Preparation and Characterization of REHY Zeolite

Rattana Liangsakul

Master of Engineering Thesis in Chemical Engineering

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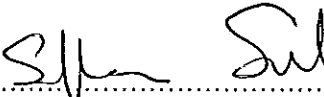
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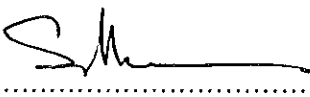
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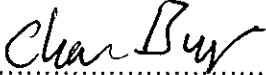
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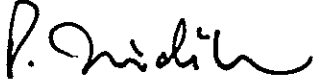|	
ชื่อวิทยานิพนธ์	การเตรียมและการหาลักษณะเฉพาะของตัวเร่งปฏิกิริยาแรร์เอิร์ท
	ไฮโดรเจนวายซีโอไลต์
ผู้เขียน	นายรัตน เลี้ยงสกุล
สาขาวิชา	วิศวกรรมเคมี
ปีการศึกษา	2543

บทคัดย่อ

แรร์เอิร์ทไฮโดรเจนวายซีโอไลต์ สามารถเตรียมได้ทั้งในสารละลาย (conventional) และสถานะของแข็ง (solid state) ในการศึกษาจะมุ่งเน้นปัจจัยที่ส่งผลกระทบต่อกระบวนการเตรียมซีโอไลต์ด้วยเทคนิคสารละลาย ซึ่งได้แก่ อุณหภูมิ, เวลา, พีเอช, ความเข้มข้นของเกลือแรร์เอิร์ท และ เกลือแอมโมเนี่ยม สำหรับในขั้นตอนการเผา (calcination) จะศึกษาอิทธิพลของ อุณหภูมิ และ เวลา รวมถึงจำนวนครั้งของการแลกเปลี่ยนไอออน สภาวะการเตรียมซีโอไลต์ที่เหมาะสมคือ อุณหภูมิ 100 องศาเซลเซียส, เวลา 1.5 ชั่วโมง, พีเอช 5, ความเข้มข้นของเกลือแรร์เอิร์ท และ เกลือแอมโมเนี่ยม เป็น 0.36 และ 0.5 โมลาร์ ตามลำดับ โดยขั้นตอนการเผาคือ อุณหภูมิ 550 องศาเซลเซียส, เวลา 2 ชั่วโมง และ จำนวนการแลกเปลี่ยนไอออน 2 ครั้ง จากสภาวะดังกล่าวสามารถเตรียมแรร์เอิร์ทไฮโดรเจนวายซีโอไลต์ที่มีลักษณะของความเป็นผลึก 29.30 % องค์ประกอบของโซเดียม และแรร์เอิร์ทในรูปออกไซด์ เป็น 0.94 % และ 11.07 % ตามลำดับ, เสถียรภาพเชิงความร้อนที่ 1,018 องศาเซลเซียส เมื่อนำแรร์เอิร์ทไฮโดรเจนวายซีโอไลต์ไปเตรียมเป็น ตัวเร่งปฏิกิริยาโดยผสมกับ pseudoboehmit (PBA) และ ดินขาว (kaolin clay) ในอัตราส่วนซีโอไลต์ 15 ส่วน, PBA 21 ส่วน และ ดินขาว 64 ส่วนโดยน้ำหนักแห้ง ตัวเร่งปฏิกิริยาที่เตรียมมีสมรรถนะใกล้เคียงกับตัวเร่งปฏิกิริยาในเชิงการค้า, โดยมีเปอร์เซ็นต์การเปลี่ยน (conversion) ของแก๊สออยล์มาตรฐาน อยู่ในช่วง 70 – 80 % และ เสถียรภาพเชิงความร้อนสูงกว่า 1,000 องศาเซลเซียส
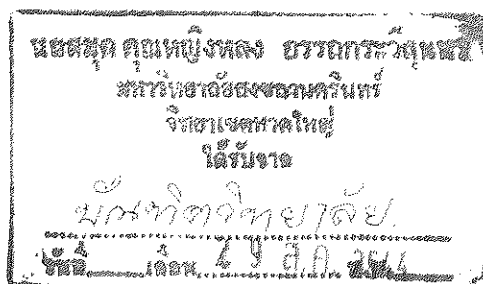
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Abstract

Rare earth hydrogen exchanged Y zeolite can be prepared by conventional and solid state ion exchange methods. In this study, the conventional ion exchange technique is focused on. There are many factors that can affect the conventional ion exchange process. These include temperature of solution, contacting time, pH, rare earth and ammonium salt concentration. In calcination step, factors such as temperature and time calcination for calcination also affect the process. Finally, the series of exchange also have a strong influence on the outcome. The conditions of interest are as followed: solution temperature of 100 °C, contacting time of 1.5 hours, pH of 5, rare earth and ammonium salt of 0.36, 0.5 M , respectively, calcination temperature of 550 °C, calcination time of 2 hours, number of exchange cycle of 2. The specific properties of prepared REHY zeolite are as followed: crystallinity 29.30%, Na_2O 0.94 wt%, RE_2O_3 11.07 wt%, thermal stability (DTA) 1018 °C. The REHY catalyst was prepared by mixing REHY with pseudoboehmite (PBA) and kaolin clay. The compositions of REHY catalysts are REHY zeolite 15 wt%, PBA 21 wt% and kaolin clay 64 wt%. Performance of prepared REHY catalysts is in the same level of the commercial one, having the conversion in the range of 70 – 80% and the thermal stability (DTA) above 1000 °C.

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Glossary

American Society of Testing and Material (ASTM) is the organization that develops analytical tests and procedure to facilitate commerce.

Beta Scission is splitting of the C-C bond two bonds away from the positively charged carbon atom.

Binder is the material used in the FCC catalyst to bind the matrix and zeolite components into a single homogeneous particle.

Catalyst Activity is the conversion of feed (gas oils) to gasoline, lighter products, and coke in the MAT laboratory.

Carbenium Ion is a positively charged $(R-CH_2^+)$ ion that is formed from a positive charge to an olefin and/or by removing a hydrogen and two electrons from a paraffin molecule.

Carbocation is a generic term for a positively charged carbon ion. Carbocation is further subdivided into carbenium and carbonium ions.

Cabonium Ion is a positively charged (CH_5^+) ion which is formed by adding hydrogen ion (H^+) to a paraffin.

Cat/Oil Ratio is the weight ratio of generated catalyst to the fresh feed in the riser feed injection

Coke is a hydrogen deficient residue left on the catalyst as a by-product of catalytic reactions.

Coke Factor is coke forming characteristics of the equilibrium catalyst relative to coke forming characteristics of a standard catalyst at the same conversion.

Coke Yield is the amount of coke the unit produces to stay in heat balance, usually expressed as percent of feed.

Conversion is often defined as the percentage of fresh feed cracked to gasoline, lighter products, and coke. Raw conversion is calculated by subtracting the volume or weight percent of the FCC products (based on fresh feed) heavier than gasoline from 100, or:

Conversion = 100 – (LCO + HCO + DO)   vol% or wt%

Cyclone is a centrifugal separator which collects and removes particulates from gases.

Equilibrium Catalyst (E-cat) is the regenerated catalyst circulating from the reactor to the regenerator.

Faujasite is a naturally occurring mineral, having a specific crystalline, alumina-silica structure, used in the manufacturing of the FCC catalyst. Zeolite faujasite is synthetic form of the mineral.

Filler is the inactive component of the FCC catalyst.

Fluid Catalytic cracking (FCC) is the primary conversion process in an integrated refinery. The FCC unit utilizes a microspherodial catalyst which fluidizes when properly aerate. The main purpose of the unit is to convert high boiling petroleum fractions called gas oil to high value, high octane gasoline and heating oil.

Free radical is an uncharged molecule formed in the initial step of thermal cracking. Free radicals are very reactive and shot lived.

Gas Factor is the hydrogen and lighter gas producing (C_1-C_4) characteristics of the equilibrium catalyst relative to the hydrogen and lighter gas producing characteristics of some standard catalyst at the same catalyst.

Hydrogen Y (HY) is one kind of Y zeolites that can be prepared by ion exchanging with ammonium salt.

Hydrogen Transfer is the secondary reaction that converts olefins (predominately iso olefins) into paraffins while extracting hydrogen from larger, more hydrogen deficiency molecules.

Matrix is a substrate in which the zeolite is imbedded in the cracking catalyst. Matrix is often used as a term for the active, non zeolitic component of the FCC catalyst.

Methyl Tertiary Butyl Ether (MTBE) is an ether added to gasoline to improve its octane and reduce air pollution.

Microactivity Test (MAT) is a small, packed bed catalytic cracking test that measures activity and selectivity of a feedstock catalyst combination.

Molecular Sieve is a term applied to zeolite. Zeolite exhibits shape selectivity and hydrocarbon absorptions.

Motor Octane Number (MON) is a quantitative measure of a fuel to knocking simulating the fuel's performance under severe operating conditions (at 900 rpm and at 300 °F).

Particle Size Distribution (PSD) is the particle size fractions of the FCC catalyst expressed as percent through a given sized hold.

Rare Earth is a generic name used for the 14 metallic elements of the lanthanide series used in the manufacturing of FCC catalyst to improve stability, activity, and gasoline selectivity of the zeolite.

Rare earth Y (REY) is one kind of Y zeolites that can be prepared by ion exchanging with only rare earth salt.

Calcined Rare Earth (CREY) is the REY.

Rare Earth Hydrogen Exchanged Y (REHY) is one kind of Y zeolites that can be prepared by ion exchanging with rare earth and ammonium salts.

Resid refers to a process, such as resid catalytic cracking, that upgrades residual oil.

Residue is the residual material from the processing of raw crude (for example, vacuum residue and not vacuum resid).

Research Octane Number (MON) is a quantitative measure of a fuel to knocking simulating the fuel's performance under low engine severity (at 600 rpm and 120 °F).

Selectivity is the ratio of yield to conversion for the desired products.

Silica Oxide to Alumina Oxide Ratio (SAR) is used to described the framework composition of zeolite.

Soda Y Zeolite is a crystallized form of Y faujasite before any ion exchange occur.

Spent Catalyst is the coke laden catalyst in the stripper.

Ultra Stable Y (USY) is a hydrothermally treated Y faujasite which has a unit cell size at or below 24.50 Å and exhibit superior hydrothermal stability over Soda Y faujasite.

Unit Cell Sized (UCS) is an indirect measure of active sites and SAR in the zeolite.

Zeolite is a synthetic crystalline alumina silicate material used in the manufacturing of FCC catalyst.

CHAPTER 1

INTRODUCTION

1.1 Introduction

In terms of product value and catalyst usage (over 500 t/day), fluid catalytic cracking is still the most important unit operation of the petroleum industry and remain the main process of large scale gasoline production even fifty seven years after its introduction. Today, more than 370 fluid catalytic cracking units are used worldwide generating capacity to produce in excess of 460 million gallon of gasoline a day. Environmental laws, politic events, oil supply and costs together with technological breakthroughs have and will continue to influence catalyst development and evolution. The HY type zeolite used in Fluid Catalytic Cracking (FCC) preparation was prepared to contain rare earth to achieve the required hydrothermal stability desired by refiners. In addition, the demand for olefins-rich gasoline is focusing attention also on new FCC compositions in which acidity can be manipulated to generate materials with a low hydrogen transfer index (Occelli and Ritz).

The development of FCC catalyst has made a powerful influence both technically and commercially on the catalytic cracking of zeolite. An important advance in this application was ion exchanged by rare earth and ammonium salt. These salts can increase, not only cracking activity, but also gasoline yield since they enhance hydrogen transfer. Hybrid rare earth exchanged high silica faujasite catalyst has recently become available, such as HY, REY, USY, REHY. However, HY zeolite is less thermally stable than others. Although the USY zeolites have better selectivity than other zeolites, its microactivity is less than REY and REHY zeolite. Unfortunately REY zeolite has too high a conversion rate so that its dry gas and coke yield are too high. REHY zeolite is an alternative choice for cracking hydrocarbon, because it has, not only good thermal stability but also lower coke and dry gas. The typical Fluid Catalytic Cracking (FCC) catalyst comprises of Y zeolite dispersed in catalyst from 15 – 25 wt.%.

The research area is to prepare rare earth hydrogen Y zeolite by conventional and solid state ion exchange. The preparation techniques included understanding of literature reviews, and further by experiments and RIPP 's techniques.

1.2 Objectives

1. To prepare rare earth hydrogen Y zeolite catalyst.

2. To study the characteristics of prepared rare earth hydrogen Y zeolite.

3. To evaluate performance of prepared rare earth hydrogen Y zeolite by microactivity test (MAT).

1.3 Literature Reviews

1.3.1 Zeolite

Zeolite, or more properly, faujasite, is the key ingredient of the FCC catalyst. Its role in the catalyst is to provide product selectivity and much of the catalytic activity. The catalyst performance depends largely on the nature and quality of the zeolite. Understanding the zeolite structure types, cracking mechanism, and properties are essential in choosing the " right " catalyst to produce the desired yield.

1.3.1.1 Zeolite structure

Zeolite are a well defined class of crystalline naturally occurring aluminosilicate minerals. They are three dimentional arising from a framework of $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$ coordination polyhedra (Figure 1-1).
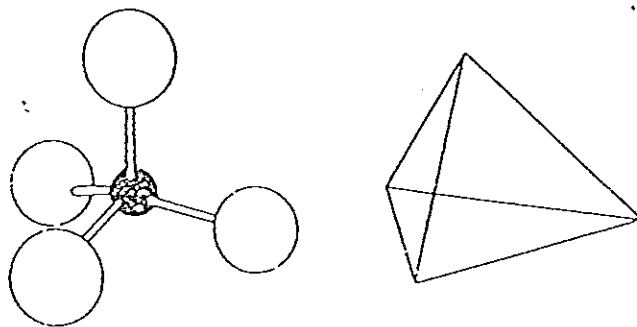
Figure 1-1 Representations of $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$ tetrahedra

From: Dryer, 1988:1

Its basic building block are silica and alumina tetrahedra. Each tetrahedron consists of aluminum atom at the center of tetrahedron, with an oxygen atom at the corner. The elementary building block of zeolite is called a unit cell. These basic building blocks combine at their oxygen atoms to form a cage structure that has well defined pores of a specific diameter. The unit cell size (UCS) is the distance between the repeating cell in the zeolite structure. One unit cell in a typical fresh Y – zeolite lattice contain 192 framework atomic positions: 55 atom of aluminum and 137 atom of silicon. This corresponds to a silica (SiO_2) to alumina (Al_2O_3) molal ratio (SAR) of 5. The unit cell size (UCS) is an important parameter in characterizing the zeolite structure.

The zeolite lattice has an organized network of very small pores. The pore diameter of nearly all of today 's FCC zeolite is approximately 8.0 angstroms (Å). These small openings, with an internal surface area of roughly 600 square meters per gram, do not readily admit hydrocarbon molecules with a molecular diameter greater than 8.0 Å to 10 Å (Sadeghbeigi, 1995).

The structure of Y zeolites consist of a negatively charged, three dimensional framework of SiO_4 and AlO_4 tetrahedra, joined to form an array of truncated octahedra. These truncated octahedra (β-cages or sodalite cages) are joined at the octahedral faces by hexagonal prisms resulting in tetrahedral stacking. This type of stacking creates large cavities (α-cages or supercages) with a diameter of about 13 Å. The

supercages can be entered through any of four tetrahedrally distributed openings (12-membered rings), each the opening has a diameter of 7.4 Å. The supercages connected through 12-membered rings to form the large pore system of the zeolite (Figure 1-2).
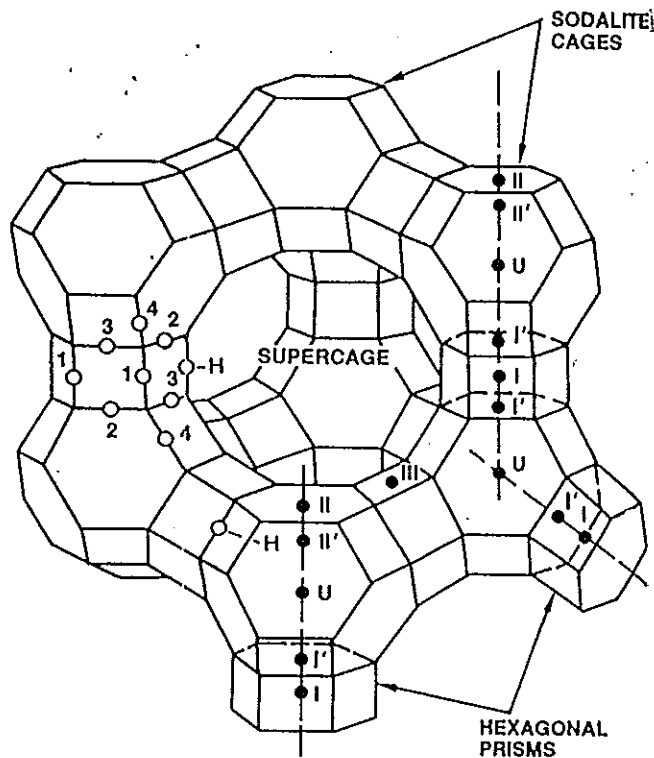
Figure 1-2 Faujasite framework showing oxygen type (o), nonframework locations (•), and Bronsted acid sites.

From Scherzer, 1989:232

The structure comprises also a small pore system. It made up of sodalite cages and the connecting hexagonal prisms. The six membered rings of sodalite cages have a diameter of about 2.4 Å.

1.3.1.2 Zeolite chemistry

A typical zeolite consist of silicon and aluminum atoms that are tetrahedrally joined by four oxygen atoms. Silicon is in a +4 oxidation state, therefore, a tetrahedral

containing silicon is neutral in charge. In contrast, aluminum is in a +3 oxidation state. This indicates that each tetrahedron containing aluminum atom has a net charge of −1 which must be balanced by a positive ion. This ionic site accounts for the catalytic activity of zeolite.

Solutions containing sodium hydroxide are commonly used in synthesizing the zeolite. The sodium ion is used to balance the negative charge of aluminum tetrahedral. 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 the sodium content. Upon drying the zeolite, ammonium is vaporized . The resulting acid site are both the Bronsted and Lewis type. The Bronsted acid site can be further exchanged with rare earth material such as cerium and lantheium to enhance their strengths. The zeolite come from these acid sites.

1.3.1.3 Zeolite type

Zeolite employed in the manufacture of the FCC catalyst are a synthetic version of naturally occurring zeolite called faujasites. There are about 40 known natural zeolite and over 150 zeolite which have been synthesized. Of this number, only a few have found commercial application. Table 1-1 shows properties of the major synthetic zeolite.

Table 1-1 Properties of the major synthetic zeolite

From : Sadeghbeigi, 1995: 82

Zeolite	Pore size Dimension (Å)	Silica to Alumina ratio	Process
Zeolite A	4.1	2 – 5	Detergent manufacturing.
Faujasite	7.4	3 - 6	Catalytic cracking and hydrocracking.
ZSM – 5	5.2 x 5.8	30 – 200	Xylene isomerization, Benzene alkylation, Catalytic cracking.
Mordenite	6.7 x 7.0	10 – 12	Hydro – isomerization, Dewaxing.

The zeolite with application to FCC are Type X, Type Y, and ZSM – 5 .Both X and Y have essentially the same crystalline structure. The major difference is that the X zeolite has a lower silica to alumina ratio than the Y zeolite. The X zeolite also has a lower thermal and hydrothermal stability than Y zeolite. Some of the earlier FCC zeolite catalysts contained X zeolite, However, virtually all of today 's catalyst contain y zeolite or variations thereof (Figure 1-3).
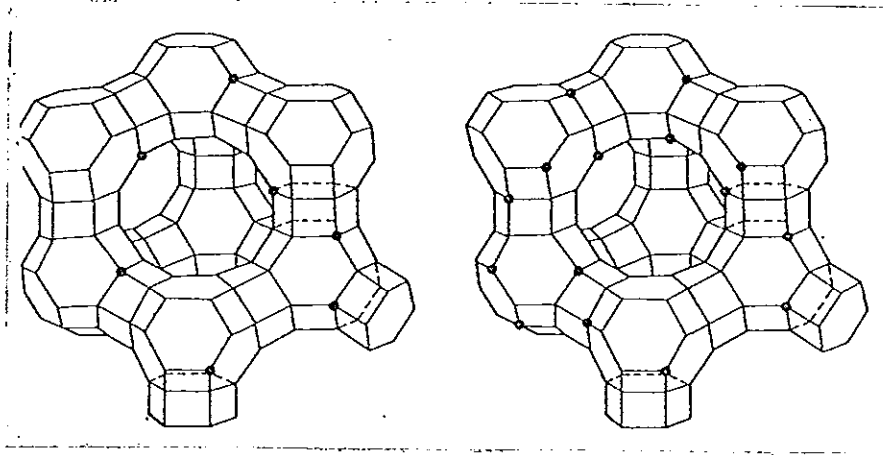
USY Zeolite (~7 Al Atoms/ u.c.)   Equilibrium REY (~23 Al Atoms/u.c.)

Unit Cell Dimension = 24.25 Å   Unit Cell Dimension = 24.25 Å

$(SiO_2/Al_2O_3 = 54)$ $(SiO_2/Al_2O_3 = 15)$

Figure 1-3 Geometry of USY and REY zeolite

From: Sadegbeigi, 1995:83

Until the 1970s, the NaY zeolite was mostly exchanged with rare earth component such as lanthanum and cerium which were used to replace sodium in the crystal. The rare - earth element, being trivalent, simply formed a " bridge" between two ro three acid sites in the zeolite framework. The bridging basically protects the acid site from being ejected from the framework and thus stabilizes the zeolite structure. Consequently, the rare earth exchange adds to the zeolite activity and thermal and hydrothermal stability.

The reaction of lead in motor gasoline in 1986 created the need for a higher FCC gasoline octane. Catalyst manufacturers responded by adjusting the zeolite formulations, an alteration that involved expelling a number of aluminum atom from the zeolite framework. The removal of aluminum increased silica oxide to alumina oxide ratio

(SAR), reduced unit cell size (UCS), and in the process, lowered the sodium level of the zeolite. These aluminum – deficient zeolite called Ultrastable Y, or USY, or simply USY, because of its higher stability than the conventional Y.

1.3.1.4 Zeolite property

The properties of the zeolite play a significant role in the overall performance of the catalyst, and familiarity with these properties increases our ability to predict catalyst response to continual changes in unit operation. From its inception in the catalyst plant. The zeolite must withstand and retain its catalytic properties under the hostile conditions of the FCC operation. The reactor/regenerator environment can cause significant changes in the chemical and structural composition of the zeolite. In the regenerator, for instance, the zeolite is subjected to thermal and hydrothermal treatments. The zeolite must also retain its crystallinity against feedstock contaminate such as vanadium and sodium.

Various analytical test can be carried out to determine zeolite properties. These tests should supply information about the strength, type, number, and distribution of acid sites. Additional tests can also provide information about surface area and pore size distribution. The three most common parameters governing zeolite behavior are as follow:

A. Unit Cell Size

B. Rare Earth Level

C. Sodium Content

A. Unit Cell Size (UCS) is a measure of aluminum site or the total potential acidity per unit cell. The negatively charged aluminum atoms are a source of active site in the zeolite. Silicon atoms do not posses any activity. The UCS is related to the number of aluminum atoms per cell (N_{Al}) by

$$N_{Al} = 111 \times (UCS - 24.215)$$

The number of silicon atoms (N_{Si}) is: $N_{Si} = 192 - N_{Al}$

The SAR of the zeolite can be determined either from the above two equations or from a correlation such as the one shown in figure1-4.
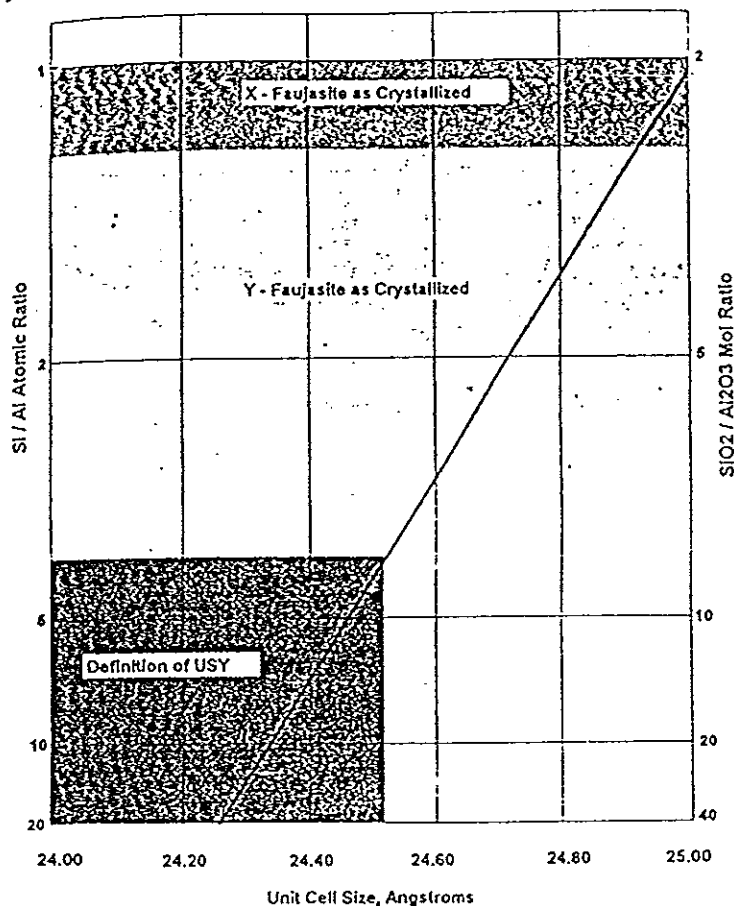
Figure 1-4 Silica – alumina ratio versus zeolite unit cell size

From: Sadeghbeigi, 1995:85

The key property of the zeolite is the unit cell size. This is the length of the smallest repeating unit in the crystal structure. The aluminum – oxygen bonds are longer than the silicon – oxygen bond. Thus, as the number of aluminum atoms in the crystal increase, the unit cell size increases. Since the aluminum atoms form the catalytically active site in the zeolite crystal, a higher unit cell size also indicates a higher activity .

In addition to the activity effect, increase unit cell size indicates the aluminum atoms, and thus the acid sites are closer together in the crystal. This means that bimolecular reactions such as hydrogen transfer are more likely to occur on a high unit cell site zeolite (Wilson, 1997).

