrix materials added to the original catalyst formulation. "Additives" are further discussed in Section 1.1.4.

1.1.4 Additives (Scherzer, 1993; Sadeghbeigi, 1995)

FCC additives with a cracking or non-cracking function can be incorporated into the catalyst by the manufactures, or can be added separately by the refiner. The main benefits to these additives (catalyst and feed additives) are to alter the FCC yields and to reduce the amount of pollutants emitted from the regenerator. The additives most frequently used in FCC catalysis are: Octane-boosting additives; SO_x reducing additives; Metal passivators and traps; and CO combustion promoters.

1.1.4.1 Octane boosting Addition

The most frequently used additive consists of ZSM-5 zeolite embedded in a matrix, and is commonly used as a distinct physical particle in conjunction with a FCC catalyst. ZSM-5 is a member of the pentasil family of high-silica zeolites and has relatively small pore opening (5.1 to 5.6 Å). In addition, the pore arrangement of ZSM-5 is different than Y-zeolite as shown in Figure 1-10. The shape selectivity of ZSM-5 allows preferential cracking of long-chain, low-octane normal paraffins as well as some olefins in the gasoline fraction. This results in the enrichment of gasoline in higher-octane branched paraffin, olefins and aromatics.

In addition to cracking gasoline range low-octane components, steamed or equilibrated ZSM-5 also favors, the isomerization of cracking products, such as n-olefins to higher-octane branched olefins. The additive represents only

small percentage (usually 1 to 3 percent) of catalyst inventory in the unit and increases both RON and MON at low concentrations.
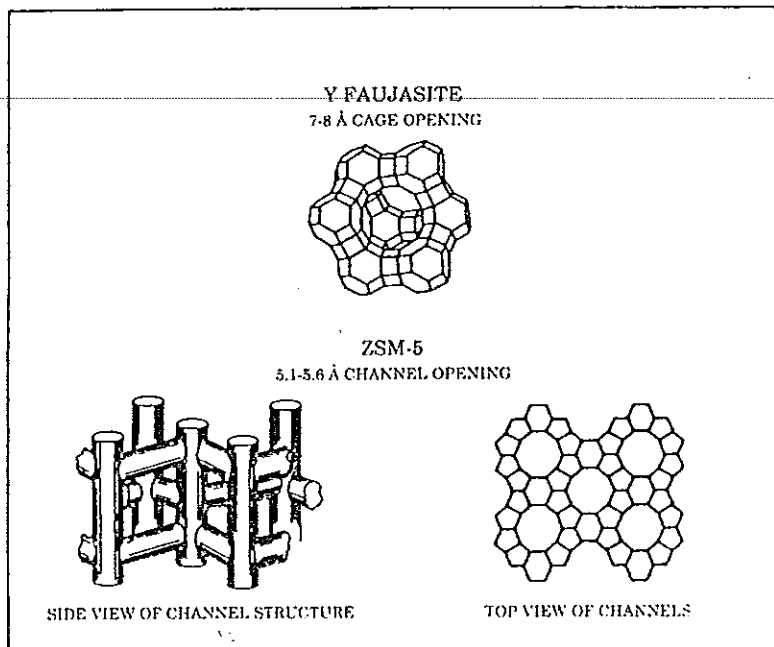
Figure 1-10 Comparison of Y faujasite and ZSM-5 zeolite.
Source: Sadeghbeigi, 1995: 117

1.1.4.2 SO$_x$ Reducing Additives

Such additives are used in conjunction with FCC catalysts when cracking high sulfur feedstocks, in order to reduce SO$_x$ emissions from the regenerator below acceptable limits. The additives are mostly inorganic oxide (e.g. Al$_2$O$_3$, MgO) or mixed oxides (e.g. spinels, rare earth oxide mixtures, vanadia-alumina, ceria-promoted spinels). The additive promotes the oxidation of SO$_2$ to SO$_3$ in the regenerator, followed by the formation of metal sulfates type compounds on the additive. In the reactor (and stripper) the metal sulfates are reduced to hydrogen sulfide, which leaves the FCC unit with the cracked products and is subsequently

removed with an amine scrubber. The additive represents usually a few percent of catalyst inventory and is often added by the refiner shortly before catalyst utilization.

1.1.4.3 Metal Passivators and Metal Traps

These additives are used primary in resid and are designed to minimize the deleterious effect on catalyst and its performance by the heavy metals present in the feedstock, such as nickel, vanadium, iron and copper. In the absence of such additives, nickel deposited on the catalyst causes partial destruction of the zeolite under steam, in addition to increasing coke and hydrogen make. Nickel is often passivated with antimony or bismuth containing additives, while vanadium is passivated with tin compounds. Metal traps are usually physically distinct particles that trap the contaminant metal. Numerous metal oxides (e.g. Al_2O_3, TiO_2) mixed oxides (e.g. $BaTiO_3$, $CaZrO_3$) and natural clays (e.g. metakaolin, sepiolite) have been recommended as metal traps. These materials are usually mixed with binder and spray dried. The resulting microspheroidal particles are blended with the catalyst.

1.1.4.4 CO Combustion Promoters

To facilitate the oxidation of CO to CO_2 in the dense phase of the regenerator, platinum-or palladium-based combustion promoters are being used. Maximizing CO oxidation in the dense phase of the regenerator prevents uncontrolled CO oxidation (after burning) in the dilute phase, which can cause metallurgical damage to the equipment. Furthermore, the heat generated during maximized CO oxidation also minimizes flue gas CO emissions.

2. Cracking Catalyst Types

Catalyst produced may be conveniently divided as a function of their primary cracking purpose – gasoline production, octane enhancement, olefin production or resid (heavy feed) cracking. A summary of the types of cracking catalysts in use or projected in the near future along with their most important catalytic control features is given in Table 1-9. (Representative commercial grades are shown in Table 1-10, divided according to their primary commercial application. A "complete" listing would be misleading since new catalyst grades are added frequently in this very dynamic branch of industrial catalysis.)

Table 1-9 Types of Cracking Catalysts in Present and Future

Source: von Ballmoos, Harris and Magee, 1997: 1971

Chief catalyst use/function	High gasoline yield	Resid conversion high metals, N or S	High octane gasoline, high light olefine yields, reformulated gasoline
Primary Zeolite UCS, Å SiO₂/Al₂O₃ Shape Selectivity Function	High U.C.S. 24.62-24.68 4.65-5.5 Possibility large-pore molecular sieve or PILC	Moderate to low U.C.S. 24.58-24.62 5.5-6.1 Possibility large-pore molecular sieve or PILC	Low U.C.S. 24.50-24.58 6.1-9.0 Small-pore molecular sieve
Matrix	Active matrix	Low to moderate	Active matrix

The three primary controls of catalyst activity and selectivity as summarized in Table 1-9 are the zeolite unit cell size (or SiO_2/Al_2O_3 ratio), the degree of cracking activity of the catalyst matrix and the presence or absence of a shape selective large or small pore molecular sieve.

Table 1-10 Commercially Available Cracking Catalysts

Source: von Ballmoos, Harris and Magee, 1997: 1971

Function	Supplier	Grade no./name
Octane and/or light olefin production	Akzo Chemicals, Inc.	Octavision-500, 600 series
	Catalysts & Chemicals Industries Co., Ltd.	Octaboost-600 series
	Engelhard Corporation	Harmorex 1240–1270 OctiDyne 1140–1170 Precision 50–70 Dimension 50–70 Millennium™
	Grace Davison	Prime 40–70 Astra series, 　Resoc-1, G Octacat-D, 　Orion series
Resid cracking, metals tolerance, bottoms cracking	Akzo Chemicals, Inc. Catalysts & Chemicals Industries Co., Ltd. Engelhard Corporation	Access, Horizon, MR HYLIC-30, 40, 50 Harmorex 2440–2470 Ultradyne Plus Dimension II 50–70 Vektor 40–70
	Grace Davison	Spectra 500–700 Orion series XP series
High gasoline yields	Akzo Chemicals, Inc. Catalyst & Chemicals Industries Co., Ltd.	Advance HYLIC 30–50
	Engelhard Corporation Grace Davison	Ultradyne 940–980 Dynasiv 740–770 Vektor 40–70 DA-250, 400 GXO-40, 41

3. FCC Catalyst Manufacture (von Ballmoos, Harris and Magee, 1997)

Two basically different methods of commercially preparing FCC catalysts are in use today: an in situ method and an incorporation method. In situ methods involve the formation of zeolite Y on (and in) a preformed predominately clay microspheres. The catalyst is basically self-binding. Incorporation methods differ fundamentally, in that the components of the catalyst zeolite, clay, matrix and binder are intimately

mixed prior to spray drying the entire composite. A summary of the preparation schemes used by the current manufacturers is given in Figure 1-11.

3.1 In Situ Catalyst Preparation-A Typical Example

(1) In situ mullite microspheres are formed by first spray drying a kaolin/water slurry followed by calcination of the micropheres.

(2) Caustic treatment of the microspheres at 38°C for six to twelve hours is followed by crystallization at 82°C for twelve to fourteen hours to form 25 to 30 wt% NaY throughout the microsphere. Added meta-kaolin micropheres allow the zeolitization to reach 60 wt%.

(3) The zeolite-containing microspheres are base exchanged to reduce Na^+ (exchanging NH_4^+ or rare earth ion (RE^{3+}) for the Na^+).

(4) Final drying or alternately calcination (to reduce zeolite U.C.S. as, for example, in octane catalyst production) with or without further base exchange steps completes the process.

Many variations in fluid catalyst properties are possible depending on crystallization time and ratio of meta-kaolin to incipient mullite as well as the extent of retention of distillate mother liquor following crystallization.

3.2 Incorporation Catalyst Preparation-A Typical Example

All components of incorporation catalyst (zeolite, matrix and binder) are prepared in plant or purchased from outside suppliers for use in the process. A typical incorporation process can be summarized as follows.

3.2.1 Component Preparation

3.2.1.1 Zeolite Preparation

NaY zeolite is prepared by reacting a mixture of sodium silicate, aluminum sulfate, sodium aluminate and initiator (seeds) at temperatures between 92°C and 103°C for approximately twelve to sixteen hours followed by rapid quenching of the mixture to below 65°C to prevent the formation of zeolite P. The sodium Y (NaY) crystalline solid is separated from the crystallizer batch by filtration and washed with water to remove occluded mother liquor. Several procedural paths can then be followed.

(a) Post-rare earth exchange: The NaY can be used directly in the catalyst makeup to be Na^+ exchanged at some later point in the catalyst manufacture. At this stage the U.C.S. of the NaY is typically ~24.65 Å, which corresponds to a framework SiO_2/Al_2O_3 ratio of approximately 4.9/1.

(b) Pre-rare earth exchange: The NaY can be rare earth exchanged and/or calcined and further exchanged to form a low soda content rare earth exchanged to form a low soda content rare earth exchanged Y (REY or CREY, if calcined). Rare earth versions of Y are typically used in gasoline and resid catalyst formulations (see Table 1-9). At this stage the U.C.S. of the REY is approximately 24.62 Å which would correspond to a NaY with SiO_2/Al_2O_3 of 5.5.

(c) Ultrastabilization: The NaY can be ammonium exchanged, calcined and further ammonium exchanged, to form a low Na_2O content, ultrastable Y (USY) with a U.C.S. of approximately 24.50-24.55 Å, which corresponds to a NaY with a SiO_2/Al_2O_3 ratio of 6.5-7.5.

3.2.1.2 Binder Formation

Three different binders are routinely used in the processes outlined in Fig. 1-11 peptized alumina sols, aluminum chlorhydrol (ACH) sol/solution, and aluminum stabilized silica sol. When Al_2O_3 sol or ACH are used as binder, the catalyst components are generally washed or exchanged to low Na^+ level prior to spray drying the mixed components. In the case of peptized Al_2O_3 bound catalysts, spray drying is the last process step. ACH bound catalysts are calcified directly following spray drying, which both hardens and densities the microspheres and also is generally the last process step. With aluminum stabilized silica sols, the spray dried product (SDP) has achieved its maximum hardness. Subsequent washing/base exchange is thus performed on the SDP.

3.2.1.3 Matrix Active Component

Peptized alumina bound catalysts need no further matrix active component as the binder itself functions as both. ACH acts to some extent as both binder and matrix active component but is insufficient where high matrix activity is desired. Therefore, with both ACH bound and aluminum stabilized silica sol bound catalysts, it is necessary that an additional component, generally some active Al_2O_3 or SiO_2/Al_2O_3 form, be added to enhance the matrix activity of the formulation.

3.2.1.4 Kaolin Addition

Kaolin, generally added as an aqueous dispersion, is used primarily to increase microsphere density and introduce some macroporosity (pores > 500 nm diameter) in the microspheres, although the necessity of this latter function is debatable, Kaolinite particle size is controlled carefully (< 2 μm diameter is desirable) since larger sizes decrease catalyst attrition resistance.

3.1.2.5 Miscellaneous Functional Additive Addition

Virtually all the materials described previously as "Additives" (Section 1.1.4) have been successfully used as catalyst matrix component-shape-selective ZSM-5, SO_x emission control, CO oxidation and bottoms cracking components. The latter are basically the cracking components. The latter are basically the matrix components described in Section 3.1.2.3. An important advantage of the incorporation method of manufacturing FCC catalysts compared to the in situ method is the flexibility afforded by the former which allows the incorporation of many diverse components in the final catalyst formulation.

3.2.2 Wet End Mixing and Spray Drying.

Catalyst components as described in Section 3.2.1 in incorporation processes are generally pumped at carefully controlled rates and carefully controlled solids contents (wt. of component/gallon of slurry) into an inline vessel under high intensity mixing conditions. Generally, residence time in this vessel is minimized because the binders present in the mixed components of the wet end are then spray dried in mixed flow or parallel flow spray dryers to form porous microspheres of approximately 60 micron diameter.

3.2.3 Base Exchange of Spray – Dried Product

Under exchange has been performed prior to spray drying (as with ACH or peptized alumina bound catalysts) the spray dried product is exchanged. Typically, ammonium ion or mixed rare earth (primarily lanthanum, cerium, praseodymium and neodymium) solutions are used.

Catalytically, the net effect or rare earth exchange is to stabilize the zeolite unit cell, retarding dealumination and subsequent decrease in both U.C.S. and the number of active sites/unit cell. Extensive ammonium ion exchange is used only when the catalyst system will be converted to a USY version or further rare earth exchanged since fully ammonium exchanged Y, if converted to "HY" is unstable.

3.2.4 Final Drying

Exchanged filter cakes are generally fed to rotary dryers operated at 150°C to 230°C. Dried finished catalyst product contains eight to twelve wt% moisture (H_2O) and is stored for shipment to the refinery in pressurized railcars or trucks.

In Situ	Silica Binder	ACH Binder	Pept. Al₂O₃
Clay Slurry	NaY Crystal	NaY Crystal	NaY Crystal
∇	∇	∇	∇
Spray Dry	NH₄⁺ Exchange (?)	NH₄⁺ Exchange	NH₄⁺ Exchange
∇	Dealumination (?)	Dealumination (?)	Dealumination (?)
Calcine	∇	∇	∇
(~980°C)	Mix Binder, Clay	NH₄⁺/RE⁺³ (?)	NH₄⁺/RE⁺³ (?)
∇	Al₂O₃, Zeolite	Exchange/Wash	Exchange/Wash
Caustic Treat	∇	∇	∇
(40°C/6 Hrs	Spray Dry	Mix Binder	Mix Binder
85°C/12-14 Hrs)	∇	etc.	etc.
∇	Reslurry	∇	∇
Filter Wash (?)/Dry	∇	Spray Dry	Spray Dry
∇	NH₄⁺/RE⁺³ (?)	∇	∇
NH₄⁺/RE⁺³(?) Exchange	Exchange/Wash	Calcine	Calcine (?)
Wash	∇	∇	∇
∇	Dry/Calcine	Further	Product
Dry/Calcine	∇	Processing (?)	
∇	NH₄⁺/RE⁺³ Exchange	∇	
Acid Wash (?)	Wash/Dry	Product	
NH₄⁺/RE⁺³(?)	∇		
Exchange/Wash	Product		
∇			
Product			

Figure 1-11 Four commercial types of FCC preparation.

