Preparation and Characterization of a Catalytic Cracking of REY-Zeolite

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ชื่อวิทยานิพนธ์	การเตรียมและการหาลักษณะเฉพาะของตัวเร่งปฏิกิริยาการแตกตัว
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บทคัดย่อ

การเตรียมแรร์เอิร์ทวายซีโอไลต์ ด้วยการแลกเปลี่ยนไอออนบวกในโซเดียมวายซีโอไลต์ สามารถทำได้ทั้งในสถานะสารละลาย และสถานะของแข็ง จากการศึกษาหาภาวะที่เหมาะสมใน การเตรียมแลนทานัมวายซีโอไลต์ ในสถานะสารละลาย พบว่าภาวะที่เหมาะสมคือ การแลก เปลี่ยนไอออนที่อุณหภูมิ 90 องศาเซลเซียส เป็นเวลา 1 ชั่วโมง ใช้อัตราส่วนเชิงอะตอมของ แลนทานัมต่ออะลูมิเนียมเท่ากับ 0.66 ในสารละลายแลนทานัมคลอไรด์เข้มข้น 2 เปอร์เซ็นต์ อุณหภูมิในการเผา 550 องศาเซลเซียส เป็นเวลา 2 ชั่วโมง และ จำนวนการแลกเปลี่ยนไอออน 2 ครั้ง แรร์เอิร์ทวายซีโอไลต์ที่เตรียมได้ มีความเป็นผลึก 33.40 เปอร์เซ็นต์ องค์ประกอบของโซเดียม และแรร์เอิร์ทในรูปออกไซด์ เท่ากับ 0.63 เปอร์เซ็นต์ และ 22.41 เปอร์เซ็นต์ ตามลำดับ และมี เสถียรภาพเชิงความร้อนที่ 1001.32 องศาเซลเซียส สำหรับการเตรียมในสถานะของแข็ง แรร์เอิร์ทวายซีโอไลต์ที่เตรียมได้ มีความเป็นผลึก 23.20 เปอร์เซ็นต์ องค์ประกอบของโซเดียม และ แรร์เอิร์ทในรูปออกไซด์ เป็น 2.44 เปอร์เซ็นต์ และ 17.91 เปอร์เซ็นต์ ตามลำดับ และมีเสถียรภาพ เชิงความร้อนที่ 919.46 องศาเซลเซียส

แรร์เอิร์ทวายซีโอไลต์ที่สังเคราะห์ได้ถูกเตรียมเป็นตัวเร่งปฏิกิริยา โดยมีองค์ประกอบของ ซีโอไลต์ 15 เปอร์เซ็นต์ pseudo-boehmite (PBA) 21 เปอร์เซ็นต์ และ ดินขาว (kaolin clay) 64 เปอร์เซ็นต์ การประเมินค่ากัมมันตภาพการแตกตัวเชิงเร่งปฏิกิริยา กระทำโดยอุปกรณ์ทดสอบ จุลกัมมันตภาพ (microactivity testing unit: MAT) โดยใช้ แก๊สออยล์ชนิดไลต์ไซเคิล (LCO) เป็น สารป้อน พบว่า มีค่ากัมมันตภาพ 81.02 เปอร์เซ็นต์ แก๊สโซลีน 48.74 เปอร์เซ็นต์ โค้ก 3.64 เปอร์เซ็นต์ และ แก๊ส 28.67 เปอร์เซ็นต์
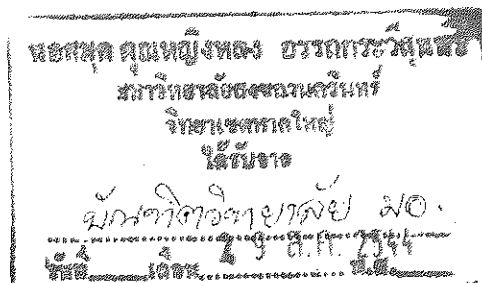
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Thesis Title   Preparation and Characterization of a Catalytic Cracking

                           of REY-Zeolite

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Abstract

     Preparation of REY zeolite by the ion exchange of cations in NaY zeolite can be performed by two methods: the conventional ion exchange and the solid-state ion exchange procedures. Various prepared conditions of LaY zeolite were studied. For the conventional ion exchange method, the suitable preparation conditions of REY zeolite are: ion exchange temperature of $90^{\circ}C$ for 1 hour, a La/Al atomic ratio of 0.66 in 2% $LaCl_3$ solution, a calcination temperature of $550^{\circ}C$ for 2 hours, and double ion exchange. The resulting REY zeolite has a crystallinity of 33.40%, and an analysis of Na_2O 0.63 wt%, La_2O_3 22.41 wt%. The thermal stability was found to be $1001.32^{\circ}C$. In the case of the solid-state ion exchange, the results are a crystallinity of 23.20%, an analysis of Na_2O 2.44 wt%, La_2O_3 17.91 wt%, and thermal stability $919.46^{\circ}C$.

     The REY catalyst was prepared by mixing 15 wt% of synthesized REY zeolite with 21 wt% pseudo-boehmite binder and 64 wt% kaolin clay filler. The activity was evaluated using a microactivity test unit (MAT) with light cycle oil (LCO, bp. $235\text{-}335^{\circ}C$) as a feedstock. The activity was found to be 81.02%. The gasoline, coke and gas yielded 48.74%, 3.64 wt%, and 28.67 wt%, respectively.

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Sutha Onkam

Contents

List of Tables

List of Figures

List of Abbreviations

AAS	=	Atomic Absorption Spectroscopy
CREY	=	Calcined Rare Earth Y Zeolite
DTA	=	Differential Thermal Analysis
EDS	=	Energy-Dispersive Spectrometry
FAU	=	Faujasite type Zeolite
FCC	=	Fluid Catalytic Cracking
GC	=	Gas Chromatograph
HREY	=	Hydrogen Rare Earth Y Zeolite
HY	=	Hydrogen Y Zeolite
ICP	=	Inductively Coupled Plasma
La	=	Lanthanum
LaHY	=	Lanthanum Hydrogen Y Zeolite
LaNaY	=	Lanthanum Sodium Y Zeolite
LCO	=	Light Cycle Oil
MAT	=	Microactivity Testing
NaY	=	Sodium Y Zeolite
NH_4Y	=	Ammonium Y Zeolite
RENaY	=	Rare Earth Sodium Y Zeolite
REY	=	Rare Earth Y Zeolite TEM
USY	=	Ultrastable Y Zeolite
WHSV	=	Weight Hourly Space Velocity
XRD	=	X-ray Diffractometer
XRF	=	X-ray Fluorescence Spectroscopy
ZSM-5	=	ZSM-5 Zeolite

Chapter 1

Introduction

1.1 Introduction

To be interested in the zeolite compounds is to become involved in many aspects of science and technology. They are materials with unique properties, which find uses in such diverse fields as oil cracking, nuclear waste treatment and animal feed supplementation. In their natural form they have a special importance in recent geology and their elegant molecular architecture has attracted an unrivalled interest from scientists seeking to apply modern instrumental methods to the determination of chemical structure (Dyer, 1988).

After the discovery of zeolite catalysts in the late 1950's it appeared for a while that hydrocarbon catalysis over zeolites could be interpreted, although not rigorously, by the characterization of structural details, particularly the cations, in the zeolite crystal. Given the advantage of the structural analysis of a crystal matrix over that of a crystal surface, the difference between zeolites and the surface of many other catalysts, the chance to decipher catalysis by characterizing the zeolite structure looked excellent. Now, after two decades of intensive work, several of the basic questions of zeolite catalysis remain unanswered. As usual, the discovery of new phenomena runs far ahead of lasting interpretation.

While a full interpretation of the catalytic phenomena occurring over zeolites remains to be spelled out in the future, the past work on zeolite catalysis and zeolite chemistry has greatly enriched the science of catalysis and surface chemistry. The study of the chemical environment within the pores and cavities of the zeolite crystal showed that the zeolitic surface is different from either the ordinary crystal surface or the ordinary crystal lattice; it has properties of both. Accordingly, a substantial part of zeolite chemistry resembles phenomena found in solid state. In addition to new and rich chemistry, zeolite catalysis introduced several new catalytic processes into petroleum refining with major economic impact.

Zeolites used in the manufacture of commercial fluid cracking catalysts are synthetic versions of the zeolite, faujasite. Before 1964, the quantity of commercially produced synthetic faujasite was negligible; however in the past decade, the rate of synthetic faujasite production for catalytic cracking applications alone was between 21 and 30 million pounds per year. The principal factors contributing to this growth were the increased conversion, gasoline yield, and much improved coke selectivity afforded by these catalysts during a period of gasoline demand and need capacity expansion (Rabo, 1976).

The sodium on the catalyst originates either from zeolite during its manufacture or from the FCC feedstock. It is important for the fresh zeolite to contain very low amounts of sodium. Since sodium decreases the hydrothermal stability of the zeolite. It also reacts with the zeolite acid sites to reduce the catalyst activity. In the regenerator, sodium is mobile. Sodium ions tend to neutralize the strongest acid sites (Sadeghbeigi, 1995). Thus, it's necessary to minimize the sodium in zeolites. The rare earth (RE) forms of Y zeolite obtained by ion exchange of synthetic NaY with RE ions are important catalysts in petroleum refining and processing (Horng Chen, 1990). Rare earth components such as lanthanum and cerium were used to replace sodium in the crystal. The rare earth elements, being trivalent, simply form "bridges" between two to three acid sites in the zeolite framework. The bridging basically protects acid sites 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 (Sadeghbeigi, 1995).

The ion exchange of cations in crystalline aluminosilicates and related materials is a standard method used for modifying their catalytic and sorption properties. Cations can be introduced into those solids by using aqueous solutions of corresponding salts. A careful control of pH is frequently required to avoid the hydrolysis of many salts, which may be followed by the deposition of oxides or hydroxy oxides on zeolitic crystals. Organic solvent may be used in some cases, but this is seldom carried out. Working with solutions has, however, many disadvantages. Large volumes are needed, and the

whole procedure must be repeated several times to reach high degree of ion exchange. The early observations by Rabo et al. and Clearfield et al., the NMR demonstration of the ion exchange upon the mere physical mixing of two different forms of zeolite A at room temperature led to systematic studies on the so called "solid-state ion exchange" or "contact-induced ion exchange" in zeolites (Sulikowski et al., 1997).

It is generally known that hydrocarbon cracking catalysts which are promoted with stabilized zeolites, particularly ion exchanged synthetic faujasite (X and Y-type), or Y-zeolites and modifications thereof, such as ultrastable Y-zeolites (USY) and calcined rare-earth-exchanged Y-zeolites (CREY), are capable of producing high yields of gasoline fractions from petroleum feedstocks such as gas oil. These cracked gasoline fractions are subsequently combined with octane enhancing additives such as tetraethyl lead to produce high-octane motor fuel. The production of high level yields of C_3 and C_4 olefins can be enhanced even more by the addition of promotional amounts of calcined rare earth exchanged zeolite (CREY) to the catalyst composite (Lussier et al., 1976). In recent times, much attention has been paid to optimizing the properties of the Y-zeolites to be used in FCC catalysts, in order to obtain FCC catalysts which produce less coke and gas and are more selective to gasoline and other desirable products. (Chamberlain et al., 1996).

These show that the modification of NaY zeolite to control or improve the catalytic properties, such as acidity, selectivity or hydrothermal resistance are very important for the petroleum refining industry.

The research area is to prepare the REY-zeolite by using rare earth ion exchange techniques from Research Institute of Petroleum Processing (RIPP) Sinopec, Beijing China. Understanding from some literature reviews and patents has developed the further applications methods of experiments.

1.2 Objectives

    1.2.1 To study the preparation of a REY-zeolite.

    1.2.2 To examine the performance and characteristics of a REY zeolite catalyst.

1.3 Literature reviews

There are some 40 natural zeolites, more than 150 zeolites have been synthesized, most of which have no known natural counterpart. Currently, only a small fraction of all these zeolites are of commercial interest. By far the major industrial process that utilizes zeolites is the catalytic cracking of petroleum and the replacement of amorphous silica-alumina materials by faujasitic (type Y) zeolites in the 1960's has saved the petroleum industry billions of dollars. Other major commercial zeolite processes include hydrocracking (faujasite), hydroisomerization (modenite), dewaxing (ZSM-5, beta), iso/n-paraffin separation (Ca-A), olefin drying (K-A) and methanol to gasoline (ZSM-5). Throughout the 1960's and well into the mid 1970's, zeolite containing FCC catalysts were modified to take advantage of the increased conversion and liquid yield and low coke production afforded by catalytic cracking over zeolites. Demands on catalyst performance were modified to include increased gasoline octane, increased activity, and improved metal tolerance. Today, new demands are requiring FCC catalysts to increase the yields of light olefins and branched isomers in reformulated gasoline (Magee and Mitchell, 1993).

1.3.1 Modification of Y zeolite

1.3.1.1 Conventional ion exchange

The ion exchange of cations in crystalline aluminosilicate and related materials is a standard method used for modifying their catalytic and sorption properties. Cations can be introduced into those solids by using aqueous solutions of corresponding salts. A careful control of pH is frequently required to avoid the hydrolysis of many salts, which may be followed by the deposition of oxides of hydroxy oxides on zeolitic crystals (Sulikowski et al., 1997).

The process for the preparation of a modified zeolite of the Y-type to be treated with a solution of a metal salt and a calcination which comprises treating a zeolite of the Y-type having an alkali oxide/aluminium oxide molar ratio of at most 0.13 with a solution of a muti-valent metal salt having a cationic radius between 0.6 and 1.0 Å and

converting the thus treated zeolite by calcination into a product having a unit cell size between 24.21 and 24.65 Å (Klazinga, 1988).

Occelli and Ritz (Occelli and Ritz, 1999) claimed that FTIR spectroscopy of pyridine thermal desorption, nitrogen sorption powder X-ray diffraction (XRD), together with elemental analysis have been used to study the physicochemical properties of a family of rare earth (RE) containing faujasite (REY) crystals having different composition, unit cell dimension, acidity and hydrothermal stability (at $760^\circ C$ with 100% steam, 1 atm). The calcined REY was prepared by ion exchange Na ions in NH_4Y with a mixture of RE chlorides prepared by acid-leaching bastneasite.

At $70^\circ C$, 2M NH_4NO_3 solution can reduce the CREY Na_2O level from 3.30% to 0.41% in only 1 hour after an intermediate calcination step at $500^\circ C/h$; A second ion-exchange reaction can further reduce the Na_2O level to 0.06% without severely affecting crystals properties. De-alumination after the intermediate calcination step is believed responsible for minor losses of La and for unit cell contraction.

The selective removal of framework of Na ions, change the distribution of Brønsted (B) and Lewis (L) acid sites as well as acid site strength. In CREY with 3.30% Na_2O, acidity is mainly of the B-type and at $200^\circ C$ the B/L ratio is 21.1. The B/L ratio monotonically decreases to 4.36 from 21.1 when the %Na_2O decreases to 0.06% from 3.30% and the crystals's Si/Al molar ratio increases to 2.83 from 2.38. Acidity, hydrothermal stability and resistance to vanadium deactivation in CREY crystals having Si/Al = 2.83 and containing trace amounts of Na, are similar to those observed for silicon-enriched HY with Si/Al in the 5.0-10.0 range.

1.3.1.2 Solid-state ion exchange

Generally, the hydrogen or ammonium form of a zeolite is reacted at relatively high temperatures (HT; above 600 K) with crystalline metal halides or oxides, resulting in the formation of the respective metal form of the zeolite and in the evolution of HCl, NH_3, and H_2O. Recently, it was reported that "contact-induced" ion exchange proceeds also between hydrated NaY zeolite and crystalline alkaline or alkaline earth metal chloride upon mere grinding at ambient temperature. In contrast to HT solid-state ion exchange,

this intracystalline water adsorbed in the pore system of the zeolitic reactant. The product obtained consists of the ion-exchanged zeolite and crystalline sodium chloride. The latter constituent may be disadvantageous, especially if the product is intended to be used as a catalyst. On the other hand, this ion exchange procedure is a very simple one and can be performed using the zeolite in the sodium form commonly obtained by synthesis. Moreover, sodium chloride, if occluded in the small cavities, should increase the thermal stability of the zeolite structure (karge, 1994).

Beyer and coworkers (Beyer et al., 1996) stated that the quantitative data obtained by thermal analysis proved to be consistent with the stoichiometry expected for incorporation of indium (sample I) ion into Y zeolite by reductive solid-state ion exchange upon treatment of ground In_2O_3/NH_4NaY mixtures in a hydrogen atmosphere at temperatures of 620-760 K. Detailed information on the complex process was obtained by IR spectroscopy. Both high frequency (HF) and low frequency (LF) hydroxyl groups are involved in the solid-state ion-exchange process, the HF ones showing higher reactivity. Reoxidation of the formed indium (I) lattice cations was found to proceed at relatively low temperatures (300-400 K) and to result, dependent on the excess of hydroxyl groups over In^+ lattice cations, in the formation of In^{3+} and /or cationic In (sample III) species comprising 'extra-framework oxygen'. The cationic indium species obtained after reduction and reoxidation were characterized by their interaction with pyridine applied as probe molecule. Adsorption of water on the cationic indium (III) species results in the formation of Brønsted-acid sites (In $(OH)_2^+$) the acid strength of which is significantly weaker than that of 'bridged' hydroxyls. The reduction/reoxidation cycle proved to be fully reversible.

Jia and coworkers (Jia et al., 1998) declared that the lanthanum-exchanged beta zeolites have been prepared by a solid-state ion-exchange procedure which consists of calcining in static conditions a mechanical of $LaCl_3.7H_2O$ and H-beta zeolite. XRD, BET, FTIR, TEM, EDS and chemical analyses have characterized the exchanged samples at various steps of their preparation. The results have been compared to those obtained on samples exchanged in solution. In the case of conventional ion exchange in solution,

the incorporation of La into the zeolitic pores is strongly limited due to the steric hindrance caused by the large hydration sphere of the La^{3+} ions. As a consequence, strongly heterogeneous samples contaminated by La-rich crystalline particles are obtained even at rather low La contents or after repeating the exchange several times. In contrast, the yield for lanthanum incorporation reaches values as high as 100% when the solid-state exchange procedure is used. Moreover, the samples are highly homogeneous and no loss of crystallinity is observed in spite of the very simple conditions used (calcination in static). The exchange by La species of protons initially present in the H-beta parent sample is confirmed by FTIR spectra of OH groups, which also reveal that part of the incorporated La species interact with the silanol groups.

Karge and coworkers (Karge et al., 1994) reported that the La,NaY zeolite (I) is prepared by contact-induced ion exchange between solid LaCl$_3$.7H$_2$O and NaY zeolite powder. La,NaY is investigate by X-ray diffraction, ^{27}Al *MAS* NMR, ^{23}Na *MAS* NMR, and i.r. spectroscopy after various treatments. Results are compared with those obtained, employing a conventionally exchanged La,NaY sample (76) (exchange degree 76%). It shows the behavior stability of the La,NaY after heat-treatment. The catalytic performance of La,NaY and La,NaY (76) is almost identical when tested for acid-catalyzed selective disproportion of ethylbenzene.

Sulikawski and coworkers (Sulikowski et al., 1997) declared that the interaction of lanthanum (III) chloride with hydrogen forms of ferrierite, mordenite, zeolite L, and faujasite, under completely anhydrous conditions, is described. The course of the interaction has been studied by *in situ* i.r. and XRD techniques. No evidence of interaction between LaCl$_3$ and small-pore H-ferrierite was found. The other three structures investigated do interact with LaCl$_3$ even under the complete exclusion of water or water vapor from the surroundings. Plausible mechanisms of the solid-state ion exchange in zeolites are also discussed.

Yin and coworkers (Yin et al., 1998) claimed that the ZnCl$_2$/NaY samples prepared by solid-state interaction between ZnCl$_2$ and NaY zeolite under microwave irradiation are characterized by XRD and i.r. It is shown that ZnCl$_2$ is completely

dispersed onto the surface of NaY at loadings up to 37.5 wt.%. Two types of bond state of $ZnCl_2$ with NaY exist: (1) part of the dispersed $ZnCl_2$ undergoes solid-state ion exchange with Na^+ in the NaY zeolite, and (2) the rest of the dispersed $ZnCl_2$ coordinates with oxygen from the NaY zeolite lattice.

1.3.2 Location and valency of rare earth ions in Y zeolite

Chao and coworkers (Chao et al., 1989) declared that the variation of the extraframework cation location in groups IA and IIA metals and rare earth metal (RE) Y zeolites as a function of the dehydration and the rehydration is monitored by ^{29}Si MAS NMR. Unheated hydrated zeolites give similar ^{29}Si spectra as they present the similar cation distributions. Upon dehydration a high-field shift is observed which correlated with the distortion of bond angles in silicon-oxygen tetrahedra. The line shapes of ^{29}Si spectra depend on the nature and the location of the exchangeable cations and the occupancy of the different sites in dehydrated and rehydrated states. The correlation between the line shape of ^{29}Si spectra and the migration of cations from the supercages to the sodalite cages after heating treatment was studied. The results of ^{29}Si NMR agree with the known structure data.