The unit cell size (UCS) was also an indicator of zeolite acidity, because the aluminum ion was larger than the silicon ion, as the UCS decreases, the acid site become further apart. The strength of the acid site is determined by the extent of their isolation from the neighboring acid site. The close proximity of these acid sites causes destabilization of zeolite structure. Acid distribution of the zeolite is a fundamental factor affecting zeolite activity and selectivity. Additionally, the UCS presents fewer active site per unit cell size. The fewer acid site are farther apart and therefore inhibit hydrogen transfer reactions, which in turn increase gasoline octane as well as production of C_3 hydrocarbon and lighter components (figure 1-5). The octane increase is due to a higher concentration of olefins in the gasoline.
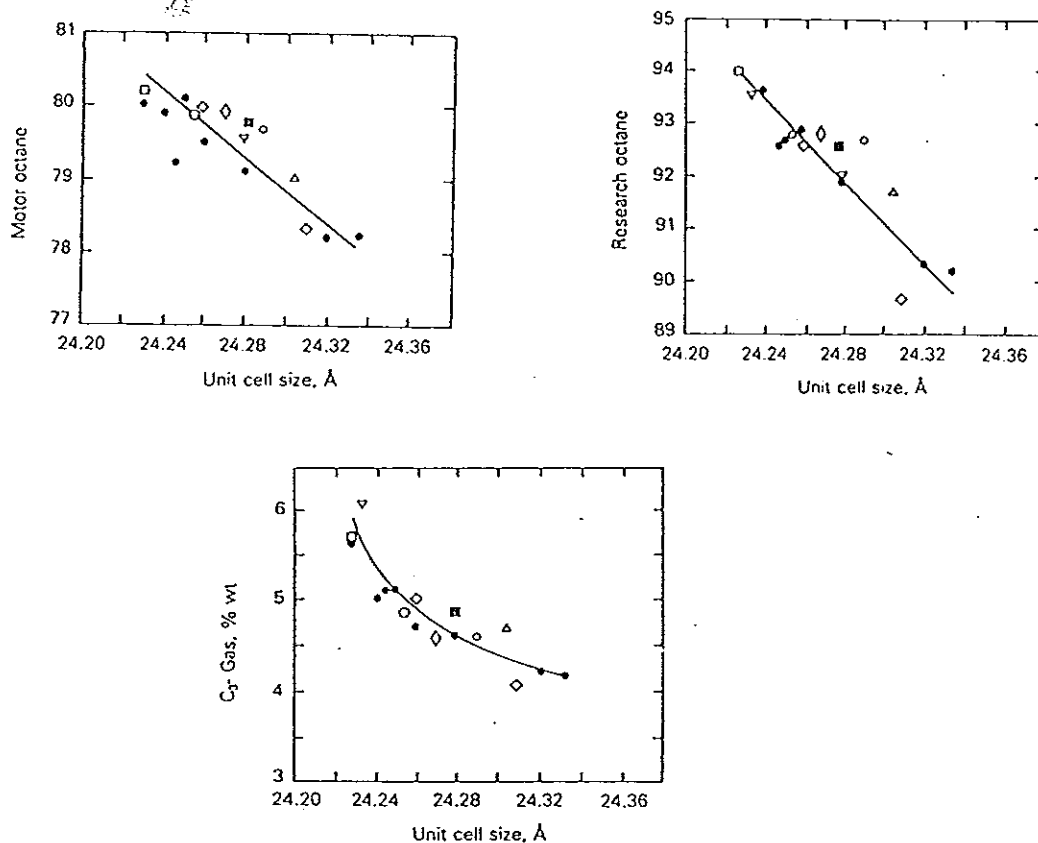
Figure 1-5 Effect of unit cell size on octane and C_3^- gas production

From: Radeghbeigi, 1995: 86

Microactivity vs. Time
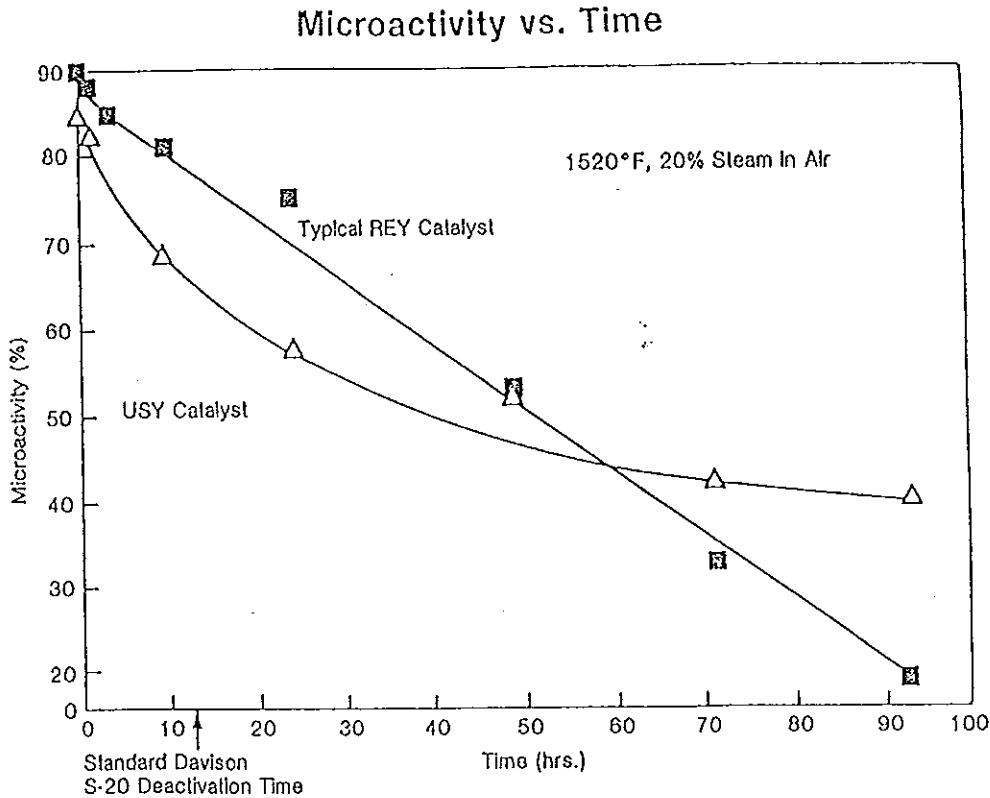
Figure 1-6 Comparison of activity retention between rare earth exchanged zeolite versus

USY zeolite

From: Radeghbeigi, 1995: 87

Zeolite with lower unit cell size (UCS) are initially less active than conventional rare earth exchanged zeolite (figure 1-6). However the lower UCS zeolite tend to retain a greater fraction of their activity under severe thermal and hydrothermal treatments, hence the name Ultrastable Y (USY).

A freshly manufactured zeolite has a relatively high unit cell size (UCS) in the range of 24.50 Å to 24.75 Å. The thermal and hydrothermal environmental of the regenerator extracts alumina from the zeolite structure and therefore reduces its UCS. The final unit cell size (UCS) level depend on the rare earth and sodium level of the zeolite. The lower the sodium and rare earth content of the fresh zeolite, the lower unit cell size (UCS) of the equilibrium catalyst (E-cat.).
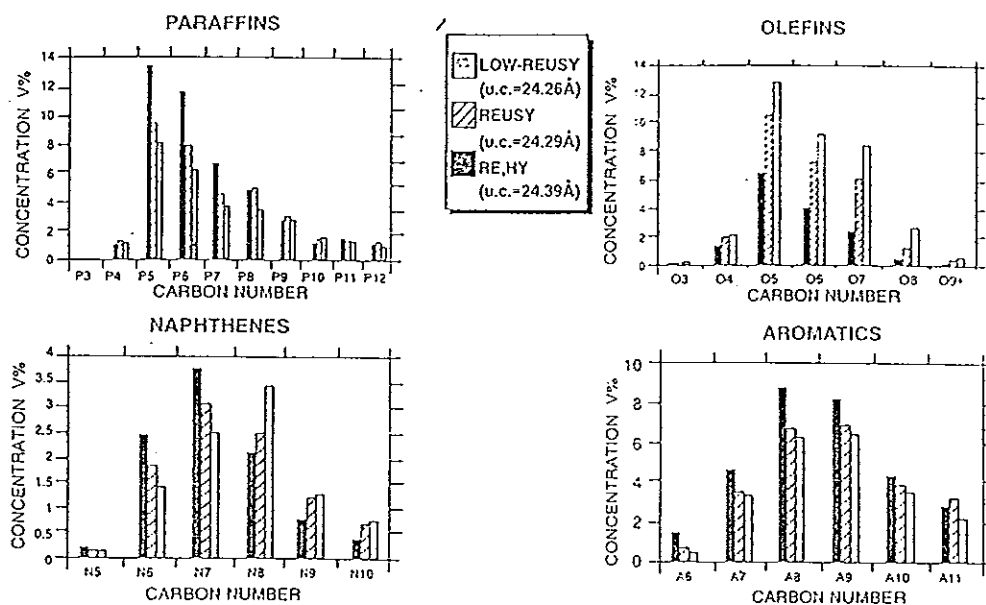
Figure 1-7 Effect of zeolite unit cell size on PONA distribution in FCC gasoline.

Conversion: 70V%, RT=527 °C; pilot plant data.

From: Magee, 1993: 160

The effect of unit cell size on hydrocarbon distribution in FCC gasoline is shown in more detail in figure 1-7. Among paraffins and olefins, the C_5 molecules have the highest concentration, regardless of the unit cell size. As the number of carbon atoms per molecule increases, the concentration of paraffins and olefins decrease. The concentration of paraffins with the same carbon number increases with increasing zeolite unit cell size, while that of olefins decreases. Among aromatics, C_8 and C_9 molecules have the highest concentration, regardless of unit cell size. The concentration of aromatics with the same carbon number generally increase with increasing unit cell size.

B. Rare Earth Level. Rare earth element serve as a bridge to stabilize aluminum atoms in the zeolite structure. They prevent the aluminum atom from separating from the zeolite lattice when the catalyst is exposed to high temperature steam in the regenerator. A fully rare earth exchanged zeolite equilibrates at a high

UCS, whereas a non rare zeolite zeolite equilibrates at a very low UCS in the range of 24.25 (Upson, 1981). All intermediate level of rare earth exchanged zeolite can be produced.
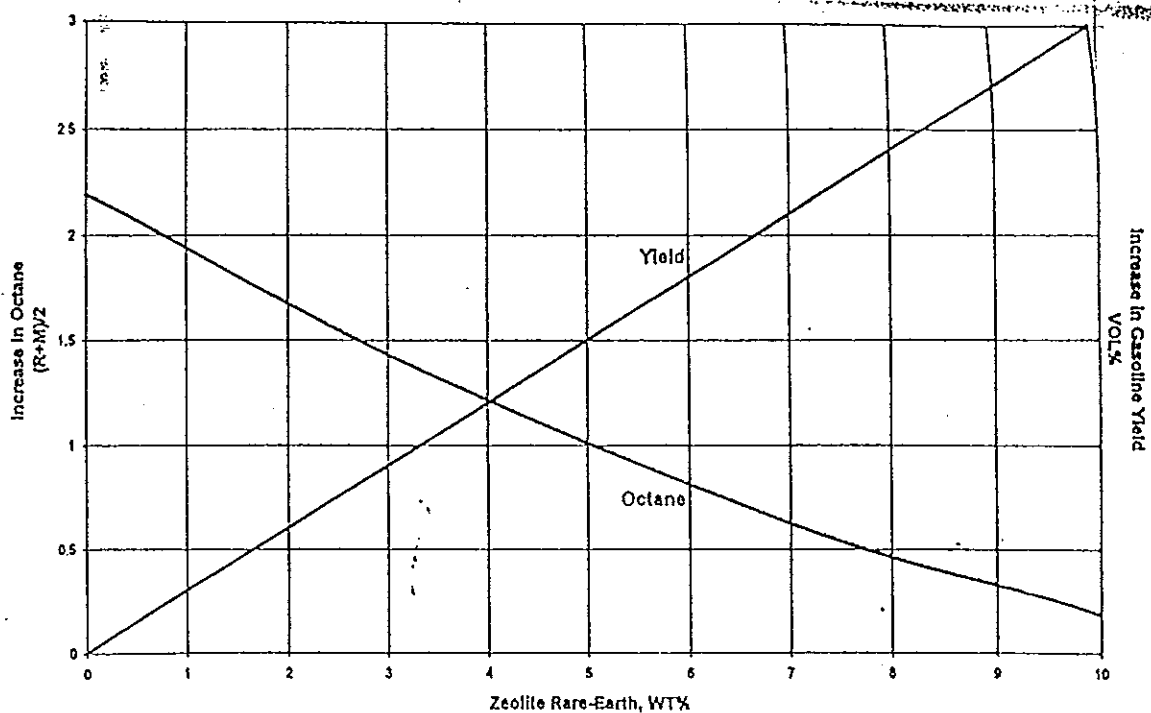
Figure 1-8 Effect of rare earth on gasoline octane and yield

From: Sadeghbigi, 1995: 89

The rare earth increases zeolite activity and gasoline selectivity with a loss in octane (figure 1-8). The octane loss is due to promotion of hydrogen transfer reaction. The insertion of rare earth maintains more and closer acid site, which promotes hydrogen transfer reactions. In additions, rare earth improves thermal and hydrothermal stability of the zeolite. To improve the activity of a USY zeolite, and suppliers frequently and some rare earth to the zeolite.

C. Sodium content. The sodium on the catalyst orginates either from zeolite during its manufacture or from the FCC feedstock. It is important for the fresh zeolite to contain a very low amount of sodium. Sodium decreases the hydrothermal stability of the zeolite. It also reacts with the zeolite acid site to reduce the catalyst activity. In the

zeolite. It also reacts with the zeolite acid site to reduce the catalyst activity. In the regenerator, sodium is mobile. Sodium ions tend to neutralize the strongest acid site. In a dealuminated zeolite where the UCS is low (24.22 Å to 24.25 Å), the sodium can have an adverse effect on the gasoline octane (figure1-9).
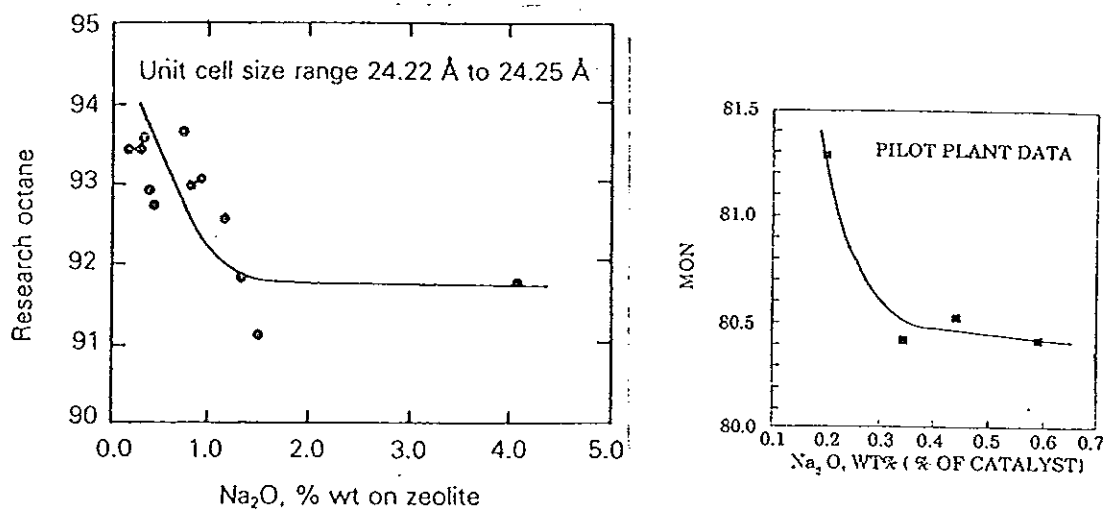
Figure 1-9 Effect of a soda motor and research octanes

From: Sadeghbigi, 1995: 90

The loss of octane is attributed to the drop in the number of strong acid site. FCC catalyst vendors are now able to manufacture a catalyst with a sodium content of less than 0.2 wt%. Sodium is commonly reported as the weight percentage of sodium or soda (Na_2O) on catalyst. The proper way to compare sodium fraction of sodium in the zeolite. This is because FCC catalyst have different zeolite concentrations.

UCS, rare earth, and sodium are just three of the parameter that are readily available to characterize the zeolite properties. They provide valuable informational tests that can be conducted to examine other zeolite properties.

1.3.1.5 Matrix

The term "matrix" has different meaning to different people. For some, "matrix" refers to components of catalysts other than the zeolite. For others, matrix is a component of the catalyst aside from zeolite having catalyst activity. Yet for others, matrix refers to the catalyst binder. In this report "matrix" means components of the catalyst other than zeolite and the term "active matrix" means the component of the catalyst other than zeolite having catalyst activity.

Alumina is the source for an active matrix. Most active matrix used in FCC catalysts are amorphous. However, some of the catalyst suppliers incorporate a form of alumina that also has a crystalline structure. The active matrix contributes significantly to the overall performance of the FCC catalyst the zeolite. The zeolite pores are not suitable for the cracking of the large hydrocarbon molecules generally having and end point >900 $^{\circ}$F; they are too small to allow diffusion of large molecule to the cracking sites. An effective matrix must have a porous structure to allow diffusion of hydrocarbons into and out of the catalyst.

An active matrix provides the primary cracking site. The acid sites located in the catalyst matrix are not as selective as the zeolite but are able to crack larger molecules that are hindered from entering the small zeolite pores. The active matrix precracks heavy feed molecules for further cracking at the internal zeolite sites. The result is a synergistic interaction between matrix and zeolite in which the activity attained by their combined effect, can be greater than the sum of their individual effect. An active matrix can also serve as a trap to catch some of vanadium and basic nitrogen. The high boiling fraction of the FCC feed usually contains metals and basic nitrogen that poison the zeolite. One of the advantages of an active matrix is that it guards the zeolite from becoming deactivated prematurely by these impurities.

1.3.1.6 Filler and Binder

The filler is a clay incorporated into the catalyst to dilute its activity. Kaolin [$Al_2(OH)_2Si_2O_5$] is the most common clay used in the FCC catalyst. Manufacturer uses kaolin clay as a skeleton to grow the zeolite in situ.

The binder serves as a glue to hold the zeolite, the matrix, and the filler together. The binder may or may not have catalytic activity. The importance of the binder becomes more prominent with a catalyst that contains a high concentration of zeolite.

The function of the filler and binder are to provide physical integrity (density), attrition resistance, particle size distribution, etc.), a heat transfer medium, and a fluidizing medium in which the more important and expensive zeolite component is incorporated.

1.3.1.7 Fresh Catalyst Property

With each shipment of fresh catalyst the supplier typically mail refiners an inspection report that contains data on the catalyst 's physical and chemical properties. This data is valuable and should be monitored closely to ensure that the catalyst received meet the agreed specifications. A number of refiners independently analyze random sample of the fresh catalyst to confirm the reported properties. In addition, quarterly review of the fresh catalyst properties with the vendor will ensure that the control targets are being achieved. The particle size distribution (PSD), the sodium (Na), the rare earth (RE), and the surface area (SA), are some of the parameters in the inspection sheet that require close attention.

1.3.1.7.1 Particle Size Distribution (PSD) of Catalyst

The PSD is an indicator of the fluidization properties of the catalyst. In general, fluidization improve as the fraction of the 0-40 micron particles is increases; however, a higher percentage of 0-40 micron particle will also result in greater catalyst loss. The fluidization characteristic of an FCC catalyst depend largely on the unit 's mechanical configuration. The percent of less than 40 microns in the circulating inventory is

a function of cyclone efficiency. In units with good catalyst circulation, it may be economical to minimize the fraction of less than 40 microns particles. This is because after a few cycles, most of the 40 microns will escape the unit via the cyclones.

The catalyst manufacturers control PSD of the fresh catalyst mainly through the spray drying cycle. In the spray dryer, the catalyst slurry must be atomized effectively to achieve proper distribution. As illustrated in figure 1-10.
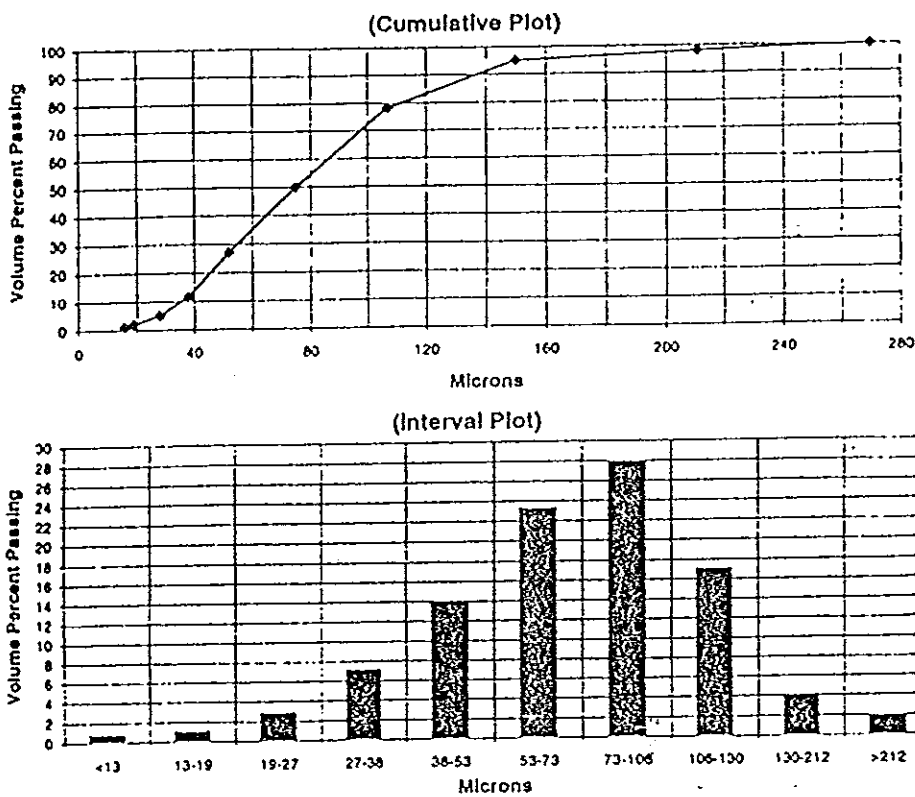
Figure 1-10 Particle size distribution of a typical FCC catalyst.

From: Sadeghbigi, 1995: 96

The PSD does not have a normal distribution shape. The average particle size (APS) is not actually the average size of the catalyst particles but rather the median value.

1.3.1.7.2 Surface Area (SA), m^2/g

The reported surface area is the combined surface area of zeolite and matrix. In zeolite manufacturing, the measurement of the zeolite surface area is one of the procedures used by catalyst suppliers to control quality. The surface area is commonly determined by the amount of nitrogen adsorbed by the catalyst.

1.3.1.7.3 Sodium (Na$_2$O), wt%

Sodium plays an intrinsic part in the manufacturing of the FCC catalyst. Its detrimental effects are well known, and because it deactivates the zeolite and reduces the gasoline octane, every effect should be made to minimize the amount of sodium in the fresh catalyst. The catalyst inspection sheet expresses sodium or soda (Na$_2$O) as the weight percent on the catalyst. When comparing different grades of catalyst, it is more practical to express the sodium content of the zeolite.

1.3.1.7.4 Rare earth (RE), wt %

Rare earth is a generic name for 14 metallic elements of lanthanide series. These elements have similar chemical properties and are usually supplied as a oxides exacted from ores such as bastnaesite or monazite.
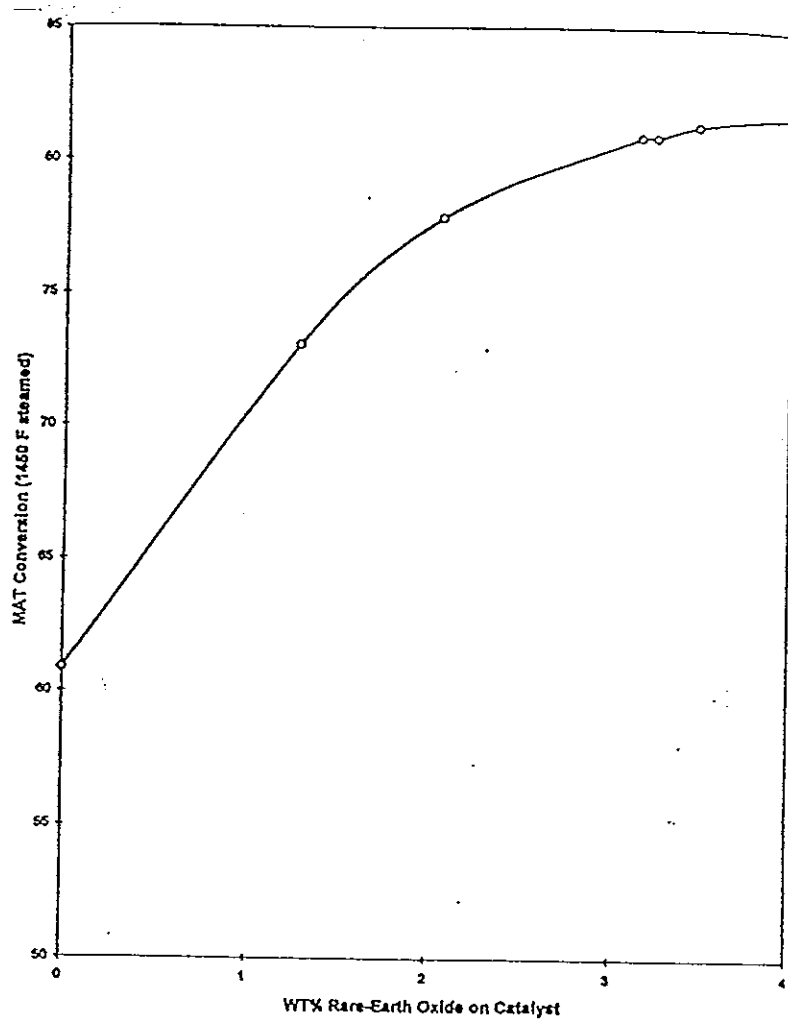
Figure 1-11 Effect of rare earth on catalyst activity.

From: Sadeghbeigi, 1995: 98

Rare earth improves the catalyst activity (figure 1-11) and hydrothermal stability. Catalysts can have a wide range of rare earth levels depending on the refiner 's objectives. Similar to sodium, the inspection sheet shows rare earth (RE) or rare earth oxide (RE_2O_3) as the weight percent of the catalyst. Again, when comparing different catalysts, the concentration of RE of the zeolite should be used.

1.3.1.8 Composition and classification of FCC catalyst

The commercial FCC catalyst can be broadly classified in three categories: (1) gasoline FCC catalysts, (2) octane FCC catalysts and (3) resid FCC catalysts. Gasoline catalysts are used when the major objective is to maximize gasoline yields.