Source: Woltermann, Magee and Griffith (Eds.: Magee and Mitchell, Jr.), 1993: 140

Objectives

1. To study the procedure for preparing REY-zeolite catalyst.

2. To characterize and evaluate the catalysts obtained from experiment.

Possible Achievement

The possible achievement is to concentrate in REY-zeolite catalyst preparation, characterization and evaluation. The knowledge from this work can be

used to prepare another cracking catalysts and also applied to prepare catalyst for other applications.

Content of Research

1. Synthesis of NaY-zeolite

2. Preparation of REY-zeolite

3. Preparation of Catalysts

   3.1 Variation of zeolite contents

   3.2 Variation of matrix types

   3.3 Variation of clay types

4. Characterization and evaluation of catalyst

Chapter 2

EXPERIMENTATION

Equipment and Material

1. Electric mixer with stirring rod (Heidolph)

2. Programming water bath (Eyela)

3. Hot air oven (Eyela)

4. Vacuum pump (Eyela)

5. Desiccator

6. Glass receiver

7. Quartz and Glass wool

8. Rubber tube

9. Porcelain ring

10. Crucible

11. Hot plate

12. Sieves

13. Agate mortar

14. Ion-exchanged column

15. Plastic container

16. Stainless vessel

Reagents

Table 2-1 Reagents Used in Experiment

No.	Reagent	Formula	Grade	From
1	Aluminium	$Al(OH)_3$	AG	AJAX
2	Aluminium sulfate	$Al_2(SO_4)_3$	AG	Carlo Erba
3	Sodium hydroxide	$NaOH$	AG	Merck
4	Sodium silicate solution (water glass)	Na_2SiO_3	CG	Oriental Silica Co., Ltd
5	De-ionized water	H_2O	-	Faculty of Agro-Industry
6	Rare earth chloride (rich-La)	$RECl_3$	CG	RIPP, China
7	Ammonium chloride	NH_4Cl	AG	Riedel-deHaën
8	Hydrochloric	HCl	AG	J.T. Baker
9	Aluminium oxide (pseudoboehmite)	$Al_2O_3.3H_2O$	CG	RIPP, China
10	Aluminium chloride hexahydrate	$AlCl_3.6H_2O$	AG	Carlo Erba
11	Strong acid cation resin (Na-form)	-	CG	Sybron Chem.
12	Kaolin Clay	$Al_2(OH)_2,Si_2O_5$	CG	RIPP, China, Ranong

AG: Analytical Reagent Grade
CG: Commercial Reagent Grade

Instruments

Table 2-2 Instruments for Evaluation and Characterization of Catalysts

No.	Instrument	Model	Brand/Company
1	Hydrothermal Aging Unit	CLY-1	RIPP
2	Microactivity Testing Unit (MAT)	WFS-1D	RIPP
3	Gas Cromatograph (GC)	GC-14BPF	SHIMUSHU
4	Integrater	HP3295	Hellet Packard
5	Brunauer-Emmett-Teller (BET)	ASAP2010	Micro metrics
6	X-Ray Diffractometer (XRD)	X'Pert-MPD	Philips
7	X-Ray Fluorescence Spectrometer (XRF)	PW2400	Philips
8	Thermogravimatric Analysis (TGA)	TGA 7	Perkin-Elmer
9	pH meter	420	ORION

Experimental Procedure

1. Preparation of REY-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 Chemical Engineering Department, PSU (Tuntragul, 2000).

Procedure for preparing NaY-zeolite based from RIPP (Tuntragul, 2000)

Input ratio: 4.66 Na_2O: 1.0 Al_2O_3: 9.52 SiO_2: 183.43 H_2O

Step 1: Preparation of initiating agent (seed, see Figure 2-1 (a))

1. Cool all working solution listed in Table A-1 of Appendix A to 5°C.

2. Place 38 ml of waterglass in a plastic container.

3. Slowly add 30 ml of high sodium aluminate and keep stirring at 5°C for 1 hour.

4. Statically age the solution obtained from (3) at 35°C for 6 hours. The gel obtained from this step was called "seed or activated waterglass".

Step 2: Preparation of gel (see Figure 2-1 (b))

1. Mix 68 g of seed (from step 1) in 460 ml of waterglass and keep stirring at 15°C for 5 minutes.

2. Aluminium sulfate was slowly added and stirred vigorously for 10 minutes.

3. Continuously add for sodium aluminate into the slurry and stirred vigorously for 2 minutes.

4. Put gel into hot air oven, then increase temperature to 100°C, and age for 13 hours.

5. Quench with water, and filter with vacuum pump to remove the solids from mother liquor.

6. Wash with deionized water several times and dry in hot air oven at 110°C for overnight.

SODIUM
SILICATE

HIGH SODIUM
ALUMINATE

Mixing 1 hr, 5 °C

SODIUM
ALUMINOSILICATE
SOLUTION

Aging 6 hr, 35 °C

SODIUM ALUMINOSILICATE
SOL/GEL (SEED)
$(15\pm2)Na_2O:Al_2O_3:(14\pm2)Si_2O:(350\pm50)H_2O$

(a) Step 1: Preparation of seed

SODIUM
SILICATE

LOW SODIUM
ALUMINATE

ALUMINIUM
SULFATE

NaY
SEED

Mixing 30-40 min, 15 °C
Make up with deionized water

SODIUM ALUMINOSILICATE
GEL
$(3-5)Na_2O:Al_2O_3:(8-12)Si_2O:(120-200)H_2O$

Crystallization (aging)
12-13 hr, 100 °C

NaY SLURRY

Filtration
Wash with deionized water

NaY ZEOLITE

(b) Step 2: Preparation of NaY zeolite

Figure 2-1 Preparation scheme for NaY zeolite.

1.2 Preparation of Rare Earth Exchanged Y Zeolite (REY) from NaY

Basis: 500 g of NaY (volatile free basis)

1. Mix 500 g of NaY (from section 1.1) in 5000 g of hot deionized water and add

   120 g of $RECl_3 \cdot 3H_2O$ containing 40.2 % RE_2O_3.

2. Reslurry and stir at 80-90°C for 1 hour.

3. Filter and wash free of chloride with hot deionized water, and put in hot air

   oven at 110°C for overnight.

4. Calcine in air at 550°C for 1 hour.

5. Repeat step 1 to 4 (second exchange). The zeolite obtained from this step was

   called "Calcined Rare Earth Exchanged Y-Zeolite" (CREY).

Deionized H₂O

NaY — — RECl₃   Deionized H₂O
                 wash

Filter → Dry → Calciner → CREY

Ion-exchange
T = 80-90°C,
t = 30-60 min
pH = 3-5

Dry
T = 100-150°C,
t = overnight

Calcine in air
T = 550°C,
t = 1 hr

NaY: (X) RE_2O_3: (10-20) H_2O
X: appointed content divided by 0.8-0.9
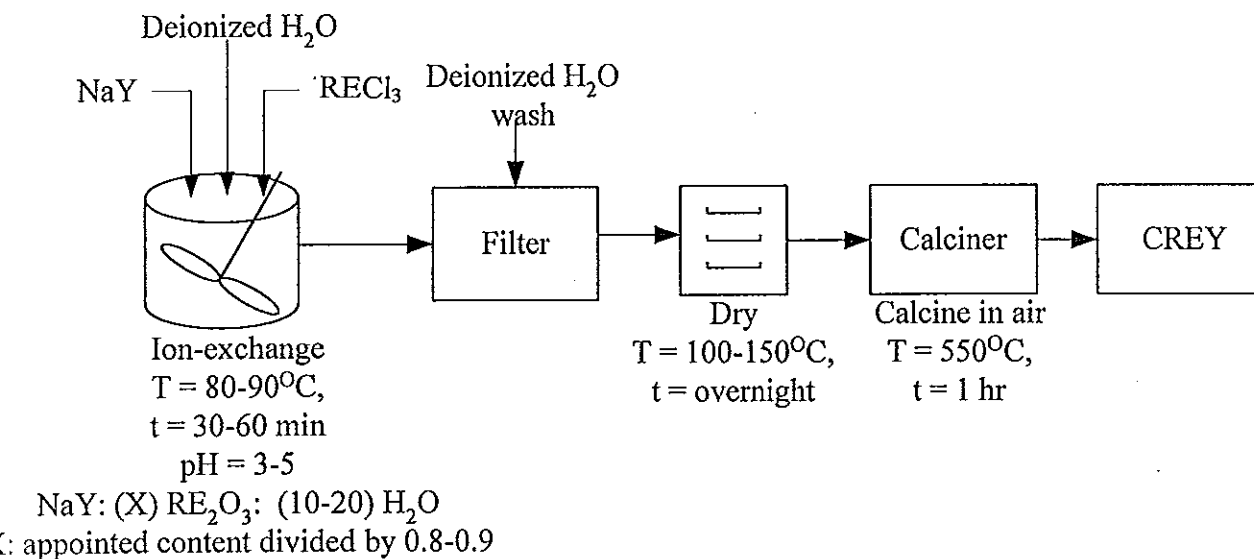
Figure 2-2 Process scheme for preparing REY zeolite.

2. Preparation of Catalysts

The procedure for preparation of cracking catalyst shown below was examined for cracking catalyst from 30% CREY promoter and 70% matrix (20% binder and 50% filler). It could be divided in three groups following the different types of binder.

2.1 Silica sol based matrix (see Figure 2-3)

Basis: 70 g batch of catalyst (volatile free basis)

1. Add 309.05 g of silica sol (4.56% SiO_2) in stainless vessel and place 47.95 g of RIPP clay then keep stirring for 30 minutes.

2. Increase pH to 5.3 (to let the sol and gel occur) with NH_4OH.

3. Add 25.11 g of REY zeolite (well dispersed in water) and stir vigorously for 30 minutes.

4. Make up with deionized water to keep the slurry solid content of 20-25 %.

5. Put the slurry in hot air oven and dry at 100-150°C for overnight.

6. Calcine in air at 500°C for 1 hour.

7. Crush and sieve to 20-40 mesh particle sizes.

8. Wash off isolated-Na by NH_4Cl solution ($CAT:H_2O:NH_4Cl$ = 1:15:0.03) at 60-70°C for 30 minutes.

9. Dry again in hot air oven at 100-150°C for overnight.

2.2 Alumina sol based matrix (see Figure 2-3)

Basis: 70 g batch of catalyst (volatile free basis)

1. Add 97 g of alumina sol (14.39 % Al_2O_3) in 0.5 litre stainless vessel and place 47.95 g of RIPP clay then keep stirring for 30 minutes.

2. Repeat step 3 to 9 of section 2.1.

Si/Al sol
Clay
Deionized H_2O

REY zeolite

Deionized H_2O

```
Colloidal
```

Mixing

Mixing of matrix component
- Stir vigorously for 30 min

Mixing

Mixing of zeolite with
matrix component
- Stir vigorously for 30 min

Drying

Drying of slurry
- Temp.: 100-150 °C
- Time: overnight

Calcining

Calination of catalyst solid
- Temp.: 500-550 °C
- Time: 1 hr.

**Crushing and
Sieving**

Crush and sieve into 20+40
mesh sizes of particle

Washing

Wash-off isolated Na^+ with NH_4Cl
- CAT: NH_4Cl: H_2O = 1: 0.03: 15
- Temp.: 60-70 °C
- Time: 30 min.

Drying

Drying of catalyst particle
- Temp.: 100-150 °C
- Time: overnight

**Fresh REY
Catalyst**

Figure 2-3 Process scheme for preparing REY zeolite catalyst (Si/Al sol based matrix).

2.3 Peptized alumina gel based matrix (see Figure 2-4)

Basis: 70 g batch of catalyst (volatile free basis)

1. Add 100 ml of deionized water in 0.5 litre stainless vessel then slowly add 47.95 g of RIPP clay and 23 g of PBA.

2. After stir for 15 minutes, slowly drop 3.5 ml of 35% HCl into the slurry and keep stirring for 1 hour.

3. Repeat step 3 to 9 of section 2.1.

The catalyst were prepared with varying matrix types and zeolite contents to demonstrate how matrix and zeolite interact for cracking of gas oil, and their activity were measure by using microactivity test. All of catalysts and matrices were listed in Table 2-3.

Table 2-3 Catalysts and Matrices Prepared in Experiments

Batch no.	REY, (%)	Binder		Kaolin clay	
		Type	Content, (%)	Type	Content, (%)
Experiment I: Variation of zeolite contents					
1	0	PBA	20	RIPP	80
2	5	PBA	20	RIPP	75
3	10	PBA	20	RIPP	70
4	15	PBA	20	RIPP	65
5	20	PBA	20	RIPP	60
6	25	PBA	20	RIPP	55
7	30	PBA	20	RIPP	50

Table 2-3 Catalysts and Matrices Prepared in Experiments (continuation)