Gaare and Akporiaye (Gaare and Akporiaya, 1997) declared that the effects of lanthanum exchange in zeolite Y and zeolite X were studied by ^{29}Si NMR. The spectra of calcined LaNaY were curve-fitted by two functions derived from the pure NaY, by keeping the Si/Al ratios of the two functions constant and similar to NaY. The fraction of the spectra shifted upfield as a result of lanthanum migration which was consistent with the percent La exchange and not with the fractional occupancy of the SI' sites. Curve fitting of ^{29}Si NMR spectra of LaNaX was more complicated due to a selective ion exchange of cations close to the Si(4Al) sites in zeolite X. However, when a redistribution of intensity between the two functions was allowed, while keeping the overall Si/Al ratio constant, high consistency between the observed and simulated spectra of LaNaX was found. It is evident from this work that the influence of lanthanum is different for the two zeolites. The results from the combination of the selective ion exchange and ^{29}Si NMR

spectra of LaNaX were found to correlate with those from Monte Carlo simulations and may be used as a complement in the study of the local ordering of framework elements.

Grunert and coworkers (Grunert et al., 1993) mentioned that the faujasite-type zeolites containing lanthanum introduced by various techniques and in different amounts were studied by X-ray photoelectron spectroscopy to elucidate the influence of the zeolite matrix on the binding energy and the shape of the La(3d) line. The results were discussed with regard to the spectral properties of the La(3d) line in La_2O_3. Significant differences in the La(3d) line shapes and binding energies between La_2O_3 and La zeolites were ascribed to final-state effects arising from the hybridization of La final states with valence bands to different extension. The La(3d) line shape of the La zeolites investigated at elevated temperatures was found to respond to structural changes in the surface region of the samples (dehydration, ion migration, formation of highly dispersed La-O structures on extraframework sites). These were also reflected in bulk phase properties of the samples (lattice parameters, determined by X-ray diffraction).

Jelinek and coworkers (Jelinek et al., 1995) proposed that the high-resolution, ^{23}Na synchronized double-rotation NMR (DOR) experiments provide site-specific information on cation-exchange processes in sodium zeolite Y. The ^{23}Na NMR spectra of $Na_{56}Y$, progressively exchanged with Cs^+, Ca^{2+}, and La^{3+} cations, respectively, indicate significantly different cation distributions in the exchanged materials. Cs^+ cations preferably deplete Na^+ cations from the supercage, while Ca^{2+} cations initially replace Na^+ cations in the hexagonal prisms. La^{3+} cation exchange, by contrast, is least disturbing to the relative distribution of the Na^+ cations. ^{133}Cs magic angle spinning (MAS) experiments provide additional information on the cation distributions in the Cs^+ cation-exchanged sodium zeolite Y. Interestingly, the positions of the ^{133}Cs resonance exhibit a significant sensitivity with respect to coexisting extraframework cations in the zeolite.

Li and coworkers (Li et al., 1994) declared that the distribution of Si and Al in the framework of LaHY zeolites were studied by ^{29}Si MAS NMR and the ordering schemes of

the distribution of Si and Al in the LaHY framework were obtained according to the results of ^{29}Si *MAS* NMR. It was found that the La ion can stabilized the Si (3Al) and Si (2Al) units of the framework of LaHY and can affect the coordination distribution of the next-nearest-neighbor Al atom (*l*-NNN) for the original Al atom. Thus, the concentration and the strength of Brønsted acid sites in LaHY zeolites can be modified by La ions.

Lee and Rees (Lee and Rees, 1987) recommend that the effect of calcination temperatures from $40^{\circ}C$ to $500^{\circ}C$ on the location and effective valency of lanthanum ions in zeolite Y (LaNaY) have been studied. At $60^{\circ}C$, lanthanum ions, initially, only sited in the supercages, started to diffuse through the six-membered ring separating the supercages to the small cavities (i.e. sodalite cages and hexagonal prisms). $La(H_2O)_x^{3+}$ species, rather than bare lanthanum ions, are believed to pass through the six-membered ring. The amount of lanthanum locked in the small cages was found to be proportional to the degree of dehydration. The sodium cation exchange capacity (Na CEC) decreased with the increasing degree of irreversible lanthanum migration. The apparent charge on the lanthanum ion was reduced from 3^+ at $100^{\circ}C$ to 2^+ at temperatures $> 200^{\circ}C$. This charge reduction was accompanied by the formation of hydroxyl groups and protons from water molecules on the hydrated lanthanum ions. Dealumination was observed during the calcination stage. Results indicate that four protons are required to remove one such aluminium from the framework.

Winkler and coworker (Winkler et al., 1989) reported that the number Ns' of rare earth (RE) ions located in the supercage can be derived from the longitudinal proton NMR relaxation time T1 of water adsorbed in 0.64 RENaY zeolite. This is because about 70% of these RE ions are paramagnetic and thus dominate the proton T1. The results do not agree completely with X-ray diffraction studies, but Ns' is in good agreement with recent results of Lee and Rees.

1.3.3 Improvement the properties of modified Y zeolite

Costa and coworkers (Costa et al., 1999) mentioned that the relationship between activity and acidity in a variety of Y zeolite for the transformation of small

olefins: ethene, propane, 1-butane and iso-butene, is presented. The acid site distribution of these samples was estimated by temperature programmed desorption of ammonia, by using a numerical deconvolution technique. This information was then correlated with catalytic activity measurements using Brønsted type equations. Despite the complexity of calculations it is clear that this gas phase solid acid catalysed reactions follow simple rules. Similar to the one observed in homogeneous processing.

Keir and coworkers (Keir et al., 1988) declared that by means of suitable ion exchange and calcination conditions, two samples of zeolite Y have been obtained in which all of the sodium ions in the original sample have been replaced by lanthanum but which contain 26 and 19 lanthanum ions per u.c., respectively. After a final calcination at 450°C, the catalytic activity of those samples for n-butane cracking at 450-550°C has been ascertained. The catalytic of the sample with 19 lanthanum ions has been shown to be very much greater than that of the sample with 26 lanthanum ions. Calcination of the active sample at 850°C produced a catalyst with much reduced activity, but on rehydration and calcination at 350°C, much of original activity was regenerated.

Lee and Rees (Lee and Rees, 1987) insisted that the dehydroxylation of lanthanum exchanged Y zeolite, LaNaY, has been studied over a calcination temperature range of 580-850°C. Approximately 12 out of the 13 lanthanum ions per unit cell, initially located in the supercage, migrated into the small cages when the calcination temperature was varied from 580°C to 650°C and decreased to about 9 ions when the temperature was raised to 850°C. The apparent charge on the lanthanum ions locked in the small cages was found to increase gradually from 2.2^+ at 580°C to 3^+ at 850°C. X-ray powder diffraction analysis indicated that the calcined LaNaY remains crystalline and has a lattice dimension similar to the starting material. Differential thermal analysis showed that the calcined LaNaY has very good thermal stability and that the crystal structure remained intact on calcination. It is proposed that during dehydroxylation a hydroxyl group associated with the lanthanum ion and a proton from the framework be removed in this high temperature calcination. The resulting lanthanum ion regains its original 3^+ charge while the zeolite still retains its ideal structure.

The total number of cations that can be accommodated within the small cages will reach a maximum of 16 per unit cell and will also be subjected to a total cationic charge criterion as a function of temperature.

Niu and coworkers (Niu et al., 1999) reported that the siliceous Y zeolite (SiO_2/Al_2O_3>150) prepared through repeated dealumination with $SiCl_4$ and steam, displays high thermal and hydrothermal stability. After it was aged at 1200°C for 4 h siliceous Y zeolite shows specific surface area as high as 510 m^2/g. Even steamed at 1000°C for 4 h it still keeps its framework perfectly. Palladium on siliceous Y zeolite shows a bit less oxidation activity of n-hexane than that on lanthanum-modified alumina. It exhibits good capability in resisting heat but poor resistance to steam. When palladium is supported on SY-A carrier, in which 12.3% alumina has been loaded on siliceous Y zeolite, the catalyst shows higher oxidation activity than Pd/La-Al_2O_3 even when heated or steamed at 1000°C for 4 h. Its excellent resistance to heat and steam make it a promising catalyst for high-temperature catalytic combustion.

Chapter 2

Fundamental of the zeolite

2.1 Introduction

The word `zeolite' is Greek in origin, coming from the words `zein' and `lithos' meaning to `boil' and `rock'. It was `discovered' by the Swedish chemist Cronstedt who found that upon heating, the zeolite sample evolved steam. There was little interest in zeolites until the late 1930's when the modern founder of zeolite chemistry, Barrer began the characterization of zeolite's structure and chemistry. His initial work studying zeolites confirmed the molecular sieving properties of the microporous solids. These discoveries sparked huge interest in the synthesis of shape selective zeolite catalysts in companies such as Union Carbide and Mobil. In the 1950s and early 1960s Union Carbide made several discoveries which proved to be of great economic significance and propelled them to the forefront of zeolite science. Milton and Breck of the Linde division of Union Carbide, over a period of 5 years, developed and characterised three novel zeolites Linde A, X and Y, which have become 3 of the most profitable synthetic zeolites. There are two very different uses of zeolites; the industrially important chemical catalysis, most notably in the petrochemical industry where zeolites are used in oil refining as cracking catalysts and as adsorbants or molecular sieves (Winder, 1997).

2.2 Natural zeolites (Hanson, 1995)

Natural zeolites are a group of hydrated aluminosilicates of alkaline and alkaline-earth metals which comprises some 40 species. Natural zeolites generally have one of three crystal structures-either fibrous, tabular or equant. Most commercial zeolites fall into the latter two categories. Zeolites are lightweight, soft minerals that are tan, buff or pale green in colour, and they have a chalky appearance.

13

Table 2-1 Some important zeolite species

Source: Hanson, 1995:40

Group/Species	Unit Cell Content	Volume of Voids(%)	S.G.	Ion-Exch. Cap (meq./g)
Group 1: Single 4-ring (S4R)				
Analcime	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}].16H_2O$	18	2.24-2.29	4.54
Phillipsite	$(K,Na)_{10}[(AlO_2)(SiO_2)_{22}].20H_2O$	31	2.15-2.20	3.87
Laumonite	$Ca_4[(AlO_2)_8(SiO_2)_{46}].16H_2O$	34	2.20-2.30	4.25
Group 2: Single 6-ring (S6R)				
Erionite	$(Ca,Mg,K_2,Na_2)_{4.5}[(AlO_2)_9(SiO_2)_{27}].27H_2O$	35	2.02-2.08	3.12
Group 3: Double 4-ring (D4R)				
A (Linde)	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$	47	1.99	5.48
Group 4: Double 6-ring (D6R)				
Chabazite	$Ca_2[(AlO_2)_4(SiO_2)O8].13H_2O$	47	2.05-2.10	3.81
Group 5: Complex 4-1, T_5O_{10} Unit (T_5O_{10})				
Natrolite	$Na_{16}[(AlO_2)_{16}(SiO_2)_{24}].16H_2O$	23	2.20-2.25	5.26
Group 6: Complex 5-1, T_8O_{16} Unit (T_8O_{16})				
Mordentite	$Na_8[(AlO_2)_8(SiO_2)_{40}].24H_2O$	28	2.12-2.15	2.29
Group 7: Complex 4-4-1, $T_{10}O_{20}$ Unit $(T_{10}O_{20})$				
Clinoptilolite	$Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$	34	2.16	2.54

Although there are many types of natural zeolites, only three are currently regarded as commercially viable-clinoptilolite, chabazite and mordenite. However, a few companies have exploited phillipsite deposits.

Generally, zeolites are formed by the alteration of silicic volcanic ash. Their lattice structure, which forms a honeycomb framework of inter-connecting channels with consistent diameter, is what gives rise to zeolites unique properties. Although each species of zeolites has a pore size of different diameter, they are generally in the range 2.5 to 10 Å.

Properties and uses of zeolites

In broad terms, zeolites properties can be divided into three categories:

- ion exchange;

- water adsorption/desorption;

- gas adsorption.

2.2.1 Ion exchange

Zeolites are blessed with a highly selective cation exchange capacity. This makes them ideally suited to a range of applications.

2.2.1.1 Nuclear waste treatment

The clean up of nuclear wastes is perhaps one of the higher profile uses for zeolites. Caesium 134, caesium 137 and strontium 90 are selectively adsorbed by zeolites when radioactive effluents are passed through filter columns packed with the mineral.

Zeolites, in particular clinoptilolite and chabazite, have been used for treating radioactive wastes for over 30 years. Some well known sites where zeolites have been successfully used are Chernobyl, Three Mile Island, Baikini Atoll, Britsh Nuclear Fuels Limited and the Hanford Atomic Energy Project.

Similarly, Teague Mineral Products of Oregon in the USA supplied a 1 short ton sample of clinoptilolite to the Bikini Atoll Reclamation Committee in September 1986. The material's absorption of caesium from the contaminated soil of the Bikini Islands was tested.

Once the zeolites have been fully loaded with caesium/strontium, the material must then be safely stored. In the case of Three Mile Island, the zeolites were vitrified in an induction furnace, encased in concrete and then placed in an underground storage facility in Hanford, Washington.

2.2.1.2 Metallurgical waste treatment

Another application for which zeolites have shown great potential is the treatment of effluents from ferrous and base metal processing plants, smelters and refineries. In the USA, the Environmental Protection Agency has designated a number of such wastes as hazardous.

Before zeolites can be used for any application, particularly complex chemical systems such as heavy-metal bearing effluents, it is important that the effluent is analysed for the concentration of:

- metal ions targeted for removal;

- competing ions, eg, alkali and alkaline earth cations;

- anions;

- pH and eH conditions.

When the above factors have been ascertained, a specific zeolite can be then be suggested. Once the effluent stream has been successfully cleaned, there are a number of different options for the safe disposal of the loaded zeolite. Like caesium/strontium laden zeolites, those bearing metals may also be vitrified and encased in concrete.

However, there are some techniques, which offer the recovery of valuable metals. The loaded material can either be added to the concentrate entering the smelter, or, alternatively, the metal content can be retrieved by using hydrometallurgical techniques-elution of a zeolite bed with a high pH sodium chloride solution, followed by electrowinning to recover the valuable metal content.

The same techniques can also be used to treat acid mine drainage (AMD) and acid waste rock (AWR), which arise when metallic sulphide minerals are mined. When water comes into contact with either an exposed mine face, in the case of AMD, or piles of waste material, in the case of AWR, it reacts with the sulphide minerals to form H_2SO_4 - sulphuric acid. The acid then passes through any surrounding material; it's waste piles or country rock, dissolving heavy metals while it does so.

2.2.1.3 Odour control

The term "odour control" covers a number of applications from cat litter to shoe care products. The reason for zeolites' suitability in these applications is based on their excellent ion exchange capacity and selectivity for ammonium.

In addition to the well known application as litter for domestic pets, zeolites are also used as a litter for poultry, dairy calves, beef cattle, pigs and horses. In such applications zeolites control both gaseous ammonia and wetness.

Manufacturers of domestic pet litter claim that zeolite-based material absorbs 4 times more ammonia than conventional clay based rivals, produces less dust and is easier to dispose of.

2.2.2 Water adsorption/desorption

Although at the moment zeolites high affinity for water is not widely exploited, their ability to adsorb and desorb water molecules without damaging the crystal structure could become increasingly important.

Perhaps the simplest application that utilises this property is desiccation. Zeolites are particularly useful at controlling moisture levels in low humidity conditions, where other desiccants are less effective.

The last few years have seen phrases like "renewably energy" become ever more application. This unique ability of zeolites to adsorb and desorb water could result in their use as heat exchangers. It has been shown that 1 short ton of zeolite spread over 200 ft^2 will produce 1 short ton of air conditioning. It is the extreme non-linearity of zeolites adsorption isotherm that results in cooling efficiencies 50% greater than other sorbent materials.

Zeolites' dehydration/rehydration properties can also be used for refrigeration. Such units have been developed that are capable of producing 6 kW-hours per square metre of collector area-equivalent to about 9 kg of ice per day.

2.2.3 Gas adsorption

Once again, although it has been demonstrated that zeolites can be used effectively to remove certain components from gas streams, they have yet to gain widespread acceptance.

When natural gas is contaminated with carbon dioxide, it is said to be "sour". In the USA, chabazite has been successful at removing up to 25% of CO_2, H_2S and H_2O from the gas from wells in the Los Angeles area.

Returning to the theme of renewable resources, zeolites can also be used to purify the methane collected from landfills. Such gases typically contain up to 40% carbon dioxide, plus the moisture, thiols and hydrogen sulphide. These latter three impurities are first removed, before the dry gas is passed through adsorption columns packed with zeolites (a mixture of chabazite and erionite has proved successful).

Although the fact that landfills generate methane gas has been known for many years, the presence of CO_2 has prevented its use as a source of energy. However, using zeolites to clean the off gases, and thus raise their BTU content, could provide a significant source of energy. The total amount of methane that could be collected from municipal sewage treatment plants, municipal waste landfills and cattle manure is vast.

Another environmental problem that could be addressed by the use of zeolites is the cleaning of stack gases. For example, the smelting of metallic sulphide ore, such as copper, results in high levels of SO_2 in the smelters' off gases. Most modern copper smelters are fitter with acid plants that convert the SO_2 to sulphuric acid (H_2SO_4), which can then either be sold as a by product, or used to leach any adjacent oxide ore using the increasingly popular ion-exchange-solvent extraction route (SXEW).

However many mining and smelting operations have no SXEW plant, and where it commands a limited price, is a major cost. Also, such acid plants also require a strong SO_2 stream to function properly, this is not a problem with modern flash smelters, but can be with old reverberatory units. Certain zeolites, such as mordenite and clinoptilolite, have been successful at removing up to 200 mg of SO_2 per gram of zeolite, even with low SO_2 and high CO_2 concentrations and high temperatures.

By the same token, zeolites can be used to clean SO_2 from the stack gases of coal fired power stations. Modern flue gas desulphurisation (FGD) plants produce gypsum ($CaSO_4.H_2O$) as a by-product/waste material.

2.3 Synthetic zeolites

Although the applications for synthetic zeolites are almost completely different to those for their natural counterparts, therefore precluding them from this feature, their similar structure and properties allows them a brief mention.

Without doubt, the major market for synthetic zeolites is the detergent sector. Before the advent of synthetically produced zeolites detergent manufactures used sodium tripolyphosphate (STPP), which has been charged with contribution to the large-scale eutrophication of lakes and streams. It was these environmental concerns that led to development of synthetic zeolites as an STPP replacement. Of the three main types of synthetic zeolite A, X and Y, the former is used by detergent manufacturers.

Zeolite A is well suited to this application because of its theoretical cation exchange capacity of 7 meq./g. It is particularly effective at exchanging sodium ions for calcium ions. In a detergent formulation this helps increase its effectiveness when used in hard water areas. The calcium ions are removed, while the subsequent sodium ions remain in solution, without precipitating onto the fabric.

However, recent years have seen something of a backlash against zeolite-based detergents. It is an increasing of popular opinion, that many environmental policies introduced over the last two decades, which saw phosphate-based detergents banned in many countries, were misguided.

In the mid-1970s, when many of today's environmental regulations were being formed (particularly in the USA and Japan), the legislation addressed the problems directly. However, the 1990s have seen the adoption of techniques such as "life cycle analysis". When the zeolites/STPP argument is looked at under these terms, studies have shown that there is little to choose between the two.

Synthetic zeolites are also used as catalysts and molecular sieves. The petrochemical industry uses synthetic zeolites widely as fluid cracking catalysts that breakdown crude oil into gasoline and fuel oils by breaking down the ling carbon chains/rings. A wide range of industries use synthetic zeolites as molecular sieves, generally in adsorption and desiccation applications (Hanson, 1995).

Zeolite Y is still the major active ingredient in FCC catalysts, but it has undergone many modifications since its introduction to meet the changing needs of the refining industry. Milton, who originally patented the synthesis of zeolite Y, used precipitated silica, sodium aluminate, and caustic soda as the starting material. An introduction or aging step of 24 hours was required at lower temperatures before actual crystallization began. Later work at the Davison Division of W.R. Grace and Co. extended the synthesis to include the use of sodium silicate and seeds to eliminate the aging step. Hayden et al., at Engelhard developed methods that allowed the in situ synthesis of zeolite Y from thermally treated kaolin and work at Filtrol developed the synthesis from acid-leached metakaolin (Woltermann, 1993).