Octane catalysts are used when the objective is to gasoline octane or octane barrels (the product between gasoline yield and octane number). Resid catalysts are used to crack resid feedstocks.

```
                        ┌─────────────────────────┐
                        │  Gasoline FCC Catalyst  │
                        └─────────────────────────┘
              ┌──────────────────┴───────────────────────┐
   ┌──────────────────────┐              ┌─────────────────────────┐
   │ Zeolite Component:   │              │     Matrix Component    │
   │                      │              └─────────────────────────┘
   │ Large pore FAU       │            ┌──────────────┴──────────────┐
   │ (Ø ~ 8 Å)            │     ┌──────────────┐          ┌──────────────┐
   └──────────────────────┘     │  Synthetic   │          │   Natural    │
                                └──────────────┘          └──────────────┘
```

● REHY (10 – 13%RE_2O_3)   ● SiO_2 ● Clay

● REY (%RE_2O_3 > 13)   ● Al_2O_3 ● Modified Clay

● (REX)   ● $SiO_2 - Al_2O_3$
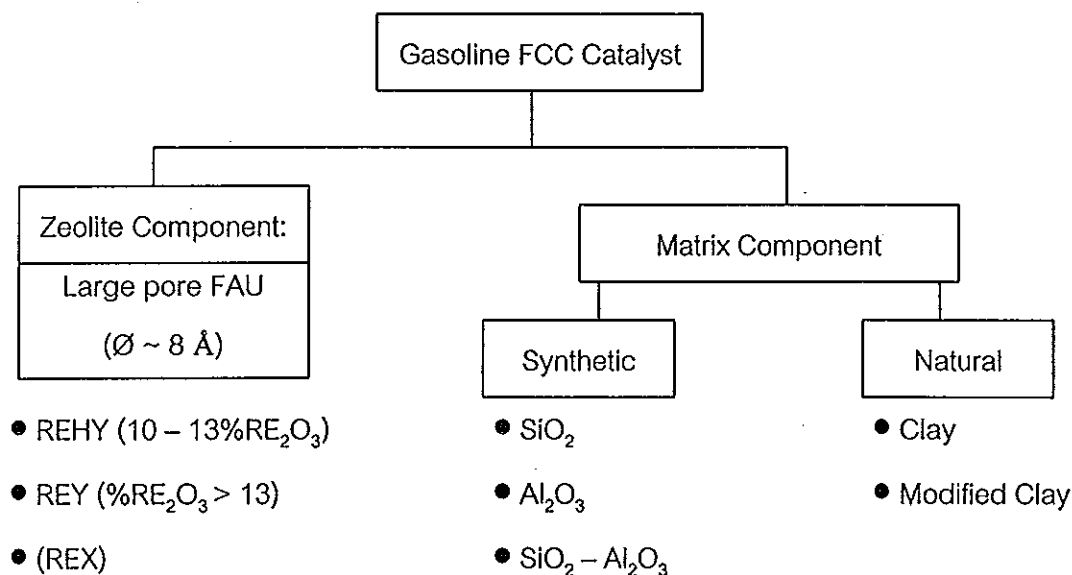
Figure 1- 12 Composition of gasoline FCC catalyst.

```
                        ┌─────────────────────────┐
                        │   Octane FCC Catalyst   │
                        └─────────────────────────┘
              ┌──────────────────┴───────────────────────┐
   ┌──────────────────────┐              ┌─────────────────────────┐
   │  Zeolite Component   │              │     Matrix Component    │
   └──────────────────────┘              └─────────────────────────┘
        ┌──────────┴──────────────┐          ┌──────────┴──────────┐
┌──────────────┐  ┌─────────────────────┐ ┌──────────┐     ┌──────────┐
│ Large Pore   │  │ Medium and Small Pore│ │ Synthetic│     │ Natural  │
│ (Ø ~ 8 Å)    │  │ (Additive)(Ø <6 Å    │ └──────────┘     └──────────┘
└──────────────┘  └─────────────────────┘
```

● HSY(RE or H - Form)   ● ZSM – 5   ● SiO_2 ● Clay

● REHY   ● ZSM – 11   ● Al_2O_3 ● Modified Clay

                          ● SAPO – 11   ● $SiO_2 - Al_2O_3$

                          ● et.al.
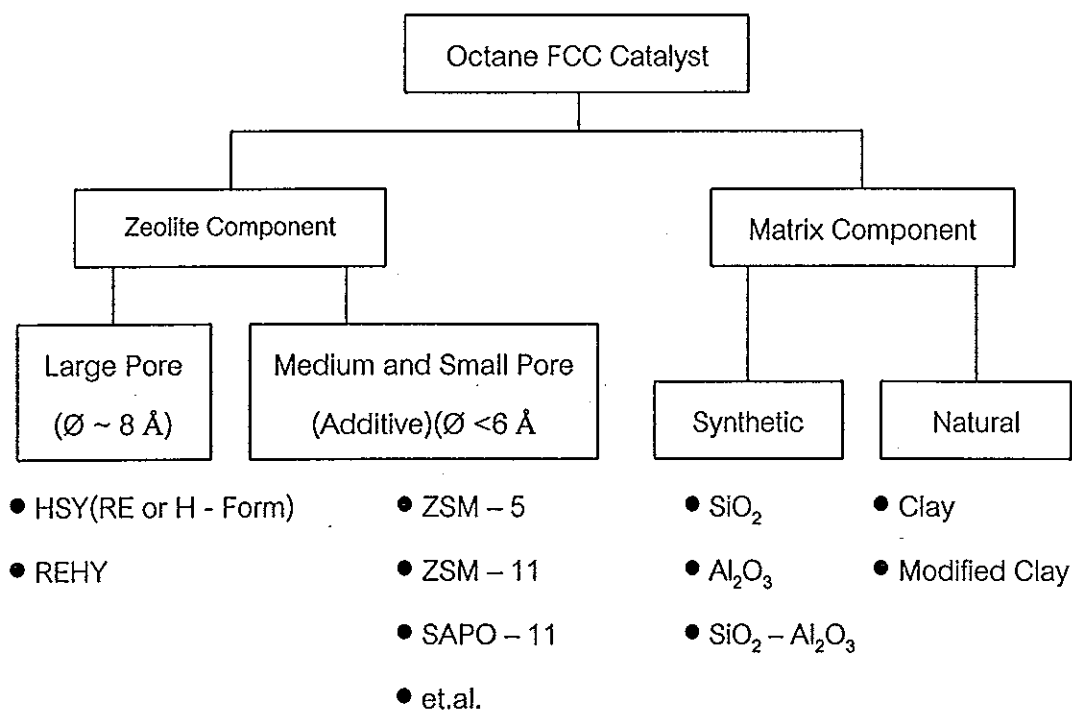
Figure 1-13 Composition of octane FCC Catalyst.
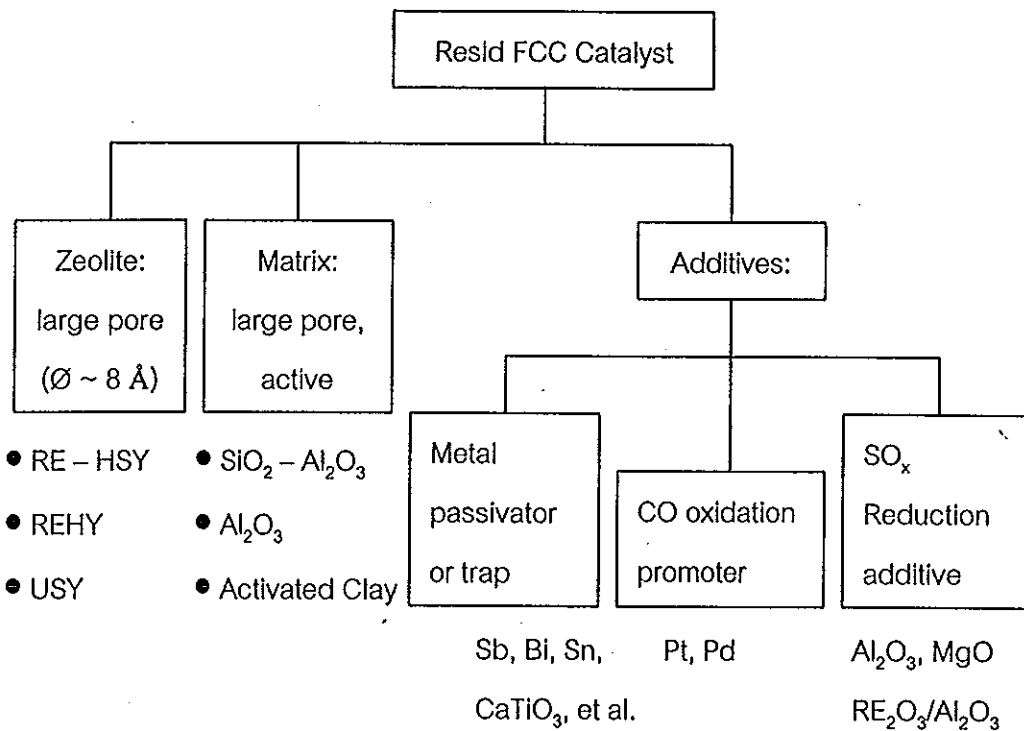
Figure 1-14 Composition of resid catalyst.

From: Magee, 1993: 148

The composition of these categories of catalyst is shown in figure 1-12, 1-13 and 1-14. The zeolite component of the gasoline catalysts is commonly a rare earth, hydrogen Y zeolite (REHY), with a rare earth content of between 10 to 13 percent RE_2O_3. Such zeolites will give high gasoline yields. The matrix usually plays a minor catalytic role in these catalysts and is therefore catalytically inactive (e.g., silica/clay matrix) or of moderate activity.

Octane catalysts contain mostly high – silica Y zeolite in rare earth or hydrogen exchanged form. They can also contain rare earth, hydrogen Y (REHY) zeolites with a lower rare earth content (RE_2O_3<10%), Furthermore, an octane – boosting additive, such as ZSM – 5 zeolite, is sometimes presents in such catalyst. The matrix is catalytically active and usually contains amorphous alumina or silica – alumina, in addition to clay.

Resid catalysts usually contain zeolites similar to those present in octane catalyst: rare earth exchange, high - silica Y and rare earth, hydrogen Y zeolites. The rare earth content of these zeolites is often high. The catalysts contain a large pore, active matrix, in which the active component is amorphous alumina, silica – alumina and, in some instances, modified clay. Furthermore, such catalysts contain metal passivators or traps, SO_x abatement additives and CO combustion promoters. The metal passivators, additive and combustion promoters are generally blended with the FCC catalyst, often by the refiner himself (Magee, 1993).

1.3.1.9 Catalyst Properties

Catalyst properties are determined by a micro activity test (MAT). A sample of the decoke equilibrium catalyst is placed in a laboratory reactor, a typical FCC feed is passed over the catalyst at cracking condition and the result is analyzed.

1.3.1.9.1 Activity

The value reported as activity is the conversion achieved in the MAT laboratory test. Because of this conversion is obtained on a decoke sample at standard test conditions, and any change in activity is due to catalyst change.

In a commercial operation, sometimes it is difficult to determine the reason for a change in unit conversion. It can be due to a change in processing conditions, change in feed quality, or change in catalyst characteristics. The MAT activity data allows the refiner to separate the catalyst effect from the process and feed effect, when they evaluate unit performance. In Katalistiks laboratory (Upson, 1981) they run each sample in duplicate and sometime in triplecate. The 95% confidence level of their MAT activity value is still ±1.5 number. Thus, it always takes at least two consecutive samples to establish confidence that the activity changes represent a real trend.

A change in catalyst activity should produce a corresponding change in the conversion of the commercial unit, providing such things as reactor temperature and feed quality remain constant. Normally, unit conversion will not change (as much) the MAT activity value much. As a general rule, the expected change in unit conversion will

be produce about 80 – 90% of change in MAT activity. Yet many factor can influence the MAT activity value. Catalyst makeup rate: For a typical unit with an average catalyst makeup rate of 1% per day, doubling the catalyst makeup rate would be expected to increase the MAT activity value 4 – 6 numbers.

Catalyst poisoning: By other contamination, particularly sodium, which can cause significant loss in activity. Sodium acts as a fluxing agent for alumina, reducing the melting point of the catalyst structure. Normal regenerator temperatures are then significantly higher to melt the contaminate part of the catalyst, destroying both sieve and matrix. Hydrothermal deactivation: Regenerator catalyst activity by the combined action of steam and high temperature. This process is known as hydrothermal deactivation.

1.3.1.9.2 Catalyst Selectivity

Catalyst selectivity normally shows in the form of a Coke Factor (CF), a Gas Factor (GF), and a H_2/CH_4. The CF and GF represent the coke and gas forming tendencies of an equilibrium catalyst (E-cat) compare to a standard steam aged catalyst sample at the same conversion. The CF and GF are influenced by the type of fresh catalyst and the level of metal decomposition on the equilibrium catalyst (E – cat). Both the coke and gas factors can be indicative of the dehydrogenation activity of the metal on the catalyst. The addition of alumina to the catalyst will tend to increase the nonselective cracking which forms coke and gas. The cracking selectivity of different Y zeolite and of active matrix is shown in table 1-2.

Table 1-2 Cracking selectivity of different Y zeolite and of active matrix

From: Magee, 1993: 62

	USY	REUSY	REHY	REY	Active Matrix
Unit cell size	← degrease				
Framework	← increase				
RE content	← decrease				
Dry yield	Low	Low	Low	Low	High
C_3/C_4 yield	High	Moder.	Moder.	Low	High
C_3/C_4 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

1.3.1.9.3 Active Site

Most industrial applications of zeolite are base upon technology adapted from the acid silica alumina catalyst originally developed for the cracking reaction. This means that the activity required is base upon the production of Bronsted site arising from the creation 'hydroxyl' within the zeolite pore structure. These hydroxyls are usually formed either by ammonium or polyvalent cation exchange followed by a calcination, viz (Dryer, 1988: 121) :

Ammonium ion exchange

$$NaZ(s) + NH_4^+(s) \longrightarrow NH_4Z(s) + Na^+(aq)$$

$$NH_4Z(s) \longrightarrow NH_3(g) + HZ(s)$$
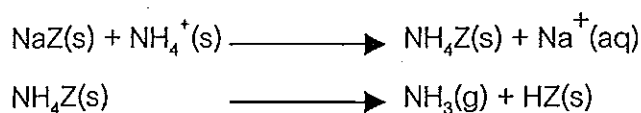
Polyvalent ion exchange

$$NaZ(s) + M(H_2O)^{n+} \longrightarrow M(H_2O)^{n+}Z(s) + nNa^+(aq) \qquad ; 1 \leq n \geq 4$$

$$M(H_2O)^{n+}Z(s) \longrightarrow MOH^{(n-1)}(s) + HZ(s) \qquad ; M \equiv Metal$$
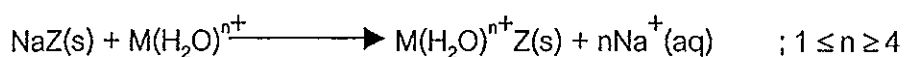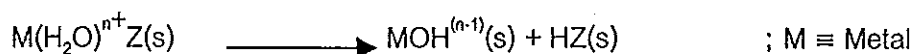
The tetrahedrally coordinated atoms in the zeolite framework each carry a negative charge. The compensate cations, however, are not of the structural and are located in several different sites throughout the pores and cavities of the zeolite. Cation occupancy in zeolite Y is confined to the small (sodalite) cage and hexagonal prism. They are easily exchanged by contacting the solid zeolite with a solution of ammonium and / or rare earth salts and this is the key to changing the acidity of the active site of the material. An obvious goal for zeolite Y is to substitute protons for sodium ions. This cannot be easily achieved directly, however, since acidic solution effects the removal of aluminium ion from the zeolite and from the framework through hydrolysis and the structure collapses. A relatively easy route to HY, is shown in figure 1–15.
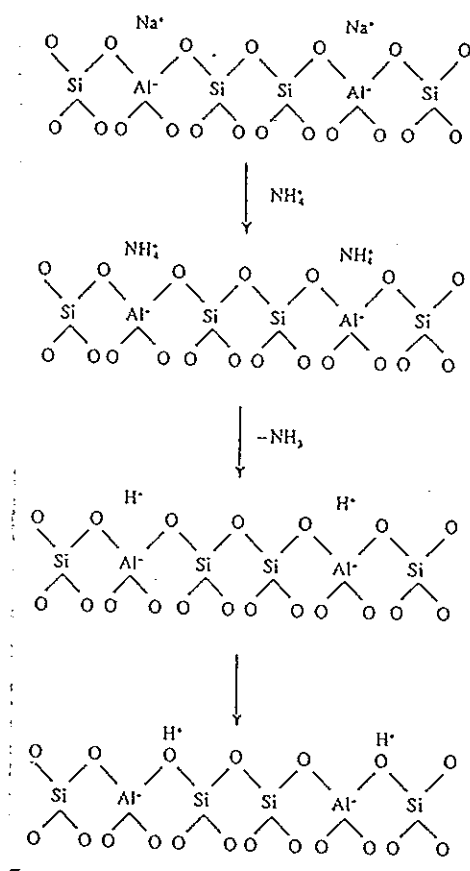
Figure 1–15 Formation of Bronsted Acid Sites.

Involves treatment with ammonium salts followed by calcination above 600 °F

the NH_4^+ ion is exchanged into NH_3 gas and H^+ the structure. The proton bonds with

oxygen atoms in the lattice to form – OH group. In this form, HY zeolite has the ability to

transfer a proton to adsorb hydrocarbon and the active site is known as Bronsted acid

site. In addition to direct proton exchange and the calcination of ammnium exchanged Y

zeolite, Bronsted acidity can also be introduced by the hydrolysis of ion exchanged

polyvalent cation, followed by partial dehydration. For example, a Y zeolite in this native

sodium form can be treated with a commercial rare earth salt solution (typical a mixture

of lanthanum, cerium, neodymium and praseodimium chloride) to replace most of

sodium ion, with polyvalent rare earth ions. The highly charged rare earth ions quickly

hydrolyze, creating acid sites as shown below

$$\cdot La^{3+} \quad + \quad H_2O \quad \longrightarrow \quad La(OH)^{2+} \quad + \quad H^+$$

$$La(OH)^{2+} \quad + \quad H_2O \quad \longrightarrow \quad La(OH)_2^+ \quad + \quad H^+$$
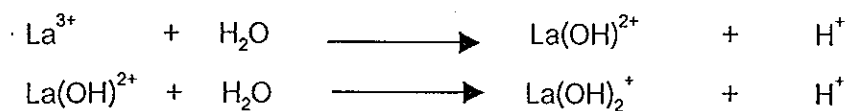
The rare earth hydroxy ions occupy site in the zeolite framework that increase

the thermal and hydrothermal stability. Bronsted acid sites formed by any of these

methods can be further dehydroxylated at temperatures in excess of about 750 °F to

form Lewis acid sites as shown in figure 1-16
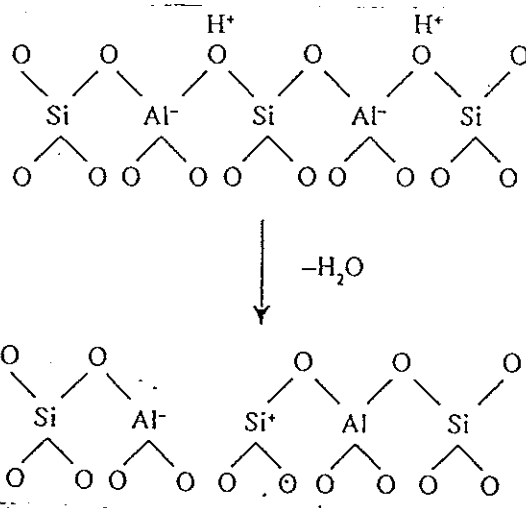
Figure 1-16 Formation of Lewis acid site

From: Magee, 1993: 47

Lewis acid site have the ability to accept an electron pair from an adsorb hydrocarbon to create a carbon (e.g. via hydride abstraction). The concept of Lewis acid sites readily formation donor – acceptor complex with, for example, H^+, is the basis of Lewis site characterization as well as dehydrogenation reaction with paraffins. The elimination of water by dehydroxylation should lead to the creation of a Lewis acid site from every two Bronsted acid sites. Nevertheless, the number of Bronsted acid sites converted to Lewis site increases with temperature up to 1500 °F, when only the latter remain see figure 1 -17
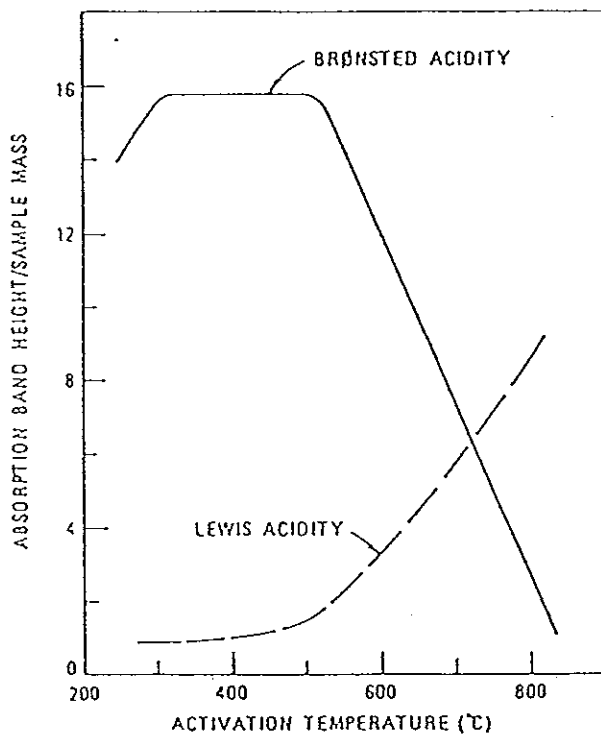
Figure 1-17 Relation Between Bronsted and Lewis acid sites as Measured by Pyridine Adsorption.

However, if the calcination temperature is kept below 1100 °F most of the Lewis acid site can be rehydrated to restore the Bronsted sites. Factors influencing the acid properties of zeolite include the method of preparation, temperature of dehydration and the silica to alummina ratio and distribution of framework atoms. For example,

the strength of the Lewis sites created via the procedure described above is higher than that of the Bronsted sites.

Correlation between the acidity of a zeolite and its catalytic properties is a difficult task. However, three factors are important here : the total number of acid sites, the ratio of Bronsted to Lewis sites, and the acid strength distribution (and density) of each type of site. For Y zeolite, a maximum in strong acid site and cracking activity occurs at silica to alumina ratios (SAR) from 7 to 15. In contrast, for ZSM – 5,hexane cracking ability increases linearly with increased aluminium content, leading to the conclusion that the maximum in acidity is a function not only of the zeolite structure but also the surrounding of the individual aluminum atoms in the framework.

The concept of "Next Nearest Neighbors" was proposed in order to provide a reasonable estimate of the acidic behavior of zeolite. The acid strength of the zeolite was related to the distribution of aluminium atoms in framework. Each framework atom (Si or Al) in the zeolite is in the tetrahedral coordination with oxygen and each aluminium atom has four silicon atoms as "Nearest Neighbors", this is Lowenstein 's Rule. The four silicon sites in zeolite Y are connected to nine other framework atom sites and these are the "Next Nearest Neighbor"(figure 1-18).

the nine Next Nearest Neighbours (NNN) of an aluminium atom, Al.

— oxygen bridges.
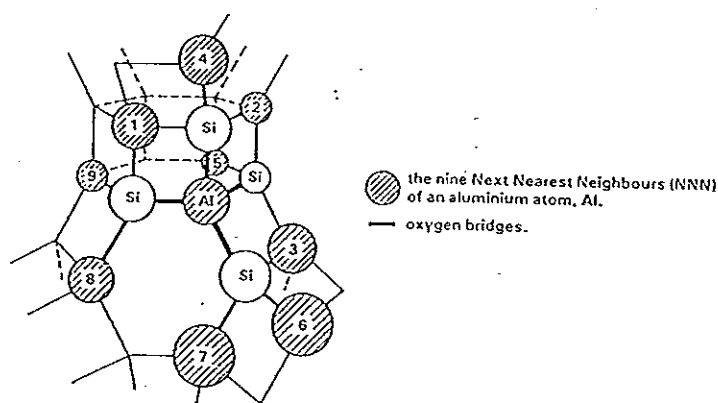
Figure 1-18 Next Nearest Neighbors.

The strongest Bronsted acid sites were associated with those framework aluminium atom which had no "Next Nearest Neighbor" (O-NNN) framework atoms. The Next strongest is associated with 1 - NNN sites, with a steady decline in acid strength through the 9 – NNN sites. Thus as the aluminum framework atom is removed from Y zeolite, stronger, more isolated O – NNN acid site are generated. As soon as all the acid sites are isolated due to O – NNN framework aluminum atoms, a maximum acidity is achieved (SAR of 9-12). The activity will then decrease linearly with the removal of more framework aluminum of similar strength.

Studies using model compounds to look at the reactions of hydrocarbon with a solid surface have concluded that both carbenium and carbonium intermediates are involved. Bronsted sites can form both, whereas Lewis sites produce only cabenium ions. Therefore, for many reactions, the activity of a catalyst should depend essentially on its Bronsted acidity, since Lewis sites alone do not appear to be active in most carbon reactions. However, Lewis sites are believed to play a significant role in reaction such as double bond shifts and cis/trans isomerization of olefins. This anomaly has been rationalized through the concept of "super acid" sites, which are believed to arise from a coupling in activity of the latter. That super acid acidity can arise from the interaction of Bronsted site extra framework. Aluminum generated after ultrastabilization with steam. Stabilization to a lower unit cell size reduces the number of acid sites on the zeolite since the latter are associated with the framework aluminium atoms. In addition to the increase hydrothermal stability, dealuminate zeolite are observed to have stronger acid sites than their higher cell size parents.

1.3.1.10 Catalytic Cracking with Zeolite

The activity and selectivity of zeolite largely depend on the type of cation that occupy the zeolite structure. FCC zeolite are synthesized in an alkaline environment such as sodium hydroxide. The soda Y zeolite have little or no stability. However, these alkaline cations can be easily exchanged. The acidity of the zeolite 's active site is enhanced upon ion exchanging of sodium with cation such as hydrogen or rare earth

ions. The most widely used rare earth compounds are lanthanium (La^{3+}) and cerium (Ce^{3+}).

The catalyst acid sites are both Bronsted and Lewis types. The catalyst can have either strong or weak Bronsted sites or strong or weak Lewis site. The catalyst acid properties depend on several parameters, including method of preparation, dehydration temperature, silica to alumina ratio, and the ratio of Bronsted to Lewis acid sites.

Bronsted 's definition of an acid is one capable of donating a proton. Bronsted acid is the traditional hydrogen donor acid, such as hydrochloric acid and sulfuric acid. Lewis 's definition of an acid is a substance that accepts a pair of electrons. Lewis acids may not have hydrogen in them but they are still acids. The classical example is aluminum chloride. Aluminum chloride in water will react with hydroxyl, causing a drop in solution pH.

The positive impact of carbenium ion cracking on FCC gasoline yields composition and octane was the major benefit in the switch from a thermal to a catalytic cracking process in the 1940 's. The product distribution from thermal cracking is different from catalytic cracking, as shown in table 1-3.

Table 1-3 Comparison of Major Features of Thermal and Catalytic Cracking

From: Magee, 1993:43

Hydrocarbon Type	Thermal Cracking	Catalytic catalyst
n – Paraffins, e.g. n – $C_{16}H_{34}$	C_2 is major product; with much C_1 and C_3, and C_4 to C_{16} α - olefins; little branching.	C_3 to C_6 is major product; few α - olefins above C_4; much branching.
Olefins	Slow double bond shifts and little skeletal isomerization; H – transfer is minor and non – selective for tertiary olefins; only small amounts of aromatic formed from aliphatics at 932 °F.	Rapid double bond shifts extensive skeletal isomerization; H – transfer is major and selective for tertiary olefins; large amounts of aromatics formed form aliphatics at 932 °F.
Naphthenes	Crack at slower rate than paraffins.	If structural groups are equivalent, crack at about same rate as paraffins.
Alkylaromatics	Cracked within side chain.	Cracking next to ring is prominent.

The shift in distribution of products clearly confirm the fact that these two process must proceed via different mechanism. Table 1-3 comparison of gasoline yield composition for thermal and catalytic cracking at about equal gasoline yield.

Both the C_4 and C_6 paraffin compositions clearly indicate a drastic shift towards a higher quantity of branch compounds with the catalytic process and the aromatics yield is strongly enhanced.