Batch no.	REY, (%)	Binder		Kaolin clay	
		Type	Content, (%)	Type	Content, (%)
Experiment II: Variation of binder types					
8	30	Si-sol	20	RIPP	50
9	30	Al-sol	20	RIPP	50
10	30	PBA	20	RIPP	50
11	0	Si-sol	20	RIPP	80
12	0	Al-sol	20	RIPP	80
13	0	PBA	20	RIPP	80
14	0	Si-sol	100	-	0
15	0	Al-sol	100	-	0
16	0	PBA	100	-	0
Experiment III: Variation of clay types					
17	15	PBA	20	England	65
18	15	PBA	20	RN-200	65
19	15	PBA	20	RN-325	65
20	15	PBA	20	RN-powder	65
21	15	PBA	20	MRD-B85	65
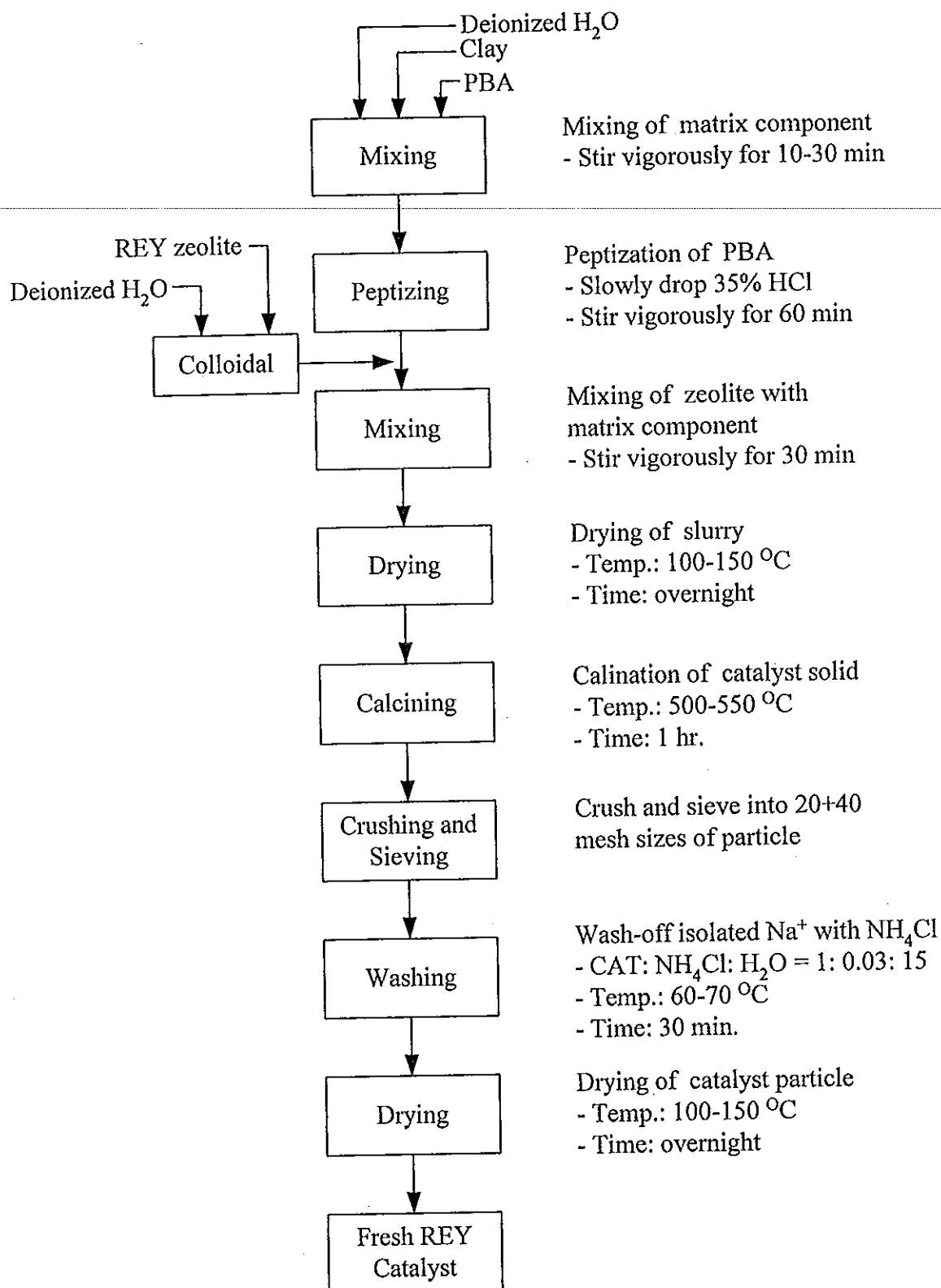
Figure 2-4 Process scheme for preparing REY zeolite catalyst (PBA based matrix).

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 2-5.

MAT PROCESS FLOW SCHEME
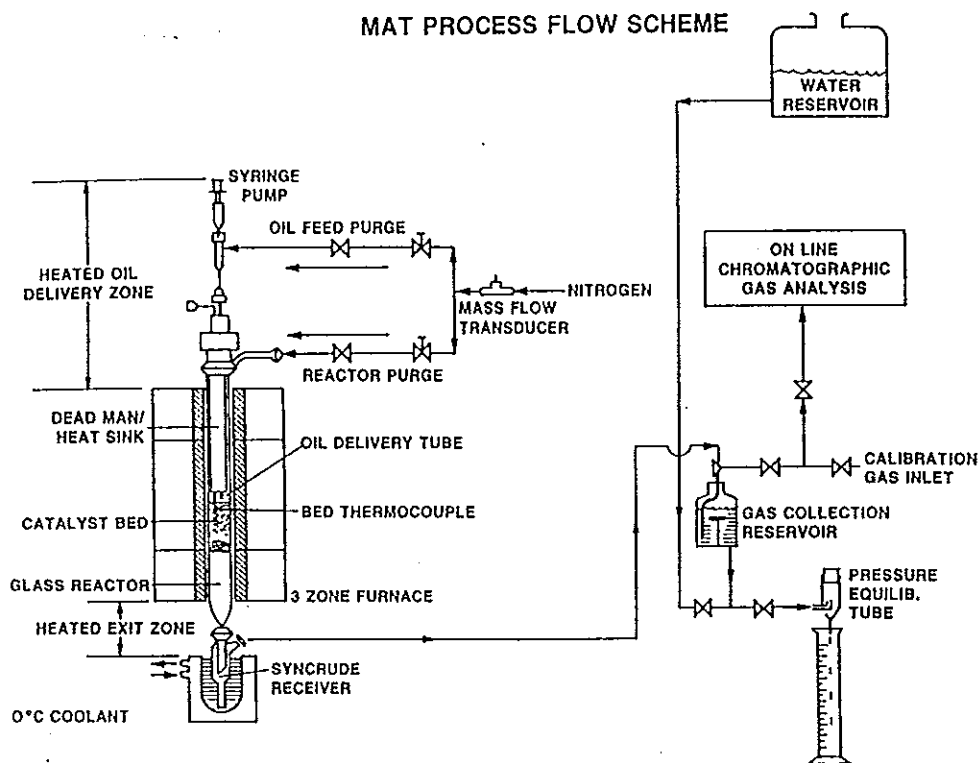
Figure 2-5 Schematic for typical MAT unit

Source: Moorehead, McLean and Cronkright (Eds.: Magee and Mittchell Jr), 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: Light Cycle Oil (LCO, bp. 235-335°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.

$$\text{Microactivity (MA,\%)} = 100 - \left[\left(\frac{100 - A}{C} \right) xB \right]$$

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 Ionize. 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 μl

Temperature of vaporization chamber (injector): 280°C

Temperature of detector chamber: 280°C

Temperature of column chamber: 35°C to 80°C with a rate of 15°C/min, then raise

from 80°C to 235°C with a rate of 8°C/min and

hold at 235°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°C

Aging time: 4 hr

H_2O/Cat: 3.0 gH_2O/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 3906-80
2	Unit Cell Size (UCS)	X-ray diffractometer (XRD)	ASTM 3942-80
3	Chemical composition, eg. Na_2O, Al_2O_3, RE_2O_3 etc.	X-ray fluorescent spectrometer (XRF)	Typical standard
4	Specific surface area	Brunauer-Bumett-Teller (BET)	ASTM D3663-78
5	Shape and size of particles	Scanning electron microscope (SEM)	Typical standard
6	Coke content	Thermogravimatric analysis	Typical standard

Chapter 3

RESULTS AND DISCUSSION

This work was focused on preparing REY catalysts which emphasized in catalyst formulation. The technique used for preparing catalyst is a typical incorporation process (conventional zeolite).

Preparation of REY Zeolite

The preparation of REY zeolite was begun with the synthetic of NaY zeolite and followed by ion exchange with rare earth.

1. NaY Synthetic

The NaY zeolite was prepared from a silica source (sodium silicate), alumina sources (sodium aluminate and aluminium sulfate), and NaY seeds consisting of amorphous sodium aluminosilicate. The resulted molar composition ratios of sodium aluminosilicate gel obtained from experiment is:

$$4.66 \, Na_2O : 1.0 \, Al_2O_3 : 9.52 \, SiO_2 : 185.37 \, H_2O.$$
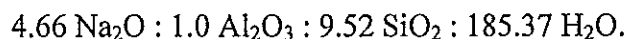
After crystallization process, the NaY zeolite was found to have a silica-to-alumina ratio of 4.74, high crystallinity (as compared to a standard and commercial NaY), and a particle sizes in the range of 1-5 μm.

Table 3-1 Comparison of NaY from this Work and Commercial

Zeolite/Properties	%Cryst.	UCS (Å)	Composition, wt%			
			SiO_2/Al_2O_3	Na_2O	SiO_2	Al_2O_3
NaY-PSU*	96.3	24.70	4.74	8.7	67	24
NaY-RIPP**	88.2	24.69	5.10	8.2	69	23

* = NaY obtained from this work.
** = NaY obtained from commercial (RIPP).
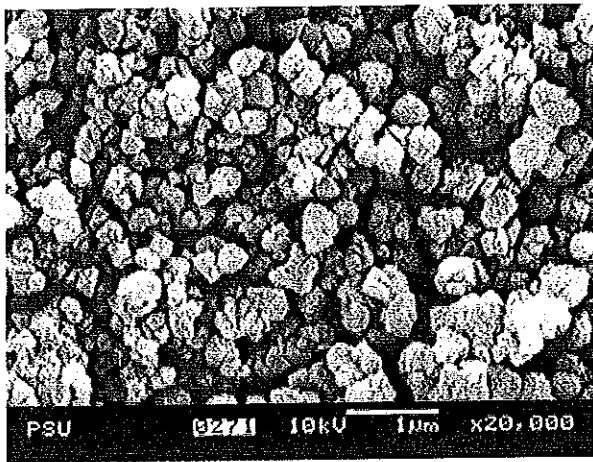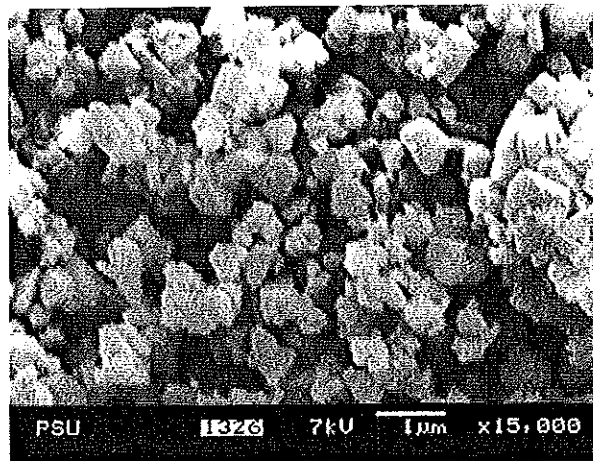
(a) NaY-PSU   (b) NaY-RIPP

Figure 3-1 SEM micrographs showing NaY zeolite sizes and shapes.
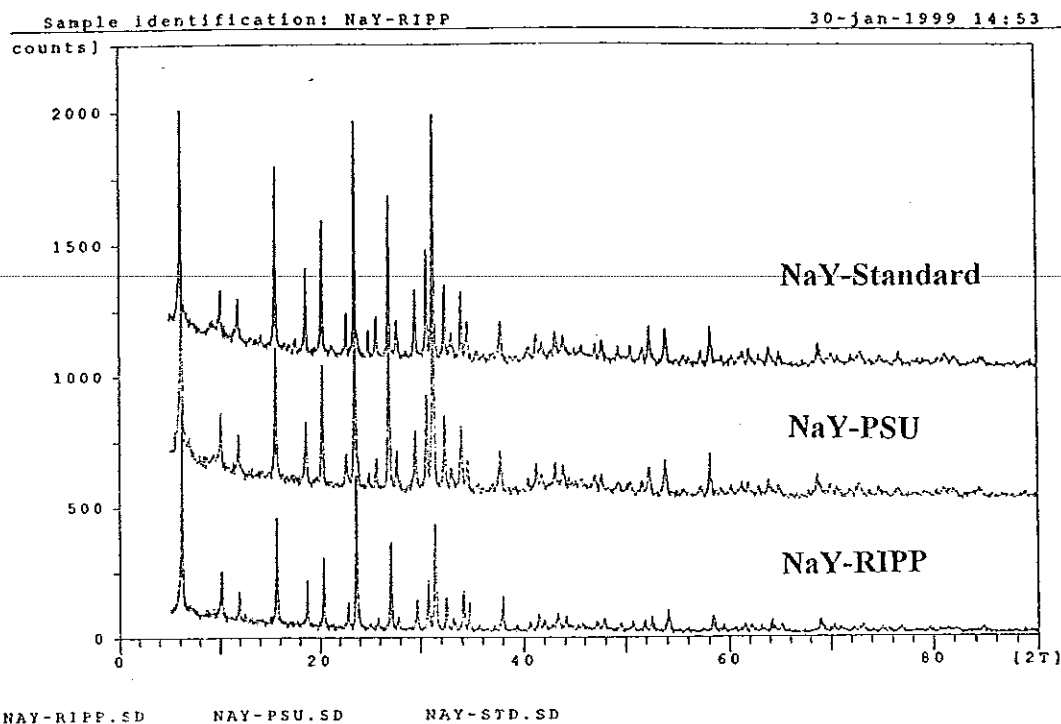
Figure 3-2 X-Ray patterns for NaY zeolite:
(a) NaY from commercial (RIPP)
(b) NaY from this work
(c) Standard NaY

2. NaY Ion Exchange

The crystallized NaY zeolite was ion exchanged with rare earth ions, in order to convert the zeolite into a catalytically active and hydrothermally material.

Generally, the level of RE_2O_3 content in REY zeolite, which fully exchanged is about 16 wt% or higher. The ion exchanged process must be carried out for two times to get a desired level of rare earth and decrease the level of sodium content to be lower than 1 wt%.

After the first rare earth exchanged (REY-1), the zeolite still contained 6.64 wt% of Na_2O. To remove the remaining sodium ions and increase the level of rare earth, the first rare earth exchanged zeolite was calcined and then carried out a second rare earth exchange.

In the final form, the rare earth Y zeolite (REY-2) contained up to 22.31% of rare earth oxide and less than 1% of Na_2O.

Table 3-2 Properties of Rare Earth Exchanged Y Zeolite

Zeolite/Properties	%Cryst.	UCS (Å)	Composition, wt%				
			SiO_2/Al_2O_3	RE_2O_3	Na_2O	SiO_2	Al_2O_3
REY-1*	74.9	24.69	4.74	15.4	6.64	67	24
REY-2**	48.2	24.67	5.53	22.31	0.38	65	20
REY-RIPP***	43.8	24.66	5.27	20.2	1.3	62	20

* 1st-exchanged REY zeolite from this work.
** 2nd-exchanged REY zeolite from this work.
*** REY zeolite obtained from commercial (RIPP).

In practice, the rare earth content of zeolite used in FCC catalysts varies, since different rare earth levels convey different activities, selectivitites, and stabilities to the final catalyst. Upon calcination, the sodium ions were migrated from the inaccessible hexagonal prism sites to more accessible site in the supercage (see Figure 1-3 of Chapter 1). Sodium in supercage sites can be readily removed by exchange ions. So, after calcined REY-1 and carried out a second exchange, it was found that the sodium ions have been quite removed from 6.63 wt% to be lower than 1.0 wt%. If the exchange is done after high temperature calcination that results in the dealumination of zeolite framework, so the number of rare earth exchange sites are lowered by dealumination. It was also decreased the zeolite crystallinity as shown in Table 3-2.

Preparation of Catalysts

The aim of this work is to concentrate in REY-zeolite catalyst preparation, characterization and evaluation. To demonstrate how zeolite and matrix components impact on cracking of gas oil molecules, catalysts with varying zeolite contents, matrix types and clay types were prepared.

1. Impact of Zeolite Content on Catalyst Activity

Microactivity cracking studies were made on catalyst samples. Each sample contained exactly the same type of matrix but the contents of REY zeolite and matrix were varied (see Table 2-3 of Chapter 2 for catalyst classifications). Thus the samples compared had distinct zeolite content. Operating conditions and feedstock were the same for each sample. From these results, conclusions may be drawn as to the effect of zeolite content on catalyst performance.

Figure 3-3 and 3-4 illustrated the impact of zeolite content on product yields using a gas oil (LCO) feedstock (see Table A-6 of Appendix A for gas oil properties). As zeolite content increases, the activity of zeolite cracking increases. When it diminishes, matrix cracking becomes more predominant.

As would be expected, an increasing of zeolite content results in microactivity, gas yield and coke yield increase, while liquid yield decrease. Unlike gasoline yield, it is highly favored by increasing of zeolite content to about 15% and slightly drops when zeolite content is higher than 15%.