Commercial NaY Synthesis

The synthesis of NaY from sodium silicate involves the use of aluminum sulfate, sodium aluminate, and initiator (seeds). The initiator is prepared by slowly mixing sodium aluminate solution into a solution of caustic and sodium silicate under conditions of high agitation and controlled temperature. The resulting clear solution must be aged for 12 to 16 hours at temperatures below $120^\circ F$ prior to use. The aging must be done in the absence of any agitation. The synthesis of the zeolite Y using the initiator and sodium silicate proceeds as outlined in Figure 2-1. Because zeolite Y is metastable, the crystallization temperature must be kept between 200 and $218^\circ F$ to prevent the formation of zeolite P. Also, after complete crystallization, the slurry must be quickly quenched to temperatures below $150^\circ F$ to prevent degradation of the product to zeolite P. The crystallization is generally done in the absence of agitation, because high shear results in low crystallinity.

After crystallization, the zeolite is usually separated from the mother liquor by filtration. The mother liquor, or filtrate, contains sodium silicate, sodium sulfate, and a small amount of sodium aluminate. The silicate is in the form of a disilicate ($2SiO_2.Na_2O$). The mother liquor is often recycled and used as a component in the batch makeup of the zeolite synthesis. Hence, the disilicate solution is neutralized with aluminum sulfate to form a silica-alumina gel, which is filtered and washed. The silica-alumina gel is then used in the synthesis to replace some of the silica and alumina obtained from other raw materials. Recycling not only avoids disposal of waste streams but also reduces raw material costs.

Figure 2-1 Seeded NaY Preparation Schematic
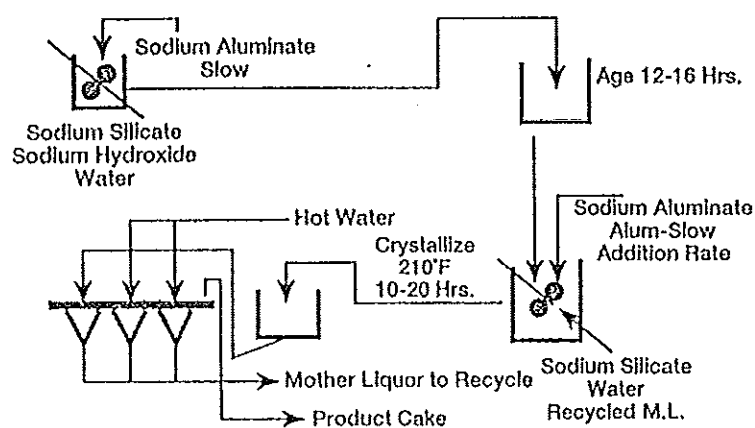
Source: Magee, 1993:108

Structural Features of Zeolites

The classic definition of a zeolite is a crystalline, porous aluminosilicate made up of a linked framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ edge sharing tetrahedra. The metal atoms are surrounded by four oxygen anions at the four corners of a tetrahedron, the tetrahedrally coordinated metals being known as T-sites.
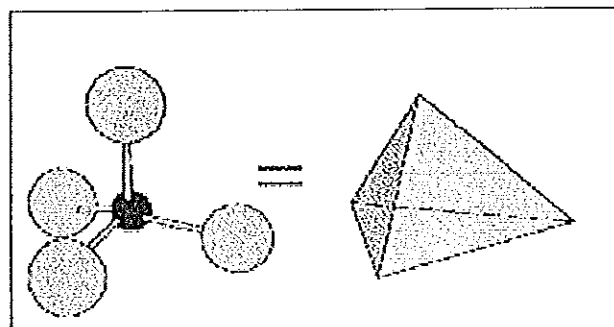
Figure 2-2 A Tetrahedral T-Site

Source: Dyer, 1988:1

The edge sharing tetrahedra join together to form a wide variety of rings and cages known as secondary building units (SBU). It is the way that these SBUs join together that gives rise to the huge number of different zeolites with and their intriguing properties. The SBUs join to form structurally and chemically important zeolite channels known as oxygen windows that pass through the zeolite. It is the pore system in the zeolites that gives rise to their interesting properties. The pores can pass through the zeolite in 1,2 or 3 directions, vary in size and in the case of ZSM-5, can also be sinusoidal. The rate of diffusion of a molecule through a zeolite will therefore be determined by a combination of the size of the sorbate and the type of zeolite used. Recent discoveries of materials virtually identical to the classical zeolite *i.e.* oxides of metals other than silicon and aluminium have stretched the definition. Virtually all oxide structures with a well defined porous structure are now included in the zeolite definition although some researchers prefering the name 'zeotypes' (Windsor, 1998).

2.4 The Chemistry of Zeolites (Windsor, 1997)

2.4.1 Brønsted Acidity

Each zeolite has an all silica polymorph; the type of zeolite is dependent on the percentage substitution of aluminium (or other metal ion) in place of silicon. In all-silica

frameworks, there is charged neutrality due to a 4^+ charge on the Si atoms and 2 oxygens with a 2^+ charge per Si.

Neutral All-Silica Framework
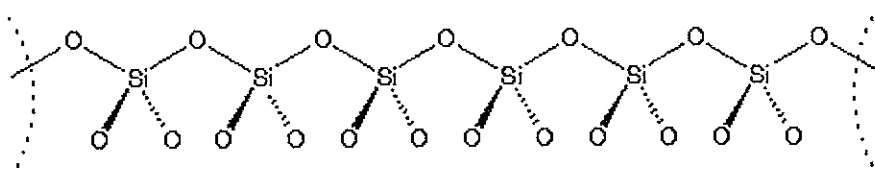
The isomorphous replacement of silicon with aluminium in a T site gives rise to a charge imbalance (aluminium having lower co-ordination ability than silicon) which must be neutralised. This is achieved in two ways in natural zeolites:

- The Al-O bond length becomes slightly longer.

- A coordination site is made available for a cation to counter the excess negative charge.

Neutral sodium balanced zeolite framework
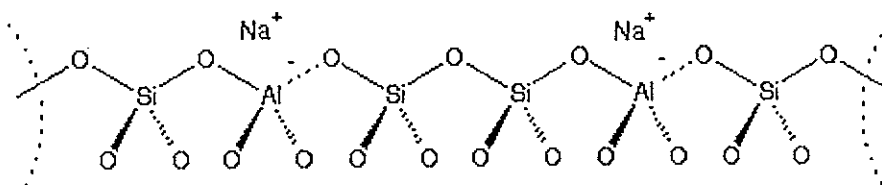
Neutral calcium balanced zeolite framework
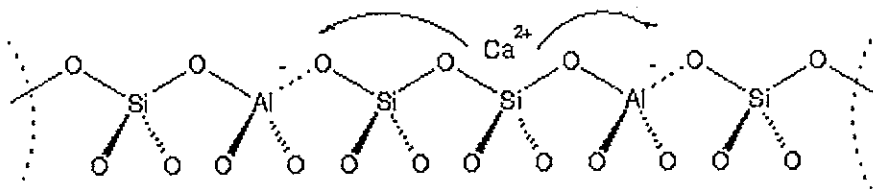
In natural zeolites, the excess negative charge is balanced by whatever ions are present in the surrounding environment e.g. K^+, Na^+, Ca^{2+} and Mg^{2+}. The type of counter ion used to balance the charge plays an important part in the use of the zeolite.

This cannot be any clearer than on the replacement of the cation with a proton by hydrothermal treatment to form a hydroxyl group at the oxygen bridge.

i) Siliceous zeolite   ii) Zeolite Brønsted acid site
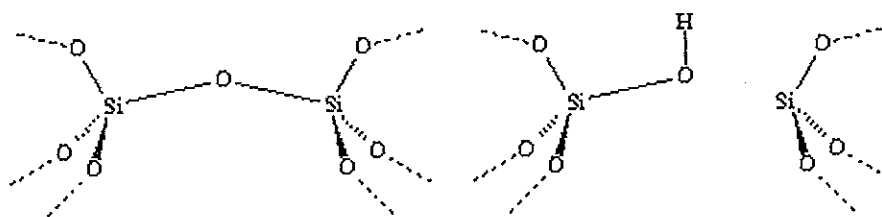
The acid site formed behaves as a classic Brønsted, proton donating acid site. The highly acidic sites, combined with the high selectivity arising from shape selectivity and large internal surface area makes the zeolite an ideal industrial catalyst. The significance of this acidic proton can be shown quite easily by comparisons of experiments in H exchanged zeolites and their equivalent cation form zeolite.

2.4.2 Shape Selective Catalysis

Zeolites have a 1, 2 or 3 directional pore structure with a well defined pore size which gives them the ability to act as efficient molecular sieves. One common use of zeolite A is in the separation of N_2 and O_2 from air. The standard method relys on cryogenically liquefying the O_2 and separating by distillation, a costly process which involves lowering the gas temperature to below $-183^{\circ}C$. The alternative is to pass the gases over a zeolite bed of Lithium zeolite X at room temperature. Both the N_2 and O_2 can fit through the pores of the zeolite but when under the influence of the electrostatic surrounding of the pore, only the smaller N_2 molecule is able to leave. The zeolite bed eventually fills up and is unable to continue separation, at this point the bed is removed from the system and heated under pressure, which evolves the O_2 and regenerates the zeolite catalyst. This process is much more efficient than the liquefaction process. Cu^{2+} chabazite is even more efficient at the separation but it is takes more work to recover the N_2 so this zeolite is only used in the removal of trace amounts of N_2 from argon.

The zeolites ability to preferentially sieve molecules can be used in a more useful way. If a reactant is sterically unable to enter the zeolite pores, where the reaction takes place, then the product resulting from that reactant is also restricted (figure 2-3). In the second case, if a product forms inside the zeolitic cavity but is unable to leave, again it is restricted (figure 2-4).
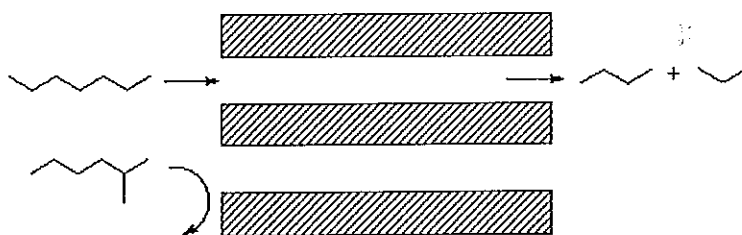
Figure 2-3 Schematic diagram of reactant shape selectivity: Rejection of branched-chained hydrocarbons

Source: Dyer, 1988:120
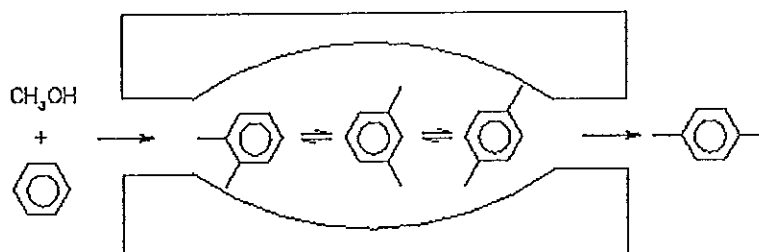
Figure 2-4 Schematic diagram of product shape selectivity: Para-xylene diffuses preferentially out of the zeolite channels

Source: Dyer, 1988:120

When molecules are absorbed into the zeolite pores, they are enveloped in a large electrostatic potential, as they would be in a solvent, an enzyme cleft or in a cyclodextrin molecule but with the added advantage of a huge internal surface area. As well as this advantage, solvent molecules can be excluded from the zeolite pores to prevent reactant/solvent interactions, which can greatly reduce subsequent reaction rates. Subsequently, if there is a high loading to supercage ratio, the concentration of

the reactants will be much more highly concentrated than solvated or in the gas phase. An example of this is the K^+ form zeolite Y catalyzed cracking of hexane at $500^\circ C$. The reaction can be catalyzed by strong acids but in this case, the zeolite counterion is K^+ not H^+. The product distribution is found to be characteristic of a free-radical mechanism rather than one proceeding via a carbenium ion intermediate. Hydrogen abstraction from the hydrocarbons by radical intermediate is favored in the pores of the zeolite whilst β-scission of the radicals is unaffected. The bimolecular steps are accelerated whilst unimolecular steps are unaffected.

The catalytic mechanism of this reaction is due to the fact that the reactants are trapped in the microactivities of the zeolite, increasing the local reactant concentration. In addition to this, there are no solvent molecules to keep the reactants separated and play any part in side reactions.

Another example of the effect of shape selective catalysis is that which takes place in the Methanol to Gasoline (MTG) process developed by the Mobil Oil Company. A stream of gaseous methanol is passed over a H-ZSM-5 catalyst bed and a dehydration-polymerization reaction takes place inside the pore. The resulting effect is a sharp cut off of product distribution at C_{11} (gasoline) length fractions, the largest length of hydrocarbon that can fit inside the zeolite pore. The result of this cut-off is that no extra reprocessing is needed to remove heavier residues.

Oxidation of hydrocarbons by molecular oxygen is a key process in the chemical industry. Small, partially oxygenated hydrocarbons are used as building blocks in the manufacture of plastics and synthetic fibers, for example, and many play a role as intermediates in the synthesis of fine chemicals. Photocatalyzed oxidation of hydrocarbons in zeolite cages, is the technique which uses molecular oxygen with visible light and results in intermediate oxidation products with unprecedented high selectivity, a recently discovered simple method that gives partial oxidation of small alkenes, alkanes, and alkyl-substituted benzenes by O_2 at unprecedented selectivity, even at high conversion of the hydrocarbon. The approach is based on visible light-induced chemistry of hydrocarbon O_2 collisional pairs in the cages of large-pore

zeolites. Reactions are conducted at an ambient temperature in the absence of solvent or photosensitizer. Here we will describe the most interesting reactions established thus far (figure 2-5) and define issues that pertain to scale-up of the method.
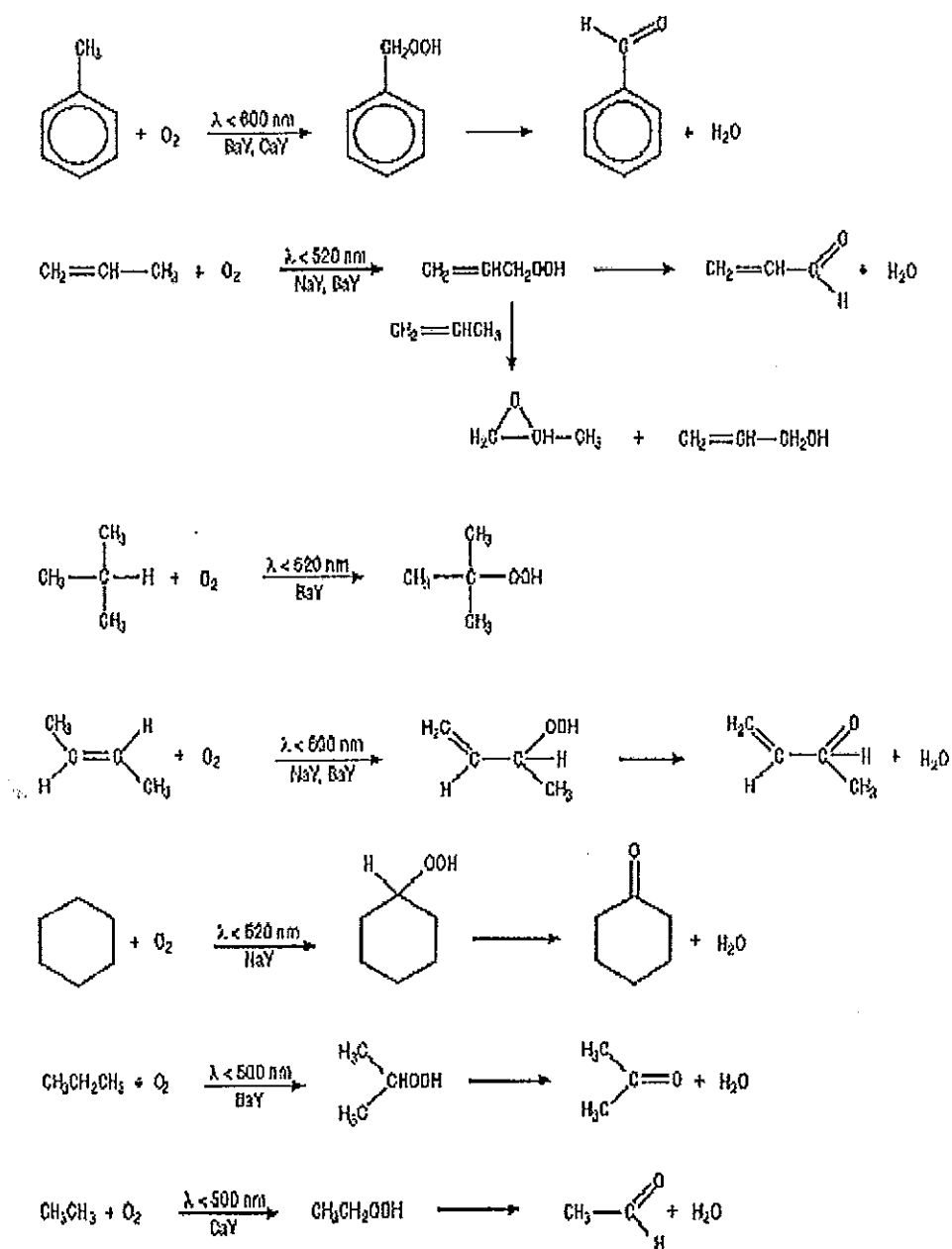
Figure 2-5 Selective hydrocarbon photooxidations with O_2 in cation-exchanged zeolite Y

Source: Heinz et al., 1996

2.5 The structure of Faujasitic Zeolites

One way to identity zeolite structures would be to relate them to the symmetry of their unit cells. This would be cumbersome and is much simplified by the observation that zeolite structures often have identical (or very similar) repeating structural sub-units which are less complex than their repeating unit cells. These recurring units are called "secondary building units" (sbus) and the simplest, most utilitarian, classification describes all known zeolite frameworks as arrangements linking eight sbus shown in figure 2-6.
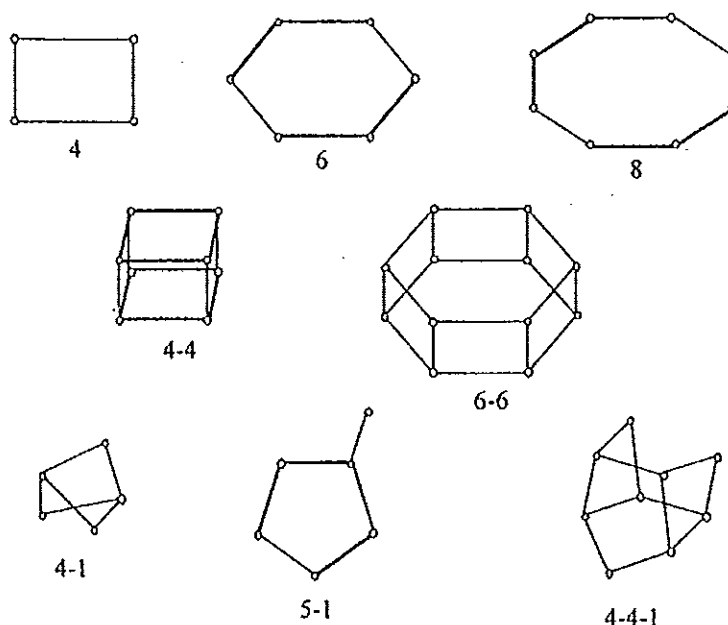
Figure 2-6 The secondary building units of zeolite framework

Source: Dyer, 1988:13

The secondary building units (sbus) recognized in zeolite framework; (4) single four ring (S4R), (6) single six ring (S6R), (8) single eight ring (S8R), (4-4) double four ring (D4R), (6-6) double six ring (D6R), (4-1) complex 4-1, (5-1) complex 5-1 and (4-4-1) complex 4-4-1.