The catalytic reaction can be classified into two categories: primary cracking of gas oil molecule and secondary rearrangement and recracking of cracked products. The reactions that occur when a hydrocarbon molecule reacts on the solid surface of a catalyst all involve positively charged organic species, usually cabenium ions. The initial reaction to form a charge species can occur via a number of paths, the most common being hydride abstraction.

(1) $CH_3\text{-}CH_2\text{-}CH_2R + L \longrightarrow CH3\text{-}C^+H\text{-}CH_2R + LH^-$

(2) $CH_3\text{-}CH_2\text{-}CH_2R + H^+ \longrightarrow CH3\text{-}C^+H\text{-}CH_2R + H_2$
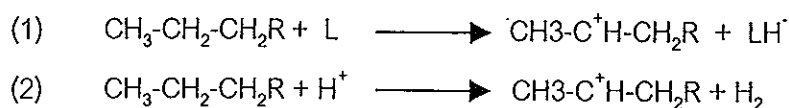
Figure 1-19 Formation of a Cabenium Ion via Hydride Abstraction.

Form: Magee, 1993: 67

Figure 1- 19 shows an example of hydride abstraction from (1) a paraffin at a Lewis site (L) and (2) via direct attack of a proton from a Bronsted site (H^+). Other paths to carbenium ion formation include the addition of a cation to an unsaturated molecule and heterolytic fission. The stability of cabenium ions increase as follows

Primary < Secondary < Tertiary

Tertiary species are thus greatly favored, accounting for the high degree of branching associated with catalytic cracking. Only an acidic type of ionic cracking involving a tertiary carbenium ion will produce branched compounds such as isobutane ($i\text{-}C_4$). On the other hand, thermal cracking, by virtue of its free radical path, will tend to produce non branched compounds and fuel gas (C_2^-).

Once formed in the initiatial reaction, cabonium ions can pursue a number of different reactions which are determined by the nature and the strength of the acid sites involved. The three dominant reactions of carbenium ion are

1.) The cracking of carbon – carbon

2.) Isomerization

3.) Hydrogen transfer

Other reaction such as alkylation, cyclization and condensation also occur, along with reverse reactions such as polymerization, dealkylation and hydrogenation.

1.) Cracking reaction

The cracking, or beta scission, is a key feature of ionic cracking. Beta scission is the splitting of the C – C bonds at two away from the positive charge carbon atom. There is a preference for beta scission because the energy required to break this bond is lower than that needed to break the adjacent C-C bonds, long chain hydrocarbons are more reactive than short chain hydrocarbons; therefore, the rate of the cracking reaction decreases with decreasing chain length to the point that it is not possible to form stable carbenium ions.

The initial products of beta scission are an olefin and new carbenium ion (equation 1-9)

$$CH_3-C^+H-CH_2-CH_2-CH_2-CH_2R \longrightarrow CH_3CH=CH_2 + C^+H_2-CH_2-CH_2R \quad (1.9)$$

The newly formed carbenium ion will then continue a series of chain reactions. Small ions such as these with four carbon or five carbons can then react with another big molecule and transfer the positive charge, and then the big molecule can crack. Cracking does not eliminate the positive charge; it stays until two ions run into each other. The smaller ions are more stable and will not crack. They stay longer and finally transfer their charge into a big molecule, because beta scission is monomolecular, and cracking is endothermic. Consequently, cracking rate is favored by high temperature; cracking is not equilibrium limited.

2.) Isomerization reaction

Isomerization reactions occur more frequently in catalytic cracking than in thermal cracking. As discussed earlier, thermal cracking is a free radical mechanism.

Breaking of a bond in thermal and catalytic mechanism is via beta scission; however, in catalytic cracking a number of carbocations tend to rearrange to form

Tertiary ions. Tertiary ions are more stable than secondary and primary ions; they shift around and crack to produce branched molecule (equation 1-10).

$$CH_3CH_2C^+HCH_2CH_2R \longrightarrow \underset{\underset{H\ CH_3}{|\ \ |}}{CH_3\text{-}C\text{-}CH\text{-}CH_2R} \text{ or } \underset{\underset{CH_3}{|}}{C^+H_2\text{-}CHCH_2CH_2R} \quad (1\text{-}10)$$
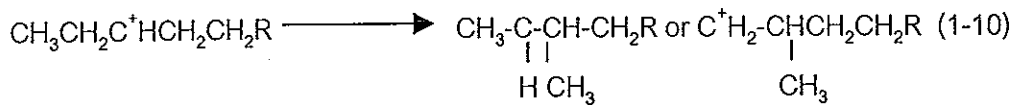
Free radicals do not do that, they yield normal or straight compounds. Some of the advantages of isomerization are as follows; high octane, high value chemical and oxygenate feedstock, lower cloud point for diesel fuel.

The isoparaffin in the gasoline boiling range have higher octane than normal paraffins. Compounds such as isobutylene will be extremely valuable as feedstocks for the production of methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). MTBE and TAME can be blended into the gasoline to reduce auto emissions. Finally, isoparaffins in the light cycle oil boiling range improve the cloud point.

3.) Hydrogen transfer reactions

Hydrogen transfer, or more correctly hydride transfer, is a bimolecular reaction in which one reactant is an olefins. An example of hydrogen transfer is the reaction of two olefins. Both olefins would have to be adsorbed on the active sites and the sites would have to be close together for these reactions to take place. One of these olefins becomes paraffin and the other becomes cycloolefins; so hydrogen is moved from one to another. Cycloolefin is now hydrogen transfer with other olefin to yield di-olefin. Cyclo di-olefin will rearrange to form an aromatic, and aromatics (equation 1-11).

$$4C_nH_{2n} \longrightarrow 3C_nH_{2n+2} + C_nH_{2n-6} \quad (1\text{-}11)$$

$$\text{Olefins} \qquad\qquad \text{Paraffins} \qquad\qquad \text{Aromatic}$$
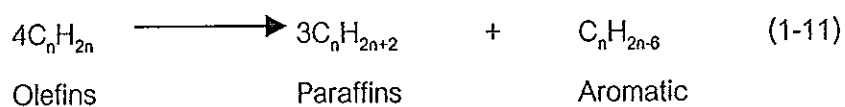
Naphthenic compounds are also hydrogen donors and can react with olefins to produce paraffin and aromatic (equation 1-12).

$$3\,C_nH_{2n} \quad + \quad C_mH_{2m} \longrightarrow 3C_nH_{2n+2} \quad + \quad C_mH_{2m-6} \quad (1\text{-}12)$$

Olefin $\qquad\qquad$ naphthene $\qquad\qquad$ Paraffins $\qquad\qquad$ Aromatics
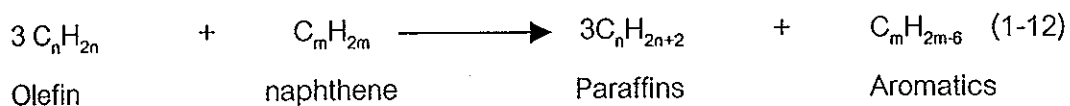
A rare earth exchanged zeolite increases indirectly hydrogen transfer reactions. In simple terms, the rare earth forms bridges between two to three acid sites in the catalyst framework. In doing so, the rare earth basically protects those acid sites being ejected from the framework. Because hydrogen transfer is promoted from adjacent acid sites, bridging these sites with rare earth promotes hydrogen transfer reaction.

Some of the drawbacks of hydrogen transfer reactions are: lower gasoline octane, lower light olefins in the LPG, higher aromatics in the gasoline and LCO, as well as lower olefins in the front end of gasoline. The light (C_3, C_4, C_5) olefins can further be processed in the alkylation and etherification unit to yield excellent blend stocks for reformulated gasoline.

1.3.2 Preparation of Rare Earth Hydrogen Exchanged Y Zeolite (REHY Zeolite)

The REHY zeolite can be prepared from NaY zeolite by two methods. The first method is called conventional ion exchange and the second is solid state ion exchange.

1.3.2.1 Conventional ion exchange method

REHY zeolites are prepared from NaY zeolite by ionic exchange with rare earth and ammonium salt in solution. The principle sources of rare earth are monasite and bastnaesite sands. Both of which give mixed rare earth chloride solutions. The rare earth metal salt employed can either be the salt of single rare earth metal or mixture of rare earth metal, such as rare earth chloride of dynimium chlorides.

Rare earth chloride solution is a mixture of rare earth chlorides consisting essentially of the chlorides of lanthanum, cerium, neodymium and praseodymium with

minor amount of samarium, gadolinium and yttrium. Rare earth chloride solutions are commercially available and the ores specificly referred to in the examples, contain the chlorides of the rare earth mixture having the relative composition: cerium (CeO_2) 48%, lanthanum (as La_2O_3) 24%, praseodymium (as Pr_6O_{11}) 5%, Neodymium (as Nd_2O_3) 17%, samarium (as Sm_2O_3) 3%, gadolinium (as Gd_2O_3) 2%, and other rare earth oxides 0.8% by weight. Dydimium chloride is also a mixture of rare earth chlorides but has a lower cerium content. It consists of the following rare earths determined as oxides: lanthanum 45-56%, cerium 1-2%, praseodymium 9-10%, neodymium 32-33%, samarium 5-7%, gadolinium 3-4%, yttrium 0.4%, and other rare earths 1-2% by weight. Although lanthanum, neodymium, praseodymium, samarium and gadolinium as well as mixtures of rare earth cations containing a predominant amount of one or more of above cations are preferred since these metals provides optimum activity for hydrocarbon conversion, including catalytic cracking. (Francis et al., 1968).

1.3.2.1.1 Ion exchange of crystalline zeolite

The exchange is carried out by mixing an access of the salt solution with the zeolite for proper time normally 5 minutes to 5 hours. The rate of exchange can be increased by carrying out the exchange at an elevated temperature. Obviously, the exchange temperature of the solution must be below the atmospheric boiling point of the solution, unless pressure equipment is used. Suitable exchange may be carried out at a temperature from about 25 to 100 °C. The time of contact between the solution and the zeolite is such as to effectively replace the easily exchangeable cation in the aluminosilicate to about 3 percent calculate as oxide of the cation, for example, Na_2O. Distribution of rare earth on the faujasite after exchange, indicates that no preferential exchange takes place, providing the exchange solution pH is such that cerium does not precipitate. An exchange pH range of 3.5 to 5.5 is necessary. Further, catalyst activity and selectivity in cracking are independent of the rare earth ratio of Ce, La and Nd in the zeolite ingredient, but zeolite stability is directly proportional to lanthanum or neodymium content and inversely proportional to cerium content. Thus in commercial practice

lanthanum rich exchange solution are generally used for zeolite exchange (Rabo, 1976: 621)

The second step of the process; the exchanged zeolite is washed to remove any excess salts. This washing is a conventional step and is normally carried out with deionized water.

After washing, the zeolite is partially exchanged with the cation desired and having 10 to 20 percent of the original cations remaining (depending on the particle zeolite) is dried and heat treated to redistribute the locked in cations. The heat treatment is normally carried out at temperature about 600 to 1200 °F. However, the temperature must be low enough so as not to cause the zeolite crystalline structure to collapse, since some of the zeolite crystalline in the low initial cations condition enter into what is known as a meta stable condition, wherein the crystalline structure will collapse when subjected to thermal treatment. Suitable results are obtained when the heat treatment is carried out at temperature of about 1000 °F for period time of 0.1 to 3 hours.

In the final stage of the process, the zeolite is cooled to room temperature and a final exchange carried out to reduce the initial cation content to the desired level. The heat treatment step has unlocked the locked initial cations may be effected. This final exchange may be carried out with any suitable salt solution depend upon the cation desired in the exchanged zeolite, the heating (to redistribute the locked in cations) and ion exchange step may be carried out as a series of repeating cycles.

For REHY zeolite, the ionic exchange occurs primarily with super cage sodium ions, due to the inability of hydrated rare earth ions ($\emptyset = 7.9$ Å) to penetrate the 6-membered ring of the sodalite cage ($\emptyset = 2.4$ Å). Some of the zeolite sodium ions are exchanged by hydrogen ions present in the acidic rare earth salt solution. Calcination of partial rare earth exchanged zeolite result in stripping of the hydration shell from the rare earth ions and migration of the hydrate ions into the sodalite cage. At the same time most of the remaining sodium ions move into super cage in positions and are subsequently removed by ammonium exchange. During calcination, some of the cerium ions present in the rare earths mixture are oxidized to the tetravalent state. Furthermore,

the rare earth ions that migrate into the sodalite cages form cationic polyhydroxy complexes. Upon calcination, $RENH_4Y$ is converted into REHY zeolite. The reaction that take place in REHY zeolite upon thermal and hydrothermal treatment are summarized in table 1-4.

Table 1-4 Reaction in REHY zeolites.

Thermal treatment

    a. Framework dehydration/dehydroxylation

    b. Cation dehydration $RE(H_2O)_n^{3+} \xrightarrow{T} RE(H_2O)^{3+} + (n-1)\,H_2O$

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

    d. Ionic migration $[REOH^{2+}]_{\alpha\text{-cage}} \xrightarrow{T} [REOH^{2+}]_{\beta\text{-cage}}$

    e. Oxidation of Ce $2Ce(OH)^{2+} + 1/2O_2 + 2H^+ \longrightarrow 2Ce(OH)^{3+} + H_2O$
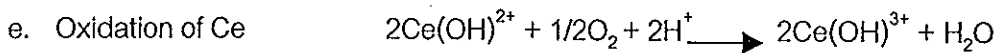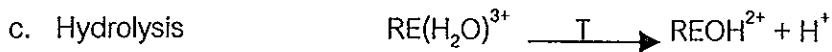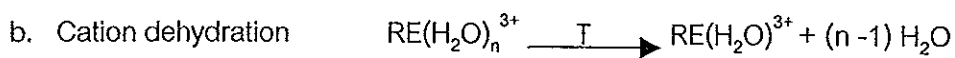
    f. Hydroxyl complex formation

$$2\,REOH^{2+} \xrightarrow{T} [RE \overset{\displaystyle \overset{H}{|} \atop O}{\underset{\underset{H}{|} \atop O}{\diamond}} RE]^{4+}$$
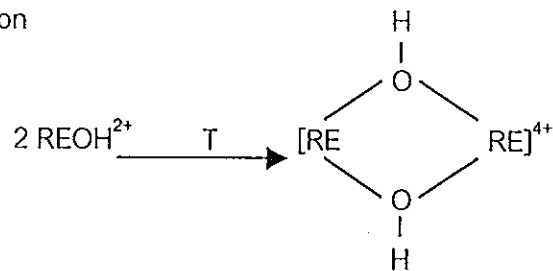
Hydrothermal treatment

    a. Hydrolysis

$RE_2O_3 \bullet 3H_2O$

$$
\begin{array}{c}
\text{Si} \\
| \\
\text{O} \quad \text{H}^+ \\
| \\
\text{b.} \quad \text{Si}-\text{O}-\overset{\cdot}{\text{Al}}-\text{O}-\text{Si} \\
| \\
\text{O} \\
| \\
\text{Si}
\end{array}
\xrightarrow{\text{Steam}}
\begin{array}{c}
\text{Si} \\
| \\
\text{OH} \\
\\
\text{Si}-\text{OH} \quad\quad \text{OH}-\text{Si} \;+\text{Al(OH)}_3 \\
\\
\text{OH} \\
| \\
\text{Si}
\end{array}
$$
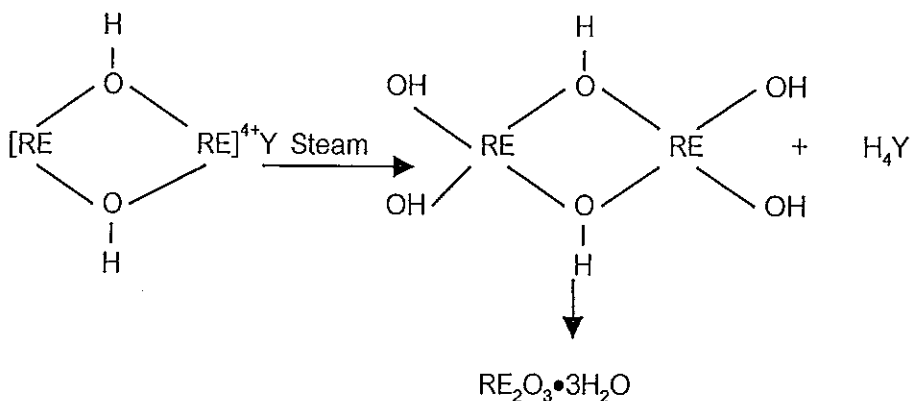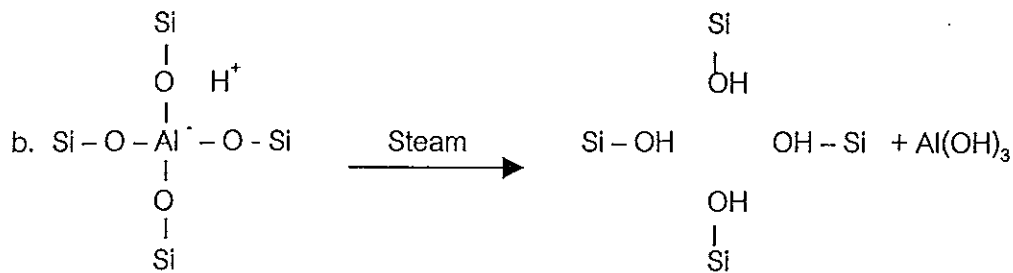
In another method, the NaY zeolite is first treated with an ammonium salt solution and then rare earth exchanged. Calcination and subsequently ammonium or rare earth exchange removes most of the remaining sodium ions. The initial ammonium salt treat removes up to about 80% of the sodium ions and reduces the alkalinity zeolite, thus preventing a possible precipitation of rare earth oxides.

It is known that the rare earth species can be used to suppress the framework dealumination of Y zeolite under hydrothermal condition through the migration of rare earth cations from supercages (α - cages) to sodalite cages (β - cage) followed by the oligomerization of rare earth cations in the sodalite cage (Xianglin, 1997):

Ionic migration $\quad\quad [RE(OH)^{2+}]_{\alpha\text{-cages}} \quad\Leftrightarrow\quad [[RE(OH)^{2+}]_{\beta\text{-cages}}$

Hydroxyl cation formation $\quad 2RE(OH)^{2+} \quad\Leftrightarrow\quad$

$$
\begin{array}{c}
\text{H} \\
| \\
\text{O} \\
/ \quad \backslash \\
[\text{RE} \quad\quad \text{RE}]^{4+} \\
\backslash \quad / \\
\text{O} \\
| \\
\text{H}
\end{array}
$$
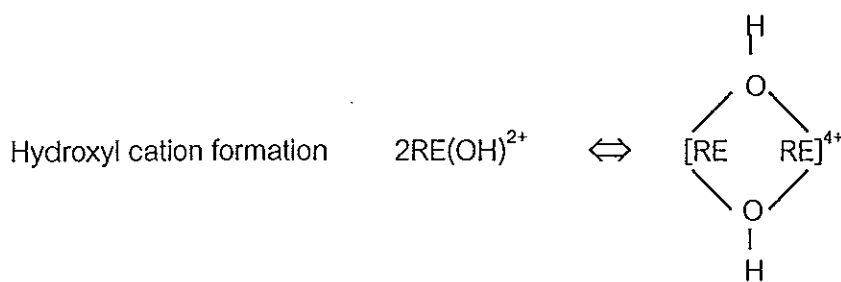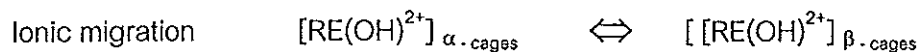
Conventional ion exchange is traditionally performed in solution, however, this method may have limitations. First of all, the steric constrains may exist due to the formation of bulky hydration shell of the cations to be exchanged such as Cs^+, La^{3+}, Ce^{3+}. As a consequence, the diffusion of the cations into the zeolite pores is hindered and intermediate calcinations are required in order to facilitate cation migration. Secondly, the solubility of cation precursor may be low, which limits the amount of cation

available in solution. The maximum degree of exchange between the cation in the solution and those in zeolite is determined by equilibrium. The third, a careful control of pH is frequently required to avoid the hydrolysis of many salts, which may be flow by the deposit of oxide or hydroxyl oxide on zeolite crystals.(Sulikowski et al., 1997). Furthermore, a single exchange most often result in only partial exchange. It is then necessary to repeat the exchange several times to reach high exchange level. As a consequence, ion exchange in solution frequently involve the handling and recycling of large volumes of zeolite.

1.3.2.2 Solid state ion exchange in zeolite

In order to avoid the above disadvantages, an alternative method, so called "Solid state" ion exchange (S.s.i.e.)(Jia et al., 1998) may be used. This method is usually performed by mixing a salt with the zeolite in ambient atmosphere; thus the latter constrains physisorbed water. Also, many salt contain crystal water, which is usually not removed before the ion exchange. The amount of water in the hydrate zeolites varies from a few percent to about 25% for Y zeolite. This method usually consists of heating in a vacuum or in a flow of inert gas a mechanical mixture of zeolite and cation precursor, which is often in the form of a chloride salt. It has been shown that solid state ion exchange can be achieved between an alkaline metal cation and the alkaline form of a zeolite. However, cation migration and trapping are strongly favored when the exchange is performed using the ammonium or protonic form of the zeolite.

1.3.3 Rare Earth Exchanged Hydrogen Y Zeolite properties.

REHY zeolite with over 10% RE_2O_3 make only a minor contribution to octane enhancement. They are used primarily to boost the gasoline yield as the major objective. Partial, rather than full, rare earth exchanged Y zeolites are use mainly to reduce coke and dry gas formation during the cracking process. As the rare earth content of REHY decreases, their contribution to octane enhancement increases while gasoline decreases. REHY zeolites have good thermal stability. Their high stability has been

attributed to the presence of polynuclear cations in the sodalite cage of the zeolite, containing oxygen bridge rare earth ions. Fresh REHY has a unit cell size in the range of 24.60 to 24.65 °A (dependent upon Si/Al ratio and rare earth content) but in equilibrium FCC catalysts the unit cell size of the zeolite is usually in the range of 24.50 to 24.55 °A. At low rare earth content, the properties of steam REHY become similar to those of rare earth exchanged HSY zeolite with equivalent amounts of rare earth.

1.3.4 Fluid Cracking catalysts

The fluid cracking catalysts are microspheroidal particles having a particle sized distribution between 10 - 150 microns. The primary active ingredient in catalysts is a synthetic zeolite. This component can be between 15-50 wt.% of the catalyst. The second active ingredient found in many catalyst today is some form of alumina. This is generally referred to as active material and is added to improve the active alumina content of FCC catalyst is generally between 0-20 wt.%.

The non active remainder of the catalyst consists of filler, generally kaolin clay, and binders. The fillers contribute to the physical properties, pore volume and surface area. The binders serve to hold the various constituent together in the catalyst particle.

In operation, fresh catalyst must be added to the unit to make up for losses and to maintain the catalyst activity. Make up rate for unit processing gas oil feeds are typically 0.15-0.20 pounds of catalyst per barrel of feed. For unit processing resid feeds, the make up rate must be higher to control the metals levels on the catalyst. For these units, the make up rate may be as high as 1.5 pounds per barrel. When the catalyst make up rate required for activity maintenance or metal control is higher than the catalyst loss rate, equilibrium catalyst must be withdrawn from the unit to balance the catalyst make up rate (Wilson, 1997).

1.3.4.1 Active alumina component

The oil industry has gradually increased demands for an attrition resistant FCC catalyst. These demands have arisen from the need to reduce particle particular air pollution from catalyst fines and to prevent the loss of expensive catalyst. At present,

four binder systems are used in the commercial production of FCC catalyst, and an extraordinary number have been examined in laboratory preparations. Table 1-5 Shows the found binder types and their main characteristics.

Table 1-5 Commercial FCC Binder.

From: Magee, 1993:117

Type	Surface Area (m^2/g)	Activity
Silica sol	20	Very low
Alumina chlorhydroy (ACH)	60 – 80	Moderate
Peptized alumina	300	High
Self – binding (In situ)	-	High

Another commonly used alumina based binder is prepared by peptizing pseudoboehmite alumina (PBA), usually with formic acid. Other monobasic acids such as HCl and HNO_3 can also be used to peptize the alumina but formic acid seems to be the commercial choice because of fewer problems in terms of stack emission or corrosion. Pseudoboehmite alumina can not 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. However, pseudoboehmite possesses a surface areas of more than 300 m^2/g and undergoes a phase change to gamma alumina at FCC unit regenerator temperature as shown in figure 1-20.
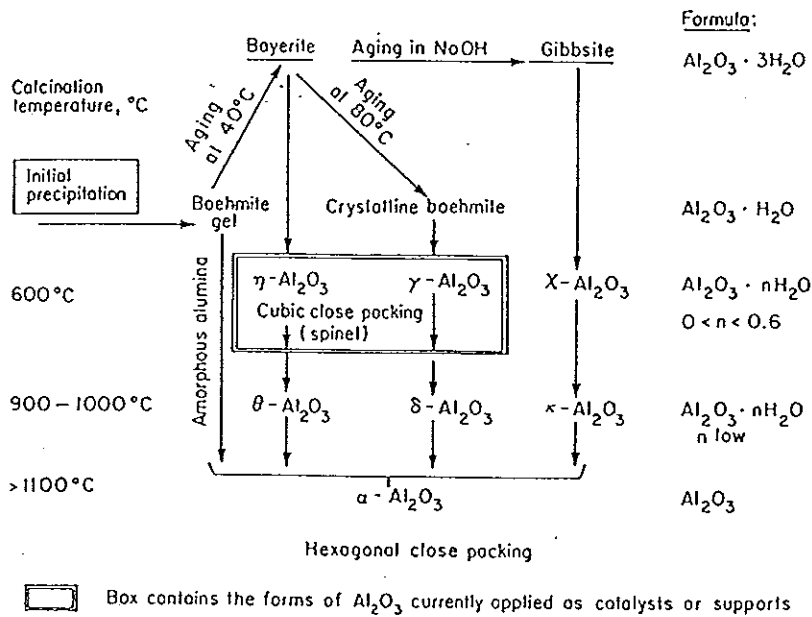
Figure 1-20 Schematic representation of various Al_2O_3

From: Gates, 1984:250

The hydrated alumina which prefer to use includes a substantial proportion above 25% and preferably substantial entirely a gelatinous alumina mono hydrate AlOOH. The acid which prefer to use in peptization reaction as HNO_3. The quantity used is about 0.08 to 0.16 grams HNO_3 per grams Al_2O_3 on a volatile free basis. This acid treatment as peptization and the resultant pseudoboehmite is peptized. Generally, peptizability index is used to selecting the pseudoboehmite. That value preferably above 0.5% (Secor et al., 1977).

For the purpose of improving the thermal stability of the catalyst, the crystalline psedoboehmite appear to act as diluent. However, purpose of improving the attrition resistance, it is found that an alumina should have a high peptizability index and be substantially free of sodium.

In general, the function of the active alumina is to crack large, heavy molecules boiling typically above 650 °F into a material with a lower molecular weight. These heavy

molecules are converted to molecules small enough to be further recracked by the zeolite into the gasoline or LPG range.

A second function serve by alumina is to absorb condensed aromatics, which are not crackable. The absorption prevents the molecules from blocking access to the zeolite and decreasing catalyst activity.