It was well known that zeolite is the most active component in catalyst for cracking of gas oil molecules. An increase in zeolite results in an increase in catalytic activity.
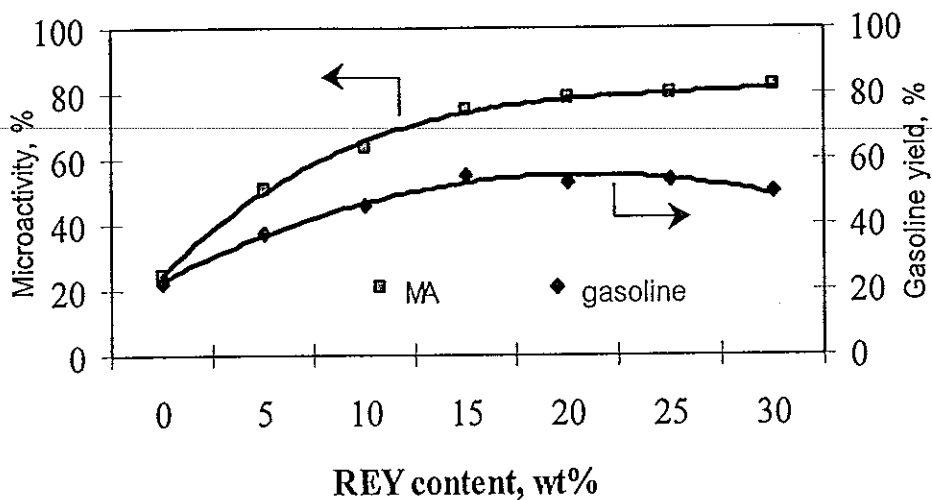
*Test condition: see section 3.1.1, page 55

Figure 3-3 Effect of zeolite content on product conversion
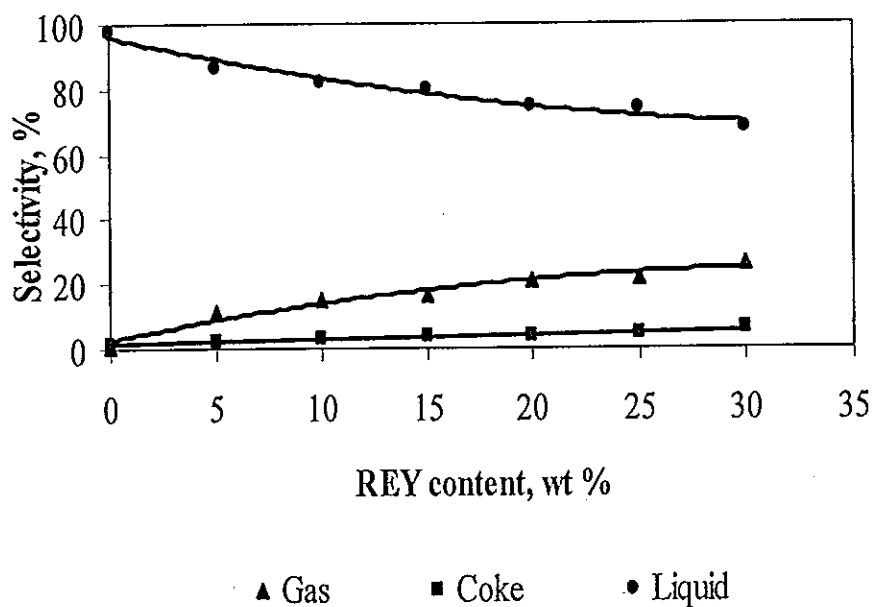
*Test condition: see section 3.1.1, page 55

Figure 3-4 Effect of zeolite content on product yield.

Table 3-3 Microactivity Test Results of Experiment I

No.	Name	MA (%)	Gasoline (%)	Coke (%)	Liq. (%)	Gas (%)*
1	REY-0	24.15	22.16	1.46	98.01	0.53
2	REY-5	50.75	37.22	1.99	86.47	11.54
3	REY-10	63.76	46.01	2.95	82.24	14.81
4	REY-15	74.94	54.85	3.57	79.90	16.53
5	REY-20	78.27	53.11	3.91	74.84	21.25
6	REY-25	79.82	53.48	4.49	73.72	21.79
7	REY-30	81.81	49.89	5.83	68.08	26.09

The concentration, strength and distribution of acid sites in the zeolite play a key role in determining its activity and selectivity. Although the reactions that take place during catalytic cracking of gas oil are rather complex and many of primary products undergo secondary reactions (see Table 3-4), most of these reactions involve carbocations as intermediates (Scherzer, 1993). While cracking of high input of zeolite contributes to high acid concentration, some primary products are converted to undesired product (e.g. gas and coke) by secondary reactions such as isomerization, cyclization and hydrogen transfer.

At high concentration of acid sites, a more secondary reactions can be take placed lead to high gas and coke make, which result in an decrease of liquid yield as shown in Figure 3-4. Although the liquid yield decreases as increasing of zeolite content, it was found that the gasoline fractions (C_{12} below, analyzed by GC) in liquid yield increase. So, the optimum zeolite content has been considered.

content, it was found that the gasoline fractions (C_{12} below) in liquid yield increase.

So, the optimum zeolite content has been considered.

Table 3-4 Main Reactions in FCC Catalysis

Source: Scherzer, 1989: 294

Paraffins $\xrightarrow{\text{Cracking}}$ Paraffins + Olefins

Olefins[a]
- $\xrightarrow{\text{Cracking}}$ LPG Olefins
- $\xrightarrow{\text{Cyclization}}$ Naphthenes
- $\xrightarrow{\text{Isomerization}}$ Branched olefins $\xrightarrow{\text{H Transfer}}$ Branched paraffins
- $\xrightarrow{\text{H Transfer}}$ Paraffins
- $\xrightarrow[\text{Condensation}]{\text{Cyclization}}$ Coke
  Dehydrogenation

Naphthenes
- $\xrightarrow{\text{Cracking}}$ Olefins
- $\xrightarrow{\text{Dehydrogenation}}$ Cyclo-olefins $\xrightarrow{\text{Dehydrogenation}}$ Aromatics
- $\xrightarrow{\text{Isomerization}}$ Naphthenes with different rings

Aromatics
- $\xrightarrow[\text{cracking}]{\text{Side-chain}}$ Unsubstituted aromatics + Olefins
- $\xrightarrow{\text{Transalkylation}}$ Different alkylaromatics
- $\xrightarrow[\text{Condensation}]{\text{Dehydrogenation}}$ Polyaromatics $\xrightarrow[\substack{\text{Dehydrogenation} \\ \text{Condensation}}]{\text{Alkylation}}$ Coke

[a]Mainly from cracking, very little in feed.

Zeolite content was consistently important and positive to most yield structure. At the present of 15% zeolite in catalyst seems to be an optimum zeolite level for gasoline catalyst. Because at this level, the maximum gasoline yield was obtained while coke and gas selectivity were very low. According to Mitchell's report, the optimum catalyst properties which contained 15% of zeolite was suggested for future catalyst formulation (Mitchell, 1993). Most commercial REY based catalysts contained between 15 and 25 percent zeolite (Scherzer, 1993).

Table 3-5 Comparison between MAT Yields and Selectivies

| No. | Name | MA (%) | Gasoline (%) | | Gas | Coke |
			yield (%)	selectivity	selectivity	selectivity
1	REY-0	24.15	22.16	0.918	0.022	0.060
2	REY-5	50.75	37.22	0.733	0.227	0.039
3	REY-10	63.76	46.01	0.722	0.232	0.046
4	REY-15	74.94	54.85	0.732	0.220	0.047
5	REY-20	78.27	53.11	0.679	0.271	0.050
6	REY-25	79.82	53.48	0.670	0.273	0.056
7	REY-30	81.81	49.89	0.610	0.319	0.071

Remark: Selectivity = yield / conversion (MA)

REY-0   REY-5   REY-10   REY-15   REY-20   REY-25   REY-30
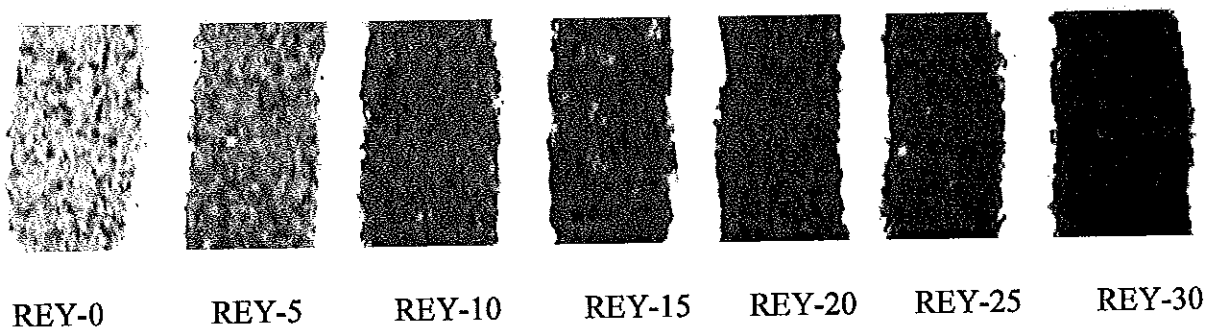
Figure 3-5 The illustration of spent catalysts from sample 1 to 7.

However, conflicting objectives made optimization difficult-zeolite levels and optimum gasoline and coke yields tended to also correlate with physical properties of catalyst such as bulk density and attrition resistant.

2. Impact of Matrix Type on Catalyst Activity

According to the different matrix compositions of catalyst, the catalysts incorporated in different matrices can play the important role in catalytic activity. To investigate the influence of matrix types on catalyst activity, the catalysts were embedded with three types of binder: silica sol, aluminium sol and peptized pseudoboehmite alumina (PBA). The result of microactivity tests for gas oil cracking over the different of matrices is shown in Figure 3-6.

■ Sample embedded with Si-sol

▤ Sample embedded with Al-sol

☐ Sample embedded with PBA
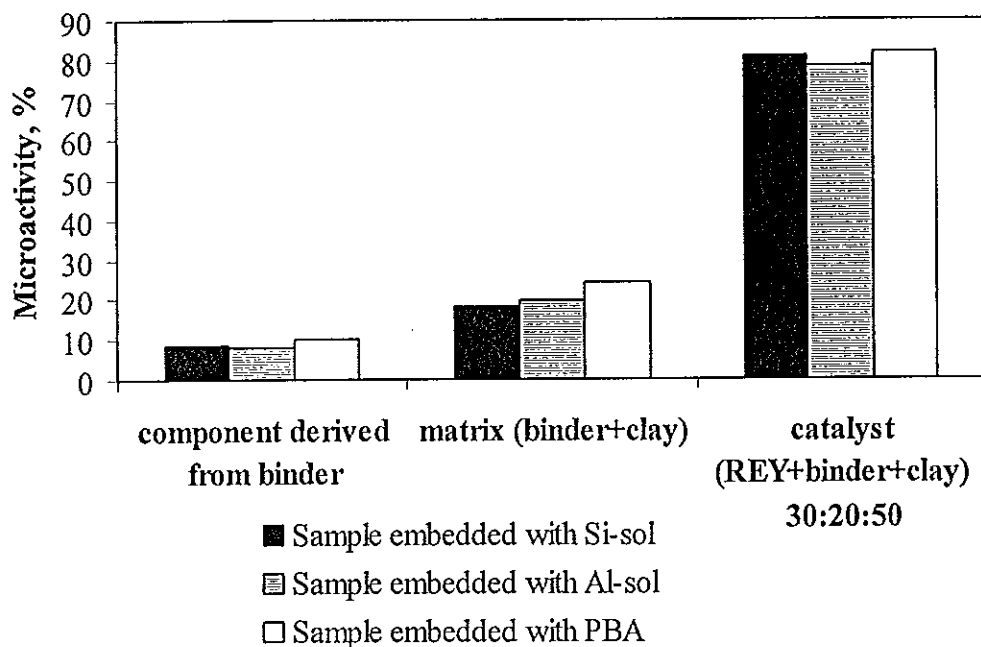
*Test condition: see section 3.1.1, page 55

Figure 3-6 The microactivity test of catalyst, matrix and binder.

Table 3-6 Specific Surface Area of Binders

Binder type	Surface area, m^2/g[*]
Silica sol	29.10
Aluminium sol	42.12
Peptized PBA	178.14

* BET surface area

From the results of three groups of sample (catalyst, matrix and binder), it was found that the microactivity among three groups of sample were slightly different. In the case of embedding with PBA, the microactivity of samples was the highest in each group. For the microactivity of the sample embedded with silica sol and aluminium sol were a bit different.

Several reviews were found that upon calcination, PBA is converted to gamma alumina at temperature about 300°C. The gamma alumina has acidic-OH groups (Brø nsted acidity) as well as Lewis acid sites but not as strong as the acid site in zeolite. As shown in Table 3-6, the PBA matrix also has a high surface area which contributed the diffusion of gas oil molecules into the acid site of catalyst. This caused alumina matrix derived from PBA, would be more active than other matrix. When considered the microactivity tests of single component which derived from binder, it were found that the PBA has the highest microactivity while silica and alumina have the same activity as packing and blank (see the definition in Table 3-7). For the cracking of gas oil over packing and blank mainly caused by thermal cracking. These results exhibit that silica and alumina (derived from aluminaium chloride sol) are an inert and have no effect on product selectivities or properties as seen in Table 3-7.

Table 3-7 Microactivity Test Results of Experiment II

No.	Name	MA (%)	Gasoline (%)
8	REY-Si	80.65	50.07
9	REY-Al	78.52	51.34
10	REY-PBA	81.81	49.89
11	Si-matrix	18.43	15.28
12	Al-matrix	19.83	18.61
13	PBA-matrix	24.15	22.16
14	SiO_2*	8.48	3.99
15	Al_2O_3* (Al-sol)	8.24	4.39
16	Al_2O_3* (PBA)	10.16	6.25
16-1	Packing (ceramics)**	8.82	4.34
16-2	Blank***	7.86	4.46

* = The component derived from binder
** = The alumina packing which has no activity in catalytic cracking.
*** = The gas oil pass through the empty reactor without catalyst loading.

As the results obtained from microactivity tests, the catalyst embedded with three matrix systems in this work exhibited a slight different in activity and selectivity. In this work the different matrices seem to be no significant impact on cracking of gas oil molecules. But in fact, the feedstock used in this work is the LCO gas oil which boiling range is 235°C to 335°C. While the pore opening to the zeolite cage structure (primary cracking site) is 7.4 Å which can accept molecules having true boiling point lower than 482°C (Leiby, 1992). This corresponds to the size of gas oil molecules within the boiling range of this work, gas oil can easily access in the pore

size of zeolite, so the cracking of gas oil (boiling point < 482°C) is less dominated by the matrix.

Although the matrix has a lesser extent than zeolite component but when the feedstock becomes heavier such as heavy vacuum gas oil (VGO) and vacuum resid, an active matrix can upgrade the heavy fraction in the feed to valuable products. Because of the large-pore of matrix can permit relatively easy access of very large feed molecules.

3. Impact of Clay Type on Catalyst Activity

Clays are natural component and used in almost all catalyst formulation. In this work, kaolin clays, which are different in property, were selected to study the effect on catalyst activity. The chemical compositions of clay are shown in Table 3-8.