The faujasite (FAU) framework, shared by the synthetic zeolites X and Y as well as the natural faujasite, the composite polyhedra are the hexagonal prism (i.e. a D6R), the sodalite cage and the type II 26-hedron (figure 2-7). Again in the FAU framework the polyhedra are linked in a "space filling" way (figure 2-8) (Dyer, 1988).
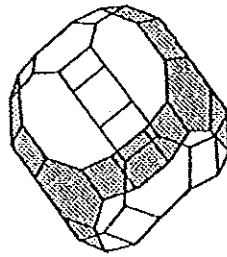
Figure 2-7 The type II 26-hedron cavity of the faujasite structure

Source: Dyer, 1988:32

Zeolite Y exhibits the FAU (faujasite) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes similar to LTA (zeolite A), and is made of secondary building units 4, 6, and 6-6. The pore diameter is large at 7.4 Å since the aperture is defined by a 12-member oxygen ring, and leads into a larger cavity of diameter 12 Å. The cavity is surrounded by ten sodalite cages (truncated octahedra) connected on their hexagonal faces. The unit cell is cubic (a = 24.7 Å) with Fd-3m symmetry. Zeolite Y has a void volume fraction of 0.48, with a Si/Al ratio of 2.43. It thermally decomposes at $793^{\circ}C$.
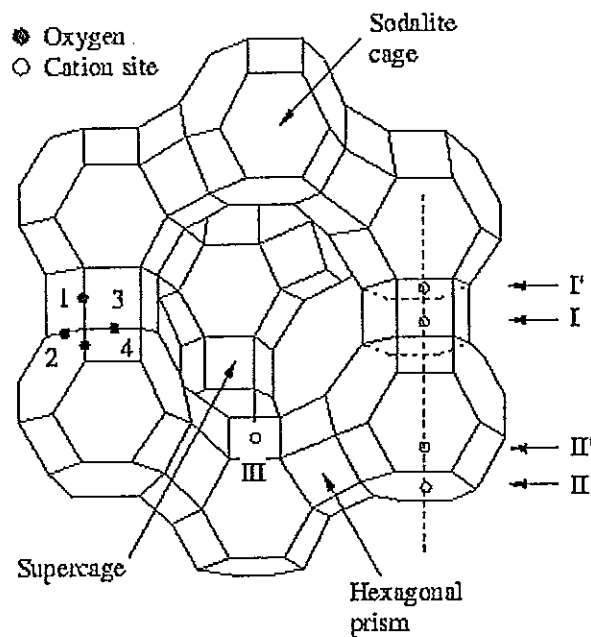
Figure 2-8 Diagram showing the differing oxygen and cation locations

Source: Windsor, 1998

The cation site occupancy in zeolites X and Y will not be dealt with in detail here, but generally it depends upon the framework charge, the nature of the cation and the amount of water present. Broadly an increase in Si:Al ratio (decrease in framework charge) depopulates the sites I and I' in the hydrated zeolites, i.e. the cations presents prefer a water environment to the framework coordination positions. The absence of water causes an increase in the population of sites I and I' regardless of framework charge. The major sites in the faujasite framework are shown diagrammatically in figure 2-8 (Dyer, 1988).

2.6 Improvement properties of zeolites (Magee and Mitchell, 1993)

The zeolite is primarily responsible for the catalyst's activity, selectivity and stability. Most commercial FCC catalysts contain Y or high-silica Y zeolites, mainly in rare earth and/or ammonia-exchanged form. Conventional Y zeolites are synthesized with a framework SiO_2/Al_2O_3 ratio between 3 and 6 (usually about 5) while high-silica Y zeolites have a higher SiO_2/Al_2O_3 ratio. Conventional Y zeolites are present primarily in gasoline FCC catalysts, whereas high-silica Y zeolites are used in the manufacture of octane and resid FCC catalysts.

Conventional Y zeolites are used in FCC catalysts mostly in the form of rare earth hydrogen Y (REHY) zeolites. Such zeolites are prepared from NaY zeolites by ionic exchange with rare earths and ammonium salts in solution. The commercial rare earth salts are a mixture of lanthanum and cerium salts, with smaller amounts of neodymium and praseodymium. The present of rare earth in the zeolite increase its stability and catalytic activity. The improved stability is attributed to the formation of polynuclear, rare earth containing hydroxy complexes in the zeolite sodalite cages. The improved activity is due to the higher number of Brønsted acid sites, resulting from the partial hydrolysis of hydrated rare earth ions:

$$RE(OH_2)^{3+} \longrightarrow REOH^{2+} + H^+$$
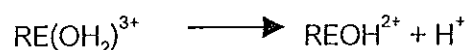
In addition to direct proton exchange and the calcination of ammonium-exchanged Y zeolite, Brønsted acidity can also be introduced by two other router. One involves the hydrolysis of ion-exchanged polyvalent cations followed by partial dehydration. For example, a Y zeolite in its native sodium form can be treated with a commercial rare earth salt solution (typically a mixture of lanthanum, cerium, neodymium and praseodymium chlorides) to replace most of the sodium ions with polyvalent rare earth ions. The highly charged rare earth ions quickly hydrolyze, creating acid sites as shown below:

$$La^{3+} + H_2O \longrightarrow La(OH)^{2+} + H^+$$
$$La(OH)^{2+} + H_2O \longrightarrow La(OH)_2^+ + H^+$$
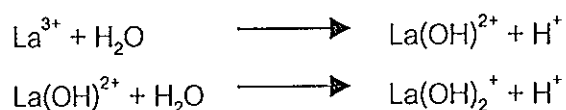
The rare earth-hydroxy ions occupy sites in the zeolite framework that increase the thermal and hydrothermal stability.

Ion exchange and calcination

A 5.0 SiO_2-Al_2O_3 ratio NaY zeolite has 55 exchange sites per unit cell, some 68% of these sites are accessible from the supercage. Approximately 32% of the sites are located in inaccessible places within the hexagonal prisms and beta cages. Removing most of the sodium from the zeolite is necessary in FCC catalysts because the sodium both poisons active sites and makes the zeolite much less hydrothermally stable.

Commercially, most of the sodium is removed by ammonium exchange using either nitrate or sulfate salts. In many cases, the zeolite is also rare earth exchanged, generally with a rare earth chloride solution. Rare earth stabilizes the zeolite, with respect to dealumination, when the zeolite is exposed to heat or steam. Increasing levels of rare earth result in higher equilibrated unit cell sizes (lower equilibrium silica-alumina ratio). This lower silica-alumina ratio in turn leads to higher catalyst activity, more hydrogen transfer, and a more paraffinic product stream. Prior to the phaseout of leaded gasoline, most FCC catalysts contained high levels of rare earth, which caused

them to equilibrate at large unit cell sizes. Such large cell sizes result in high activity and gasoline yield. With an increasing need for high octane gasoline, rare earth levels were gradually decreased so that the unit cell size could be lowered and the hydrogen transfer reactions reduced to increase olefin yields and gasoline octane.

After ion exchange and drying at 300 - 400°F, the zeolite or catalyst is usually subjected to some form of calcination to induce the migration of sodium ion from the inaccessible hexagonal prism sites to more accessible sites in the supercage. Sodium in the supercage sites can be readily removed by exchange ions. Calcination is achieved in large rotary kilns, which can be fired either directly or indirectly. After calcination, a final exchange with either ammonium or rare earth ions is done to remove residual sodium ions. Fully exchange and calcined Y zeolite contain from 0.2 to 1.0 weight percent sodium oxide.

Rare Earth Exchange

The exchange of sodium or ammonium ions by rare earth impedes zeolite dealumination during hydrothermal treatment. Hence, equilibrium or steam deactivated catalysts containing highly rare earth exchanged zeolites exhibit unit cell sizes near 24.40 Å, while very low levels of rare earth exchange result in unit cell sizes less than 24.30 Å. By preventing alumina loss from the zeolite framework under hydrothermal conditions, rare earth exchange increases activity per weight of zeolite and increases the rate of hydrogen transfer. The resulting loss in octane and olefinicity is caused by the rare earth stabilization of unit cell size. The majority of commercial FCC catalyst sold contains some amount of rare earth on zeolite. The rare earth is present mainly to moderate the activity loss observed in going to completely hydrogen exchanged forms.

Rare earth, which is generally a solution containing lanthanum, cerium, praseodymium, and neodymium with traces of other rare earths can be exchanged directly onto zeolite sites after the zeolite is incorporated in the catalyst before or after calcination. If exchange is done after high temperature calcination or other methods that

result in dealumination, the maximum amount of rare earth exchange will be significantly lowered, because the number of exchange sites are lowered by dealumination.

Figure 2-9 shows the exchange isotherm for lanthanum replacing sodium at two temperatures. Again, a type D isotherm is observed. The steep slope at La(s)=0 shows the rare earth to be highly preferred at low levels up to approximately 50 - 60 mole % exchange. Because calcination is required to allow penetration of rare earth into exchange sites in hexagonal prisms or Beta cages, the maximum exchange in the absence of calcination is approximately 70%. Because of octane needs, no commercial catalysts designed for octane enhancement contain such high rare earth levels on zeolite. Furthermore, exchange is not done under equilibrium conditions, and much of the rare earth exchanges for ammonium rather than sodium ions.
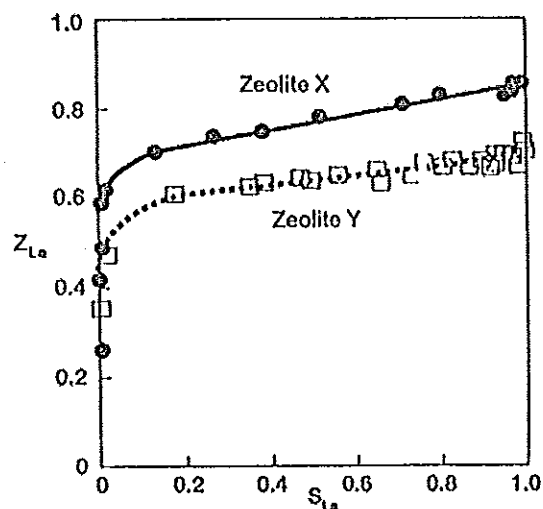
Figure 2-9 La-Na Isotherms at 25°C and 0.1 Total Normality

Source: Magee and Mitchell, 1993:132

At low rare earth levels based on zeolite exchange capacity, rare earth is highly favored over sodium or ammonium ions, and exchange is close to stoichiometric. At higher levels of exchange, excess rare earth must be used to reach the required final exchange level. If ammonium sulfate is used as the exchange solution, washing of the catalyst between ammonium and rare earth exchange is critical to prevent formation of pink salt.

As with ammonium exchange, elevated solution temperatures (150 to 180°F) are used to improve exchange kinetics. The maximum level of rare earth exchange is also accomplished at higher temperatures. In addition, concentrated rare earth solutions are quite acidic and dilute solutions are generally used to prevent zeolite destruction.

2.7 Composition and classification of FCC catalysts (Magee and Mitchell, 1993)

The zeolites used in FCC catalysts are mostly synthetic, faujasite type zeolites: Y and high-silica Y zeolites. In the past, X zeolites have also been used but have been replaced by the more stable Y zeolites. Some commercial catalysts contain mixtures of Y and high-silica Y zeolites. The zeolites are being used mostly in the rare earth or ammonium exchanged form. Most commercial FCC catalysts contain between 15 and 40 percent zeolite, which is the major contributor to the catalytic activity and selectivity of the FCC catalyst.

The catalyst matrix consists usually of a synthetic and a natural component. The synthetic component in most commercial catalysts is amorphous silica, alumina or silica-alumina, while the natural component is clay. Thermally and/or chemically modified clays are also used. The matrix is responsible primarily for the physical properties of the catalyst, although it can also have a catalytic role. For example, FCC catalysts used for cracking heavy feedstocks (e.g., resid) usually have catalytically active matrices.

Regarding their main applications, commercial FCC catalysts 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 maximize 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 (∅ ~ 8 Å)     │          ┌─────────────┴─────────────┐
└──────────────────────────────┘   ┌──────────────┐      ┌──────────────┐
                                    │  Synthetic   │      │   Natural    │
  -RE, HY (10-13%RE₂O₃)             └──────────────┘      └──────────────┘
                                     -SiO₂                 -Clay
  -REY (%RE₂O₃ > 13)
                                     -Al₂O₃                -Modified Clay
  -(REX)
                                     -SiO₂-Al₂O₃
```
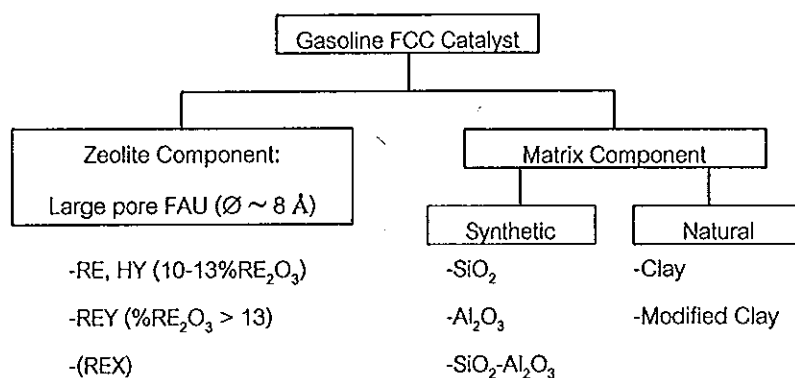
Figure 2-10 Composition of gasoline FCC catalysts

```
                      ┌──────────────────────┐
                      │  Octane FCC Catalyst │
                      └──────────────────────┘
             ┌────────────────┴───────────────────┐
   ┌──────────────────────┐              ┌──────────────────────┐
   │  Zeolite Component:  │              │   Matrix Component   │
   └──────────────────────┘              └──────────────────────┘
      ┌───────┴────────┐                    ┌──────────┴──────────┐
┌────────────┐ ┌──────────────────────┐ ┌────────────┐  ┌────────────┐
│ Large pore │ │ Medium and small pore│ │ Synthetic  │  │  Natural   │
│  (∅ ~ 8 Å) │ │ (additive) (∅ < 6 Å) │ └────────────┘  └────────────┘
└────────────┘ └──────────────────────┘  -SiO₂           -Clay
-HY (RE or H-form) -ZSM-5
                                          -Al₂O₃          -Modified Clay
-RE, HY            -ZSM-11
                                          -SiO₂-Al₂O₃
                  -SAPO-11

                  -et al.
```
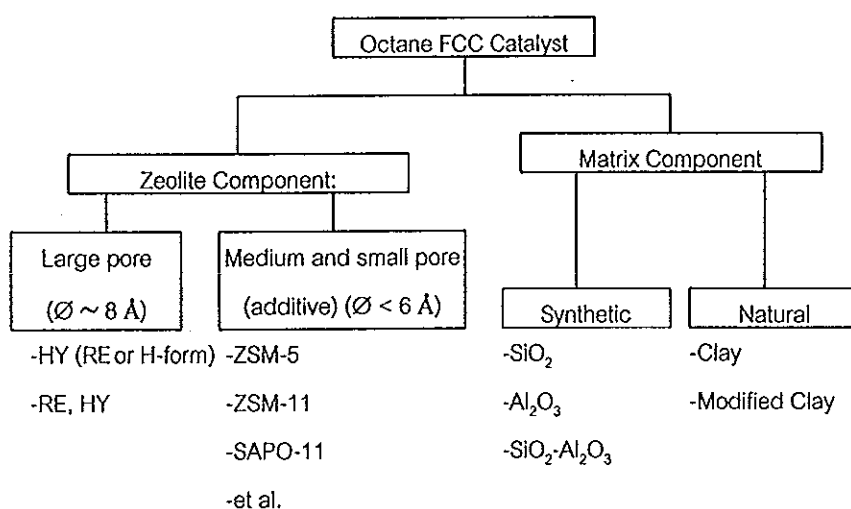
Figure 2-11 Composition of octane FCC catalysts

```
                       ┌──────────────────────┐
                       │  Resid FCC Catalyst  │
                       └──────────────────────┘
          ┌──────────────────┬──────────────────────┐
┌───────────────────┐ ┌──────────────┐      ┌──────────────┐
│ Zeolite: large pore│ │ Matrix: large│      │  Additives:  │
│    (∅ ~ 8 Å)       │ │ pore, active │      └──────────────┘
└───────────────────┘ └──────────────┘   ┌──────────┴─────────────┐
                                 ┌────────────────────────┐  ┌────────────────────────┐
                                 │ Metal passivator or trap│  │ SOₓ reduction additive │
                                 └────────────────────────┘  └────────────────────────┘
 -RE-HSY              -SiO₂-Al₂O₃      Sb, Bi, Sn              Al₂O₃, MgO