A third function of the alumina is to react with the vanadium metal contained on porphyrin structures, where they are present to a greater or lesser degree in all feed stocks, and prevent its migration to the zeolite. Migration to the zeolite will result in crystall destruction by vanadic acid from V_2O_5 and H_2O in regenerator. Unfortunately, alumina also serve as good support for both nickle and vanadium, and increase their coke and gas making tendencies. Alumina by itself is not a particularly good metal passivator. Finally, the alumina also imparts stability to the catalyst by migrating the destructive effects of hydrothermal dealumination on the crystal structure of the zeolite. Hence, overall catalyst stability and activity is improved.

1.3.4.2 The clay component

Clay is added to most FCC catalyst as an inert densifier, In order to improve the apparent bulk density (ABD) of catalyst without having an effect on catalyst activity and selectivity. In all know FCC catalyst, the clay of choice is kaolin. Its ability to form high solid pumpable slurries, low fresh surface area, and case of packing as a result of its platelet structure make kaolin particurly suitable.

Some parameters of the kaolin are critical for FCC manufacturing. Specially, the kaolin particle sized must be small to ensure that the resulting FCC catalyst good ABD and attrition resistance. Average particle size of 0.3 to 0.4μ with 90% point of approximately 1μ are normal for FCC use. The ion and titania content of clay can also be important. High ion or titania levels can lead to undesirable secondary reactions, such as gas and coke formation and increase CO combustion in the regenerator, when such clays are use in the manufacture of cracking catalyst. Titania level below 3.0 wt.% and ion content of 0.4 to 0.8 wt% are considered acceptable.

1.3.5 Designing FCC Catalyst

The design of FCC catalyst is determined by the following factors: feedstock type, products desired (yield and quality), unit design, environmental impact, and cost. For example, the processing of a resid feedstock requires a different catalyst than the processing of a light gas oil; maximizing gasoline yield requires a different catalyst to gasoline octane; limitation on the unit air blower capacity or LPG capacity will effect the design of FCC catalyst; a well designed FCC catalyst will minimize SO_x and CO emission during the cracking process.

When designing a FCC catalyst, both the mechanical/physical and catalytic properties should be taken into consideration. The following mechanical/physical properties are important: attrition resistance, thermal/hydrothermal stability, particle sized distribution, pore size distribution, surface area, bulk density and x-ray crystallinity. Some of these physical properties, such as thermal/hydrothermal stabitlity, pore size distribution and surface area effect the catalyst performance of the catalyst. Other properties, such as attrition resistance, particle size distribution, and density affect primarily the mechanical behavior of catalyst in the FCC unit.

When designing the catalytic properties of catalyst, catalytic activity, selectivity and stability should be considered. The correlation between catalyst formulation and catalyst performance is shown in figure 1-21.

SMALL
UCS

OCTANE INCREASE —
RE CONTENT INCREASED

A
CAT. WITH
• BEST BOTTOMS CRACKING
• HIGHEST C₃+C₄
• HIGHEST OCTANE

C
CAT. WITH
• LOWEST COKE MAKE
• MODERATE GASOLINE MAKE
• MODERATE OCTANE

E
CAT. WITH
• HIGHEST OCTANE-BBL.

B
CAT. WITH
• GOOD BOTTOMS CRACKING
• LOWER C₃+ C₄
• HIGHEST COKE MAKE

D
CAT. WITH
• HIGHEST GASOLINE MAKE
• LOWEST OCTANE
• LOWEST C₃+ C₄
• LOWEST BOTTOMS CRACKING

LARGE
UCS

1   2   3   4

LOWER
Z/M

Z/M ACTIVITY RATIO

HIGHER
Z/M

◄——— MATRIX ACTIVITY INCREASE
◄——— COKE MAKE INCREASE

Figure 1-21 Optimized catalyst compositions for specific application.

From: Mage, 1993:175

The figure illustrates the correlation between zeolite Y unit cell size, zeolite/matrix activity ratio and catalytic performance. The catalyst can be divided in several groups, based on composition and performance. Catalysts in group A consist of zeolites with small unit cell size and a low zeolite/matrix ratio. Such catalysts are best suited for cracking bottoms, since both low – unit cell size zeolites and active matrices favor the cracking of heavy hydrocarbons. Such a composition also maximizes total C_3+C_4 as well as C_3+C_4 olefin yields, which is advantageous when alkylation capacity is available. The yield of C_3+C_4 and gasoline octane can be further enhanced by using ZSM – 5 additive.

Catalysts in group B consist of zeolites with a large unit cell size and an active matrix. Such catalysts are able to crack bottoms, although to a less extent than the previous category. They also generate more coke and less C_3+C_4 hydrocarbons. The catalysts can be used for bottom or resid cracking when limitations exist on the C_3+C_4 capacity. Such catalysts have good gasoline selectivity.

Catalyst group C consists of low – unit cell size zeolites and low activity matrices. The gasoline selectivity and gasoline octane are moderate. Due to the low production such catalysts, the FCC unit can be operated at higher conversion, which results in higher gasoline yields and better octane numbers. Due to the low – activity matrix such catalysts are not well suited for bottom cracking.

Catalyst in group D contain active zeolites with relatively large unit cells and low activity matrices. Such catalysts have the highest gasoline selectivity, but gasoline octane C_3+C_4 yields and the ability to crack bottoms are low. Such catalysts are used to maximized gasoline production, but are unfit for bottoms cracking.

Catalyst in group E consist of zeolites with medium – unit cell sizes and matrices of medium activity. Such catalysts, which have a composition and properties between those of group A and D, are designed to maximize octane-barrels. The catalysts have a moderate ability to crack bottoms and give moderate yields of C_3+C_4 hydrocarbons. The catalyst selection is often determined not only by the desired product yields and quality, but also by unit constraints. For example, when blower capacity is a limiting factor and the objective is maximizing gasoline yield and octane, a catalyst from group C is best suited. Due to its low coke production, such a catalyst can be run at high conversion, resulting in higher gasoline yields and octane. When alkylation unit capacity is the limiting factor (C_3+C_4 yield limitation) and the objective is maximizing gasoline yield and octane, a catalyst from group E is selected. (Catalysts from group D would maximize gasoline and minimize C_3+C_4 yields, but would also minimize gasoline octane.) Similar considerations apply when compressor limitations exist, requiring the reduction of dry gas and C_3+C_4 yields.

The environmental impact of the FCC catalyst during its use in the cracking unit is of considerable importance. A well designed catalyst will not only reduce SO_x and CO emissions, but will also contribute to the making of quality products, which have a diminished environmental impact.

CHAPTER 2

EXPERIMENT

The experiments were mainly focused on the ionic exchange, both conventional and solid state ion exchange were included the catalyst preparation.

2.1 Materials and Equipment

1. NaY zeolite
2. Mixed rare earth chloride (obtained from RIPP institute)
3. Ammonium chloride (AR grad)
4. Deionized water
5. NaCl (AR grad)
6. HCl (AR grad)
7. NH_3 (AR grad)
8. Mortar
9. Electric mixer with stirring rod (pitched blades turbine join inside truncated cone) (Heidolph made in Germany). The electric mixer type R2R1 was used to mixing in conventional ion exchange step.
10. Hot air oven (Eyela made in Japan), the hot air model NDO-600N use to drying the exchanged zeolite before calcination step.
11. Muffle oven (maximum temperature as 800 °C) used in the calcination step.
12. Water bath.
13. Vacuum pump (Eyela made in Japan) was used to for vacuum filtration of the exchanged zeolite.

2.2 Instrumentations

1. Hydrothermal Aging Unit, Model CLY-1
2. Microactivity Test (MAT) Unit, Model WFS-1D

3. Gas Chromatograph (GC-14 BPF, SHIMUSHU) and Integrater (HP3295, Hellet Packard)

4. X-Ray Fluorescence Spectrometer (XRF), Model PW2400, Philips

5. Differential Thermal Analyzer (DTA), Model DTA7, Perkin Elmer

6. X-Ray Diffractometer (XRD) Model X'Pert-MPD, Type 3040/00NC, Philips

7. ICP-MS Model UltraMass-700, Varian

8. Atomic Absorption Spectrophotometer (AAS) model AA (GBC Scientific Equipment Pty.Ltd. 901)

2.3 Conventional Ion Exchange

2.3.1 Sequences for ion exchange

The synthetic NaY zeolite was prepared by following Tuntragul method. (Tuntragul, 2000). In order to study the consequence of ionic exchanging, NaY zeolites were exchanged with ammonium and mixed rare earth salt in three pathways. These were carried out under the same conditions which were temperatures 97-100°C, pH 5.5 and exchange time of 1 hour. The different methods as follows:

Method 1

NaY zeolites were exchanged with rare earth salt and ammonium salt simultaneously for 1 hour.

Method 2

NaY zeolites were exchanged with ammonium salt for 1 hour, then exchanged zeolites were carried out with rare earth salt for 1 hour.

Method 3

NaY zeolites were exchanged with rare earth salt for 1 hour, then exchanged zeolites were exchanged with ammonium salt for 1 hour.

In order to choose the one of three methods that is the most appropriate method for ionic exchange, these methods were done under the same conditions such as temperature, pH, etc.

2.3.2 The study of factors that can effect in exchange step.

NaY zeolite (support from RIPP, China) is exchanged with ammonium and rare earth salt in the following condition:

a. Temperature is varied from 28 to 100 °C.

b. Exchanging time is varied from 0.5 to 4 hours.

c. The pH of working solution is varied from 3 to 7.

d. The amount of rare earth to aluminum atomic ratio is varied from 0.33 to 1

e. The amount of ammonium to aluminum atomic ratio is varied from 0.33 to 1.

f. The number of exchange is reached to 4 times.

2.3.3 The study on the effect of time and temperature in calcination step

a. The temperature is varied from 350 to 750 °C

b. The time is varied from 0.5 to 4 hours.

2.4 Solid state ion exchange

NaY from RIPP with 8.71 percentages sodium oxide content has been ion exchanged with ammonium salt 0.33 equivalent of aluminum in Y zeolite at 100 °C for an hour. The sample was washed with deionized water until it was chloride free and dried overnight at 120 °C. The calcination was done at 550 °C for 2 hours under N_2. It was repeated twice in the exchange series. It became HY zeolite. This HY zeolite is divided into two parts as following:

Part 1 was carried out with rare earth salt by conventional ion exchange at 80 °C, pH 5, for 3 hours. The resulting sample was washed with deionized water 5 times and dried overnight at 110 °C. This sample was compared with solid state ion exchange sample.

Part 2 was carried out with rare earth salt by solid state ion exchange as follows: HY zeolites and rare earth salts were ground in a mortar for 0.5 hour. Moisture was removed from them by using a vacuum pump at temperature above 80 °C pressure 29

lb/in^2 for 1 hour. Then the sample was ball milled for 6 hours and calcination was done in N$_2$ at 550 °C for 3 hours. The resulting sample was washed with deionized water 5 times at the room temperature with deionized water. Finally, it was dried overnight at 110 °C.

For REUSY zeolite, the second exchanged of NH$_4$Y zeolite was calcined at 540 °C for 4 hours under steam at the flow rate of water of 0.41 ml/min. The ion exchange was then repeated by conventional ion exchange at 100 °C for 1 hour and the sample was then calcined under steam at 820 °C for 2 hours at the same water flow rate. This form was treated twice with a mild 0.1 and 0.2 M HCl per 100 grams of sample at 91°C for 1 hour. The resulting sample was tested as same as the part 2. Finally, the sample was washed with deionized water for 5 times and was dried overnight at 110 °C.

Both conventional and solid state ion-exchange used the rare earth concentration of La/Al atomic ratios of 0.33, 0.66 and 1, respectively. The minimum ratio was chosen for the following reason: assuming that each RE^{3+} cation acts as a compensating cation for three framework negative charge (for example one RE^{3+} balances three AlO^{4-}).

2.5 Re - exchanging of rare earth hydrogen Y zeolite with NaCl salt

In order to study the locked rare earth in zeolite structure, the prepared rare earth hydrogen Y zeolites were carried out with saturated sodium chloride by using conventional ion-exchange at room temperature and at 105 °C, pH 5 for 1 hour.

2.6 Preparation of rare earth hydrogen Y zeolite catalyst

The prepared rare earth hydrogen Y zeolites were mixed with pseudoboehmite and clay to form the catalyst. The ratio of REHY zeolite: pseudoboehmite: kaolin clay was 15: 21: 64 basis of 100 parts of dry weight (Secor et al.). The ratio of deionized water to zeolite was 1:10 by weight. In this way, the pseudoboehmite is the matrix and kaolin is the binder. The process is as followed, first kaolin clays and water were added into vessel; next it was stirred for about 10 minutes and then stirred until mixing was complete, 1:1 hydrochloric acid was added into this vessel, pH as indicated by litmus paper should be about 3-4. After pseudoboehmite was added, it was stirred for about

30 minutes until it was homogenous. Now, this liquid became a slurry. Consequently, the slurry was heated above 60-70 °C. As the temperature decreased to room temperature, the slurry became a gel. After pH was checked, REHY zeolite was added into slurry and stirred for about 20 to 30 minutes. The slurry was dried overnight at 120 °C. This product is called a catalyst. The catalyst was ground before it was separated into two parts. The first part having a particle size of approximately 20 – 40 mesh. The other part was powder catalyst, that was used to determine the quantity of rare earth composition in catalyst by XRF. Finally, the small particle size catalyst was taken to aging by Aging Unit instrument. It was carried out at 800 °C for 4 hours in a water flow rate of 0.41ml./minute. This final product is called aging catalyst. Finally, fresh catalyst is determined MAT activity by MAT unit (see appendix B).

2.7 The sample analysis

2.7.1 The zeolites

1. The sodium element is determined by Atomic Absorption Spectrophotometer (AAS), that is shown in the appendix A.

2. The rare earth elements are determined by Inductive plasma (ICP MS), see appendix A

3. The crystallinity of exchanged zeolite is determined by X-Ray Diffractometer (XRD), see appendix C.

4. The thermal stability of exchanged zeolite is determined by Differential Thermal Analyzer (DTA), see appendix D.

2.7.2 The catalysts

1. The rare earth elements are determined by X-Ray Fluorescence Spectrometer (XRF).

2. The aging process is carried out with aging unit, see appendix E.

3. The MAT activity is determined by MAT unit and gas production is carried out with GC, see appendix B.

4. The coke on catalyst is determined by TGA, see appendix F.

RESULTS AND DISCUSSION

3.1 Conventional Ion Exchange

3.1.1 Sequence of the method for ionic exchange
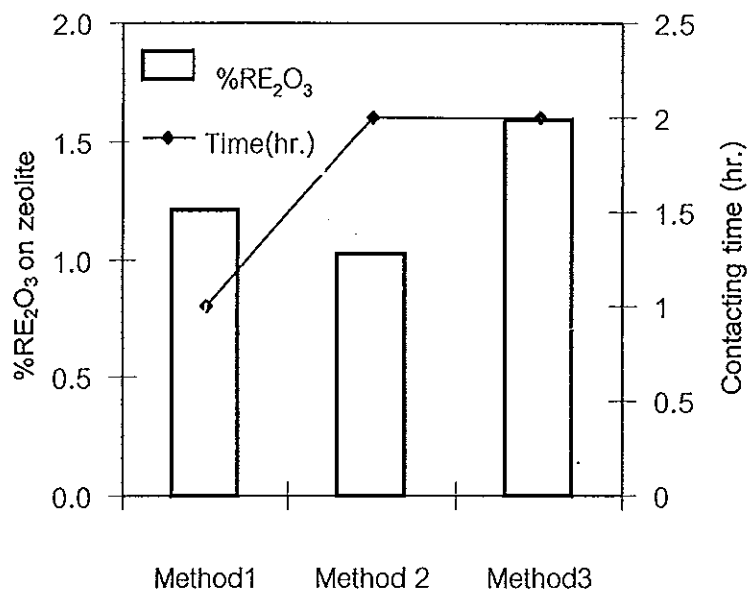
Figure 3-1 sequence of the exchange

The objective of this experiment is to study the sequence of exchange. The three methods were carried out under the same conditions except the sequence of exchange. For method 1, NaY zeolite was ion exchanged with rare earth and ammonium salt simultaneously for 1 hour. Method 2, NaY zeolite was ion exchanged with ammonium salt solution for 1 hour and then was ion exchanged with rare earth salt solution for 1 hour. The last method, method 3, NaY zeolite was ion exchanged with rare earth solution for 1 hour, then exchanged zeolite was carried out with ammonium salt solution for 1 hour. From figure 3-1, method 3 produces higher rare earth than the method 2 that uses the same exchanging time of two hours. However, method 1 is

interesting, since it can produces the rare earth oxide on zeolite satisfactorily and only uses a contact time of about one hour.

Li (Li et al.,1994) have prepared LaHY by the following sequence: NaY$\rightarrow$ LaNH$_4$$\rightarrow$LaHY. This resulted in the exchange degree of up to 81%. It was found that higher degree of La ions, which have occupied more weak proton acid site, gave the same result as in the paper of Scherzer (Scherzer, 1975). As is known, the stronger and more acid sites there are, the more advantageous the catalyst will be for cracking. Thus, the sample with a high exchange degree of La ions is not suitable for maintenance of strong acid sites, eventhough it is advantageous to the stability of the framework Al. Therefore, the LaHY with a low exchange degree may be a more suitable catalyst for cracking.

Scherzer (Scherzer et al., 1975) prepared LaHY by the following sequence: NaY$\rightarrow$REY$\rightarrow$LaNH$_4$Y$\rightarrow$LaHY. It was found that freshly exchanged LaNaY zeolite, after steaming at 540 °C, resulted in more lanthanum ions occupying positions within the sodalite cages. The average distance between these ions increased due to electrostatic repulsion. This repulsion caused the lanthanum ions to occupy average position closer to the center of the hexagonal prism.

Occelli (Occelli and Ritz, 1999) prepared REHY from CREY zeolite by the following sequence: NaY$\rightarrow$REY$\rightarrow$LaHY. It was found that post-synthesis treatment of CREY with ammonium ion increases the crystals surface area during unit cell contraction.

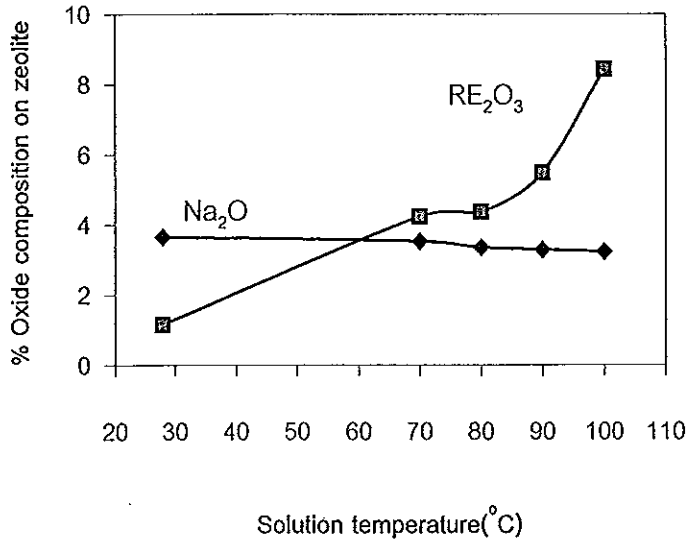### 3.1.2 The influence of the temperature in the conventional exchange

Figure 3-2 Effect of solution temperature

For conventional ion exchange, the ionic exchanging is done in a solution so that the temperature of solution will have an effect on the exchanging. Figure 3-2 shows that when the temperature of solution increases, the rare earth content on zeolite increases. The sodium content trend line does not noticibly change. The exchange degree increases with temperature, because the exchanging is controlled by diffusion. So when temperature is increasing, the diffusion of ions in solution can move rapidly into supercage (β cage). The counter diffusion exchange process is very fast, and therefore, control by diffusion (Wojciechowski, 1995: 50) which can occur more readily than at lower temperatures. In addition, the ion exchange process can be described as a reversible equilibrium that relates to Gibb's free energy (ΔG^{θ}), since the Gibb's energy increases in negative value as the temperature rises which allows the ion exchange to proceed data faster rate.

Olson (Olson et al., 1968) prepared exchanged rare earth zeolite X and Y at room temperature. It was found that hydrate rare earth ion can only exchanges only with the supercage sodium ions. The extent of exchange at 100 °C was used as a measure

of lanthanum ion transfer from SIV (SIV is a 32-fold supercage site located just inside the plane of the supercage 6MR) to the sodalite cage. The rate of transfer was at least four times faster in zeolite Linde X than in Y. As he suggested, the activation energy for this transfer may be the heat of hydration of metal ion. If so, the faster transfer rate in zeolite X than Y are caused by a lower heat of activation for the transfer, which results from the partially dehydrated state of the SIV lanthanum ions. At 25 °C there is insufficient thermal energy to strip the remaining water and allow the 2.30 Å diameter La^{3+}ion to pass through the 1.8 Å diameter SIV 6MR opening.

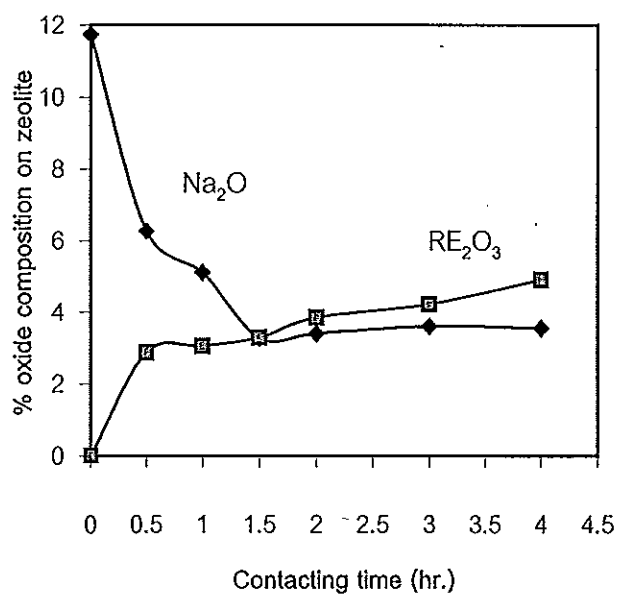### 3.1.3 Effect of contacting time

Figure 3-3 Effect of contacting time

Figure 3-3, it shows that, the exchanged rare earth on zeolite increases directly with contacting time. On the other hand, the sodium content decreases rapidly in range from 0 to 1.5 hour and is quite stable after 1.5 hours. For this reason, contacting time of 1.5 hour is chosen for the next experiment in studying the other effects.
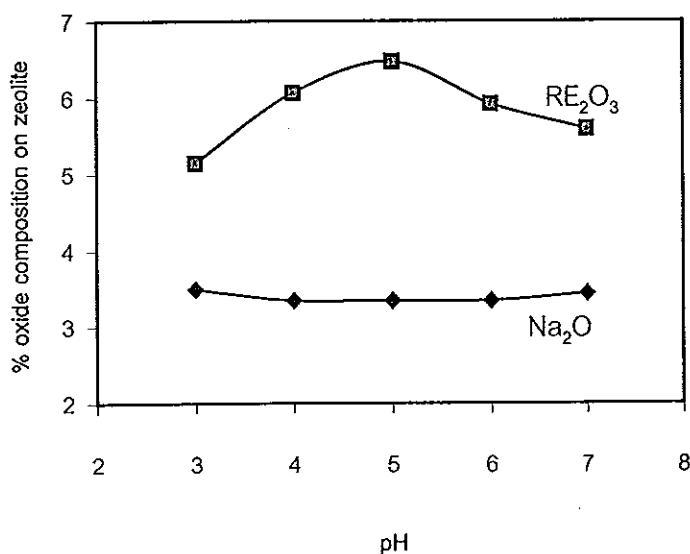
Figure 3-4 Effect of pH in exchange solution

Figure 3-4, it shows that the maximum rare earth on zeolite is at pH 5. However, at pH levels lower or higher than 5, it shows decreasing rare earth content on zeolite. This suggests that the solubility of rare earth salt is not satisfied in higher pH range, because rare earth can be precipitated in non-acidic solution. The another reason is its sensitivity to low pH solutions. At low pH, alunimium ions are removed from the crystalline framework and the structure collapses, leaving an amorphous material (Wojcieshowski, 1995:51). However, the ionic exchange is carried out in acidic solution under control pH in order to avoid precipitation of the rare earth during the exchange process and to suppress the oxidation of Ce^{+3} to Ce^{+4} (Scherzer, 1989). Furthermore, the catalyst activity and selectivity on cracking are independent of rare earth ratio of Ce, La, and Nd in the zeolite gradient. However, the zeolite stability is directly proportional to lanthanum or neodymium content and inversely proportional cerium content. Thus, commercial practice lanthanum rich exchange solutions are generally used for zeolite exchange (Rabo, 1976:621). In the same way, Campana (Campana et al., 1986) found that the ratios of rare earth components in the zeolite are also important. Most significant

is the ratio of La/Ce. For a given rare earth content, a higher La/Ce ratio will result in a significantly more stable zeolite.

3.1.5 The effect of rare earth concentration
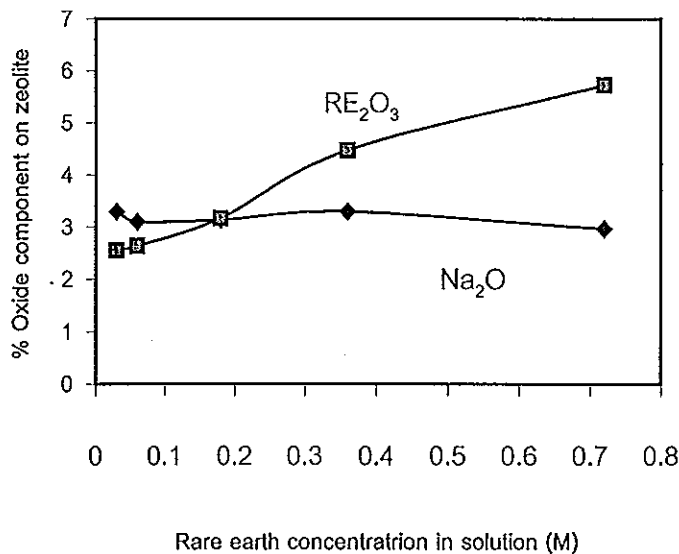
Figure 3-5 Effect of rare earth concentration

Figure 3-5, it shows that when the concentration of rare earth salt in solution increases, this results in raising the exchange rare earth on zeolite, as the remaining sodium content in zeolite slightly decreases. Increasing amount of reactant can produce higher products, because more reactant molecules react with the remaining sodium molecule, and ionic exchange reaction can proceed more effectively. However, the theoretical exchange capacity can continuously be derived from elemental composition of zeolite (Dryer, 1998). Scherzer (Scherzer et al., 1972) suggested that rare earth chloride solution contains about 10 to 30 percent excess rare earth ions which is required to theoretically exchange the alkali metal ions of faujasite.