Table 3-8 Chemical Compositions of Clays

Clay type	Composition, wt%				
	SiO_2	Al_2O_3	Na_2O	TiO_2	Fe_2O_3
RN-Powder	46.10	36.20	1.15	0.10	1.05
RN-325	46	38	<0.001	0.03	0.80
RN-200	46.50	37	<0.001	1.05	1.10
MRD-B85	46	38	<0.001	0.03	0.60

As shown in Table 3-8, the main compositions of clay were SiO_2 and Al_2O_3. The quantities of these compositions are in the same level among four types of clay, but different in the case of Na_2O, TiO_2 and Fe_2O_3 content. Four catalyst samples which incorporated with different types of clay have been performed the activity by microactivity test and the results were shown in Figure 3-8.
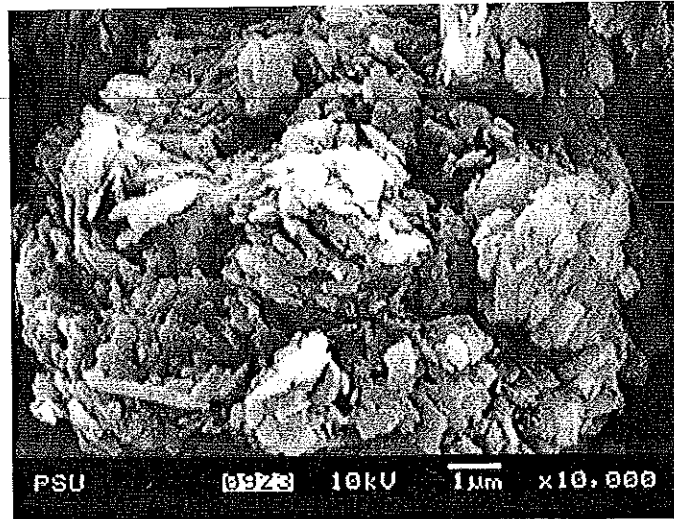
(a) RN-Powder
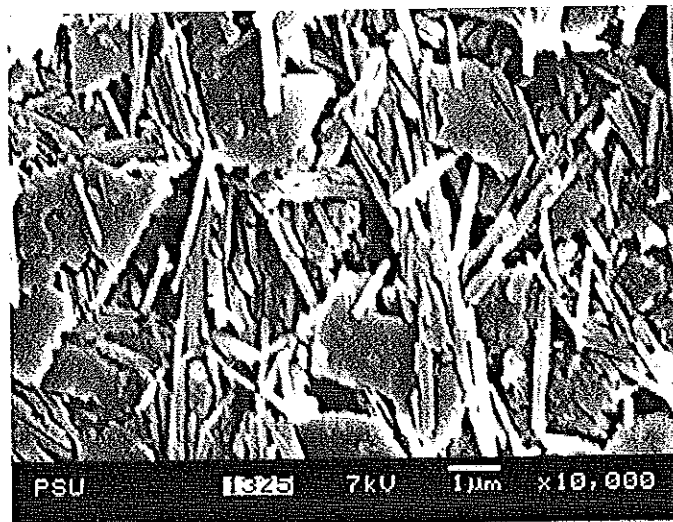
(b) RN-325

Figure 3-7 SEM micrographs of clays.
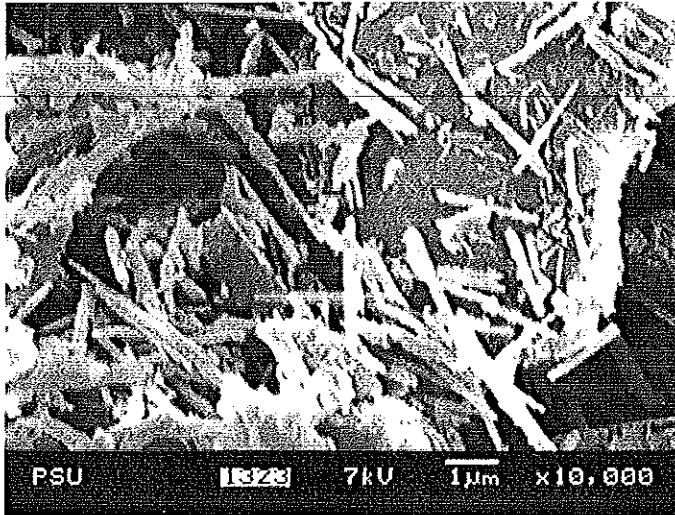
(c) RN-200
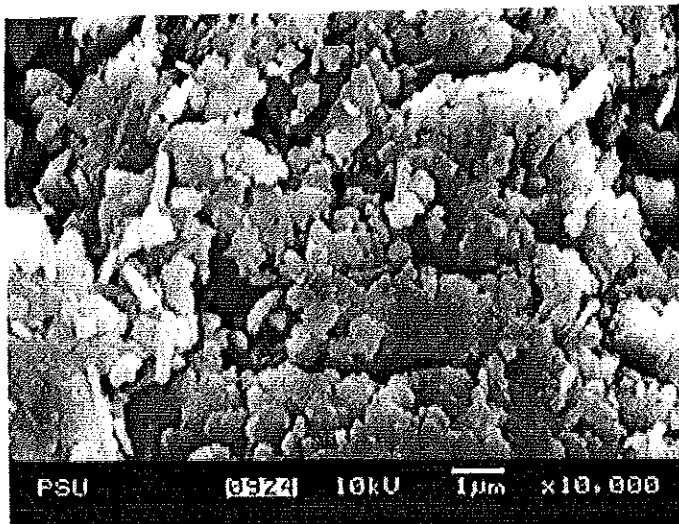
(d) MRD-B85

Figure 3-7 SEM micrographs of clays (continuation).
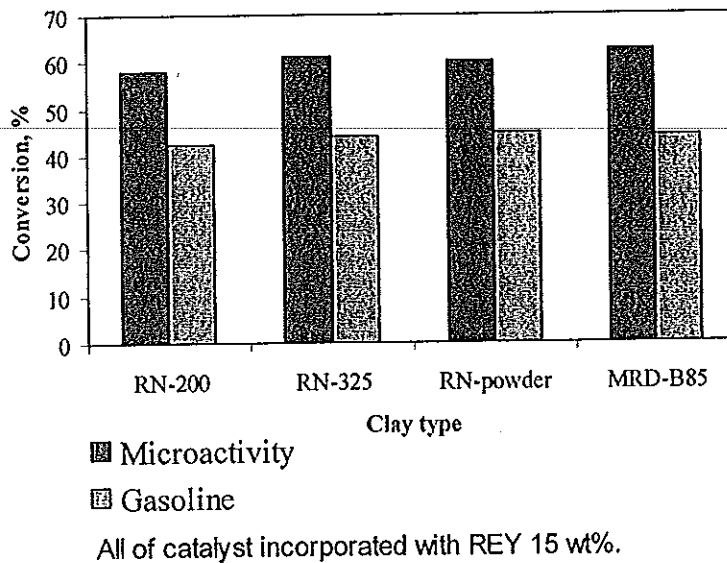
Figure 3-8 The microactivity of catalyst incorporated in different types of clay.

As the results, there is a slightly different in microactivity and gasoline selectivity. By the chemical structure, kaolin clays have a two-layer structure, consisting of alternating sheets of SiO_4 tetrahedra and AlO_6 octahedra as shown in Figure 3-9. The ideal composition corresponds to the formula $2SiO_2.Al_2O_3.2H_2O$. According to their structure, they have no such acid site, so they exhibit as an inert component for cracking catalyst. That the reason why kaolin clays are used as a filler for diluting catalyst activity.

However, natural clays frequently contain impurities, such as iron, magnesium, titanium etc. as well as different mineral impurities such as quartz (see Table A-5 in Appendix A for more characterization of clays). These impurities, such as iron and titania can also be important. High iron or titania levels can lead to

undesirable secondary reactions such as gas and coke, when such clays are used to prepare cracking catalysts. Titania levels below 3.0 wt% and an iron content of 0.4 to 0.8 wt% are considered acceptable (Woltemann, Magee and Griffith, 1993). Since, the slightly content of impurities of clays in this work can be acceptable, so the effect of their present is not significant.
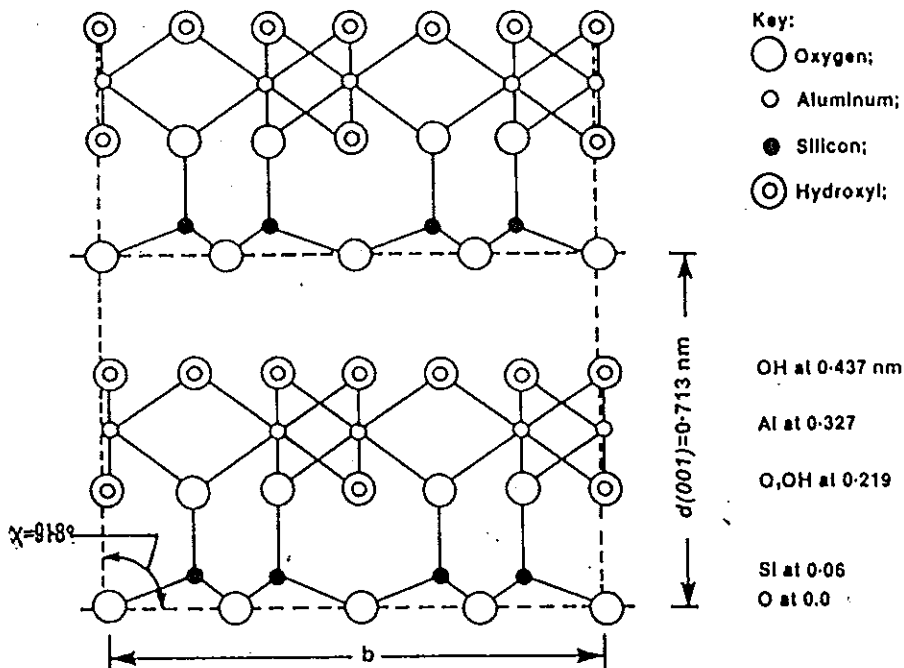
Figure 3-9 Kaolinite layer viewed along the α-axis.

Source: Scherzer, 1989: 267

Chapter 4

CONCLUSIONS

In this work, preparation of REY zeolite catalyst was studied which emphasized in catalyst preparation. The work carried out in this study was divided in two parts: REY zeolite preparation and catalyst preparation.

The preparation of REY zeolite was conducted by synthesis of NaY zeolite first and following with an exchange of rare earth cations.

The NaY zeolite was synthesized by reaction of sodium silicate, aluminium sulfate, sodium aluminate and initiator (seeds). The input molar ratios of reaction were

$$4.66 \ Na_2O : 1.0 \ Al_2O_3 : 9.52 \ SiO_2 : 185.37 \ H_2O.$$
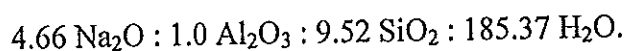
The NaY powder was then exchange with rare earth cations for twice times to get a desire level of rare earth and decrease sodium content to be lower than 1 wt%.

The catalyst can be prepared by embedding REY zeolite with binder and filler (clay). Several matrix components can be used to incorporate with REY zeolite and the evaluations of their impacts on catalyst activity were made on microactivity test. Specific conclusions resulting from this study are as follows.

1. An increase in zeolite content of catalyst results in an increase in catalyst activity and undesired product yields such as gas and coke. By considering on gasoline yield and undesired product selectivity, the optimum zeolite content is about 15 wt%. %. However, the optimum zeolite content would be varied

75

when the reaction condition changed. So the varying of test condition such as temperature should be conducted to find out the suitable zeolite content for cracking catalyst in further study.

2. The different types of matrix in this work (Si-matrix, Al-matrix and PBA matrix) have less significant impact on catalytic activity for cracking of gas oil (LCO, bp. 235-335°C) used in this study. However, the activity of catalyst containing alumina in the matrix is higher than that containing silica in matrix. Up to now, the matrix activity becomes more important, since most of feed stock is much heavier than before. So, the study on varying type of feedstock can be done to select and modify the suitable matrix for cracking of heavy feedstock.

3. Four types of clay, which are different in sizes and shapes of particle but approximately the same chemical composition can be used as a filler in cracking catalyst without significant impact on catalyst activity. But it is also believed to affect on physical properties of catalyst.

However, the activity of catalyst not only plays a key role in FCC process but also the physical property. The physical property such as bulk density, surface area and attrition resistant are also critical parameter for FCC operation. So the key physical characteristics of catalyst such as acidity, bulk density, attrition resistance, thermal and hydrothermal stability, surface area, particle size distribution, pore volume and pore size distribution of catalyst should be performed for the study on preparation of cracking catalyst.

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PREPARATION OF ZEOLITES AND MATRIX COMPONENTS

Synthesis of NaY Zeolite

Table A-1 Chemical Compositions of Working Solution

No	Solution/Composition (g/l)	Na_2O	SiO_2	Al_2O_3	H_2O	Density (g/l)
1	Waterglass	91.81	262.38	-	915.75	1269.94
2	High sodium aluminate	254.56	-	43.39	1061.05	1359
3	Low sodium aluminate	130.48	-	104.54	1037.48	1272.5
4	Aluminium sulfate	-	-	83.14	1183.16	1266.3
5	Deionized water	-	-	-	1000	1000

Step I: Preparation of initiating agent (seed)

Basis on 200 ml seed

Basis ratio : (13-17) Na_2O : (1) Al_2O_3 : (12-16) SiO_2 : (300-400) H_2O

Input ratio : 14.73 Na_2O : Al_2O_3 : 15 SiO_2 : 313.08 H_2O

Step II: Preparation of aluminosilicate gel (whole gel)

Basis on 2000 ml whole gel

Basis ratio : (3-5) Na_2O : (1) Al_2O_3 : (8-12) SiO_2 : (120-200) H_2O

Input ratio : 4.66 Na_2O : Al_2O_3 : 9.52 SiO_2 : 185.4 H_2O

Table A-2 The Quantity of Working Solution for Synthetic of NaY Zeolite

Working Solution	Volume (ml)
Step I: Preparation of initiating agent	
Water glass	107
High sodium aluminate	73
Deionized water (make up)	20
Step II: Preparation of whole gel	
Water glass	1180
Initiating agent (from step I)	200
Aluminium sulfate	360
Low sodium aluminate	260

Table A-3 The Composition Balance Derived from Table A-1 and Table A-2

Working Solution/Composition (g)	Na$_2$O	Al$_2$O$_3$	Si$_2$O	H$_2$O
Step I : Preparation of seed				
Water glass	9.77	-	27.92	97.38
High sodium aluminate	18.57	3.16	-	77.40
Demonized water				20.62
Total weight (g)	28.34	3.16	27.92	195.40
Total mole (mole)	0.457	0.031	0.465	10.86
The molar ratio	14.73	1.0	15	313.08
Step II : Preparation of whole gel				
Water glass	108.34	-	309.6	1080
Initiating agent (seed)	28.34	3.16	27.92	195.4
Low sodium aluminate	33.92	27.21	-	269.7
Aluminium sulfate	-	29.93	-	425.9
Demonized water	-	-	-	-
Total weight (g)	170.6	60.3	337.5	1971
Total mole (mole)	2.752	0.591	5.625	109.5
The molar ratio	4.66	1.0	9.52	185.4

Preparation of REY Zeolite

Table A-3 Distribution of Individual Rare Earth Oxide used in Experiments

Type/RE_2O_3 (wt%)	La_2O_3	Ce_2O_3	P_2O_3	Nd_2O_3	Sm_2O_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

Table A-4 Solid Content of Catalyst Components

Material	% Solid
NaY	76.60
REY	83.62
Rich La $RECl_3$	51.73
Mixed $RECl_3$	54.37
PBA	60.86
Clay RIPP	73.13
Clay England	86.87
Clay RN-200	80-37
Clay RN-325	74.61
Clay RN-powder	85.68
Clay MRD-B85	82.0

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

Table A-5 Properties of Clays

Properties\Clay types	RN-200	RN-325	RN-Powder	MRD-B85
Chemical composition (wt%)				
SiO_2	46.50	46.0	46.10	46.0
Al_2O_3	37.0	38.0	36.20	38.0
TiO_2	1.05	0.03	1.05	0.03
Na_2O	<0.001	<0.001	1.15 (max)	<0.001
K_2O	1.25	1.00	1.05 (max)	1.00
MgO	<0.001	<0.001	-	<0.001
CaO	<0.001	<0.001	-	<0.001
Fe_2O_3	1.10	0.80	1.05	0.60
Mineral composition				
Kaolinite	79	83	82	87
Quartz	5	3.5	4	4.0
Micaceous	11	8.5	10	5.0
Gibbsite	3	3	2	4
Feldspar	<1	<1	<1	<1
Others	2	2	2	< 1
Physical properties				
Finer than: 10 micron (wt%)	56.6	60.0	60.0	56.0
: 1 micron (wt%)	10.9	12.0	10.0	8.0
Residue on 325 mesh (wt%)	3.5	0.6	1.4	0.6

Table A-6 Properties of Gas Oil (LCO) Feedstock

ASTM D-2887		ASTM D-86 correlation	
wt %	Temp. (°C)	wt %	Temp. (°C)
IBP	173	IBP	221
5	220	2	241
10	234	10	250
20	251	20	261
30	264	30	270
50	292	50	287
70	321	70	309
80	338	80	322
90	358	90	336
EP	395	EP	355

Table A-7 Properties of Binder

Properties/Binder types	Si-sol	Al-sol	PBA
Na_2O, wt %	≈ 0	-	-
Al_2O_3, wt %	-	14.39	n/a
SiO_2, wt %	4.56	-	-
pH	3	2-3	-
Solid content (%)	n/a	n/a	60.86

n/a = data not available

Preparation of Binder

2. Silica Sol

The silica sol is formed by passing a sodium silicate solution (water glass) through a column of an ion exchange resin. The effluent from the column is a sodium free silica sol that contains about 1 to 8% preferably about 5% silica (Hoffman, et. al., 1976). The product has a pH of about 3. This sol exhibits a gellation time of approximately 2-5 days depending on concentration, pH and temperature and can advantageously be used as is.