 -RE, HY              -Al₂O₃          CaTiO₃, et al.           RE₂O₃/ Al₂O₃,

                      -Activated Clay                         CeO₂/spine I,

                                                              Pt/ Al₂O₃, et al.
                                 ┌────────────────────────┐
                                 │  CO oxidation promoter │
                                 └────────────────────────┘
                                           Pt, Pd
```
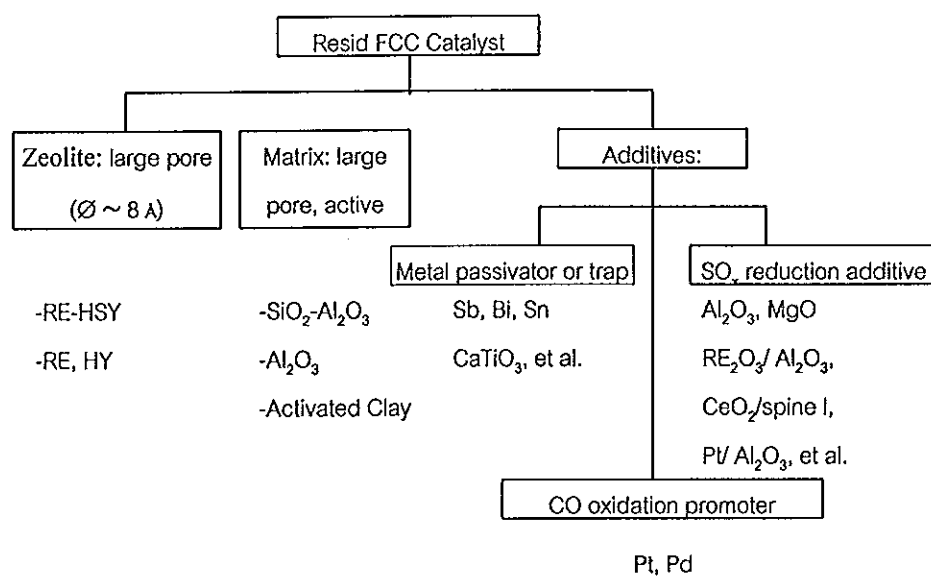
Figure 2-12 Composition of resid FCC catalysts

The composition of these three categories of catalysts is shown in figures. 2-10, 2-11, and 2-12. The zeolite component of the gasoline catalysts is commonly a rare earth, hydrogen Y zeolite (REHY), with a rare earth content between 10 and 13 percent RE_2O_3. Such zeolites will give high gasoline yields. However, they will also generate high coke 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 zeolites in rare earth or hydrogen exchanged form. They can also contain rare earth, hydrogen Y (REHY) zeolites with a lower rare earth content. Furthermore, an octane-boosting additive, such as ZSM-5 zeolite, is sometimes present in such catalysts. 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 catalysts: rare earth exchanged, 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, additives and combustion promoters are generally blended with the FCC catalyst, often by the refiner himself.

2.8 Characterization of FCC Catalysts (Magee and Mitchell, 1993)

Catalyst characterization as used in the industry describes both the physical attributes (analyses) and the catalytic performance characteristics (evaluation) of the materials under investigation. Physical measurements of FCC catalysts combine a wide range of disciplines from macrosopic (bulk) level down to the microscopic (molecular) level, and testing, such as elemental analysis, surface area, particle size, attrition, and bulk density. Catalyst evaluation, on the other hand, utilizes highly sophisticated, custom designed equipment, intended to mimic the commercial FCC process, or parts of the

process, but on a laboratory scale. Activity, selectivity, and stability measurements fall into this category.

Because of this complexity, the characterization scientist must deal with an extremely broad range of instruments and techniques to fully define the system under study. In the specific case of FCC catalysts, for example, equipment currently in use, can range in cost from $0.30 glass bottle for water titrated pore volume to over $500,000 for a computerized circulating pilot plant. The fundamental goal of all testing is to provide laboratory information about the catalyst, which can then be used to accurately predict performance of the catalyst in the field.

2.8.1 Analyses

In analyses of FCC materials three bulk techniques of elemental analysis predominate; atomic absorption spectroscopy (AAS), X-ray fluorescence spectroscopy (XRF), and inductively coupled plasma (ICP). Each has its own strengths and weaknesses, and in many respects is complementary.

AAS has been available for many years and its methods are well known. This technique measures the absorption of radiation by an ionized vapor of the sample under investigation. Its major advantages are relatively inexpensive equipment and well developed methodology. Its disadvantages are the need to completely dissolve the sample (very time consuming for FCC catalysts) and correctly match the calibration standard solution to the unknown, and the fact that each element must be determined individually.

ICP uses the same characteristic radiation lines. However, because the temperature of the plasma flame is higher, emission radiation rather than absorption are used. Computer software is available to analyze most elements simultaneously, without the need to match the solution matrix of the standards and the unknown. However, as with AAS, the sample must first be dissolved before the analysis is performed.

XRF differs from ICP and AAS in that it uses emission lines from the innermost electron shells of an element. Because these lines are far removed from the valence

electrons (those used in chemical bonds), chemical composition does not affect the analysis. Hence, samples need not be dissolved prior to analysis. In FCC catalyst elemental analysis, simple pressed pellets are suitable for routine determinations. The major disadvantages of XRF are the relatively high cost of the instrument ($150,000+) and the need to match the major element matrix in the calibration standards. Even relatively minor changes in matrix or particle size can effect the analysis. Matrix effects can be eliminated by fusing powder using a flux and high temperature into a clear 'glass' pellet. However, this technique is more labor intensive and precludes accurate sodium analysis at low concentrations. The latter is critical in determining catalyst quality.

2.8.2 Evaluation

Catalyst evaluation in the FCC industry is routinely performed using equipment that can be eight orders of magnitude (100 million times) smaller than the commercial units they are trying to simulate. The long term goal of catalyst evaluation, in the FCC industry, is to simulate commercial cat crackers in the laboratory by using the smallest scale equipment compatible with the generation of reliable and accurate data. Accuracy is defined as agreement with commercial performance. Despite these enormous differences, such laboratory studies have led to significant improvements in catalysts performance. These improvements result in higher gasoline yields, higher octane, lower coke production, and better bottoms cracking.

FCC catalysts are evaluated by three test methods in most laboratories. These methods are microactivity (MAT), fixed fluidized bed, and circulation pilot plant. They differ primarily in scale. The MAT is the smallest, and the circulating pilot plant is the largest. They also vary in their thermodynamic and kinetic similarity to commercial operations. The MAT is the least similar to the process, whereas the circulation unit is a small version of the FCC unit. However, most circulating pilot plants are not run adiabatically.

The evaluation of fresh catalysts normally includes a deactivation step that precedes the actual MAT evaluation. This deactivation typically involves the steaming of a catalyst sample at temperatures ranging from $100^{\circ}F$ to $1700^{\circ}F$ for 2 to 14 hours. The primary objective is to deactivate a fresh catalyst such that its performance in the MAT is representative of what is observed when testing a commercially deactivated sample of the same catalyst. In this way, prediction of commercial performance for new catalysts can be made. An additional deactivation parameter that is widely studied is that induced by the presence of metals in the hydrocarbon feedstock, typically nickel and vanadium. These contaminants are relatively non-volatile and when deposited on the catalyst, are not removed during catalyst regeneration. Their presence on the catalyst is known to negatively impact both catalyst stability and product selectivities.

The current ASTM referenced MAT procedure has its roots in the work by Gustafson and Ciapetta and Henderson. This standard test procedure operates at $900^{\circ}F$, uses 4 grams of catalyst and 1.33 grams of oil, giving a catalyst/oil ratio of 3. The oil is injected over a 75 second time period. The weight hourly space velocity (WHSV), defined by 3600/(Cat/Oil*Injection Time) is 16. It is this standard test method that is most widely referenced, but not generally practiced as written. It should also be noted that the ASTM test is technically applicable only for catalyst activity determinations and does not address measurements of catalyst selectivities. A suitable test for selectivity determinations is being reviewed by ASTM. A tabular summary comparing the MAT procedures of Ciapetta et al, Gustafson, and the ASTM procedure is presented in table 2-2. A schematic of typical MAT unit is presented in figure 2-13.

Table 2-2 Comparative Microactivity Test Conditions

Source: Magee and Mitchell, 1993:225

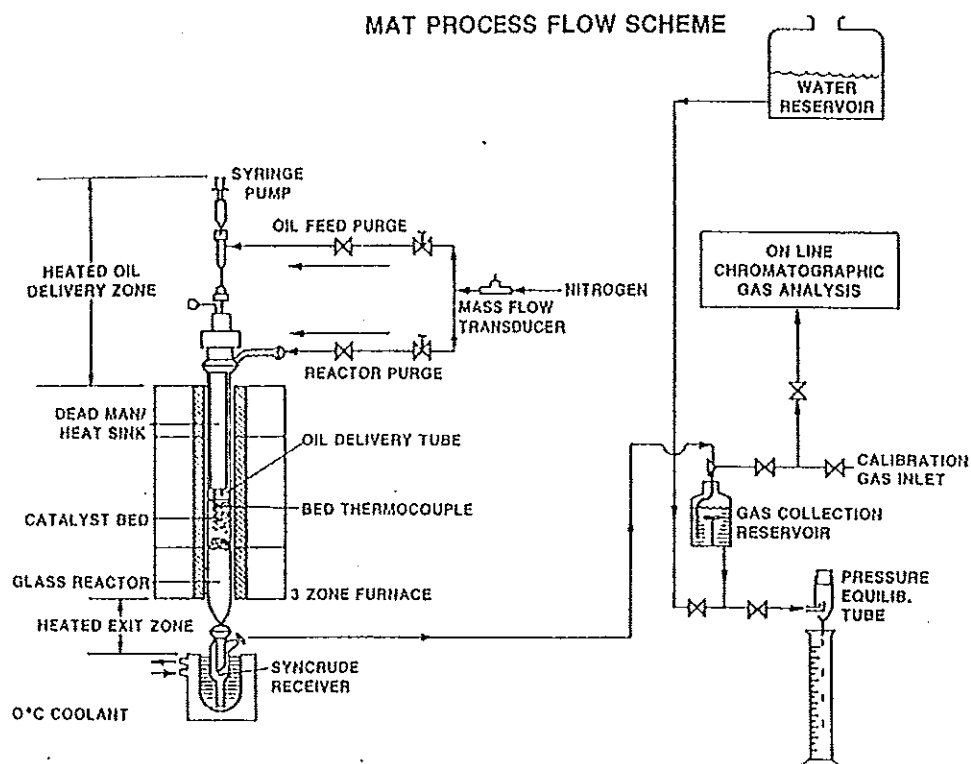|	Ciapetta	Gustafson	ASTM
Catalyst Charge, grams	5	N/A	4
Catalyst Shape	3/32 in	microsphere	microsphere
Oil Charge, grams	0.86	N/A	1.33
Catalyst/Oil (w/w)	5.8	35.-4.0	3.0
Temperature, $^{\circ}$F	900	900-950	900
WHSV, Hr^{-1}	2-16	16-64	16

Figure 2-13 Schematic of Typical MAT Unit

Source: Magee and Mitchell, 1993:226

An alternative approach to evaluating catalysts, without steam deactivation, is to test commercially deactivated (equilibrium catalysts) samples of the catalysts in the MAT. The principal advantage of this approach comes from eliminating the uncertainties associated with laboratory deactivation procedures. For cases where the history of catalyst samples is well known, and operating conditions of the commercial unit(s) is not a variable, this approach has merit. However, it is often very difficult to get equilibrium samples that have seen the same commercial operation. When the objective is to evaluated several catalysts from different vendors, getting samples having equal levels of metal contaminants that have also been exposed to similar severity of catalyst regeneration and unit operations is difficult. Making comparisons on the relative performance of these catalysts having such different histories can be misleading.

Chapter 3

Experimentation

The scope of experiment in this study was divided into two parts. The first part was concerned with the preparation of rare-earth Y zeolite by ion exchange method and its preparation to catalyst whereas the second part was the catalyst characterization.

3.1 Equipment

3.1.1 Electric mixer (Heidolph type RZR 1 made in Germany)

3.1.2 Hot air oven (Eyela model NDO-600N made in Japan)

3.1.3 Vacuum pump (Eyela model A-3S made in Japan)

3.1.4 Water bath (Memmert type W350 made in Germany)

3.1.5 Furnace

3.2 Instruments

3.2.1 Differential Thermal Analysis (Perkin Elmer model DTA 7)

3.2.2 Gas Cromatograph (SHIMUZHU model GC-14BPF)

3.2.3 Integrater (Hellet Packard model HP3295)

3.2.4 Hydrothermal Aging Unit (RIPP model CLY-1)

3.2.5 Microactivity Testing Unit (RIPP model WFS-1D)

3.2.6 X-Ray Diffractometer (Philips model X'Pert-MPD)

3.2.7 X-Ray Fluorescence Spectrometer (Philips model PW2400)

3.2.8 Thermogravimatric Analysis (Perkin-Elmer model TGA 7)

3.3 Materials

3.3.1 NaY zeolite from RIPP

3.3.2 Lanthanum chloride from RIPP

3.4 Preparation of a REY catalyst

3.4.1 Ion exchange in NaY zeolite

The ion exchange of cations in crystalline aluminosilicate (sodalite cages) can be made in two methods. The conventional ion exchange in solution and the solid-state ion exchange procedures.

3.4.1.1 Conventional ion exchange

The conventional ion exchange in NaY zeolite in this research was modified from the procedure of RIPP.

1) Lanthanum exchange

The sodium form of Y zeolite was obtained from RIPP. A calculated amount of $LaCl_3$ was dissolved in deionized water (2% $LaCl_3$ dry base in solution) and added to the grinded zeolite at ambient temperature. The atomic ratio of $LaCl_3$ applied to Al in the zeolite were 0.33, 0.66, and 0.99. The minimum ratio of 0.33 was chosen for the following reason: assumtion that each La^{3+} cation acts as a compensating cation for three framework negative charges (i.e. one La^{3+} balances three AlO_4^-), this ratio represents a La/cationic-sites charge equilibrium in the zeolite. In other words, this ratio would correspond to the La content for "stoichiometric" exchange. The suspension was then stirred with an electric stirrer in a water bath (see figure 3-1) at various temperatures in the range $30 - 90°C$ for different periods of time $30 - 150$ min.

2) Filtration

The slurry was filtered with vacuum pump (shown in figure 3-2) to remove contaminant salts by exchange.

3) Washing

The filter cake was washed to be free of the exchange anion (usually chloride ion) with hot deionized water and was passed to the drying step.

4) Drying

In order to remove water from the product, the washed samples were dried at $120°C$ for 2 hrs. Water in the product might decrystalline the zeolite in calcination process.
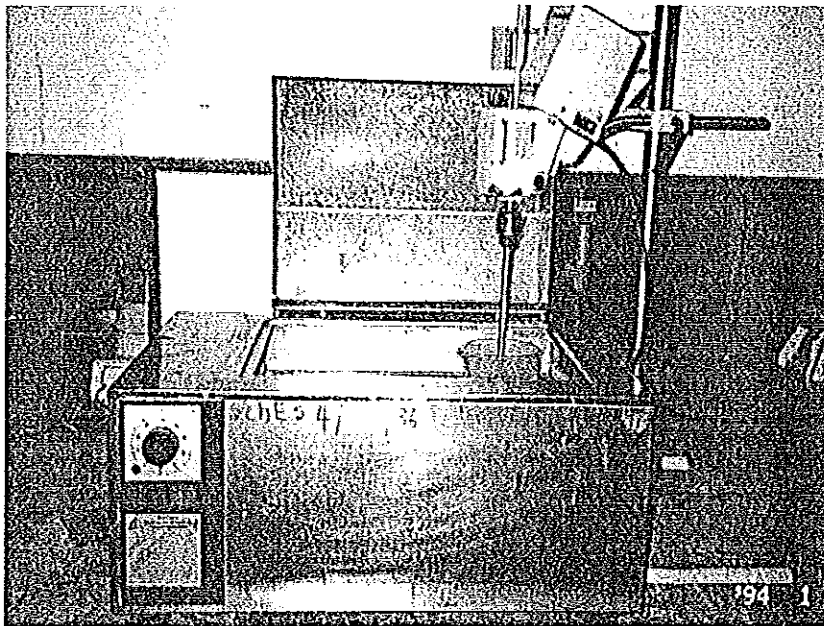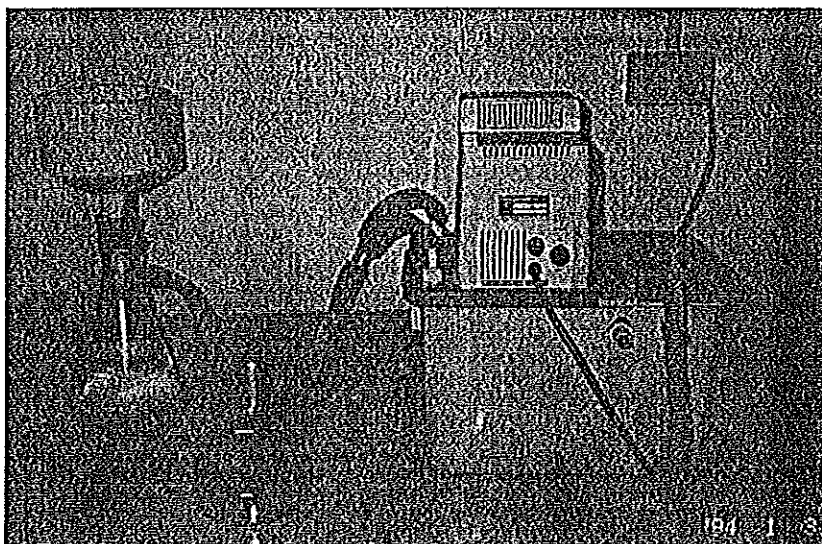
Figure 3-1 Water bath

Figure 3-2 Vacuum pump

5) Calcination

The final calcination step in the furnace was shown in figure 3-3. The samples were calcined at various temperatures in the range 200 – 650°C for 2 hrs. At 90°C of cation exchange in Y zeolite, lanthanum ions are located in their supercages. Calcination of lanthanum exchanged Y zeolites leads to the irreversible migration of the lanthanum ions into the small cages.