3.1.6 Effect of ammonium salt concentration
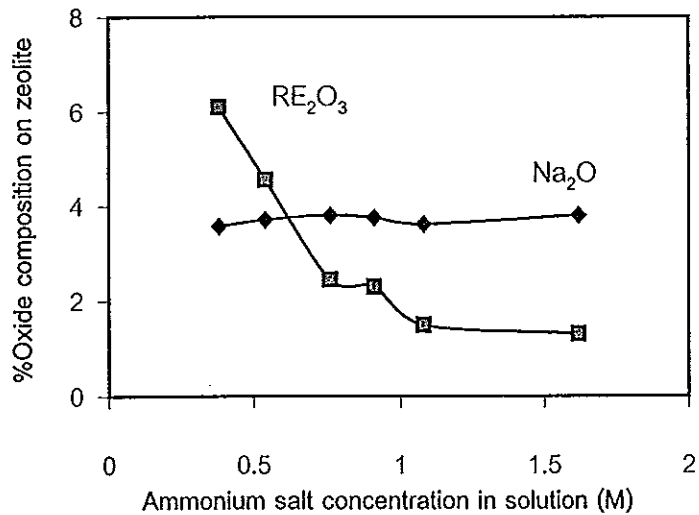
Figure 3-6 Effect of ammonium salt concentration

Figure 3-6, it shows that the rare earth decreases in exchange capacity as ammonium salt concentration increases, while the sodium content does not change. This suggests that the exchange reaction is competitive between rare earth and ammonium ions. So increasing ammonium concentration results in decreasing exchangeable rare earth ions. However, when ammonium salt concentration is lower than 0.75 M, rare earth production rapidly decreases, while a higher ammonium concentration slowly increases the rare earth content on exchanged zeolite.

3.1.7 Effect of temperature in calcination step

Figure 3-7 Effect of temperature in calcination step for 2 hrs.

Changing calcination conditions not only results in framework dealumination. cation movement and associated framework distortions also results from the hydrothermal of zeolite. Quoting Bennett and Smith have shown that dehydration and dehydroxylation of calcium exchanged Y zeolites causes migration of the calcium ions which in turn result in framework distortion and change infrared spectrum. There is a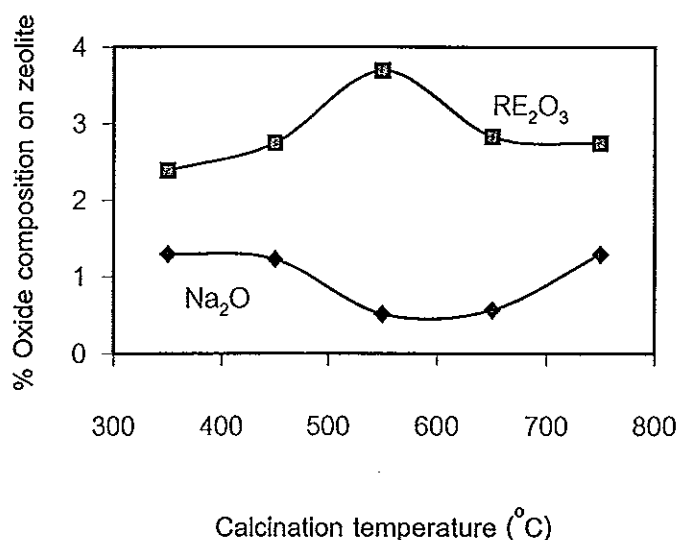lso evidence for migration of lanthanum ions in LaY at the high temperature (Scherzer et al., 1975). Jung Chao (jung Chao, 1989) found that for unheated REY zeolite, all the RE cations bonded to water molecules are in the supercages. At or above 60 °C, RE ions in the supercages start stripping their hydration sphere and migrating into small sodalite cages where each RE ion is coordinated to framework oxygens and hydroxyl oxygens. Upon dehydration at 350 °C all rare earth ions move into the sodalite cages and form the stable sodalite cage complex, La^{3+} is locked in site I'. The trivalent ion distribution cannot be changed by rehydration at room temperature, because of the reversible migration of RE ions from the supercage to the sodalite cage. Although the distributions

of trivalent ions in dehydrate and rehydrated states are similar, the difference in water content can affect the ^{29}Si spectra.
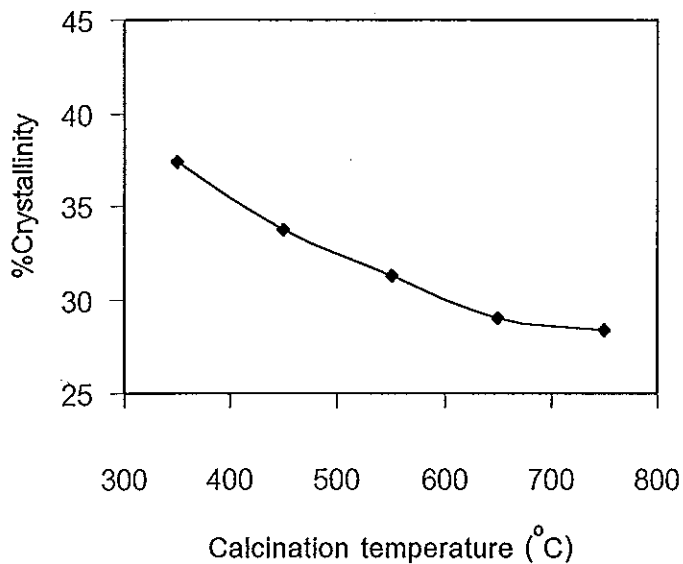
Figure 3-8 Effect of temperature to crystallinity

The calcination is the main factor for ionic exchange, because thermal treatment can redistribute exchangeable ions from supercage to sodalite cage and decompose ammonium ions, leaving behind a proton in place of the original sodium (Wojciechowski, 1995: 52). However, figure 3-7 shows that, with the temperature increased from 350 to 550 °C, the exchange process can proceed directly with the rare earth on zeolite, because thermal diffusion can increase with temperature. The higher temperature may diffuse the rare earth ions into the sodalite cage at the same time that sodium ions diffuse out to supercage. Unfortunately, at higher temperatures above 550 ° C, exchange process is not satisfactory. Rare earth content can be decreased at temperatures higher than 550 °C. The reversible reaction of Bronsted to Lewis acid can occur rapidly, and water can be removed from zeolite framework and induced to hydrothermal condition., As a result, the dealumination process suppresses the exchange capacity. For the same reason, this loss of crystallinity is due to the dealumination that occurs as the sample is calcined (Nery et al., 1997). Figure 3-8,

shows that crystallinity decreases significantly with increasing temperature because the dealumination process can occurres rapidly on crystalline zeolite.

Scherzer (Scherzer et al., 1975) found that an increase in calcination temperature from 540 to 820 °C will further enhance the dealumination process. This is reflected by the infrared spectra. As a result of the dealumination process, the unit cell size decreases, since there are voilds in the framework. However, it is probable that the voids created by the dealumination have been filled by the migration of silica.

3.1.8 Effect of time in calcination step
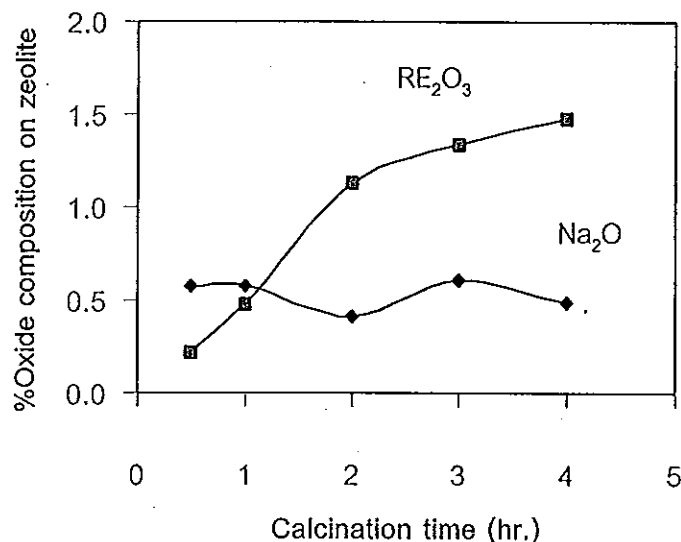
Figure 3-9 Effect of calcination time at 550 °C

Figure 3-9 shows that higher calcination time produces higher rare earth content on zeolite, however the sodium content does not change. This suggests that when the calcination time is increasing, the reaction time for redistributing exchangeable ions from supercage into sodalite cage is increasing also. However, after two hours of calcination the amount of the rare earth on zeolite is slowly increasing.
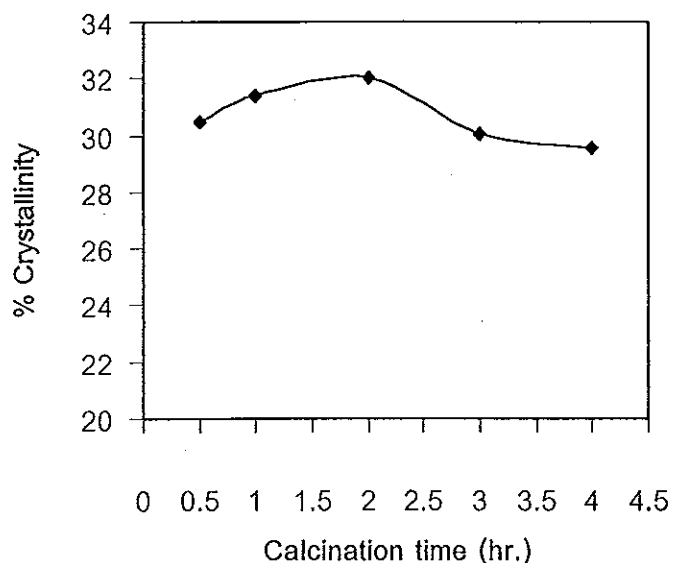
Figure 3-10 Effect of calcination time to crystallinity at 550 °C

From figure 3-10, it shows that the calcination time has a slight effect on crystallinity. The loss of crystallinity is due to the dealumination process caused by the hydrothermal effect during calcination.

The location of rare earth cations in faujasite structure and the dependence of their distribution on thermal treatments have been discussed in paper of Occelli (Occelli, 1999). After calcination, bulky complexs, such as $[Ce_2O_2]^{+4}$ $[Ce_2(OH)_2]^{+2}$, $[La_2O_2]^{+2}$ and $[La_2(OH)_2]^{+4}$ are believed to be preferentially formed in the faujasite main channels. Whereas the smaller La ions can migrate to the sodalite cage where they become part of the zeolite framework by forming –La(OH)– bridges that impart stability to zeolite structure. Two –La(OH)– linkages per sodalite cage contribute to the zeolite thermal stability whereas ions such as $La(OH)^+_2$ act as charge compensating cations. The presence of –La(OH)– species have been observed by neutron diffraction studies.

3.1.9 Number of exchange cycle
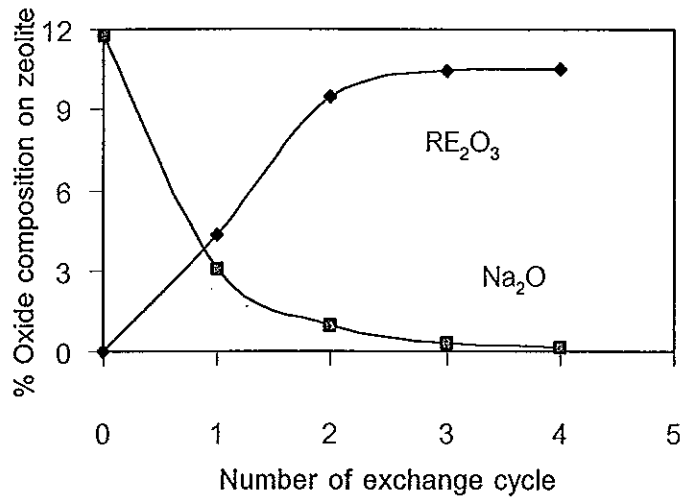
Figure 3-11 Number of exchange cycle to exchangeable rare earth on zeolite
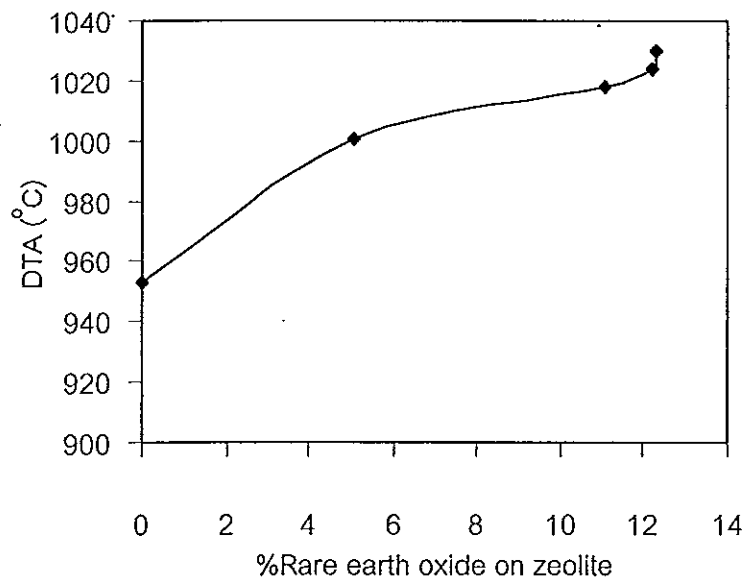
Figure 3-12 Effect of rare earth on thermal stability

A number of exchange cycles can increase rare earth component on zeolite whereas sodium rapidly decrease from 0 to 2 cycles. Generally, rare earth hydrogen Y zeolites contain rare earth content in a range of 10-13% by weight. Figure 3-11 shows that Y zeolite can reach 11 wt.% of rare earth and lower than 1 wt.% of sodium content at the second exchange cycle. However, higher number of exchange cycle effects largely on decreasing crystallinity of zeolite. Especially, the crystallinity of zeolite which decreases very slowly after the second exchange cycle as shown in figure 3-13. However, It was found that the rare earth cations can stabilize the framework and increase the thermal stability of the framework of zeolite Y (Li et al.,1994).
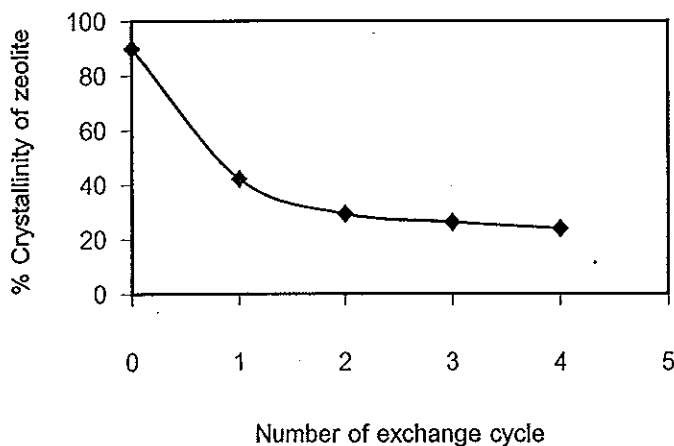
Figure 3-13 Effect number of exchange cycle to crystallinity.

Figure 3-13, it shows that the number of exchange cycles has the effect of decreasing zeolite crystallinity. This suggests that each exchanging cycle creates the hydrothermal effect in the calcination step and hydrothermal induces dealumination process making framework collapse and results in crystallinity decreasing. Li (Li et al., 1994) found that after steam treatment the decrease of relative crystallinity of HY is greater than that of LaHY whose crystallinity can remain above 60%. So, the La ion can stabilize the framework of Y zeolite.

3.2 Solid state ion exchange

The disadvantage of conventional ion exchange may present limitations of rare earth ion exchange. First of all, steric constrains may exist due to the formation of bulky hydration shell of cations to be exchanged such as Cs^+, La^+ or Ce^+. As a consequence, the diffusion of the cations into the zeolite pores is hindered and intermediate calcinations are required in order to facilitate cation migration. Secondly, the solubility of the cation precursor may be low, which limits the amount of cations available in solution. Furthermore, the maximum degree of exchange between the cations present in the solution and those in the zeolite is determined by equilibrium, and the single exchange most often results in only partial exchange. It is then necessary to repeat the exchange several times to reach high exchange level. As a consequence, ion exchange in solution frequently involves the handling and recycling of large volumes of solution. In order to avoid the above disadvantages, an alternative method, so called "solid state" ion exchange, reported by Jia (Jia et al., 1998) and Sulikowski (Sulikowski et al., 1997), is an interesting method.

3.2.1 Comparison between conventional and solid state ion exchange
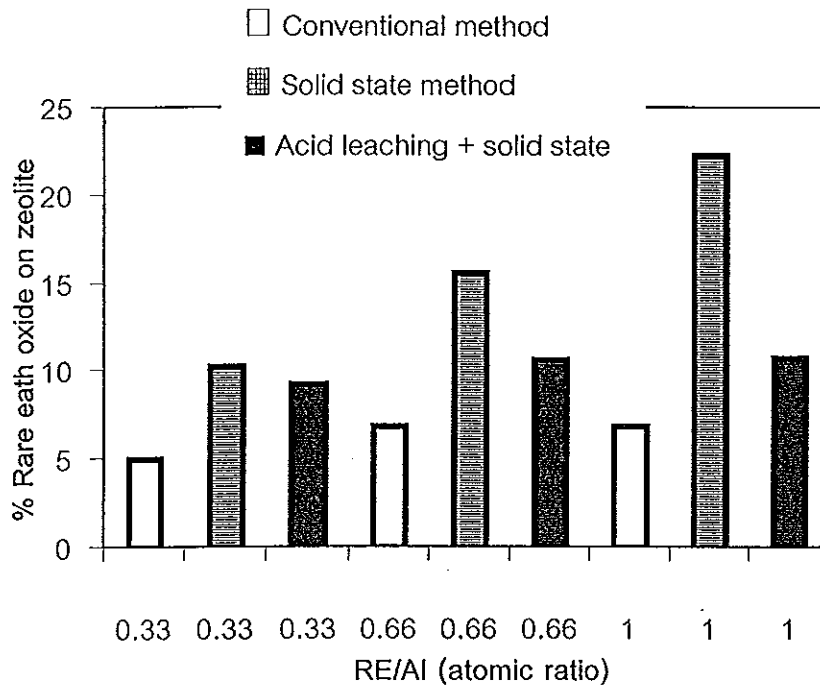
Figure 3-14 Comparison exchanging method with rare earth to aluminum ratio

The rare earth oxide from three methods is determined by XRF instrument. Figure 3-14 shows that both solid state (S.S.i.e.) and method of acid leaching plus solid state method (acid leaching+S.S.i.e) have exchangeable rare earth content on zeolite higher than the conventional method (C.i.e.). Since conventional ion exchange method has many disadvantages such as effect of hydration shell cation and steric constrains as previously mentioned.
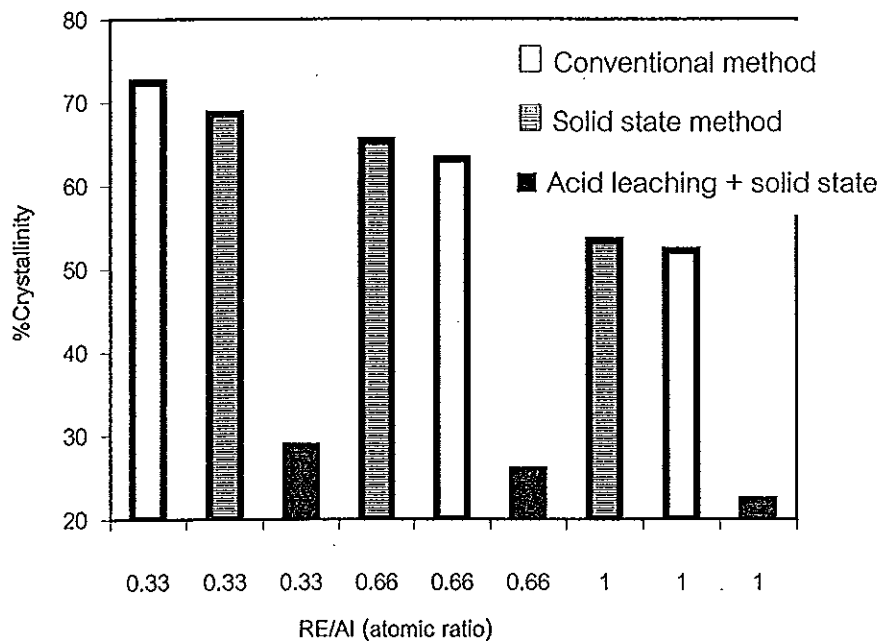
Figure 3-15 Comparison of crystallinity of the three methods

Figure 3-15 shows that conventional ion exchange has higher crystallinity than the other methods because solid state ion exchange contains rare earth salt in hydrated form. In the calcination step, water in hydrated rare earth is decomposed and created hydrothermal condition, and results in dealumination process was suppressed. This is the same reason that the method of acid leaching including solid state ion exchange have low crystallinity.

Solid state ion exchange can produce satisfactory exchanged zeolite. However, this method is very complex and there must be concerned about homogeneity of grinding between zeolite and rare earth. Also, it is very difficult to prepare water-free lanthanum chloride. Finally, DTA data and XRD spectra patterns (see appendix G) indicate that there are many impurities and non-homogeneous rare earth in zeolite.

3.2.2 Re-exchange of REHY zeolite with saturated NaCl
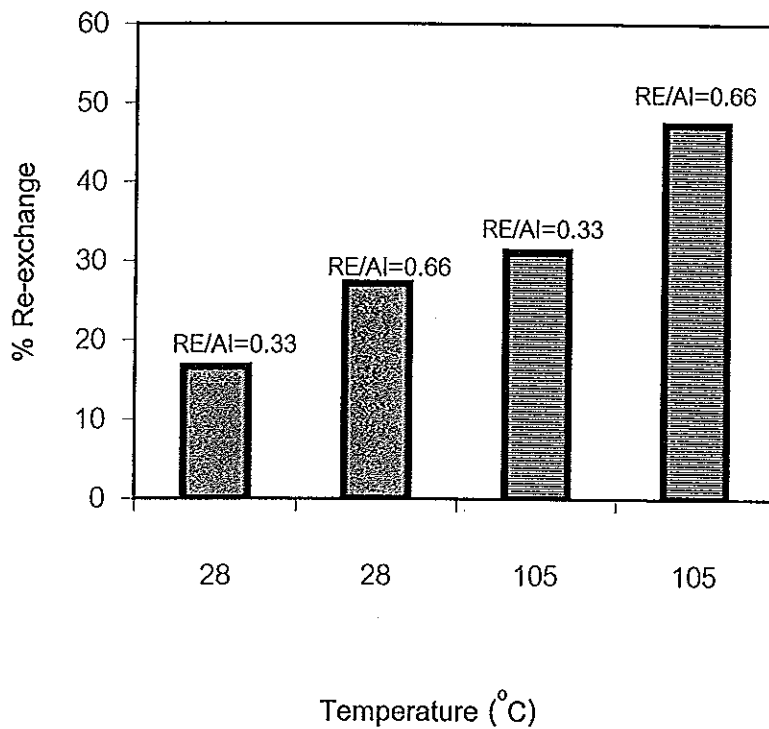
Figure 3-16 Re-exchange with saturated NaCl

Thermal treatment in the calcination step redistributes exchangeable ions from supercage (α cage) by migration into sodalite cage (β cage). However, the remaining ions in supercage (α cage) can be removed by simple sodium salt re-exchanging. Generally, ions in sodalite cage can not be removed by conventional exchange. Figure 3-16 shows that % re-exchange largely increases with temperature. It indicates that at higher temperatures, rare earth ions in supercage are more re-exchangeable than at room temperature (28 °C).

3.3 Catalyst performance

3.3.1 Microactovity
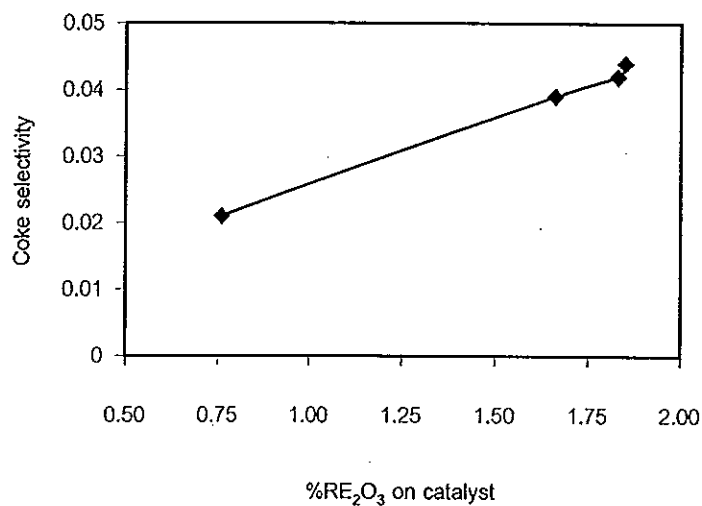
Figure 3-17 Effect of rare earth content on coke selectivity

Figure 3-17 shows that coke selectivity increases directly to rare earth content on catalyst, because the presence of rare earth in Y zeolite increases its stability and catalytic activity (Scherzer, 1989:247). Also, rare earth ions could increase the acidity of the OH groups by withdrawing electrons from the O-H bond (Gates et al., 1984). As acid sites are increased the activity and reaction more result in coke of catalyst.
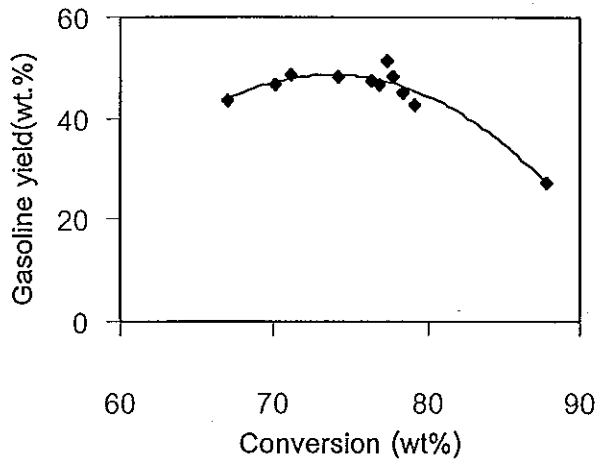
Figure 3-18 Relation of conversion and gasoline yield on REHY aging catalyst

The yield of gasoline from catalytic cracking is not linear with conversion. At lower conversions, the gasoline yield increases as conversion increases. The yield of gasoline goes through a maximum and decline as conversion increase as shown in figure 3-18. This result is the same trend obtained by Chiang (Chiang et al., 1988). The conversion at which this maximum gasoline point occurs primarily a function of the feed quality and reaction temperature. The maximum gasoline yield is function of feed quality, catalyst type, and reactor temperature (Wilsom, 1997:63).
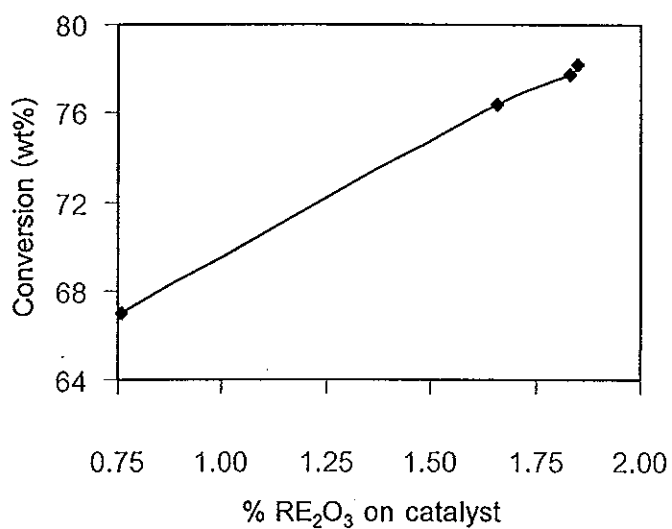
Figure 3-19 Effect of rare earth on conversion.
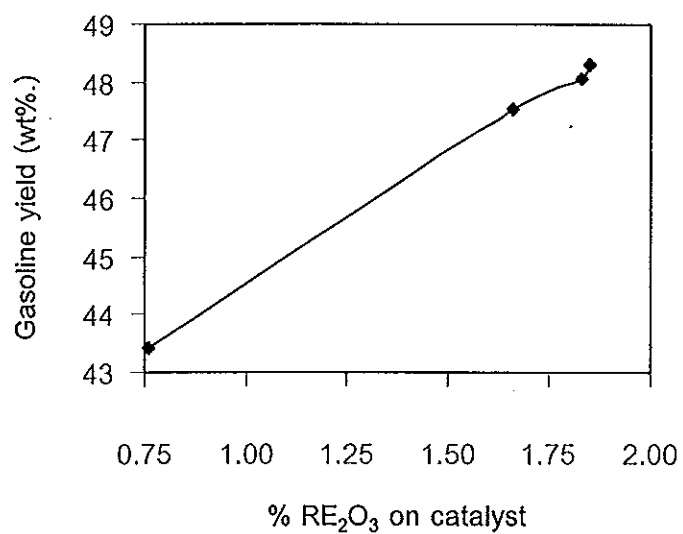
Figure 3-20 The relation of rare earth on catalyst to gasoline yield.