The fresh sol can be allowed to gel with long residence times or be synthetically gelled by raising the pH to 5 to 9 preferably 6. However in cases where gellation is desired, the sol can be easily gelled by increasing the pH about 5.3 with sodium silicate or any other base.

Procedure for preparing silica sol

A silica sol was prepared by diluting commercially sodium silicate ($SiO_2/Na_2O = 3.30$) to a solution containing 5 wt% SiO_2 with water. The resulting solution was passed through a cation resin of the strong acid type, namely IONACRC-249. The column was packed with cation resin about 2/3 of the column high (2 inches in diameter). The sodium silicate solution was fed to the top of column and passed through the bed of resin by gravity (flowrate about 50-80 ml/min). The effluent from the column was a polysilic acid containing about 5 wt% silica the pH of the sol was about 3.
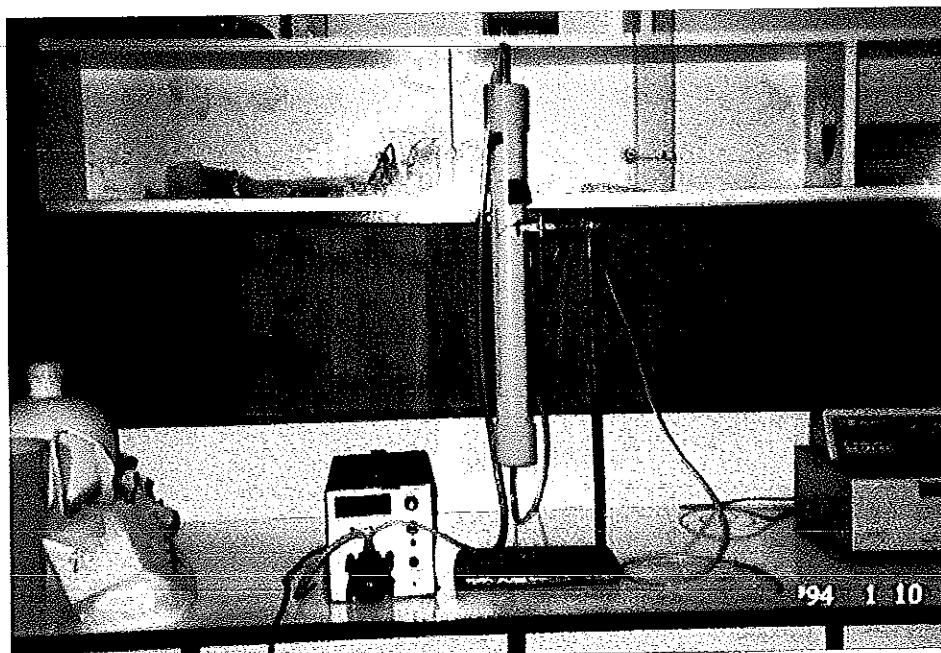
Figure A-1 Illustration of experiment set up for an ion exchanged unit.

2. Aluminium/alumina sol

An aluminium or alumina sol in this work was prepare by the slow hydrolysis of a solution of aluminium chloride hexahydrate (AlCl$_3$. 6H$_2$O) with base.

Procedure for preparing aluminium sol

Place 240-250 g of AlCl$_3$.6H$_2$O (MW = 241.5) in 1000 ml beaker and dilute with distilled water until the volume get 5000 ml. The pH of the aluminium is very low (pH is about and keep stirring until the pH get higher preferably pH 2 or 3). Finally the clear solution which slightly green in color is obtained and the AlCl$_3$ content is about 10 wt% preferably Al$_2$O$_3$ content of 10 to 20 wt%.

3. Peptized Alumina

Peptized alumina based binder is prepare by peptizing pseudobehmite alumina (PBA) with monobasic acids such as HCl and HNO_3. The action of the acid on the reactive alumina produces an alumina so with particle size of several hundred manometers.

Procedure for preparing peptized alumina

Place PBA powder into stainless vessel and add some deionized water. Slowly add HCl (35-36wt%) into the PBA slurry and keep stirring until the sol or gel is formed. The ratio of HCl to PBA used is about 0.05 to 0.25, preferably 0.1. The effect HCl/PBA ratios on catalyst activity is shown in Figure A-2.

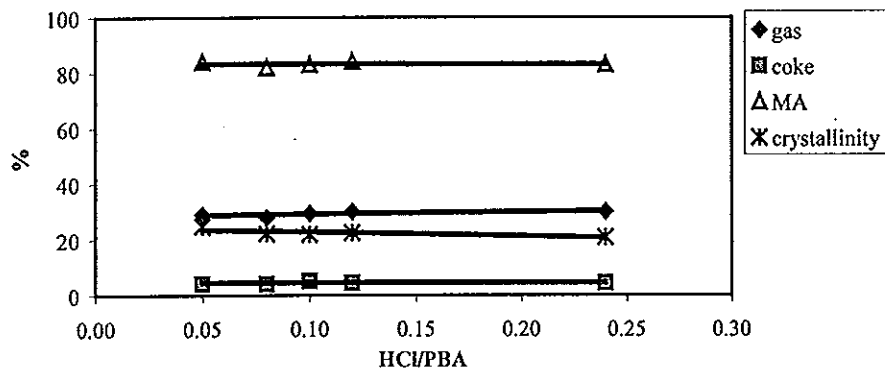**Figure A-2** Activity and properties of catalyst incorporated in PBA, which was peptized different ratios of HCl/PBA.

Source: Kritsanaphak et al., 2000: 133

Appendix B

INTRUMENTAL METHODS OF CRACKING CATALYST

Microactivity Test (by WFS-1D Microactivity Testing Unit)

There are two parts in the test system: test unit (MAT unit) and gas chromatography set.

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 235-337C

Reaction temperature	: 460 $\pm$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
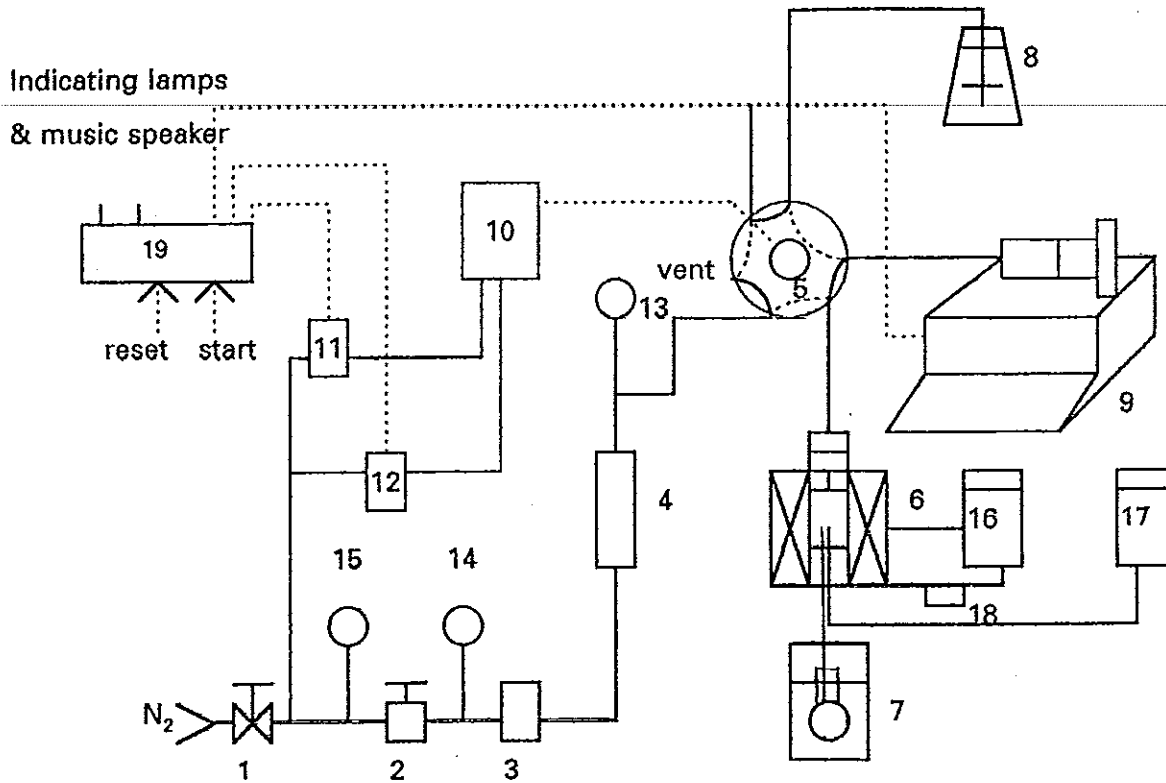
Figure B-1 The process diagram of MAT unit.

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 a 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 :

$$0 \leq 1 \leq 150s$$

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

$$T3 = T2 - T1 \text{ (s)}$$

$$T4 \leq 991 - T1 \text{ (s)}$$

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 Gas Chromatography Set and Integrator

The G.C. is Shimadzu GC-14B, the integrator is Shanghai HP 3295. For the use of detecting cracking catalyst microactivity index, the conditions in analysis are

Carrier gas   : nitrogen (OFN), flow rate : 35-40 ml/min

Combustion gas   : hydrogen, flow rate : 40 ml/min

Auxiliary gas   : air, flow rate : 400 ml/min

Temperature of vaporization chamber (injector) : 280°C

Temperature of column chamber   : 280°C

Temperature of column chamber   : rises from 35°C to 80°C by rate of 15°C/min, then rises from 80°C to 235°C by rate of 8°C/min, hold at 235°C for 10 min.

Sample injection volume   : 1μl

Range   : set to 10

The recommended integrator's parameters are:

Attenuation   : 8

Half-pack width: 0.04 min. after 1.5 min. changes to 0.16 min

Use Integrate function 14 to sum up all the peak areas (%wt) before C12 (including C12). It is the cut point of gasoline and feed oil (gas oil or diesel oil). Use integration function 5 to set the base line horizontally.

4. Preparation before Operation

4.1 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 ± 1C. It can be obtain by adjusting the furnace temperature controller's set value.

4.2 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 110-120°C.

4.3 Feed Oil

Heavy oil isn't suitable for this apparatus

4.4 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 ± 0.01 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							

4.5 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

5. 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.

6. Analyses of Reacted Product and Aata Disposal

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

6.1 Calibrate the retention time of n-dodecane

Put a little standard n-dodecane ($CH_3 (CH_2)_{10} CH_3$) into the mixture of gasoline and the standard feed oil or used only standard n-dodecane, Analyze the sample with G.C., The n-dodecane retention time is the cut pint (n-dodecane belong to the gasoline)

6.2 Calculation the microactivity index

Put weight of feed oil, weight of liquid product, gasoline area (%wt) in program WSF-1D in report command, it will calculate the MAT index.

$$\text{Microactivity (MA,\%)} = 100 - \left[\left(\frac{100 - A}{C} \right) \text{x} B \right]$$

Where

A = Gasoline yield, analyzed by GC, %wt
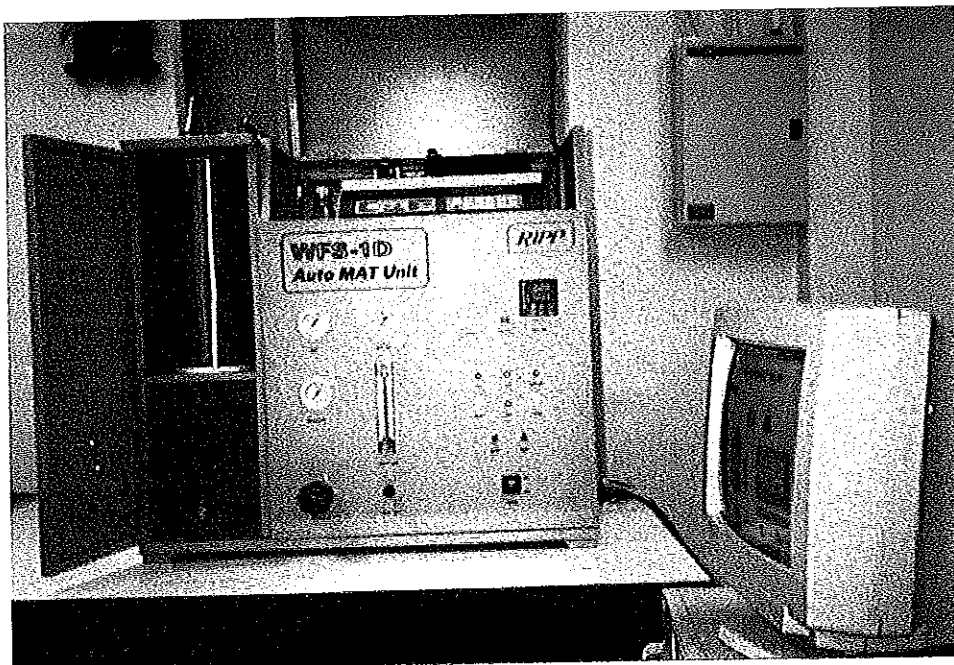
B = Liquid product from MAT, g.