The whole procedure must be repeated several times to reach the high degree of ion exchange. In this work, the NaY zeolite was ion exchanged at various order of exchange 1 to 3 times.
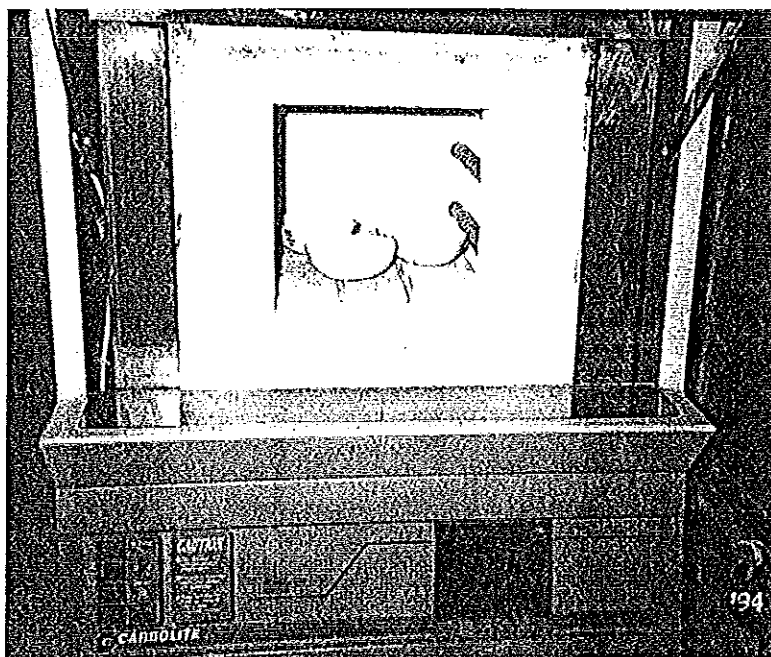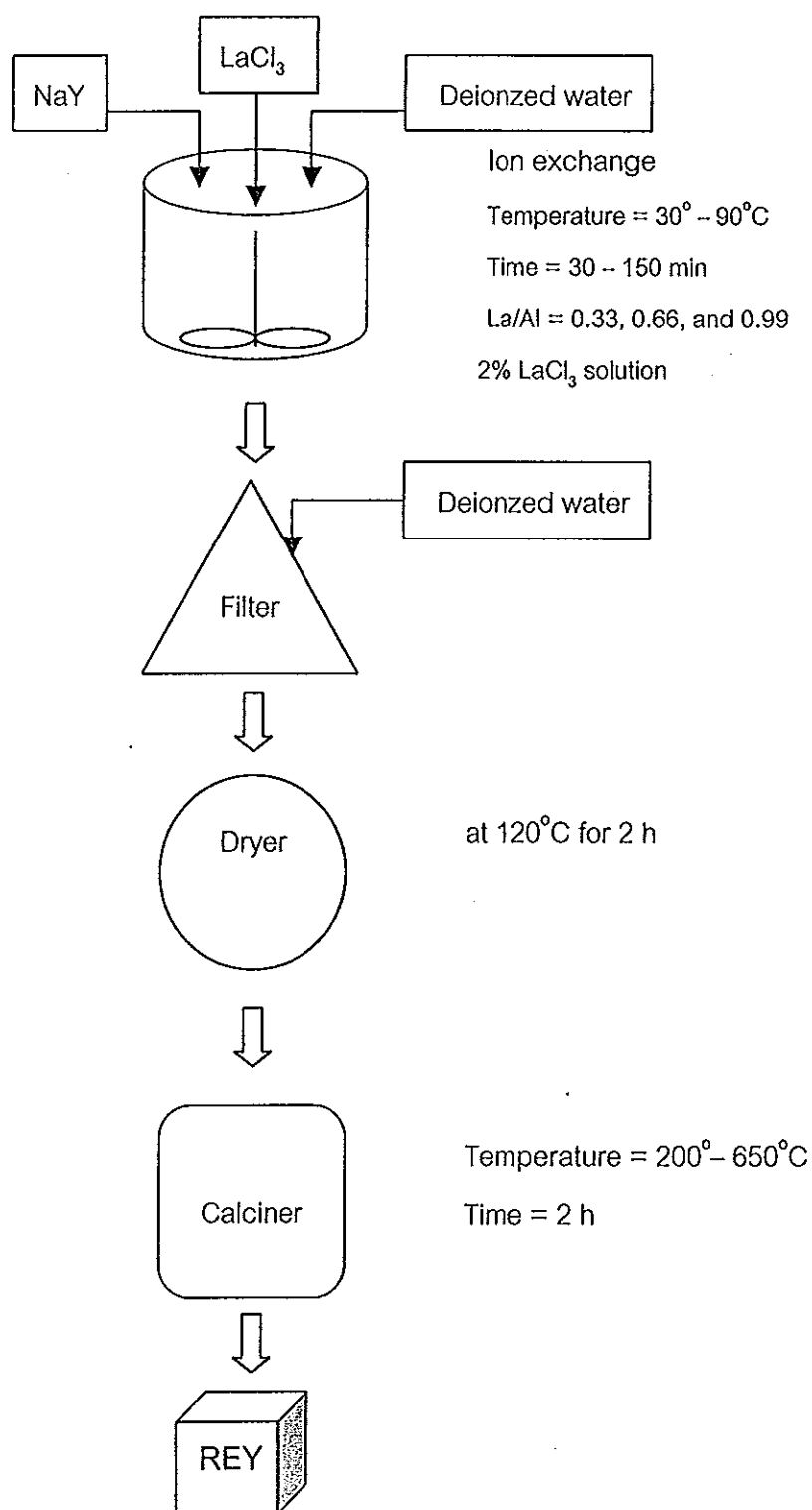

Figure 3-3 Furnace

Figure 3-4 Process scheme for the conventional ion exchange.

47

3.4.1.2 Solid-state ion exchange

Conventional ion exchange in solution was performed by the incorporation of La into the zeolitic pores is strongly limited due to the steric hindrance caused by the large hydration sphere of the La^{3+} ions. A single exchange most often results in only partial exchange. It is then necessary to repeat the exchange several times to reach high exchange levels. As a consequence, ion exchange in solution frequently involves the handling and recycling of large volumes of solution.

The solid-state ion exchange procedure is a very simple one and can be performed using the zeolite in the sodium form commonly obtained by synthesis. This proceeds between hydrated NaY zeolite and crystalline alkaline or alkaline earth metal chloride were ground at ambient temperature.

The procedure of solid-state ion exchange used in this work was very simple. In the subsequent preparation steps.

1) Mixing

The La/Al atomic ratios also in the mechanical mixtures were 0.33, 0.66, and 0.99. A mixture of $LaCl_3$ and the NaY zeolite was carefully ground in a ball mill shown in figure 3-5 for 1 h.

Figure 3-5 Ball mill

NaY → [Ion exchange chamber] ← LaCl₃

Ion exchange
Ambient temperature
Time = 60 min
La/Al = 0.33, 0.66, and 0.99

Calciner

Temperature = 550°C
Time = 2 h

Filter ← Deionzed water

Dryer

at 120°C for 2 h
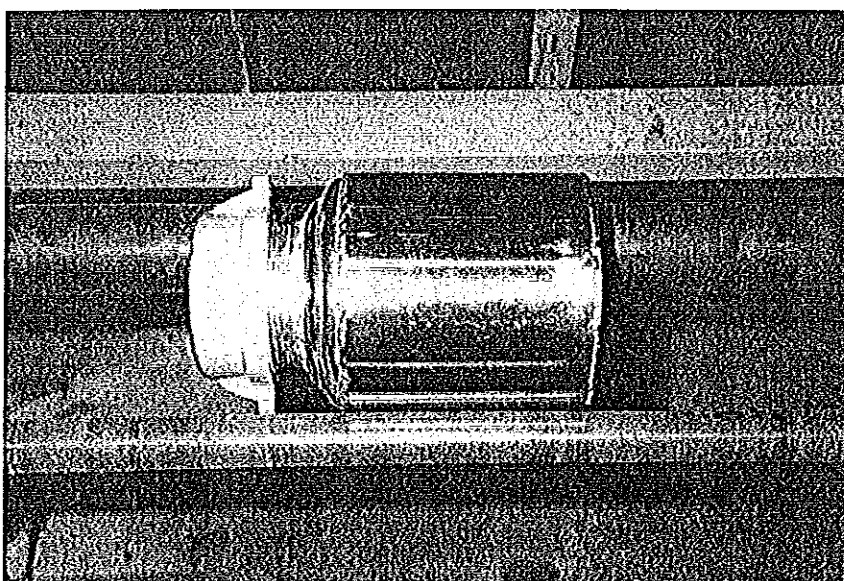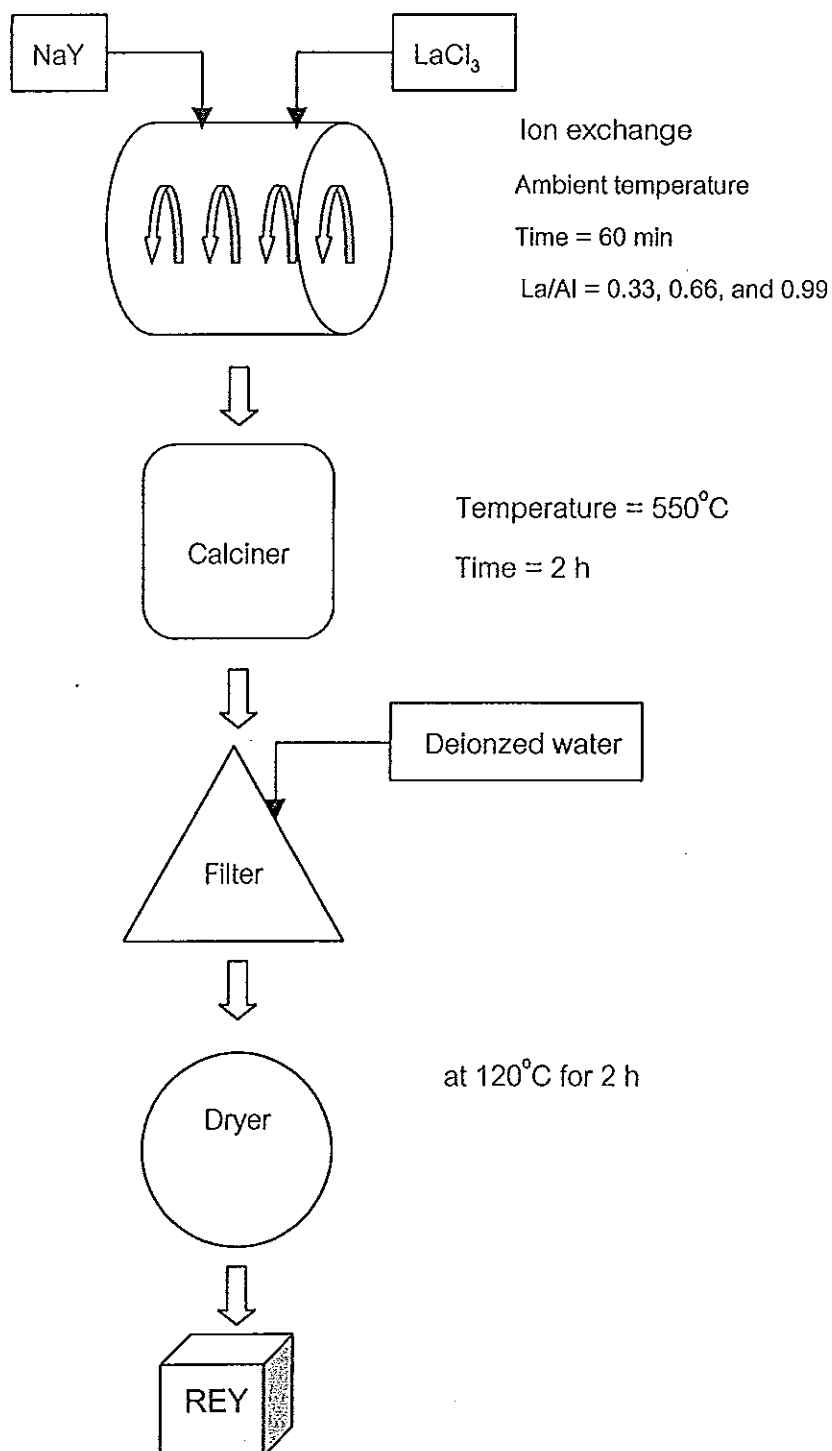
REY

Figure 3-6 Process scheme for the solid-state ion exchange.

2) Calcination

The ground mixture was then transferred to a reactor of hydrothermal aging unit (see figure B-8 in appendix B) and calcined at $550^\circ C$ in a stream of nitrogen for 2 hrs. This method usually consists of heating in vacuum or in a flow of inert gas to avoid framework collapse resulting from the production of HCl during calcination.

3) Washing

The calcined sample was washed several times with hot deionized water.

4) Drying

This drying step was the same drying step in conventional ion exchange.

3.4.2 Mixing of REY catalyst

Rigorous mixing of the various components of the FCC catalyst is required to produce a hard, dense, homogeneous catalyst. The primary consequences of poor mixing are poor attrition and density as well as poor particle morphology. However, stratification of the active components caused by incomplete mixing can also significantly effects the activity and selectivity of the final catalyst. Generally the mixers are high shear because of the thixotropic nature of many of the slurries used in FCC manufacture. Also stirrer blades are designed to induce significant up and down mixing.

Most commercial FCC catalysts contain between 15 and 40 percent zeolite. In this research, REY zeolite is used in considerably small amounts resulting in catalysts with zeolite contents 15 percent.

Preparation of powder catalyst from REY-zeolite was performed by the binder is pseudo-boehmite and the filler is kaolin, both are mixed with REY. This dry weight ratio of kaolin:pseudo-boehmite:REY as 1:0.33:0.232 respectively. In this step, 100 g of kaolin and 250 g of deionized water are added into a vessel. This is stirred for about 10 minutes until the mixing is completed, after 5-7 ml of 1:1 HCl is added into this vessel. The pH is indicated by litmus paper about 3-4 after the acid is added. After the 91.42 g of pseudo-boehmite are added, it is stirred for about 30 minutes until it is homogeneous. Now, this liquid becomes slurry. Consequently, the slurry is heated above $60-70^\circ C$. As the mixture cools to room temperature, the slurry becomes gel. After pH is checked,

the REY is added into the slurry and stirred for about 20-30 minutes, then the slurry is dried at 100-200°C for 2 h until the water is removed completely. Actually, this product is called catalyst. The catalyst is ground to particle size about 20-40 mesh.

The filler is clay incorporated into the catalyst to dilute its activity. Kaolin [$Al_2(OH)_2,Si_2O_5$] is the most common clay used in the FCC catalyst. One FCC catalyst manufacturer uses kaolin clay as a skeleton to grow the zeolite *in situ*. The binder serves as glue to hold the zeolite, the matrix, and the filler together. Binder may or may not have catalytic activity. The importance of the binder becomes more prominent with catalysts that contain high concentrations of zeolite.

3.5 Characterization of catalyst products

The characteristics of exchanged zeolite and catalysts were examined, catalyst preparation involves the intimate mixing of many components. The quantity and quality of each component is critical to the physical and catalytic properties of the FCC catalyst. Proper and accurate characterization is thus essential to sufficiently define the product and insure quality catalyst.

Catalyst characterization describes both the physical attributes (analyses) and the catalytic performance characteristics (evaluation) of the materials under investigation.

3.5.1 Chemical analyses

Catalysts are analyzed chemically for alumina (Al_2O_3), silica (SiO_2), soda (Na_2O), and rare earth oxide (RE_2O_3) which originated in the exchange. Soda and rare earth oxide contents are by far the most important. In most zeolite catalysts, intrinsic thermal and hydrothermal stability of the catalyst depend on the absolute level of these two components.

X-ray fluorescence spectroscopy (XRF) was used for elemental analysis, such as the content of lanthanum (La) or rare earth oxide (RE_2O_3), Si(SiO_2), and Al(Al_2O_3). The method requires very careful calibration and needs gram quantities for analysis.

Atomic absorption spectroscopy (AAS) measures the content of soda (Na_2O) NaY zeolite and exchanged zeolite. The need to completely dissolve the sample

(see the method in appendix A) and correctly match the calibration standard solution to the unknown, and the fact each element must be determined individually.

3.5.2 Physical analysis

The important physical properties of the catalyst are its crystallinity and thermal stability.

The crystallinity of zeolite was determined by x-ray diffraction (XRD) spectroscopy by using a reference database. The XRD patterns of the zeolite containing sample and the reference sample (NaY) are obtained under the same conditions. Intensities of the (533) peak (23.5 deg with Cu Kα radiation) are compared to provide "% XRD intensity/NaY (533)." If the XRD pattern of the zeolite is sufficiently strong, comparison of the sums of intensities of eight peaks is used to give "% XRD intensity/NaY". This latter measure is commonly used in zeolite technology and is referred to as the ambiguous term "% crystallinity" (ASTM D3906, 1991).

In thermal analysis, differential thermal analysis (DTA) is the monitoring of the difference in temperature between a sample and a reference compound as a function of temperature. A plot of mass versus temperature permits evaluation of thermal stability.

3.5.3 Evaluation

Laboratory testing and evaluation of fresh FCC catalysts, when refinery change feedstock or specific demand, involves two steps: a deactivation step, usually uses hydrothermal deactivation (hydrothermal aging) and catalytic step (MAT testing).

This deactivation typically involves the steaming of a catalyst sample at the flow rate of water 0.41 ml/min and temperatures 800°C for 4 hours. The primary objective is to deactivate a fresh catalyst so that its performance in the MAT is representative of what is observed when testing a commercially deactivated sample of the same catalyst. The water used for aging should be deionized water.

The use of the MAT unit as the primary tool for the laboratory evaluation of FCC catalysts was focused on index of China is RIPP 92-90 referenced MAT procedure. The test procedure operates at 460°C, uses 5 grams of catalyst and 1.56 grams of oil, giving a catalyst/oil ratio of 3.2. The oil is injected over a 70-second time period. The weight hourly space velocity (WHSV), defined by (3600/Cat/Oil*Injection Time) is 16.

The MAT procedure of RIPP is presented in table 3-1. A schematic of a typical MAT unit is presented in figure 2-13 (chapter 2).

Table 3-1 Microactivity Test Conditions of RIPP

(see MAT set up and operation in appendix B)

Catalyst Charge, grams	5
Oil Charge, grams	1.56
Catalyst/Oil (w/w)	3.2
Temperature, °C	460
WHSV, h^{-1}	16
Feed stock	Light Cycle Oil (LCO, bp. 235-335°C)
Feeding rate, g/min	1.337
Feeding time, sec	70
Purging time, sec	600

Liquid produced from MAT was then analyzed by Gas Chromatograph (GC). The condition for Gas Chromatograph is given in table 3-2.

Table 3-2 Conditions for Gas Chromatograph

(see Gas Chromatography set and Integrator in appendix B)

Column	Pack Column (OVI, methylsilocone)
Detector	Frame Ionization. Detector (FID)
Carrier gas	Nitrogen (Purity 99.99%, OFN), flow rate 35-40 ml/min.
Combustion gas	Hydrogen, flow rate 40 ml/min
Auxiliary gas	Air, flow rate 400 ml/min
Sample injection volume, μL	1
Temperature of vaporization chamber (injector), °C	280
Temperature of detector chamber, °C	280
Temperature of column chamber: 35 °C to 80 °C with rate of 15°C/min, then raise from 80°C to 235°C a rate of 80°C/min and hold at 235°C for 10 min	

Chapter 4

Results and Discussion

The aim of this work was to investigate of the ion exchange of lanthanum in Y zeolite. Since lanthanum Y zeolites are widely used as the catalytically active components of catalysts for petrochemical processes. Through the REY catalyst was prepared and evaluated in physical, chemical and catalytic characterization.

4.1 The effect of experimental conditions during conventional ion exchange treatment

The parent material was a NaY zeolite with relatively high Si/Al. It was obtained from RIPP, China. This zeolite was treated with lanthanum chloride solution to replace sodium ions in the structure of zeolite with lanthanum ions.

4.1.1 Effect of exchange time

The results of the Y zeolite after first lanthanum ion exchange at $90^{\circ}C$ was selected to study exchange time effect. The NaY/LaCl$_3$ ratios (dry basis) in mixed solution were 1/0.25. Figure 4-1 gives the content of La$_2$O$_3$ (%) and exchange degree (%) vs. exchange time. It can be observed that the number of lanthanum in exchanged Y zeolite (LaY) was slightly increased along with increasing exchange time and is about 15.0% La$_2$O$_3$ content. The number of Na was defined in terms of "exchange degree". It was also increased along increasing exchange time, indicating that the sodium ions in the original sample have been released by lanthanum. Exchange degree was obtained from:

$$Exchange\ Degree = \frac{(initial\ Na - final\ Na)}{initial\ Na} \times 100$$
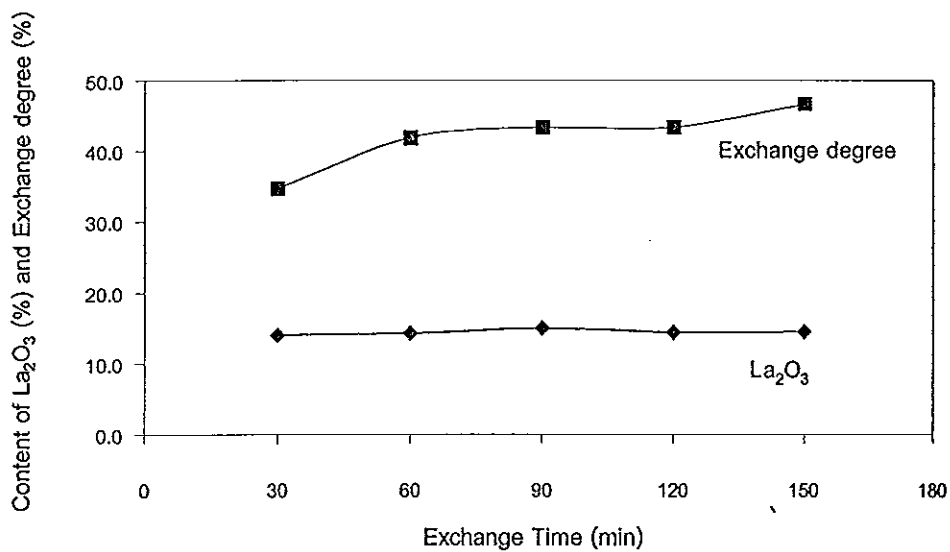
Figure 4-1 Effect of exchange time

(NaY/RE=1/0.25, 1st exchange, $90^{o}C$)

4.1.2 Effect of exchange temperature

The experiments were carried out at 60 min of exchange time. The $NaY/LaCl_3$ ratio (dry basis) in mixed solution was 1/0.25. The effects of ion exchanged temperature at $30^{o}C$ and $90^{o}C$ are presented in figure 4-2.
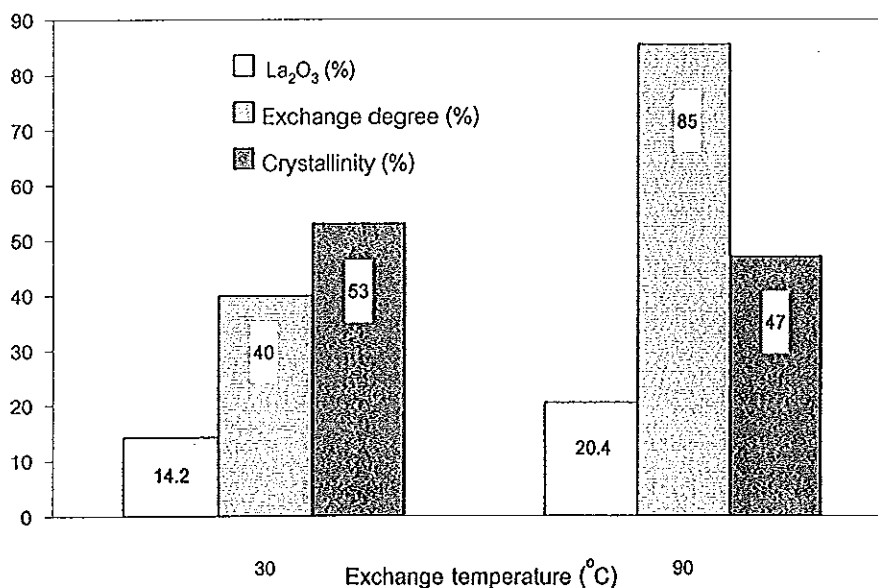

Figure 4-2 Effect of exchange temperature

(NaY/RE=1/0.25, 2nd exchange, 1 h)

The exchange degree and lanthanum content at $90^{\circ}C$ for 1 h treatment (LaY(90)) are higher that at $30^{\circ}C$ (LaY(30)). Higher exchange temperatures lead to diffusion rate of lanthanum ions through the structures of zeolite.

X-ray powder diffraction analysis was used to evaluate crystallinity of the starting NaY (85% crystallinity) and exchanged samples. From figure 4-2, the decrease of relative crystallinity of the LaY(90) was greater than of LaY(30) whose crystallinity can remain above 50%. The loss of crystallinity is due to the high rate of ion exchange and high rare earth content. Nevertheless, both samples were found to be at highly crystalline.

4.1.3 Effect of calcination temperature on the migration of La ion

After exchange process, lanthanum ions are mostly located in the supercages. It is necessary to move the lanthanum ions from the supercage to small cages by using calcination process. The calcination temperature employed during the course of the lanthanum exchange of zeolite is important in determining the final number of lanthanum ions present in each unit cell.