Figure 3-19 and 3-20, both the gasoline yield and conversion depend directly on the rare earth content. Rare earth can increase catalytic activity and gasoline yield. Sugunan (Sugunan et al., 1997) found that the acidity of the Y zeolite increases as the concentration of rare earth cations in Y zeolite increases.
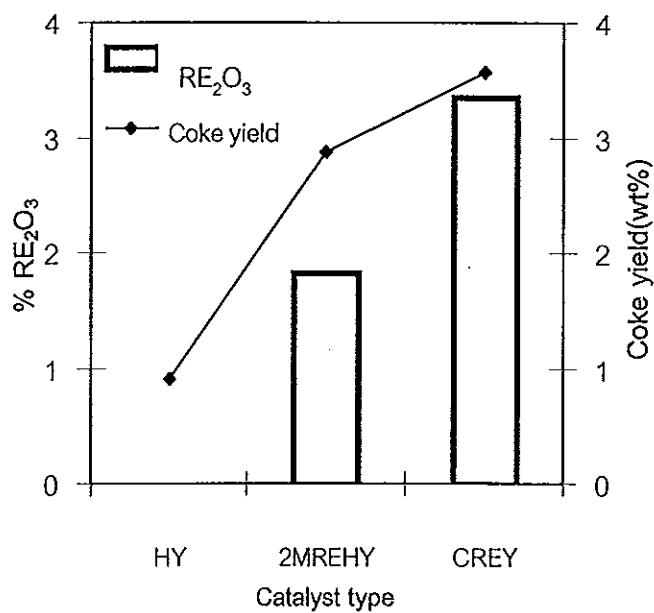
Figure 3-21 Comparison catalyst type to MAT properties.
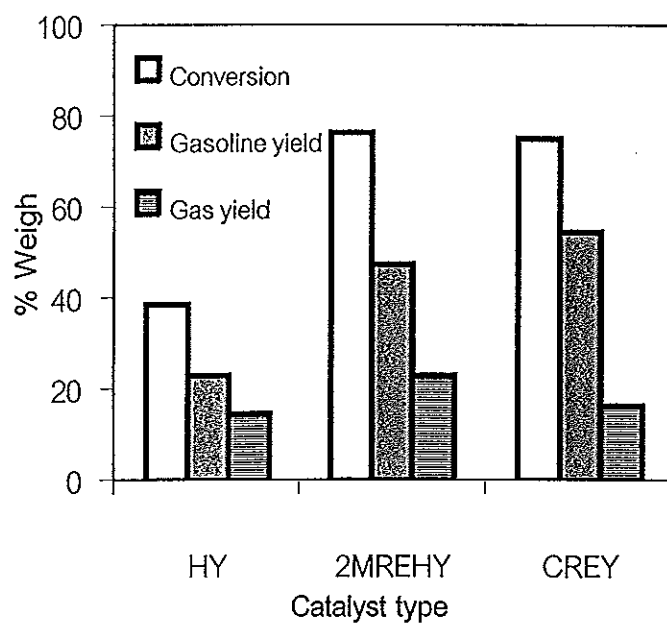
Figure 3-22 Comparison of HY, REHY and CREY catalyst.

Remark: 2MREHY is defined as the second conventional ion exchange of REHY.

Figure 3-21 and 3-22 show that, although CREY (fully rare earth Y) catalyst can produce high gasoline yield but the coke yield is very high too. However, REHY shows

the interesting MAT product such as lower coke and high conversion as CREY catalyst. Finally, HY catalyst shows low conversion.

The low zeolite coke yield is explained by relatively high rates of hydrogen transfer between cracked product molecules rather than hydrogen transfer from coke precursors (Gates et al., 1984).

REHY zeolites having RE_2O_3 content of over 10% are used primarily to boost the gasoline yield, especially where maximizing octane-barrels rather than gasoline octane is the major objective. Partially, rather than fully, rare earth exchange Y zeolites are used mainly to reduce coke formation during the cracking process. As the rare earth content of REHY decreases, their contribution to octane enhancement increases while gasoline production decreases (Scherzer, 1989:246). Ammonium exchange zeolite catalyst (HY) appears to have minor coke and light gas selectivity advantages over rare earth exchanged materials but they are substantially less catalytically active on an equal weight basis (Rabo, 1976:622). For product yield distribution, Scherzer (Scherzer et al., 1972) found that REHY sieves give higher yields in C_3 and C_4 olefins compared to CREY and the yield in total C_3+C_4 hydrocarbons is also higher for REHY sieves tested compared to CREY but coke selectivity of all REHY sieves tested is similar or better than CREY.

Table 3-1 Comparison between synthetic aging catalyst and commercial catalyst

Properties	REHY Catalyst				Commercial Catalyst	
	1MREHY	2MREHY	3MREHY	4MREHY	GongY (REY)	Lanet-35 (REHY-USY)
Chemical Properties, wt%.						
Al_2O_3	21.70	23.46	20.72	21.68	24.6	53.5
SiO_2	55.41	58.77	63.32	62.95	N/A	N/A
Na_2O	0.46	0.14	0.04	0.02	0.18	0.32
RE_2O_3	0.76	1.66	1.83	1.85	2.5~2.8	0.78
Fe_2O_3	0.38	0.34	0.42	0.32	0.47	1.1
Physical Properties						
DTA Collapse temp. °C	998.48	1015.28	1021.53	1026.29	1014.15	996.48
Microactivity, LGO feed, %wt (800 °C/4hrs., Cat/Oil 3.2)						
MAT	67.01	76.39	77.73	78.21	73	76
Gasoline yield (%wt)	43.42	47.55	48.06	48.31	42.72[a]	
Coke yield (%wt)	1.44	2.87	3.22	3.44	2.04[b]	

Remark: 1.) The prefix 1M, 2M, 3M and 4M defines the number of exchange cycle as first, second, third and forth cycles respectively.

2.) Superscript of a and b is reported by using mean value from commercial catalysts (Patprasit, 2001).

3.) N/A means data not available.

Table 3-1 shows the comparison between aging REHY catalyst and commercial catalyst in chemical, physical and microactivity properties. It was found that,

although the rare earth contents of the catalyst are lower than Gong Y, the sodium contents, thermal stability (DTA collapse) and microactivity are at the same level of REY catalyst. However, aging REHY have more thermal stability than Lanet-35.

CHAPTER 4

CONCLUSION

Rare earth hydrogen exchanged Y zeolite (REHY) can be prepared by two methods. First, is conventional ion exchange (C.i.e.) and the other is solid state ion exchange (S.S.i.e.). However, in practical ways, by using solid state, it is more difficult to prepare homogeneous REHY zeolite. For conventional ion exchange, there are many factors that can effect both the exchange step and the calcination step. The conditions for conventional ion exchange are as follows:

Ion exchange step:	temperature of solution	= 100 °C
	Contacting time	= 1.5 hrs.
	pH	= 5
	Rare earth concentration	= 0.36 M
	Ammonium concentration	= 0.5 M
Calcination step:	Calcination temperature	= 550 °C
	Calcination time	= 2 hrs.
Series	Number of exchange	= 2 times

After the cracking process, the advantage of REHY catalyst is not only lower coke yield but also higher conversion than REY catalyst. Furthermore, REHY can produce gasoline yield that is nearly the same as using REY catalyst. Rare earth content of the catalyst can depend positively on conversion, gasoline yield and thermal stability. Finally, only the second cycle of conventional ion exchange (2MREHY) prefers the use of REHY catalyst which have desired properties like those found in the commercial catalysts.

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APPENDIX

Appendix A

Atomic Adsorption Spectroscopy (AAS)

Atomic Adsorption Atomic Absorption Spectrophotometer (AAS) model AA (GBC Scientific Equipment Pty.Ltd. 901) is used to determine the chemical composition of zeolite samples.

Samples are typically made up by first dissolving approximately 0.1 gram of zeolite sample in a solution of 1ml. HF/5ml. deionized water. Dissolution times are generally in the region of 1 hour.

After complete dissolution of the zeolite, the solutions are then diluted to decrease their element concentrations to within the linear range for the particular element under study. Ionization suppressants, which consisted of alkali metal salts (e.g. KCl are added to the solutions for Al, Ca and Na; CsCl is added to the solutions for K). The following table shows the wavelengths and flame type used in the analysis of various elements (Hampson, J.,1995).

Element	Wavelength	Flame
Si	251.6	NO_2/Acetylene
Al	309.3	NO_2/ Acetylene
Ca	432.7	NO_2/ Acetylene
K	589.0	Air/Acetylene
Na	766.5	Air/Acetylene

Inductive Couple Plasma Mass Spectrometer (ICP-MS)

ICP-MS Model UltraMass-700 (Varian) is used to analyze the rare earth component in the exchange zeolite. The sample is digested by the same method as AAS method for the zeolite sample. The operating conditions of ICP-MS are as following:

Plasma Ar flow   = 15.5 L / hr.   Extraction lens   = -392 V

Nebulizer Ar flow	= 0.69 L / hr.	First lens	= -113 V
Auxiliary Ar flow	= 1.20 L / hr.	Second lens	= -0.8 V
Power	= 1.3 KW	Third lens	= -28 V
Pump rate	= 25 rpm	Forth lens	= -128 V
Photon stop	= -9.40 V	Entrance plate	= 2.0 V
Exit plate	= -167 V		

General Characteristics of ICP

In inductive couple plasma spectrometry, the sample is usually transported into the instrument as a stream of liquid sample. Inside the instrument, the liquid is converted into an aerosol through a process known as nebulization. The sample aerosol is then transported to the plasma where it is desolvated, vaporized, atomized, and exited and/or ionized by the plasma. The exited atoms and ions emit their characteristic radiation which is collected by wavelength. The radiation is detected and turned into electronic signals that are converted into concentration information for the analyst.
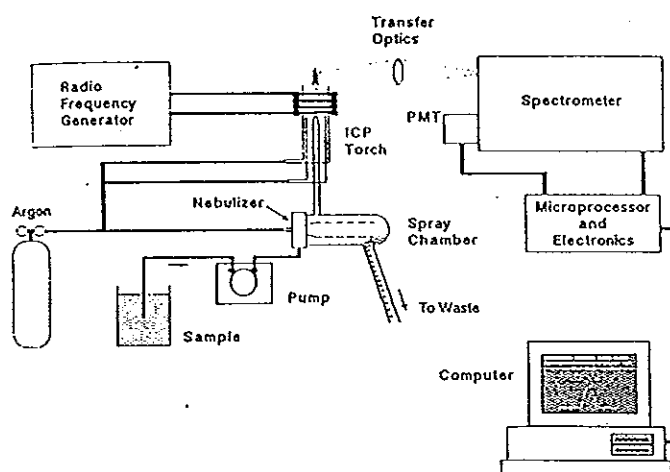
Figure A-1 Major components and layout of ICP instrument.

Most samples begin as liquids that are nebulized into an arosol, a very fine mist of sample droplets, in order to be introduced into the ICP. The sample aerosol is then

carried into the center of the plasma by the nebulizer argon flow. The function of the ICP discharge at this point are several fold. Figure A-2 depicts the processes that take place when a sample droplet is introduced into an ICP (Boss, 1977).

$$
\begin{array}{lll}
\text{(ion)} & M^+ \xrightarrow{\text{excitation}} M^{+*} \\
& M^+ \xleftarrow{\sim\!\sim\!\sim} h\nu \\
\text{ionization} & \updownarrow \\
& M \xrightarrow{\text{excitation}} M^* \\
\text{(atom)} & M \xleftarrow{\sim\!\sim\!\sim} h\nu \\
\text{atomization} & \updownarrow \\
\text{(gas)} & MX \\
\text{vaporization} & \uparrow \\
\text{(solid)} & \odot \quad (MX)_n \\
\text{desolvation} & \uparrow \\
\text{(solution)} & \bigcirc \quad M(H_2O)_m^+ , X^-
\end{array}
$$

Figure A-2 Process that takes place when a sample droplet is introduced into an ICP discharge.

Appendix B

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

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

B.1 MAT Unit

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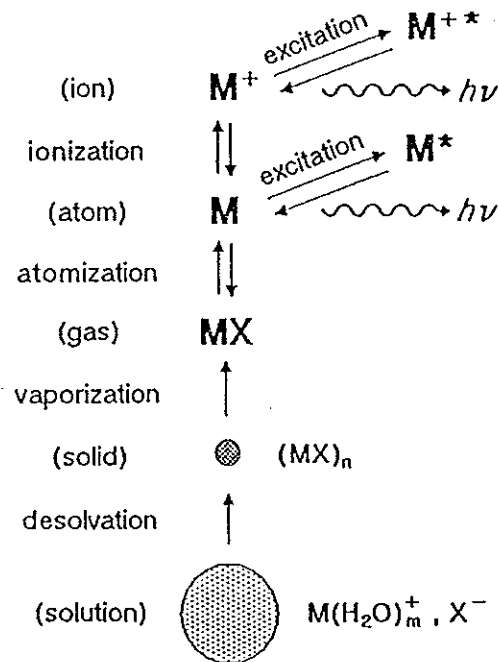inly used to test the activity index of cracking catalyst microactivity index in China is RIPP-92-90. The conditions are:

Standard feed gas oil: Straight-run light gas oil, boiling range of 235 - 335 °C

Reactor temperature : 460±1 °C

Feed oil weight : 1.56±0.01 gram

Feed time : 70 seconds

Post stripping time : 10 minutes

Stripping nitrogen flow rate : 20-30 ml./min.
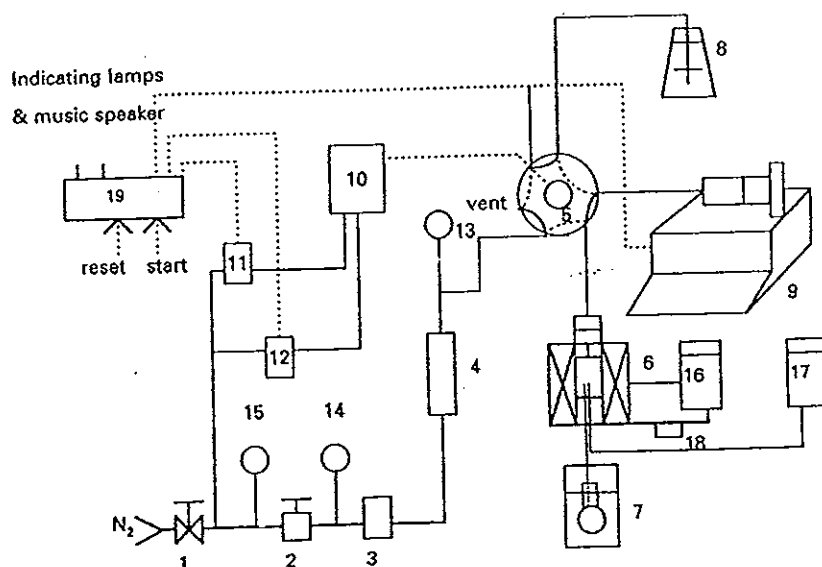
1: valve   2: pressure regulator   3: flow regulator   4: rotary flow meter

5: six-port valve 6: reactor & heater   7: ice bath & collect bottle   8: feed oil bottle

9: injection pump 10: six-port valve driver   11: selenoid valve   12: selenoid valve

13: reaction pressure gauge 0-0.16 MPa   14: regulated pressure gauge 0-0.4 MPa

15: inlet pressure gauge 0-0.16 MPa 16: temperature controller (furnace)

17: temperature monitor (reactor) 18: solid relay

19: programmable logic controller

Figure B-1 The process diagram of MAT unit.

B.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, the length is about 7 cm where the catalyst is to be loaded. At the bottom, liquid product is collected in reciever bottle by passing though a long needle that is joined with the reciever bottle by rubber tube. The bottle is immersed in the condensed well filled with ice and water. A medical syringe needle sticks into the rubber tube, from which the cracking gas exits.

B.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 70 sec.

B.1.3 Stripping System

This 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 tube into the reactor and strip out all reaction production from reactor.

B.1.4 Measurement and Control System

The system includes the temperature controllers, the selenoid valves and the programmable logic controller (PLC). The two temperature controllers are the same, one indicates the catalyst bed temperature, the other controls temperature of the furnace. They are intelligent controllers produced by Shimandan (Shimazu), Japan, with PID self tuning, automatic cold conjunction temperature compensation, thermocouple linearization and deviant correction. Due to the uniqueness of the furnace manufacture

technology, the reactor has a 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 is turned on, the PLC will draw the six-port valve to the position shown by dotted lines. That is the pre-stripping.

2. Oil injection step: After the reactor bed temperature is stable, push the start button, then the six-ways valve will turn to the position shown by the solid lines, the syringe plug goes forward, and the feed oil is injected into the reactor through the six-ways value.

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, and 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 minutes when the alram sounds and the system goes back to the preparation step again. In order to keep the syringe plug to stay at a certain position, the rest button is enabled.

B.2 Gas Chromatography Set and Integrator

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

Carries gas　　　　　: nitrogen (OFN), flow rate: 35 – 40 ml./min.

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

Auxilliary gas　　　　: air, flow rate: 400 ml./min.

Temperature of vaporization chamber (injector): 280 °C

Temperature of detector 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   : 1 µl

Range   : set to 10^2

The recommended integrator's parameters are:

Attenuation   : 8

Half peak width: 0.04min. after1.5min. change to 0.16 min.

Use integrate function 14 to sum up all the peak areas (%wt.) before C_{12} (including C_{12}). It is the cut point of gasoline and fed oil (gas oil or diesel oil). Use integration function 5 to set the base line horizontally.

B.3 Preparation Before Operation

B.3.1 Reactor's Temperature

In order to have the 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 ± 1 °C. It can be obtained by adjusting the furnace temperature controller's set value.

B.3.2 Test Catalyst

In order to have the test catalyst correctly weighed, before loading it into reactor, it should be dried in oven for an hour at 110 – 120 °C.

B.3.3 Feed Oil

Heavy oil is not suitable for this apparatus.

B.3.4 Feed oil Weight Calibration

In order to have a correct injected oil weight, it is suggested to calibrate the weight every day before the experiment. The method is to insert the joint into a small bottle, then push the "start " button, when the squeezing step has finished, push the

"reset" button and weigh the bottle. If the oil weight is not over 1.56 ± 0.1 gram, adjust the pump's speed and calibrate again.

Example Calibration of the feed pump.

Feed oil: standard gas oil (RIPP)

Flow rate (ml./min.)	1.52	1.52	1.52
Measured Value (g.)	1.567	1.565	1.566
Average = 1.566 grams			

B.4.5 Material Balance Test

In this test the cracking gas is not collected and the coke deposit is not detected either. So in the practice test, the material balance is not done. The material balance test here is as followed: instead of using catalyst, use quartz sand to do the same process as with catalyst, weigh the collected oil. It should be more than 98% of the inject feed.

Example Blank test for checking liquid recovery

Feeding amount(g.)	1.562	1.562	1.562	1.562
Liquid Recover (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

B.5 Operation Steps

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

2. Put some quartz fiber at the reactor's bottom, weigh 5 grams of catalyst and load it into the reactor. Put the reactor into the furnace and also to the six port valve.

3. Link the collection bottle to the reactor with a rubber tube and then put the bottle into the ice water well.

4. When the reactor's temperature has stabled for 5 min., push the "start" button. The unit works automatically for injection, suction, squeezing and post stripping. After 10 minutes of stripping, the speaker sounds an alarm indicating that the test has finished.

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

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

Example: Find the MA (%wt.) of catalyst
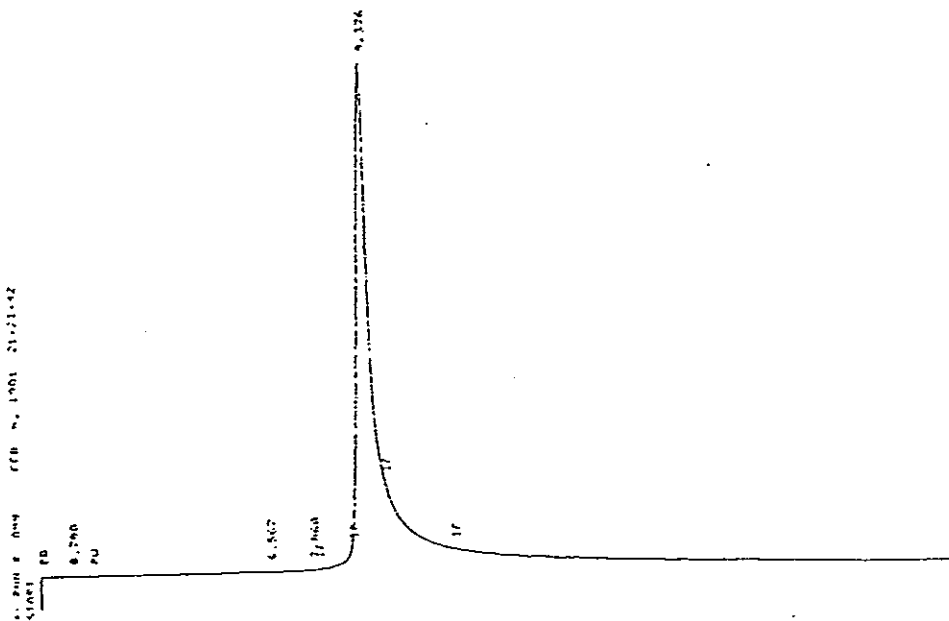
Figure B-2 Chromatogram of n-dodecane (n-C_{12})

From figure B-2 the retention time of gasoline cut point is about 9.4 minutes.

2. The reaction of catalyst with gas oil: let catalyst to react with RIPP standard gas oil in MAT unit.
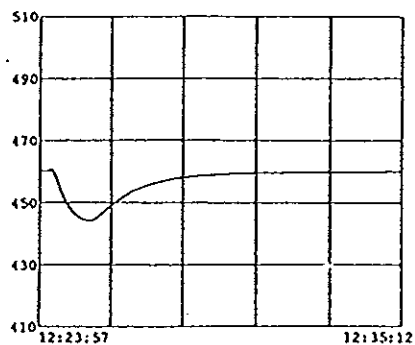
Figure B-3 Temperature profile of catalyst

3. Gasoline yield (gasoline area, %wt.): Analyze liquid product from MAT unit with Gas chromatograph
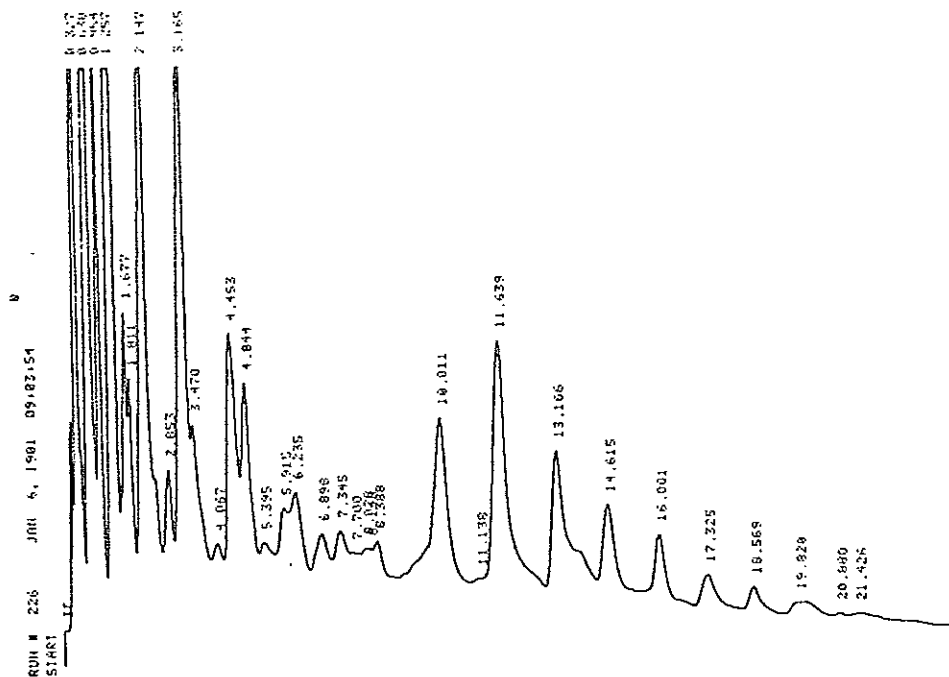
Figure B-4 Chromatogram of catalyst REHY catalyst

B.6 Analyses of Reacted Product

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

B.6.1 Find the cut point of gas oil and the gas oil:

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

B.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.

Conversion (MAT)　　=　　$100 - [(100 - A) \times B] / C$

Where:

A　　=　　Gasoline yield, analyzed by GC, %wt.

B　　=　　Liquid product from MAT, gram

C　　=　　Feed oil, gram

Appendix C

X-Ray Diffraction (XRD) spectroscopy (Crystalline analysis)

1) Place the sample zeolite and the reference in the drying oven at 100 °C for 1 hour.

2) Cool the sample in the dessicator at 35% relative humidity controlled by a saturated solution of ammonium chloride at the room temperature for at least 16 hours.

3) Grind the sample into very fine particles and pack the sample into XRD sample holder and put it into the goniometer.

4) Close the XRD window.

5) Start up the power source and adjust the detector speed.

6) Set the starting angle at 5°.

7) Turn on the goniometer and the recorder.

8) The graph of 2θ eight peaks shown in Table C-1 was used to calculate the area under each peak.