C = Feed oil, g

Figure B-2 Microactivity test unit
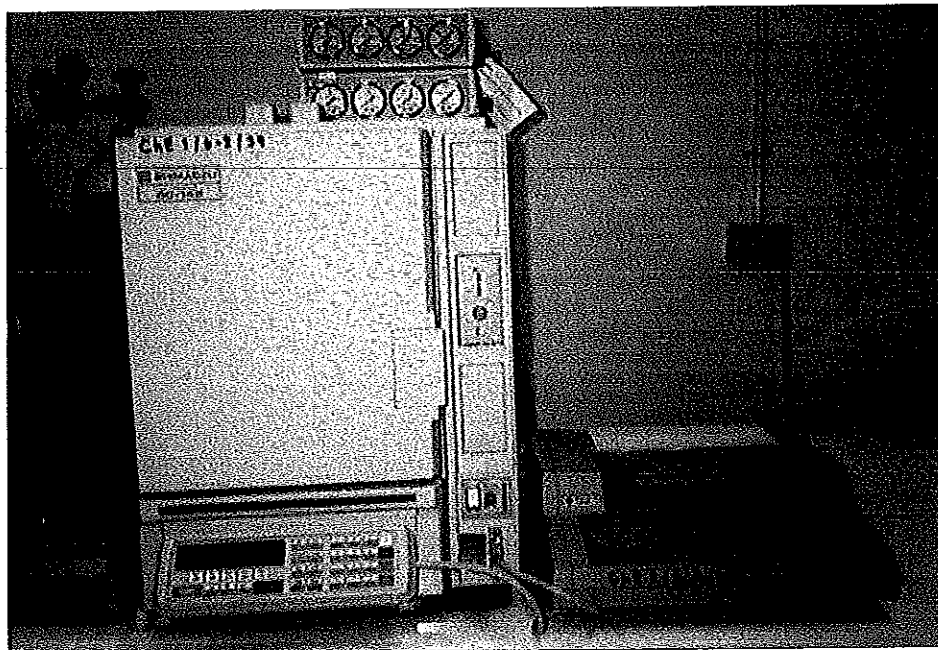
Figure B-3 Gas Chromatograph unit

Example: Measures the MA (%wt) of catalyst sample no. 7 of Table 3-3 from Chapter 3.

1. Measure gasoline cut point or retention time of n-dodecane (C_{12}) by injection of standard n-dodecane to the GC column or mixing standard n-dodecane with gas oil and gasoline, and inject to GC. From Figure B-4, the retention time of C_{12} is 9.4 minutes, so gasoline fraction can be integrated from initial to the retention time of 9.4 minutes (C_{12} below).
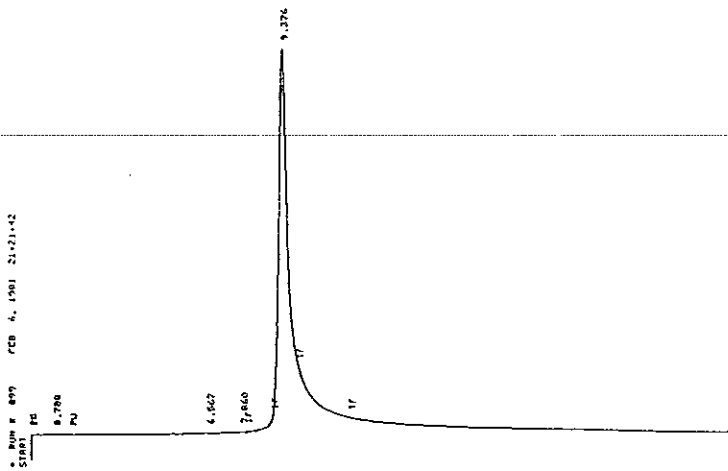
Figure B-4 Chromatogram of n-dodecane (n-C$_{12}$)

2. Cracking of gas oil with catalyst sample no. 7 (REY-30) and inject

the liquid produced from MAT to the GC.
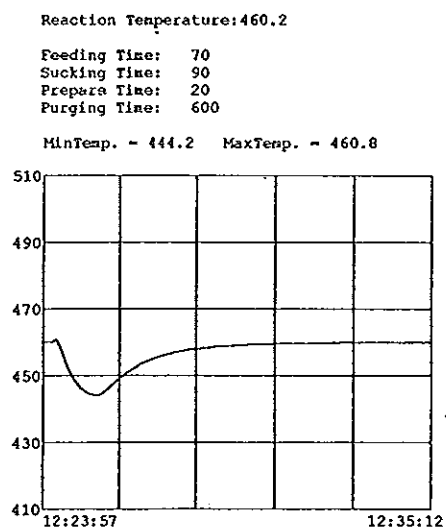
Figure B-5 Temperature profile during catalytic cracking of sample no. 7 (REY-30)

3. Calculate gasoline yield from the integration of area under the resulted chromatogram which retention time from initial to 9.4 minutes (C_{12} below).
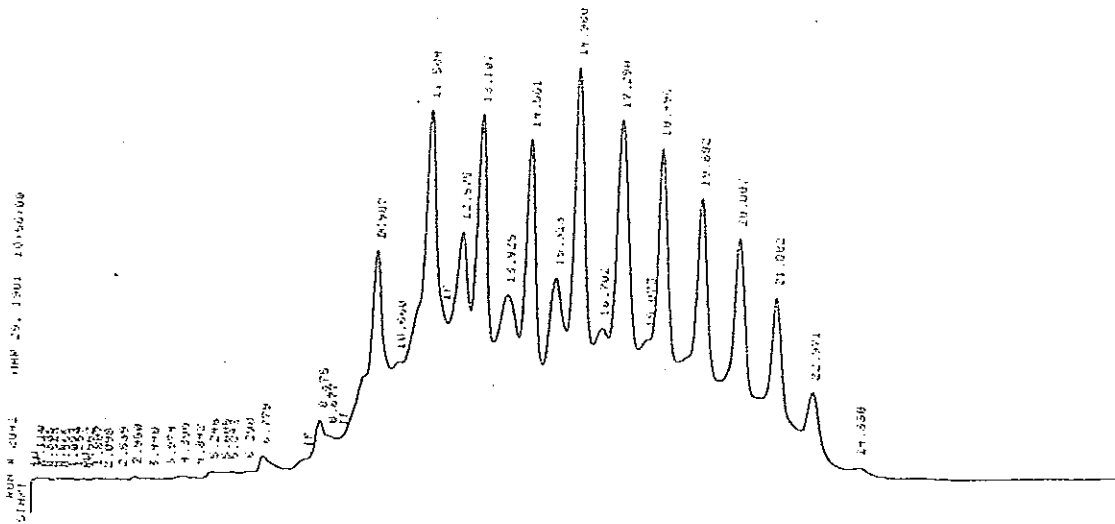
Figure B-6 Chromatogram of gas oil (LCO) before react with catalyst.
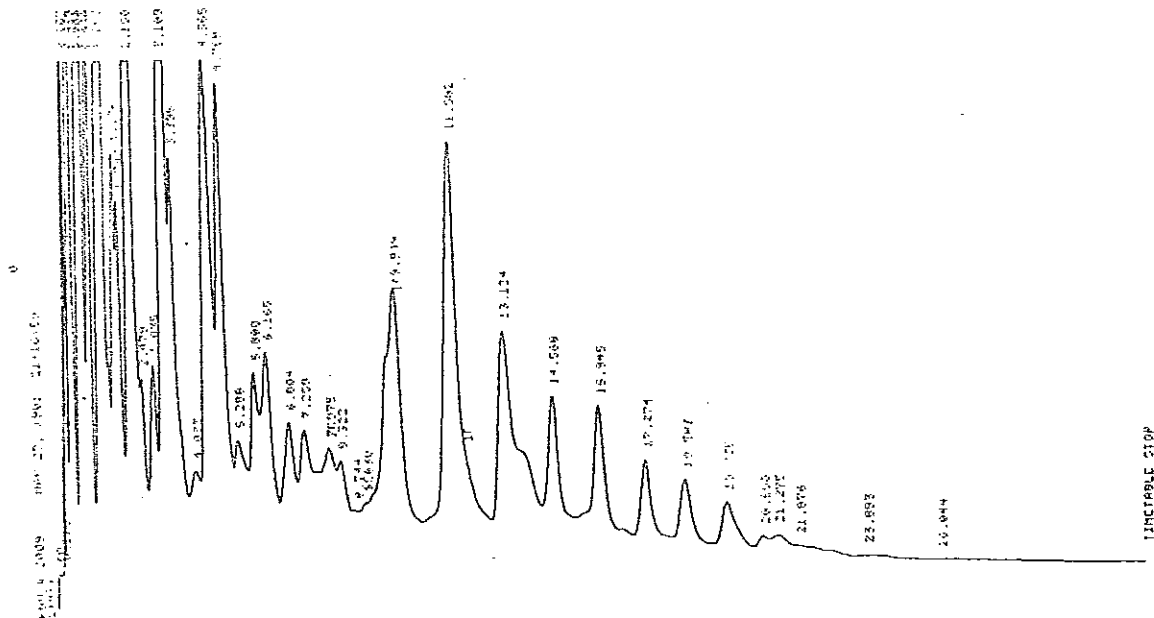
Figure B-7 Chromatogram of liquid after reacted with catalyst sample no. 7 (REY30)

4. Put the gasoline yield (gasoline area, %wt), liquid products yield in

program WSF-1D to calculate the microactivity.

| Test Date Operator	10-05-1998 Kritsana
Test Condition :	
Reaction Temp. (^{O}C)	460
Feeding Time (sec.)	70
Space Velocity Weight (h^{-1})	16
Feed oil (g)	1.56
Catalyst No.	A8.1
Reaction No.	2
Item :	
Feeding Time (sec.)	70
Reaction Temp. (^{O}C)	460.2
Catalyst Load (g)	5.004
Feed oil Quantity (g)	1.565
Liquid Product Weight :	
Oil and Receiver weight (g)	1.332
Receiver weight (g)	0
Oil weight (g)	1.332
Light oil yield	0.4823
Micro Activity	55.938
Average Value	55.938
Note	

Figure B-8 MAT operation report

Hydrothermal Deactivation (by CLY-1 Hydrothermal Aging Unit)

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). It 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, 6, 8, 12 17 (16) hrs. respectively.

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
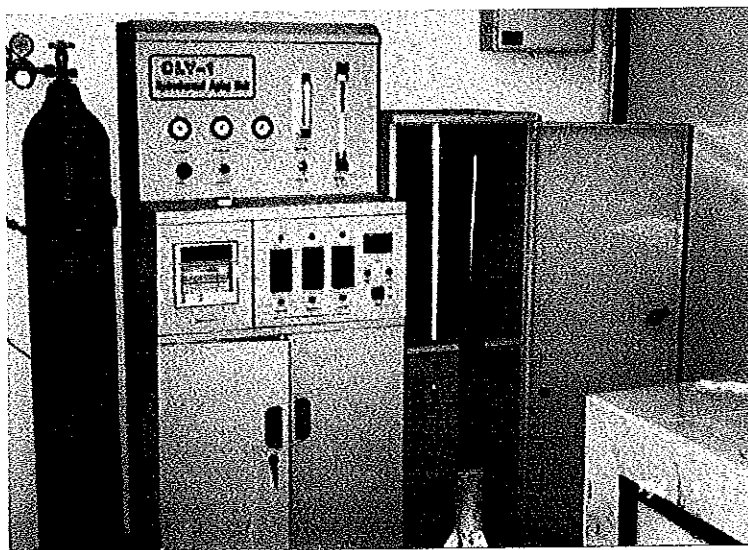
out the catalyst and separate it from porcelain rings.

Figure B-9 Hydrothermal aging unit

Diffraction Analysis by X-ray Diffractometer (XRD)

1. Relative Zeolite Diffraction Intensities

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 $110^{O}C$.

3. Hydrator maintained at 35% relative humidity by a saturated solution of salt, such as $CaCl_2.H_2O$.

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.

2. Place about 1.5 g of the sample in the drying oven at $110^{O}C$ for 1 h. 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 a 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:

   % XRD intensity/NaY = S_X/S_R

   where: S_X = sum of peak heights for the sample and

   S_R = sum for the 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
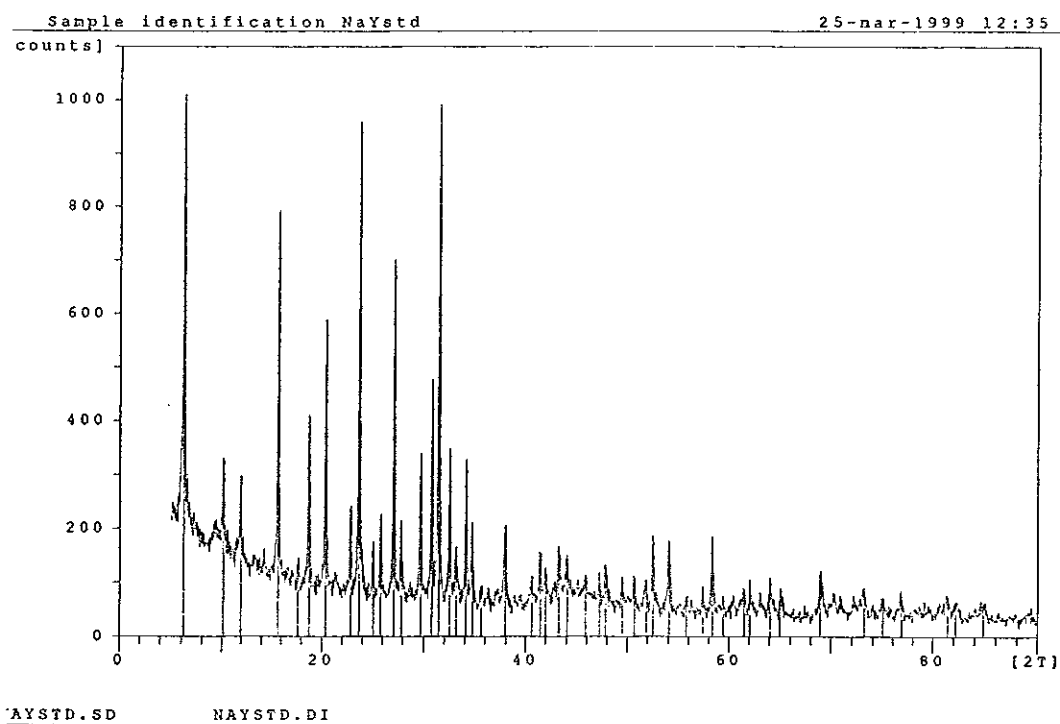
Figure B-10 X-Ray diffraction patterns of reference (standard) NaY zeolite.
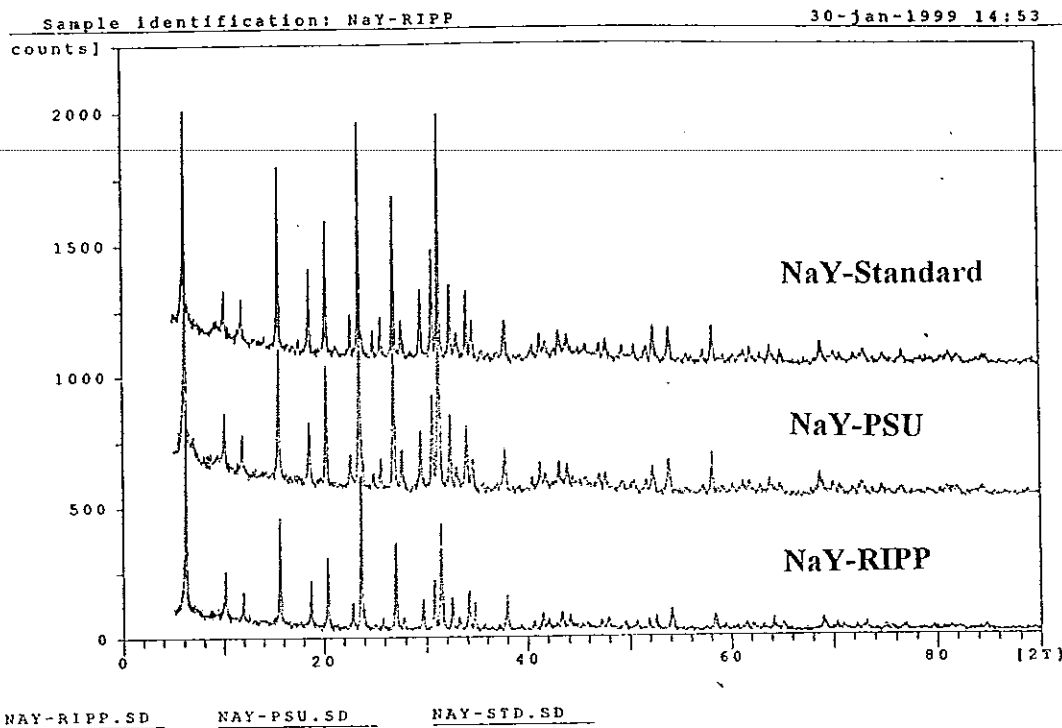
Figure B-11 Identification of NaY zeolite samples from this work.