The effect of calcination temperature on the migration of lanthanum ions is demonstrated in figure 4-3. More than 80% of lanthanum migration occurs initially at temperatures $200^{\circ}C$. The amount of lanthanum locked in the small cages become highest at calcination temperatures $500^{\circ}C$, which is in agreement with a study by Lee and Rees (1987). In the case of the calcination at $60^{\circ}C$, lanthanum ions, initially only are sited in the supercages, diffuse through the six-membered ring leaving the supercages to the small cavities of sodalite cages.

The amount of lanthanum locked in the small cage decreases slightly when the temperature was raised above $600^{\circ}C$. The aluminium was found to be removed from the framework of the lanthanum exchanged samples during the high temperature calcination stage. Some of the water in the product might decrystalline of zeolite. The maximum amount of rare earth exchange will be significantly lowered.
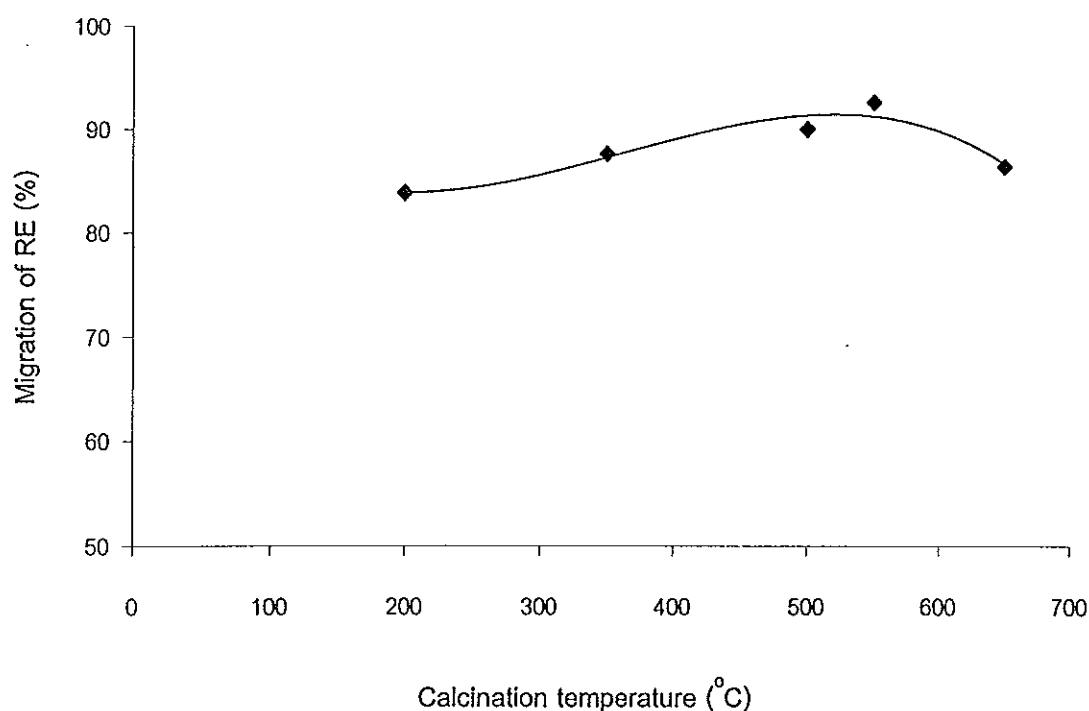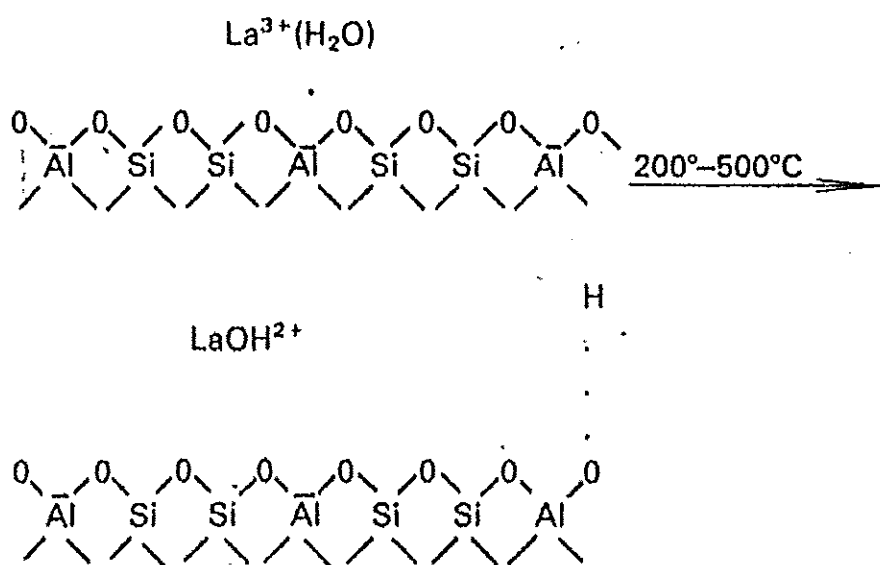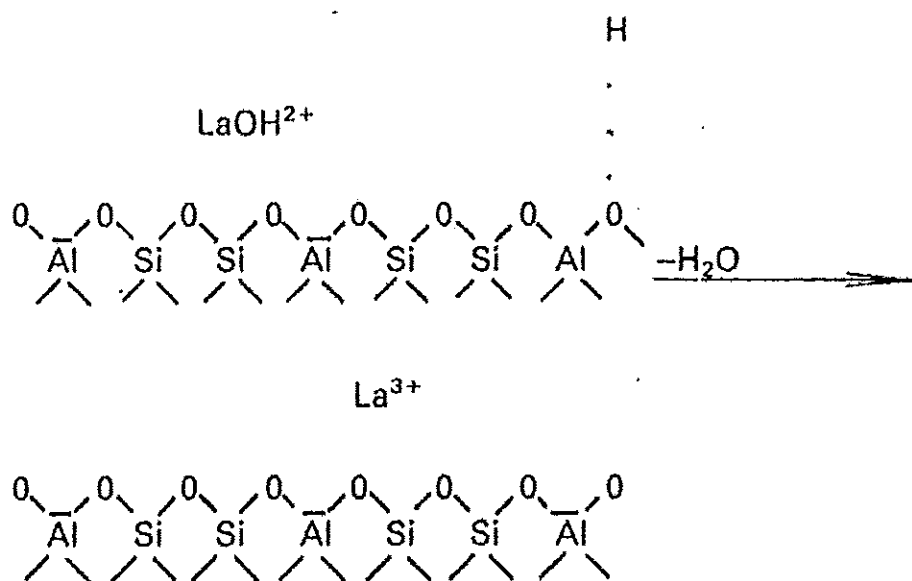
Figure 4-3 Effect of calcination temperature on the migration of La ion

(NaY/RE=1:0/25, 2nd exchange, $90^{\circ}C$, 1 h)

When lanthanum ions are associated with water molecules in zeolites they exist as trivalent cations. Calcination results in the decomposition of some of the remaining water molecules. These few, tenaciously held, when water molecules are desorbed at elevated temperatures some of the remaining water molecules are split to produce Brønsted acid sites in the dehydrated structure and OH^- groups on the lanthanum ions. Reducing the effective charge on the lanthanum ion 2^+ that increase the thermal and hydrothermal stability.

Lee and Rees (1987) have reported that on calcination of lanthanum Y zeolites between $200^{\circ}C$ to $500^{\circ}C$, the apparent charge on the lanthanum ion is reduced from 3^+ to 2^+. This charge reduction was accompanied by the irreversible formation of hydroxyl groups and protons from water molecule complexes to the lanthanum ions as shown below.

$$\text{La}^{3+}(\text{H}_2\text{O})$$

O—O—O—O—O—O—O—O
Al Si Si Al Si Si Al $200°\text{–}500°\text{C} \longrightarrow$

$$\text{LaOH}^{2+}$$

H

O—O—O—O—O—O—O—O
Al Si Si Al Si Si Al

In other word, the effective charge on the lanthanum ions in the small cages has been found to increase from 2.2^+ to 3^+ on calcination at temperatures from $580°\text{C}$ to $850°\text{C}$. The following dehydroxylation mechanism is, therefore, proposed:

H

$$\text{LaOH}^{2+}$$

O—O—O—O—O—O—O—O
Al Si Si Al Si Si Al $-\text{H}_2\text{O} \longrightarrow$

$$\text{La}^{3+}$$

O—O—O—O—O—O—O—O
Al Si Si Al Si Si Al

This dehydroxylation mechanism removes a hydroxyl group from the lanthanum ion and a proton from the framework oxygen and thus retains the zeolite structure. This is favored compared with removal of a hydroxyl group from the framework leaving an oxygen vacancy.

4.1.4 La/Al atomic ratios in the suspension

For classical exchange (conventional) in solution, the Y zeolite was poured into $LaCl_3$ solution. The respective effects of La/Al ratios, the zeolite with different ratio of La/Al were analyzed.

The results of La/Al ratios in ion exchange treatment are demonstrated in figure 4-4, observed that the lanthanum ion is initially preferred, but the exchange does not go to completion on La/Al ratio of 0.33. For the La/Al mixture ratio of 0.66 and 0.99 measured after washing suggests a full lanthanum exchange.

At low rare earth levels based on zeolite exchange capacity, rare earth is highly favored over sodium ions, and exchange is close to stoichiometric. To obtain the maximum levels of rare earth exchange, excess rare earth is required to reach the desired final exchange level.
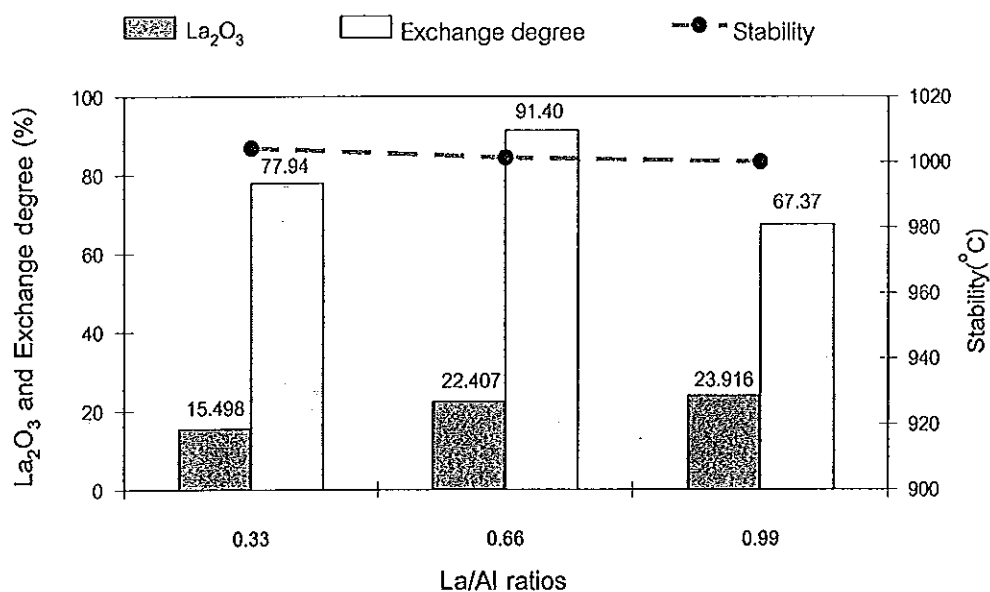

Figure 4-4 The ratios of La/Al in suspension

(2nd exchange, $90°C$ exchange temperature, $550°C$ calcination temperature)

Y zeolite exchanged with rare earth cations is one of the most useful catalysts for cracking hydrocarbons. It was found that the rare earth cations could stabilize the framework of Y zeolite. The lattice collapse temperature of the original NaY was 875°C. Different thermal analysis of the Y zeolite after lanthanum exchange at 90°C showed that all of the samples possessed very good thermal stability, a minimum value at 1000°C. The zeolite stability is controlled by the content of rare earth and sodium ions are referred to as level of exchange or exchange degree. The low Na concentration is responsible for the enhanced hydrothermal stability of REY crystal.

Zeolites are synthesized in a solution of sodium hydroxide and initially, the ionic sites on the aluminum atoms are occupied by positively charged sodium atoms. These sodium ions would reduce the stability of the zeolite at typical regenerator conditions. This would have a negative effect on the long-term activity maintenance of the catalyst.

Enhancing the native sodium ions for rare earth ions shows an increase in the hydrothermal stability of the zeolite. The presence of rare earth on the ion exchange sites stabilizes the aluminum atoms in the crystal structure. This prevents the loss of aluminum atoms during subsequent heat treatment and later during exposure to high temperatures in the FCC regenerator. By holding the aluminum atoms in the zeolite structure, the rare earth limits the shrinkage of the unit cell.

4.1.5 Order of exchange

Chemical analysis of the starting NaY gave the rare earth content less than 0.1 wt%. Generally, the level of RE_2O_3 content in REY zeolite, which fully exchanged is about 16 wt% or higher. The ion exchanged process must be carried out several times to get a desired level of rare earth and decrease the level of sodium content to lower than 1 wt%.

Figure 4-5 shows that the low exchange degree after first rare earth exchange. To remove the remaining sodium ions and increase the level of rare earth, the first rare earth exchanged zeolite was carried out a second and third rare earth exchange. The efficiencies of the two exchange method are evaluated by comparing the exchange

degree and level of La. Both exchange degree and level of La curves show a maximum value, which suggests that complete exchange of the sodium ions by lanthanum ions at this order of exchange.
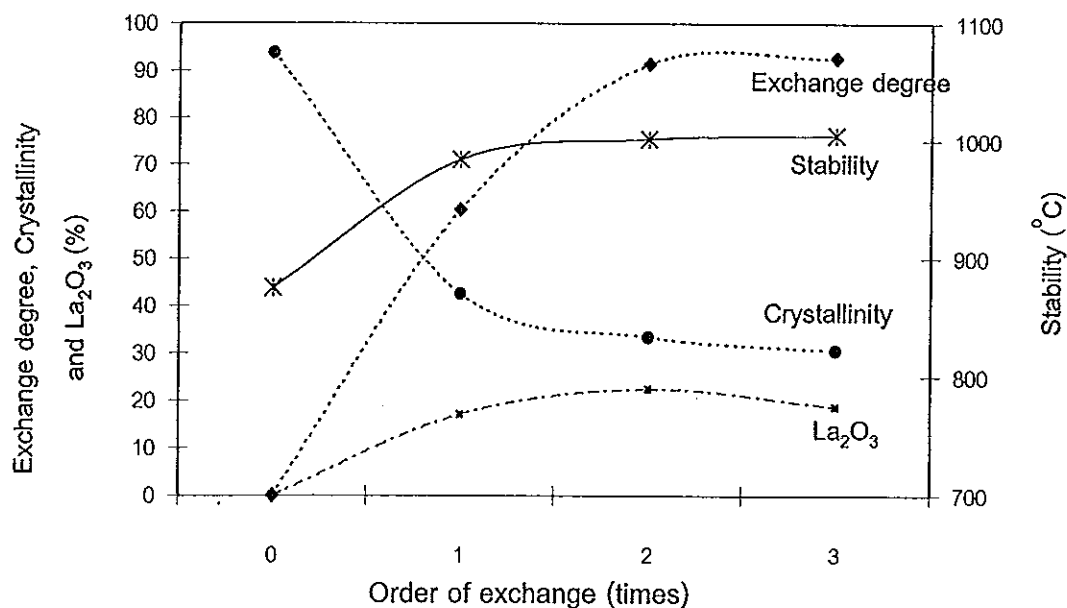

Figure 4-5 The order of exchange

(La/Al=0.66, 90°C exchange temperature, 550°C calcination temperature)

The chemical compositions of REY are summarized in table 4-1. From this table we can see that the decrease of relative crystallinity of REY after first exchange is greater than that of REY after the second exchange. It is reasonable that the loss of crystallinity is due to the dealumination occurred as the samples are calcined. In fact, as proposed by Rees and Lee (1987), dealumination upon calcination of rare earth containing Y zeolites is likely to occur due to the presence of protons produced in the formation of hydroxyl groups associated with the rare earth cations. Such protons would catalyze the reaction of aluminum hydrolysis.

Table 4-1 Order of ion exchange

Order of ion exchange (times)	La$_2$O$_3$ (%)	Na$_2$O (%)	Exchange Degree (%)	Crystallinity (%)	Stability (°C)
0	< 0.1	7.33	0.00	93.8	875.00
1	17.08	2.91	60.29	42.5	983.49
2	22.41	0.63	91.40	33.4	1001.32
3	18.70	0.54	92.65	30.6	1004.46

(La/Al=0.66, 90°C exchange temperature, 550°C calcination temperature)

So, after the third exchange, the crystallinity decreases slightly. As is well known, the La ion can stabilize the frame framework of Y zeolite. For the third exchange sample, the stability is not significantly higher than the second exchange sample but the La content. is much lower.

4.2 Comparison of conventional and solid-state ion exchange procedures

The solid-state ion exchange procedure by performing the calcination of mechanical mixtures in static conditions is compared to those obtained by conventional ion exchange.

Figure 4-6 reveals the comparison of La contents in the LaY, La incorporation into the zeolitic crystals is strongly favored when the exchange is conducted in the conventional rather than the solid-state. The La content increases as the La/Al ratios increase from 0.33 to 0.99. But the La content increases slightly from La/Al ratio of 0.66 to 0.99.

For the solid-state ion exchange, the zeolite still contains 2.44 wt% of Na$_2$O at La/Al ratio of 0.99 (see figure 4-7), while very low levels of Na$_2$O content for the conventional ion exchange is observed.

Figure 4-6 Effect of La/Al ratios on content of La

(Conventional = 2nd exchange, $90^{o}C$ exchange temperature, 1 h, $550^{o}C$

calcination temperature

Solid-state = ambient temperature, 1 h, $550^{o}C$ calcination temperature)
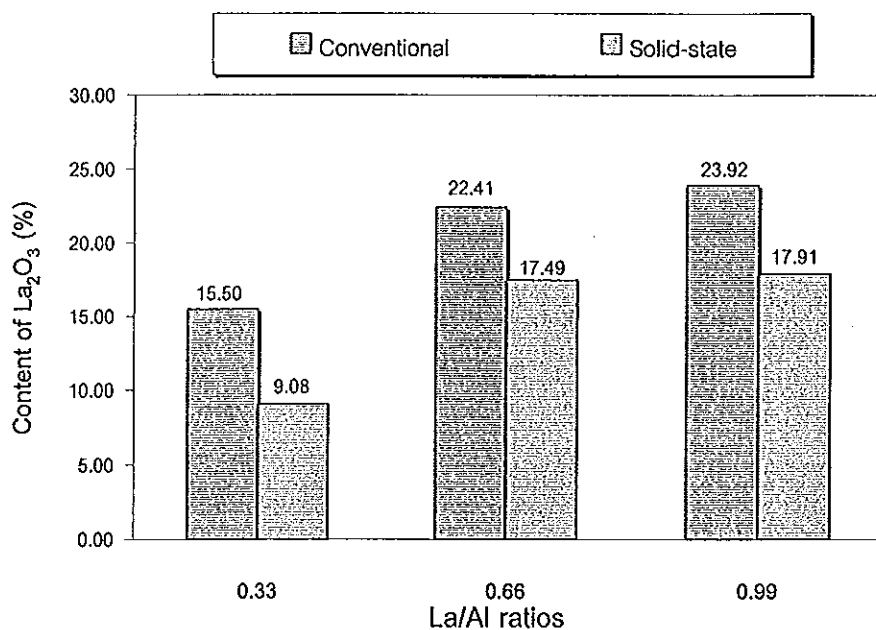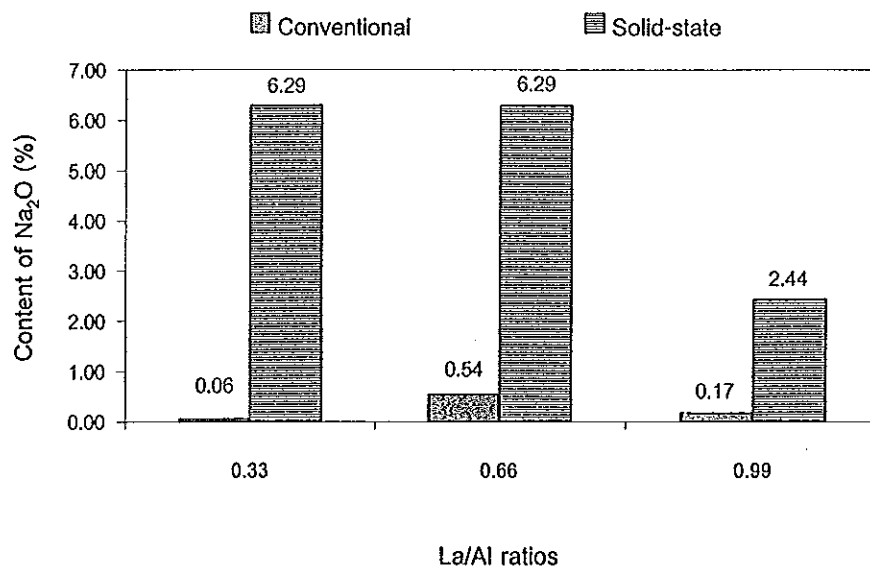

Figure 4-7 Effect of La/Al ratios on content of Na

(Conventional = 3rd exchange, $90^{o}C$ exchange temperature, 1 h, $550^{o}C$

calcination temperature

Solid-state = ambient temperature, 1 h, $550^{o}C$ calcination temperature)

Figure 4-8 shows that whatever the La/Al ratio used for the conventional ion exchange, there is no significant loss of crystallinity. In contrast, the increase in the La/Al ratios from 0.33 to 0.99 upon solid-state ion exchange indicates the increasing loss of crystallinity.

Solid-state ion exchange is performed by mixing a salt (lanthanum chloride) with the zeolite in ambient atmosphere; thus the latter contains physisorbed water. Also, many salts contain crystal water, which was not removed before the ion exchange. In the case of the La-rich mechanical mixture (La/Al of 0.66 or 0.99), the water content of the mixture is high. The amount of water in the hydrated lanthanum is about 48 wt%. In the calcination process, the presence of this amount of water promoted hydrolytic attack on the framework alumina resulting in aluminum ions being removed from the zeolite framework. This removal necessarily leaves holes or defects in the crystal and causes some loss of crystallinity.
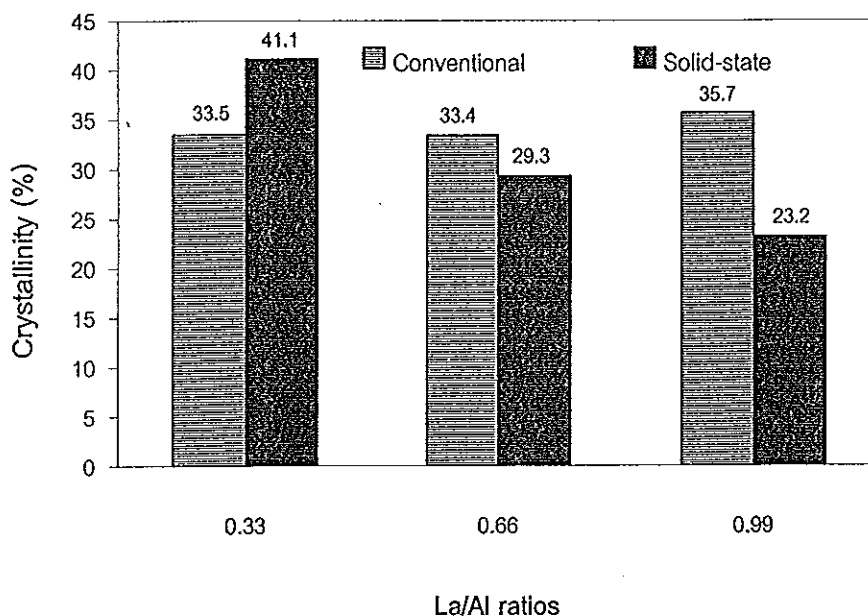

Figure 4-8 Effect of La/Al ratios on crystallinity

(Conventional = 2nd exchange, $90^{o}C$ exchange temperature, 1 h, $550^{o}C$ calcination temperature

Solid-state = ambient temperature, 1 h, $550^{o}C$ calcination temperature)

The calcination of LaY for conventional ion exchange resulted in an increase in hydrothermal stability of NaY above 1000°C (see figure 4-9), while lower thermal stabilities of zeolite were obtained when the exchange was conducted by the solid-state. It is well known that the zeolite stability is proportional to the content of rare earth. In other words, there is no significant change of hydrothermal stability in the conventional ion exchange although the levels of La in zeolite are quite different.

It is well established that lanthanum ions migrate from supercages into small cages and are formed as hydroxyl group at elevated temperatures. Lee and Rees (1987) reported that the number of lanthanum ions migrating into the small cages is a function of temperature. The number of lanthanum ions locked in small cages becomes constant at calcination temperature > 300°C. In this work, the calcination temperature was carried out at 550°C. Thus, most or all of cations located in the small cages reached a maximum at this temperature.
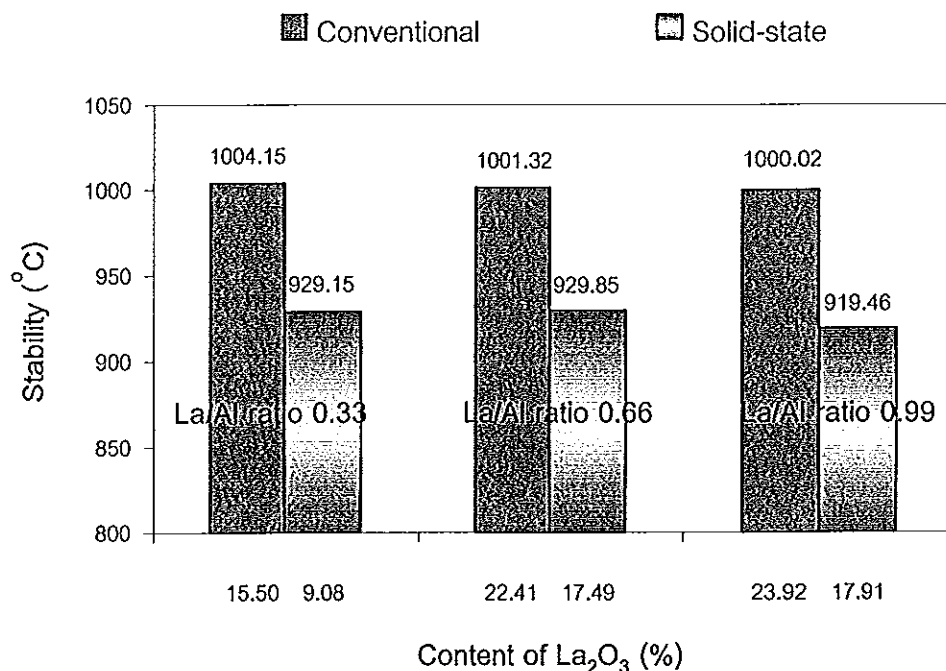

Figure 4-9 Effect of La/Al ratios on stability of LaY

(Conventional = 3rd exchange, 90°C exchange temperature, 1 h, 550°C calcination temperature

Solid-state = ambient temperature, 1 h, 550°C calcination temperature)

The rare earth content in zeolite is not really indexed to the thermal stability. The location of La in zeolite framework, La ion species such as La^{3+} or $LaOH^{2+}$ and their homogeneous distribution are more effect to the thermal stability. However, at high La content the attrition resistance of many catalysts deteriorates.

4.3 Microactivity testing of prepared REY catalyst

All FCC catalysts, regardless of their specific applications, are designed to have the following catalytic properties: activity, selectivity and stability. Catalytic activity is due to the presence of acidic sites in the catalyst. It is determined by zeolite content. Zeolite content was consistently important and positive to most yield structure. Most commercial REY based catalysts contain between 15 and 25 percent zeolite (Scherzer, 1993).

In this work, REY zeolite was prepared in small amounts resulting in catalysts with zeolite contents 15 percent. According to Mitchell's report, the optimum catalyst properties which contained 15% of zeolite was suggested to future catalyst formulation (Mitchell, 1993).

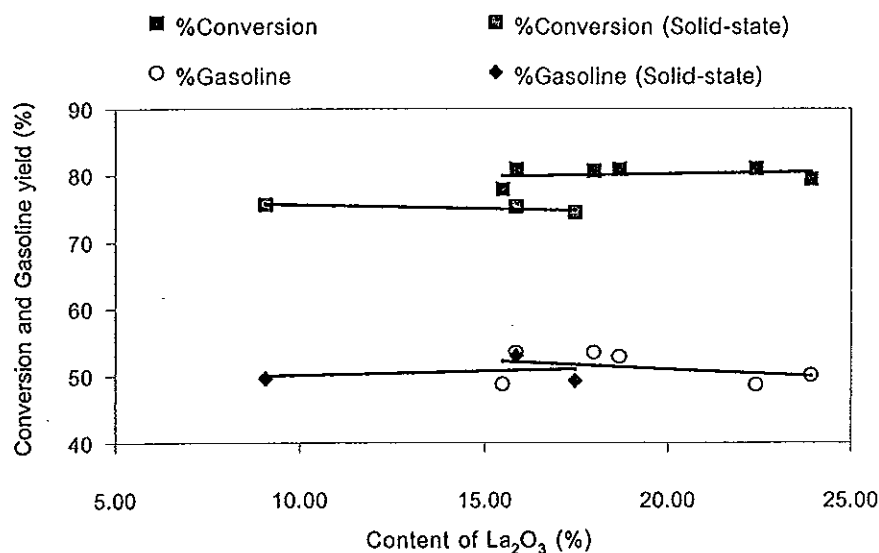Figure 4-10 Effect of La content on microactivity of LaY catalysts