9) Calculate % of crystallinity by using the formular:

%Crystallinity $= F \times 100 \times (S_X / S_R)$,

where F = cofactor of crystallinity (100/90)

S_X = Sum of peak areas for the sample

S_R = Sum of peak areas for the reference (90%) NaY zeolite

Values frequently obtained for pure zeolites are given for general guidance

	%XRD (Intensity / NaY)
NaY, NaX	90 to 105
NH_4Y	100 to 115
REY	25 to 50
Ultrastable Y	80 to 95

10) Calculate the unit cell size and silica to alumina ratio as in the following equations,

Unit cell sized $(a_0) = 5.0509 / sine(\theta)$

Silica to alumina ratio $(SiO_2 / Al_2O_3) = [25.858 - (a_0) / a_0 - 24.191] \times 2$

By chemical analysis

$$R = Si / Al = (\%SiO_2 \times 51) / (\%Al_2O_3 \times 60)$$

$$2R = SiO_2 / Al_2O_3$$

$$\#Al / Unit\ cell = 192/(R+1)$$

By XRD analysis $\quad \#Al / Unit\ cell = 1152(a_0-2.4191) \quad$ (Breck equation)

Cation exchange can reduce the unit cell size by as much as 0.004 nm compared to the same decationate zeolite. Removal of cation, such as sodium from as – synthesized faujasite or nonframework alumina from steam dealuminated faujasite, results in an increase in unit cell 0.002 to 0.004 nm (S.Magee, J., 1993).

Table C-1 Diffraction angles 2θ hkl Miler Indices (ASTM D3906-80, 1991)

Peak	2θ	hkl
1	15.2 ± 0.2	331
2	18.7 ± 0.2	511, 333
3	20.4 ± 0.2	440
4	23.7 ± 0.2	533
5	27.1 ± 0.2	642
6	30.8 ± 0.5	822, 660
7	31.5 ± 0.5	555, 751
8	34.2 ± 0.6	664

Appendix D

Differential Thermal Analysis (DTA) (Thermal analysis)

1) Tare the DTA aluminium sample lid and pan.

2) Weigh the indium sample in the pan and put the lid on the pan

3) Crimp the sample

4) Record the weight of sample

5) Place the sample in the left DTA cup and place an empty DTA aluminium sample pan and lid in the right DTA cup.

6) Make a run using the following criteria:

    Run a baseline under analyzer parameter

    Scan rate = 10 °C/min.

    Temperature range = 500 –1000 °C

    Use the key "GO TO LOAD"

    End condition; use the hard key "GO TO LOAD"

Appendix E

Hydrothermal Deactivation (by CLY-1 Hydrothermal Aging Unit)

E.1 Installation and preparation

E.1.1 Power Supply

It is better to have three – phase electric power. Each L-N voltage is 220V, AC 20 A. If the laboratory is not equipped with three phase power supply, the three lines should be shorted in the power switch. The water pump and the recorder is wired to AC, 220V.

E.1.2 Nitrogen Supply

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

E.1.3 Water

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

E.1.4 Temperature Adjustment

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

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

E.2 Aging Procedure

E.2.1 Load Catalyst

The catalyst is to be loaded in the middle of the isothermal section of the aging tube as followed:

1. Fill porcelain rings at the bottom of the aging tube up to the isothermal section (about 17 cm. from the bottom). At its top, put some broken rings, to a thickness of about 1-2 cm.

2. Put a quartz cotton layer of about 1-2 cm. on top of this.

3. Then place 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. Put in some broken porcelain chips.

6. Fill the tube with porcelain rings.

7. Put the tube in the furnace and line up.

E.2.2 Pre-Nitrogen Stripping and Start Heating

1. Open the nitrogen in valve on the unit panel, adjust the air pressure to 0.3 MPa, regulated pressure be 0.1 MPa, and adjust the nitrogen flow to 30 ml./min.

2. Turn the "power" switch on.

3. Set the heating time for 2 hrs.

4. Set the aging time for 4 hrs.

5. Set the alarm time at the 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.

E.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, with the water valve open and the nitrogen valve closed, and aging time will start automatically).

E.2.4 Post Nitrogen Stripping

When the aging time has passed, the water pump stops, the water valve closes and the air valve opens automatically by LOGO. The post nitrogen stripping begins.

E.2.5 Finish

After about 10 minutes post nitrogen stripping, cool it down in the open air, and then take out the catalyst and separate it from porcelain rings.

APPENDIX F

The Thermogravimetric Analysis (TGA)

Thermogravimetric analysis is used to determine the framework weight of zeolite samples. Synthesised zeolite samples typically contain remnants of zeolite template and water. For adsorption/diffusion studies, it is important to remove all volatile material from within the zeolite framework.

Thermogravitmetric analysis allows the analysis of volatile material given off from the zeolite when the sample undergoes a temperature ramp. The temperature range is usually between 350 °C to 800 °C. A typical heating rate is 10°C a minute using air as the carrier gas (Hamson, J., 1995).

SM1707/44, No.1/13, April30 2001   Temperature (°C)   patchara
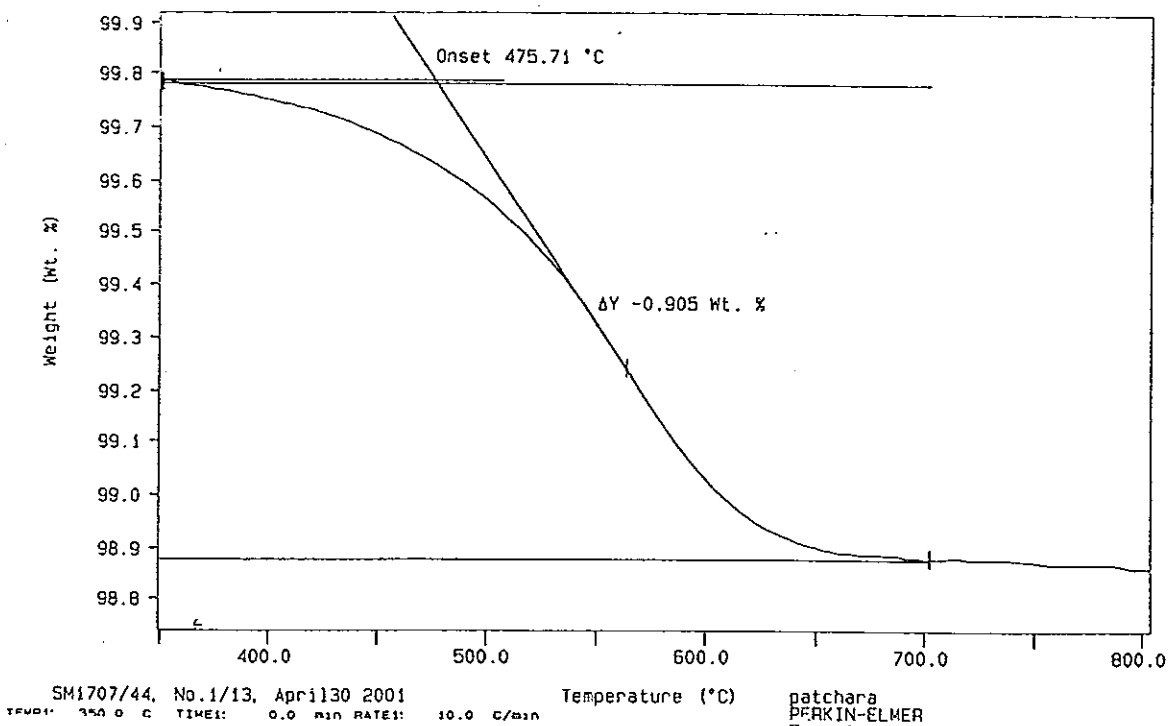TEMP1: 350.0 C TIME1: 0.0 min RATE1: 10.0 C/min   PERKIN-ELMER

Figure F-1 The resulting coke analyze of TGA

F.1 Calculation of the coke selectivity and coke yield

From figure F-1, ΔY is defined weight loss from burning spent catalyst with TGA instrument (by weight)

$$\%coke \text{ (catalyst basis)} = \Delta Y$$

so   %coke (feed basis) $= A * B / [C*(1-B/100)]$

where

A = Weight of fresh catalyst passing the MAT unit (g.)

B = Percentage of coke on spent catalyst (ΔY, %wt.)

C = Weight of Feed oil (g.)

Coke selectivity $= A*B/[(100-B)(C-(D*E/100)]$

Where

A = Weight of fresh catalyst passing the MAT unit (g.)

B = Percentage of coke on spent catalyst (ΔY, %wt.)

C = Weight of Feed oil (g.)

D = Weight of liquid product from MAT unit (g.)

E = Percentage of C_{16} in liquid product from MAT unit (%wt.)

Appendix G

The DTA and XRD pattern of conventional and solid state ion exchange
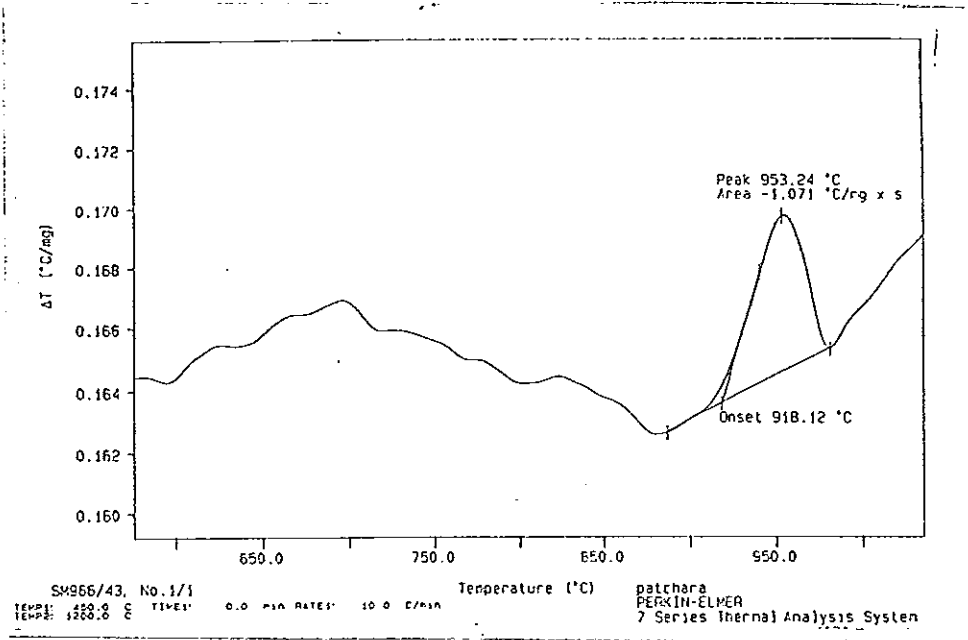
Figure G-1 DTA of NaY zeolite
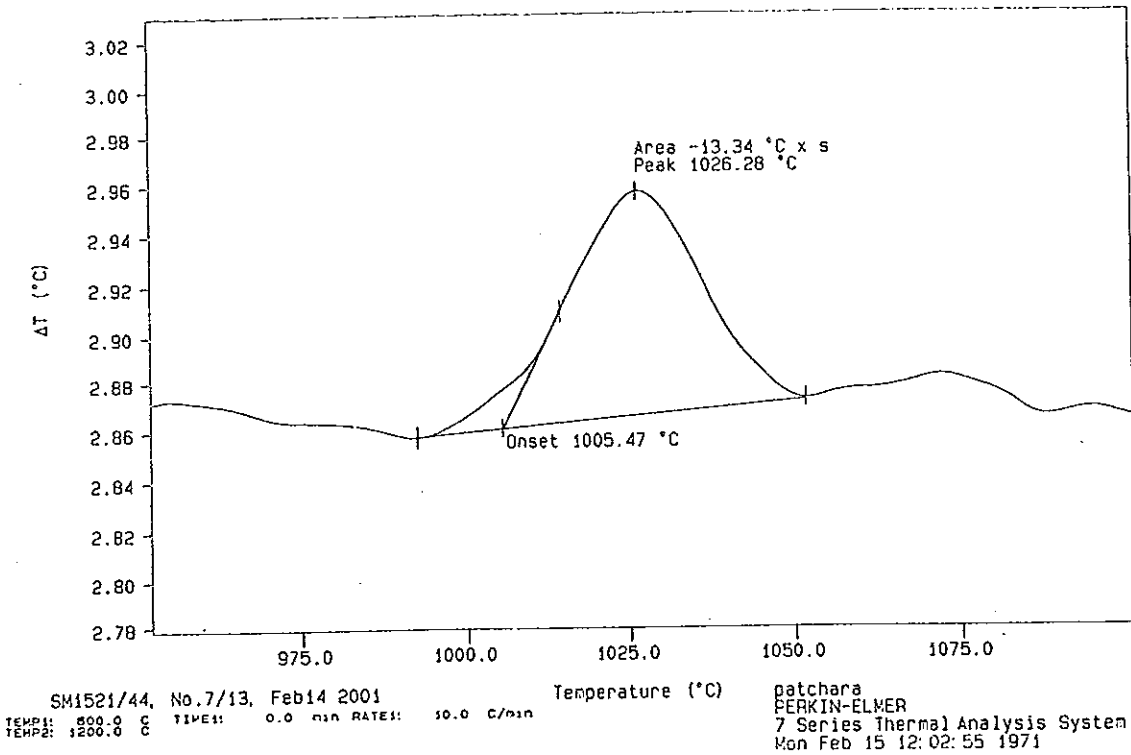
Figure G-2 DTA of sample from conventional ion exchange (RE/Al = 1)
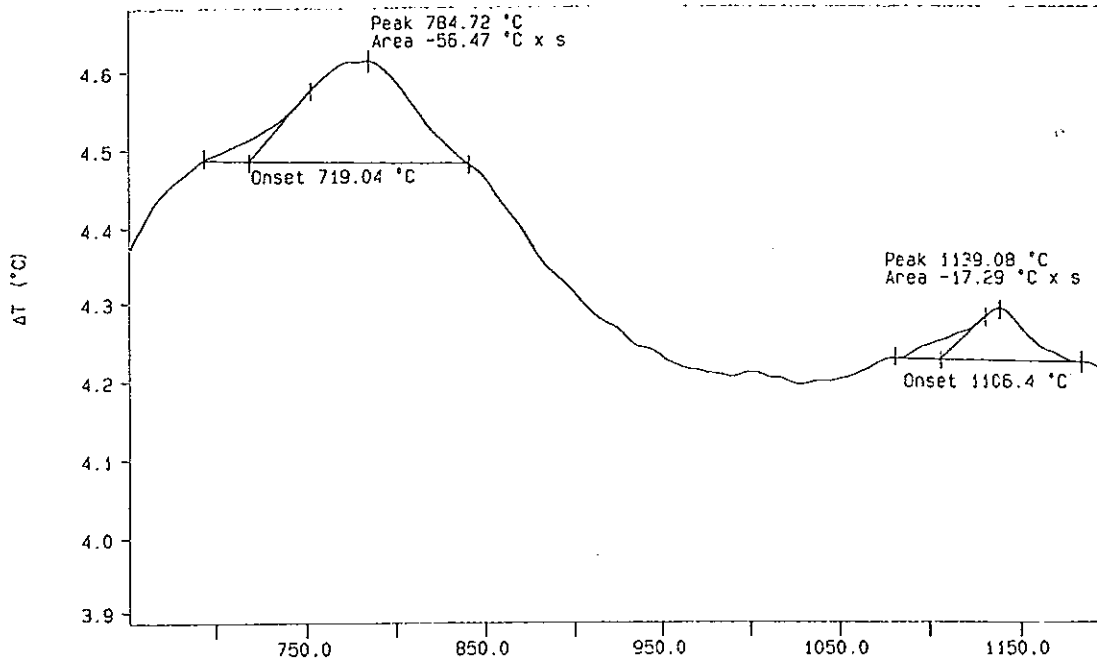
Figure G-3 DTA of sample from solid state ion exchange (RE/Al = 1)
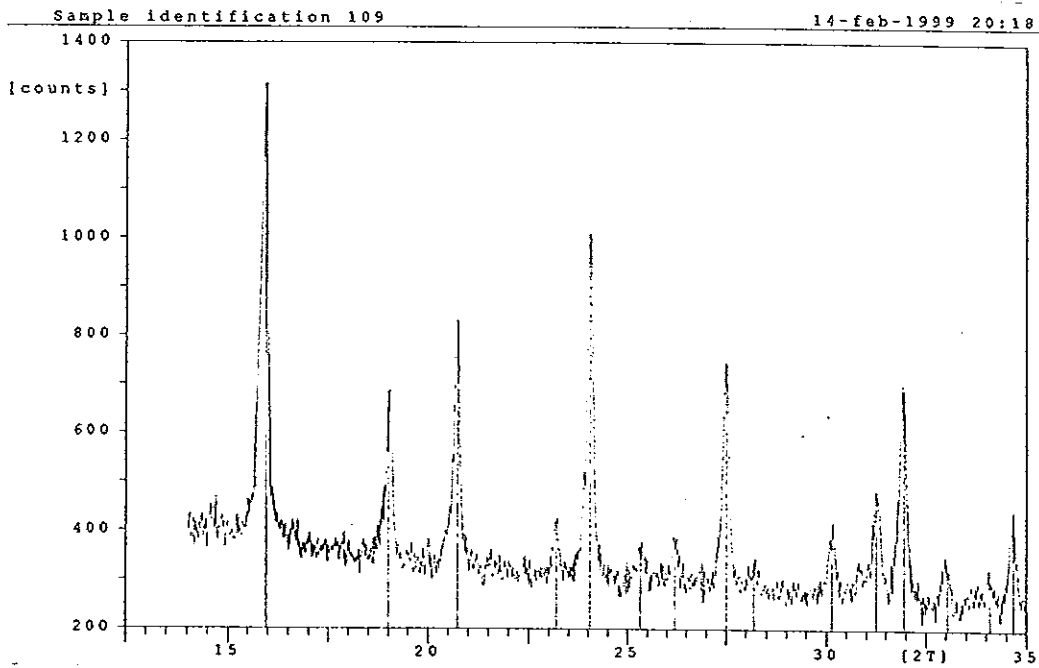
Figure G-4 XRD of sample from solid state ion exchange (RE/Al = 1)
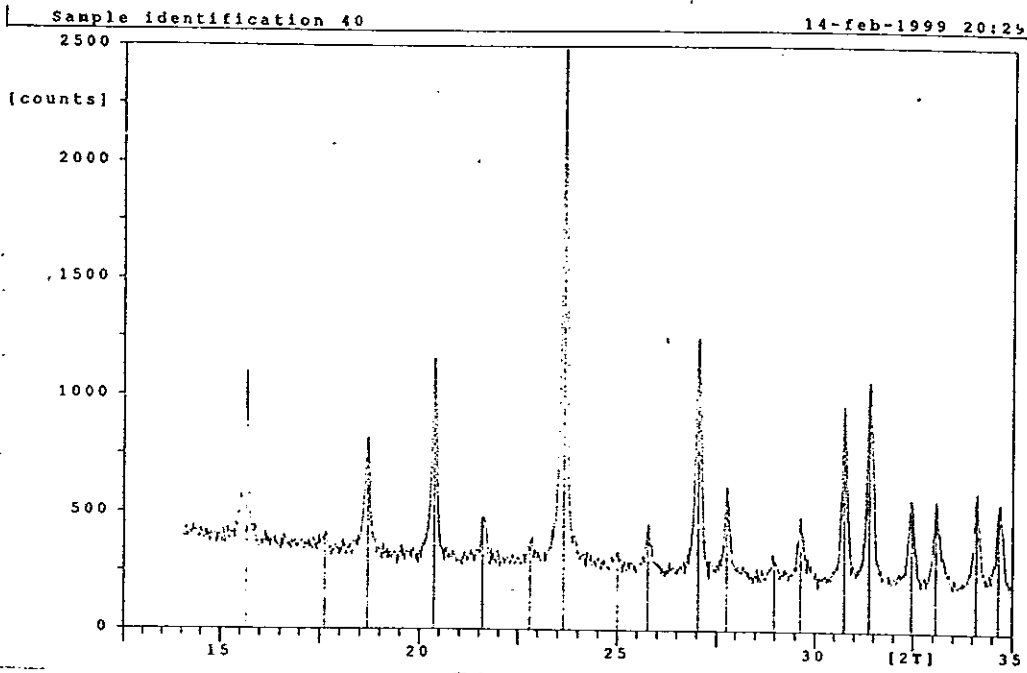
Figure G-5 XRD pattern of sample from conventional ion exchange (RE/Al = 1)
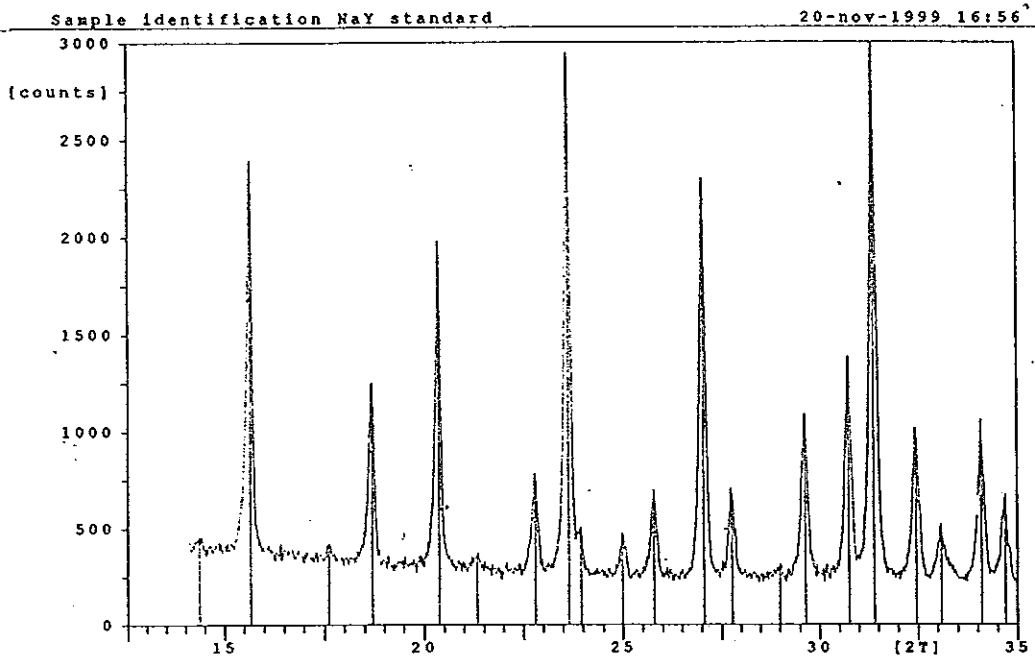
Figure G-6 XRD pattern of standard NaY zeolite.

Appendix H

Experimental data

Table H-1 Sequence of the exchange

Method	%RE$_2$O$_3$ on zeolite	Contacting time(hr.)
1	1.21	1
2	1.02	2
3	1.59	2

Table H-2 Effect of solution temperature

Solution temperature (°C)	%Na$_2$O	%RE$_2$O$_3$
28	2.71	1.16
70	2.62	4.23
80	2.49	4.37
90	2.44	5.49
100	2.4	8.43

Table H-3 Effect of contacting time

Contacting time (hr.)	%Na$_2$O	%RE$_2$O$_3$
0	11.74	0
0.5	6.27	2.87
1	5.11	3.05
1.5	3.28	3.28
2	3.40	3.84
3	3.60	4.22
4	3.54	4.90

Figure H-4 Effect of pH in exchange solution

pH of solution	%Na$_2$O	%RE$_2$O$_3$
3	3.49	5.15
4	3.34	6.06
5	3.34	6.47
6	3.34	5.92
7	3.44	5.59

Table H-5 Effect of rare earth concentration

Rare earth concentration (M)	%Na$_2$O	%RE$_2$O$_3$	%Rare earth consumption
0.03	3.29	2.55	1
0.06	3.10	2.64	0.71
0.18	3.13	3.16	1.32
0.36	3.29	4.47	2.11
0.72	2.97	5.73	2.23

Remark: %Rare earth consumption = 100 {1- ($[RE]_{initial} - [RE]_{zeolite}$) / $[RE]_{initial}$ }

Where $[RE]_{initial}$ = initial rare earth concentration use

$[RE]_{zeolite}$ = rare earth concentration in exchanged zeolite

Table H-6 Effect of ammonium salt concentration

Ammonium salt concentration (M)	%Na$_2$O	%RE$_2$O$_3$
0.38	3.57	6.10
0.54	3.71	4.55
0.76	3.80	2.44
0.91	3.75	2.29
1.08	3.61	1.49
1.62	3.80	1.30

Table H-7 Effect of temperature in calcination step for 2 hrs. (number of exchange = 2 times)

Calcination temperature (°C)	%Na$_2$O	%RE$_2$O$_3$	%Crystallinity
350	1.29	2.39	37.37
450	1.23	2.75	33.76
550	0.51	3.69	31.21
650	0.57	2.83	28.97
750	1.29	2.75	28.37

Table H-8 Effect of calcination time at 550 °C (number of exchange = 2 times)

Calcination time (hr.)	%Na$_2$O	%RE$_2$O$_3$	%Crystallinity
0.5	0.58	0.22	30.5
1	0.58	0.48	31.41
2	0.42	1.13	32.03
3	0.61	1.34	30.07
4	0.49	1.48	29.57

Figure H-9 Number of exchange to exchangeable rare earth on zeolite

Number of exchange (time)	%Na$_2$O	%RE$_2$O$_3$	%Crystallinity	DTA collapse (°C)
0	11.74	0	89.97	953.24
1	3.09	5.505	42.22	1000.46
2	0.94	11.07	29.3	1017.88
3	0.30	12.20	26.18	1024.17
4	0.12	12.32	23.95	1029.75

Figure H-10 Comparison between conventional and solid state ion exchange

Method	RE / Al	%N$_2$O	%RE$_2$O$_3$	DTA collapse (°C)	%Crystallinity
Conventional	0.33	0.36	5.08	1023.34	72.42
Solid state	0.33	0.70	10.22	990.7	68.57
Acid laching + solid state	0.33	0.01	9.28	895.74	28.73
Conventional	0.66	0.26	6.83	1025.66	65.35
Solid state	0.66	0.59	15.49	1086	63.16
Acid laching + solid state	0.66	0.01	10.66	1105.7	25.84
Conventional	1	0.23	6.88	1026	53.37
Solid state	1	0.49	22.24	1149.8	52.20
Acid laching + solid state	1	0.01	10.76	1139.08	22.27

Table H-11 Re-exchange of REHY zeolite saturated NaCl

Temperature (°C)	RE / Al	%Re-exchange
28	0.33	16.65
28	0.66	27.14
105	0.33	31.14
105	0.66	47.32

Table H-12 Effect of rare earth on coke selectivity, gasoline yield of REHY catalyst

Sample	%RE$_2$O$_3$	Coke selectivity	Gasoline yield (wt%)	Coke selectivity
1MREHY	0.76	0.021	43.42	0.021
2MREHY	1.66	0.039	47.55	0.039
3MREHY	1.83	0.042	48.06	0.042
4MREHY	1.85	0.044	48.31	0.044

Table H-13 Relation of conversion and gasoline yield on REHY aging catalyst

Sample	Gasoline yield (wt%)	Conversion (wt%)
41cat	46.68	70.08
42cat	44.98	78.44
43cat	43.42	67.01
3mixed cat1	46.59	76.91
2mixed cat	47.55	76.39
3mixed cat2	48.31	77.73
4mixed cat	48.06	74.21
2NH$_4$+2RE	48.55	71.05
2RE+2NH$_4$	51.4	77.42
2(RE+NH$_4$)	42.5	79.1

Table H-14 Comparison catalyst type to MAT properties of HY, 2MREY, CREY

Catalyst	%RE$_2$O$_3$	Conversion	Gasoline yield	Coke yield	Gas yield
HY	0	38.68	23.09	0.9	14.65
2MREHY	1.83	76.39	47.55	2.87	23.28
CREY	3.35	74.94	54.85	3.57	16.53

VITAE

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