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

At peak 533,

$$S_X \qquad = (0.14) \times (2746) \qquad = 384.44$$

$$S_R \qquad = (0.12) \times (3025) \qquad = 363$$

The relative crystallinity $= (384.44)/(363) \qquad = 1.059$

The sample crystallinity $=$ (relative crystallinity $\times$ % crystallinity of ref.)

$$= (1.059) \times (90)^* = 95.31\%$$

Note: The crystallinity of reference (standard) used is 90%.
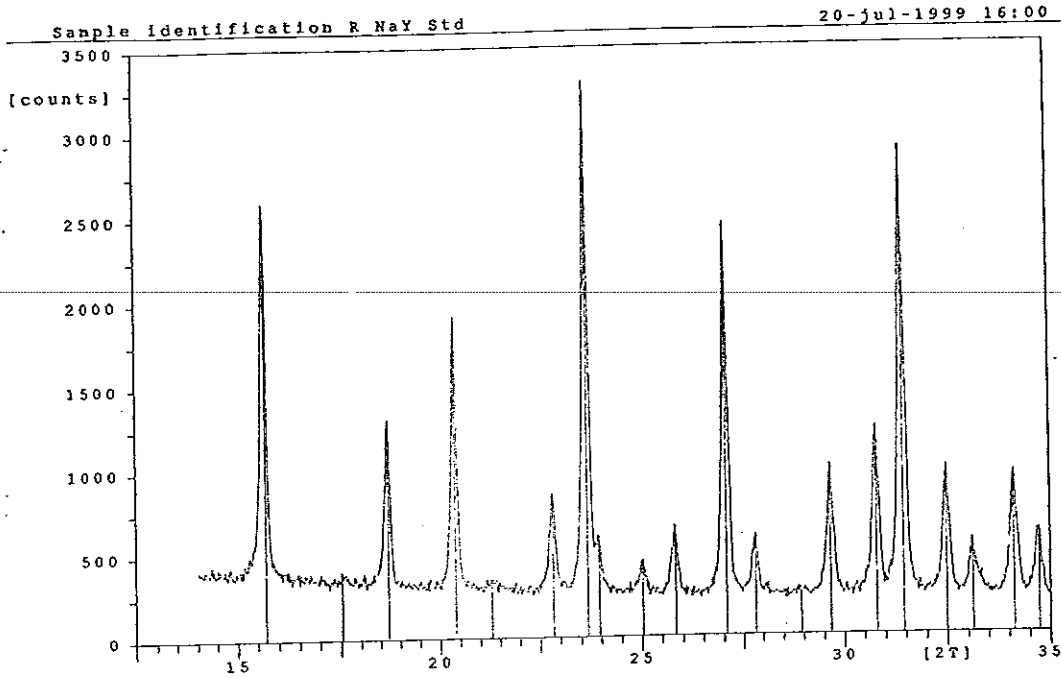
```
File: C:\APDW\DATA\R_NAYSTD.DI                    20-jul-1999 16:01
================================================================
Philips Analytical                      PC-APD, Diffraction software
```

```
DI FILE:

        Sample identification: R_NaY Std

                 DI file name: R_NAYSTD.
               Input file name: R_NAYSTD

             Start angle [°2q]: 14.010
               End angle [°2q]: 34.990
             Start d-value [Å]: 6.31621
               End d-value [Å]: 2.56235
        Maximum number of counts: 3025

                Anode material: Cu
            a1 Wavelength [Å]: 1.54060
            a2 Wavelength [Å]: 1.54439

    Intensities for FIXED slit

    Peak positions defined by: Minimum of 2nd derivative of peak
        Minimum peak tip width: 0.00
        Maximum peak tip width: 1.00
        Maximum peak base width: 2.00
          Minimum significance: 0.75
               Number of peaks: 20


    DIFFRACTION LINES:
```

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T.width [°2q]	Height [counts]	Backgr. [counts]	Rel.int. [%]	Signific
15.685	5.64527	5.65916	>0.100	2144	376	70.9	11.03
17.545	5.05077	5.06319	0.240	30	346	1.0	0.89
18.710	4.73882	4.75048	>0.120	986	328	32.6	9.72
20.390	4.35201	4.36271	>0.100	1608	306	53.2	8.55
21.305	4.16712	4.17737	0.240	40	296	1.3	1.20
22.825	3.89294	3.90251	0.140	529	282	17.5	7.91
23.675	3.75506	3.76430	<0.120	3025	276	100.0	16.67
23.960	3.71103	3.72016	0.060	313	276	10.4	2.19
25.025	3.55546	3.56421	0.140	182	266	6.0	3.58
25.830	3.44645	3.45493	0.080	388	262	12.8	1.56
27.075	3.29073	3.29883	>0.180	2200	253	72.7	33.16
27.810	3.20541	3.21329	0.180	357	246	11.8	8.34

(a) Diffraction data of reference NaY.

Figure B-12 The diffraction data for determination of the relative zeolite intensity.
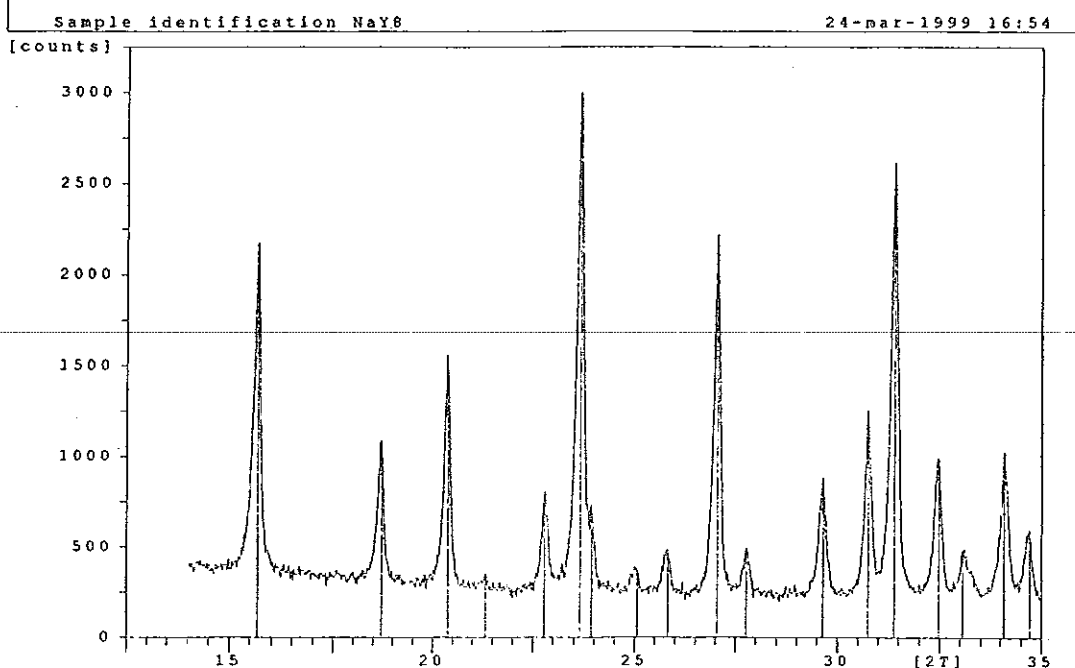
File: C:\APDW\DATA\R_NAY8.DI   24-mar-1999 16:56
===
Philips Analytical   PC-APD, Diffraction software

D I   F I L E :

       Sample identification: NaY8

              DI file name: R_NAY8.DI
            Input file name: NAY8

       Start angle [°2q]: 14.010
         End angle [°2q]: 34.990
      Start d-value [Å]: 6.31621
        End d-value [Å]: 2.56235
   Maximum number of counts: 2746

             Anode material: Cu
       a1 Wavelength [Å]: 1.54060
       a2 Wavelength [Å]: 1.54439

   Intensities for FIXED slit

   Peak positions defined by: Minimum of 2nd derivative of peak
       Minimum peak tip width: 0.00
       Maximum peak tip width: 1.00
       Maximum peak base width: 2.00
          Minimum significance: 0.75
             Number of peaks: 18

       D I F F R A C T I O N   L I N E S :

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T.width [°2q]	Height [counts]	Backgr. [counts]	Rel.int. [%]	Signific
15.665	5.65244	5.66634	0.120	1815	372	66.1	11.10
18.705	4.74007	4.75174	0.120	729	320	26.6	6.82
20.370	4.35623	4.36695	0.160	1149	292	41.9	16.55
21.315	4.16519	4.17543	0.120	64	276	2.3	1.14
22.775	3.90137	3.91097	0.140	462	259	16.8	5.76
23.645	3.75975	3.76900	0.140	2746	256	100.0	19.68
23.930	3.71562	3.72476	0.060	420	256	15.3	2.77
25.045	3.55267	3.56141	0.080	128	253	4.7	1.20
25.810	3.44908	3.45756	0.200	231	250	8.4	7.13
27.045	3.29431	3.30242	0.160	1980	243	72.1	22.09
27.755	3.21163	3.21953	0.120	253	243	9.2	2.60
29.635	3.01203	3.01944	0.160	645	240	23.5	8.94

===

(b) Diffraction data of NaY sampled from this work.

Figure B-12 The diffraction data for determination of the relative zeolite intensity

(continuation).

2. Determination of the Unit Cell Dimension of a Faujasite-type Zeolite

2.1 Apparatus and Reagents

1. X-ray diffractometer

   - Model X' Pert-MPD

   - Scan at 0.25 °2θ/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 ± 3°C

4. Silicon powder

2.2 Procedure

1. Place 1 g. of powdered catalyst sample the drying oven at 110°C for hr.

2. Blend 1 g. of powered 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 h. 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 53 to 60° 2θ

4. Measure the angle of the zeolite reflections at about 53.4° and 57.8° 2θ and that of the 56.1° 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 23.5, 26.9 and 31.2 and the silicon reflection at 28.443° 2θ

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

   $CuK\alpha_1$ radiation is measured, the calculated angle is 56.123°.

Note: The corresponding calculated angles when lower angle reflections must be used

is 28.443° 2θ $(CuK\alpha_1)$

2. 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 1.54060 Å for

   $CuK\alpha_1$ Note that the angle used in this calculation is

   only θ.

3. 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	($h^2 + k^2 + l^2$)
57.8°2θ	243
53.4°	211
31.2°	75
26.9°	56
23.5°	43

Note: Certain component of a catalyst matrix can interfere with individual peaks. For example, quartz may interfere with the reflection at 26.9° when interference occurs, other reflections should be used in the calculation.

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

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

Calculation

Degrees 2θ

Measured	Corrected	($h^2 + k^2 + l^2$)	(α, Å)
53.890	53.873	211	24.70
56.140	56.123	silicon	-
58.190	58.173	243	24.70
		Average	24.70

Note: the correction factor in the above calculation is {56.123 (standard diffraction angle of Si) – 56.14 (measured diffraction angle of Si) = - 0.017°} and is simply added to the measured angle of the two zeolite reflections.

Sample identification uh_NaY8   24-mar-1999 17:14
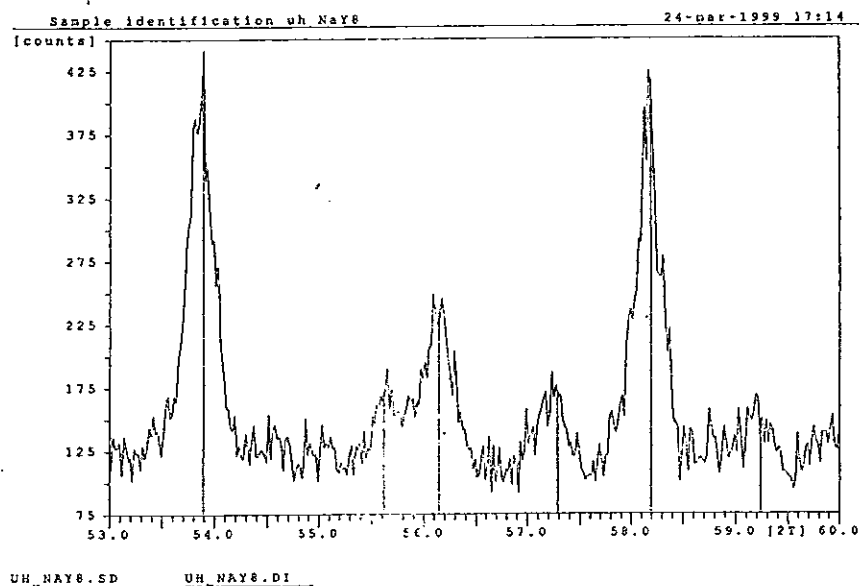
UH_NAY8.SD   UH_NAY8.DI

File: C:\APDW\DATA\UH_NAY8.DI   24-mar-1999 17:15

Philips Analytical   PC-APD, Diffraction software

    DI FILE:

        Sample identification: uh_NaY8

            DI file name: UH_NAY8.D
            Input file name: UH_NAY8

            Start angle [°2q]: 53.010
            End angle [°2q]: 59.990
            Start d-value [Å]: 1.72606
            End d-value [Å]: 1.54083
        Maximum number of counts: 320

            Anode material: Cu
            a1 Wavelength [Å]: 1.54060
            a2 Wavelength [Å]: 1.54439

        Intensities for FIXED slit

        Peak positions defined by: Minimum of 2nd derivative of peak
            Minimum peak tip width: 0.00
            Maximum peak tip width: 1.00
            Maximum peak base width: 2.00
            Minimum significance: 0.75
                Number of peaks: 6

        DIFFRACTION LINES:

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T.width [°2q]	Height [counts]	Backgr. [counts]	Rel.int. [%]	Signific
53.890	1.69993	1.70412	0.060	320	121	100.0	1.06
55.615	1.65122	1.65529	0.120	52	121	16.2	1.05
56.140	1.63702	1.64105	0.200	117	121	36.4	2.15
57.285	1.60699	1.61094	0.160	49	121	15.3	0.77
58.190	1.58413	1.58803	0.120	296	121	92.3	2.33
59.235	1.55866	1.56249	0.240	29	121	9.1	0.79

Figure B-13 Diffraction data of NaY sampled from this work.

Vitae

Name Kritsana Kritsanaphak

Birth Date June 9, 1975

Educational Attainment

Degree	Name of Institution	Year of Graduation
B.Eng. (Chem.)	Prince of Songkla University	1998

Scholarship Awards during Enrolment

- The scholarship support by the National Science and Technology Development Agency (NSTDA).

- The Teacher Assistantship support by the Graduate School.