(Conventional = 2nd & 3rd exchange, $90^{\circ}C$ exchange temperature, 1 h, $550^{\circ}C$ calcination temperature

Solid-state = ambient temperature, 1 h, $550^{\circ}C$ calcination temperature)

The conventional ion exchange and solid-state ion exchange samples have been evaluated by microactivity test.

Figure 4-10 and table 4-2 illustrated the impact of La content on product yields using gas oil (LCO) feedstock. Since the lanthanum content per gram of zeolite was not the same in each sample, the results were normalized to La content in zeolite versus microactivity (conversion) and gasoline yield. In the case of conventional ion exchange, as La content increases, the activity of zeolite cracking tends to increase (figure 4-10). REY catalysts, with a higher rare earth content will give a higher conversion. However, they will also generate high coke and gas yields, which result in a decrease of liquid yield (shown in table 4-2). Some primary products are converted to undesired products by secondary reactions such as isomerization, cyclization and hydrogen transfer.

In the case of solid-state ion exchange, the level of La content in zeolite was not responsible for the catalyst's activity. This may be due to the heterogeneous distribution of La atoms and the position where La ions are located. Some of La ions are located at the supercages where they are less active than in sodalite cages. And this is a reason why REY catalysts prepared from solid-state ion exchange zeolite have a lower activity than conventional REY.

The double conventional ion exchange is enough of order of exchange, which resulted in a high La content and stability of $1001.32^\circ C$. Rare earth elements serve as a "bridge" to stabilize aluminum atoms in zeolite structure. They prevent aluminum atoms from separating from zeolite lattice when the catalyst exposed to high temperature steam in the regenerator. However, catalyst can have a wide range of rare earth levels depending on the refiner's objectives.

Table 4-2 Microactivity test results of REY Catalysts (La/Al 0.66)

Catalysts	Solid-state 17.49 wt%La$_2$O$_3$ 929.85°C DTA	Conventional (2nd exchange) 22.41 wt%La$_2$O$_3$ 1001.32°C DTA	Conventional (3rd exchange) 18.70 wt%La$_2$O$_3$ 1004.46°C DTA
Conversion (%)	75.35	81.02	80.96
Gasoline (%)	53.03	48.74	52.89
Liquid (%)	77.76	67.69	70.64
Coke (%)	1.98	3.64	2.81
Gas (%)	20.26	28.67	26.55
Gasoline selectivity	0.689	0.613	0.591
Coke selectivity	0.027	0.044	0.036
Gas selectivity	0.276	0.350	0.339

A previous study by Angkasuwan (1999) on the activity of commercial FCC catalyst illustrates that the microactivities of REY catalyst (obtained from Thai Oil Company Ltd., Co., Star Petroleum Refinery and RIPP) are in the range of 70-73. It was found that the microactivity of REY from this work is higher than the commercial REY catalyst. But the selection of catalyst used in the FCC unit does not only depend on the activity. Many specific characteristics like high gasoline and light cycle oil selectivities, low coke and dry gas made and low decant oil made have to be considered.

The optimum virgin catalyst properties proposed by Mitchell (Mitchell et al., 1993) are shown in table 4-3. While it is doubtful that these precise values are necessary, they do demonstrate directions for future catalyst formulation.

Table 4-3 Derived optimum virgin catalyst properties.

Source : Mitchell et al., 1993

Surface Area	180-200 m^2/g
Total Pore Volume	0.40-0.50 cc/g
<60 Å	Maximize
60-80	
80-100	Maximize
100-200	Maximize
200-400	Maximize
400-1000	Minimize
1000+	
Zeolite Intensity	15%
Unit Cell Size	24.59-24.62 Å
Alumina	>45%
Rare Earth Oxides	3-4%

Chapter 5

Conclusions

The conclusions, which emerged from this research, are as follows:

1. The optimum conditions for the conventional ion exchange treatment are:

Conditions	Points
La/Al atomic ratios	0.66
Exchange temperature ($^{\circ}$C)	90
Exchange time (min)	> 60
Calcination temperature ($^{\circ}$C)	500-550
Order of exchange	2

The prepared LaY zeolite have the following properties: crystallinity 33.40%, Na_2O content 0.63 wt%, La_2O_3 content 22.41 wt% and thermal stability 1001.32°C.

2. The effectiveness of the conventional ion exchange (solution) procedure for the exchange of La in Y zeolite is higher than the solid-state ion exchange. The conventional ion exchange results in the degrees of exchange Y zeolite above 90%. By a one step of the solid-state ion exchange between NaY and hydrated $LaCl_3$ as precursors could be obtained only 67% degree of exchange. When the ion exchange was performed in the solution, the yield of rare earth incorporation and their homogeneity distribution are higher than the solid-state method.

3. The present of rare earth in the zeolite increases its stability and catalytic activity. The catalyst can be prepared by mixing LaY zeolite with 21 wt% pseudo-boehmite binder and 64 wt% kaolin clay filler. The activity of LaY catalysts (15 wt% zeolite content) was 81.02, the gasoline yield was 48.74%, coke yield was 3.64 wt%, and gas yield was 28.67 wt%.

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Appendix A

The acid digestion process for zeolite

1. Grinding the samples into fine powers and drying at $120^{\circ}C$.

2. Weighing 0.2 g of sample treated under step 1, putting it into a Teflon vessel and then adding 5 ml HF, 4 ml $HClO_4$ and 10 ml HCl (1:1 $HCl:H_2O$ v/v).

3. Heating the Teflon vessel under the low temperature ($<180^{\circ}C$), until the fog of $HClO_4$ vapors was observed.

4. Cooling the vessel and putting 2 ml H_2O_2. After waiting a few minutes, heat the vessel again until see the fog of $HClO_4$ vapors appears again.

5. Cooling it to the room temperature.

6. Adding 20 wt% HCl into the vessel to 25 ml.

Appendix B

Instrumental Methods for determining the properties of Cracking Catalyst

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

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

B-1.1 MAT Unit (Angkasuwan, 1999)

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

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

Reaction temperature	: 460 $\pm$ 1°C
Feed oil weight	: 1.56 $\pm$ 0.01 g
Feeding time	: 70 sec
Post stripping time	: 10 min
Stripping nitrogen flow-rate	: 20-30 ml/min
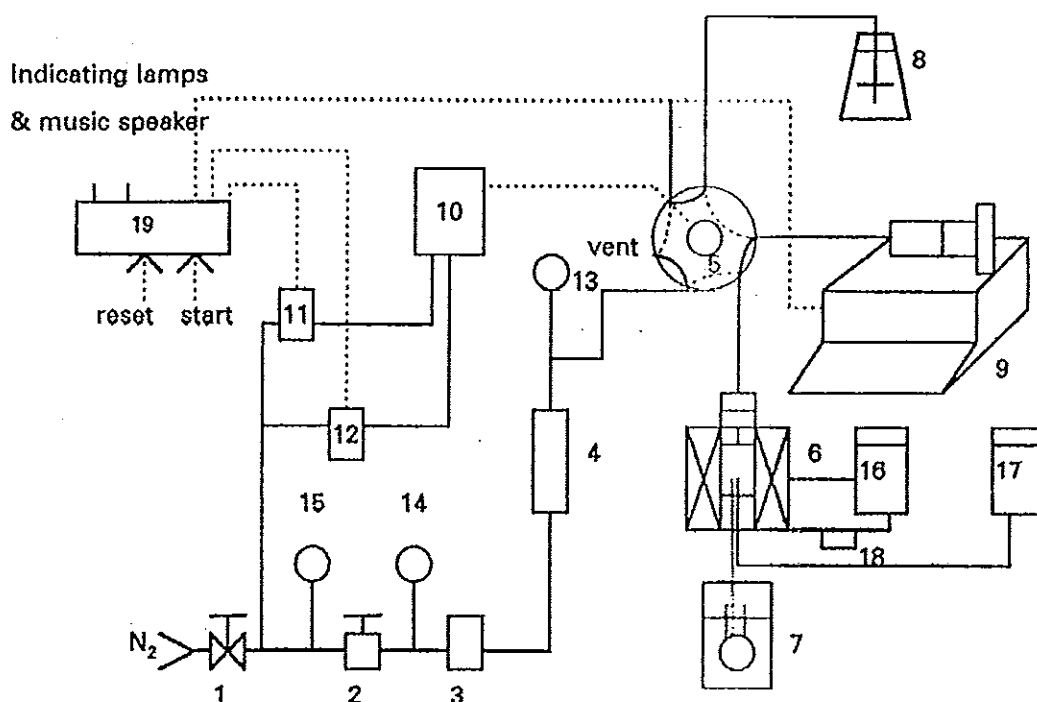
Figure B-1 The process diagram of MAT unit.

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

B-1.1.1 Reaction and Collection System

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

B-1.1.2 Feed Oil Injection System

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

B-1.1.3 Stripping System

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

1) Pre-stripping : The nitrogen stripping before oil injection can ensure the catalyst is in the nitrogen atmosphere and water-free

2) Post-stripping: After oil injection the nitrogen stripping can get residual oil in the tube into the reactor and strip out all reaction production from reactor.

B-1.1.4 Measurement and Control System

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

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

1) Preparation step: If the nitrogen source is supplied, when the power switch turns on the PLC will draw the six-port valve to the position shown by the dotted lines. That is the pre-stripping.

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

3) Oil suction step: After 70 seconds of oil injection, the six-way valve turns back to the dotted line position. Then post-stripping begins and syringe plug goes backward, the feed oil is sucked into the syringe from the feed oil bottle.

4) Squeezing step: When the oil-suction has lasted for 70 seconds the syringe plug goes forward again for 20 seconds to squeeze out the gas bubbles.

5) Post-stripping: When post-stripping lasts about 10 min (the speaker song music), the system goes back to the preparation step again. In order to keep the syringe plug always stay at a certain position, only in this period the reset button is enable.

B-1.2 PC Work Station (Optional)

B-1.2.1 Functions

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

B-1.2.2 Operations

1) Start up

1.1) Enter Window 3.11

1.2) Double click Group WFS-1D

1.3) Double click the icon WFS-1D of the group

1.4) Input the operator's name and click "OK" then go into the working window

2) Operations in the main working window:

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

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

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

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

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

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

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

B-1.2.3 Commands

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

1. "RUN"   : begin to run

2. "RESET"   : to reset the system

3. "EXIT"   : to quit from the main working window

4. "SAVE"   : to save the parameters onto the system's hard disk

5. "LOAD"   : to load the parameter from the system's hard disk

6. "QUIT"   : to quit from the WINDOWS

7. "CALCULATOR   : to use system's calculator

8. "REPORT"   : to print test report. Each report can contain two test reports. According to the prompt input parameters, and then click "OK", the computer

can calculate out the needed parameters, and then click "PRINT" and the report can be print out Click "EXIT" to quit from the window.

9. "TRACE" : to display the temperature's trace. In this window there are several command blocks.

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

- "SET SCALE" : to set the temperature's scale by input the minimum/maximum temperature.

- "EXIT" : to quit from this window

B-1.3 Gas Chromatography set and Integrator

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

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

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

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

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

Temperature of column chamber : $280^\circ C$

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

Sample injection volume : $1\mu L$

Range : set to 10

The recommended integrator's parameters are:

Attenuation : 8

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

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

B-1.4 Preparation before Operation

B-1.4.1 Reactor's Temperature

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

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

B-1.4.2 Tested Catalyst

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

B-1.4.3 Feed Oil

Heavy oil isn't suitable for this apparatus

B-1.4.4 Feed Oil Weight Calibration

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

Example: Calibration of the syringe pumps.

Table B-1 Feed oil: gas oil (Light Cycle Oil, LCO) obtained from RIPP

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

B-1.4.5 Material Balance Test:

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

Example:

Table B-2 Blank test for checking liquid recovery

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

B-1.5 Operation Steps

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

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

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

4. When the reactor's temperature has been stable for 5 min, push the "start" button then the unit works in automatic for injection, suction, squeezing and post-stripping. After 10 minutes stripping, the speaker sings music indicating that the test has finished.

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

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

B-1.6 Analyses of Reacted Product and Aata Disposal

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

B-1.6.1 Calibrate the retention time of n-dodecane

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

B-1.6.2 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.

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

Where

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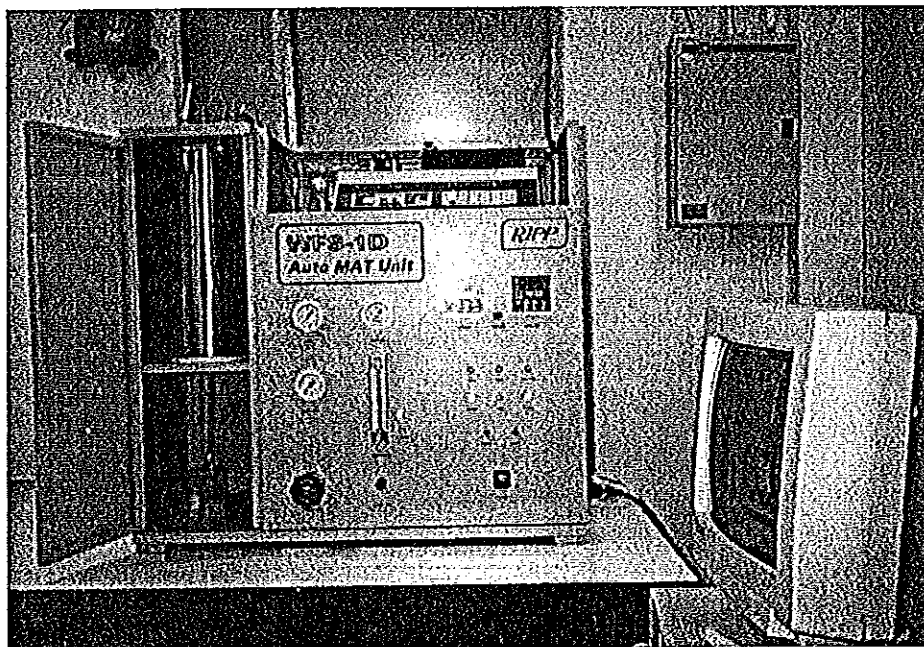
B = Liquid product from MAT, g.

C = Feed oil, g

Figure B-2 Microactivity test unit

Figure B-3 Gas Chromatograph unit

Example: Measures the MA (%wt) of catalyst sample 2nd conventional exchange of Table

4-2 from Chapter 4.

1. Gasoline cut point: Analyze the mixture of gasoline+gas oil+standard n-dodecane or pure n-dodecane with Gas Chromatograph

Figure B-4 Chromatogram of n-dodecane (n-C_{12})

2. Cracking of gas oil with catalyst sample 2nd conventional exchange and inject the liquid produced from MAT to the GC.
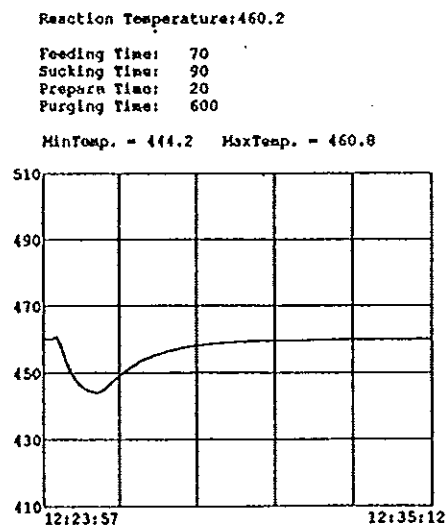

Figure B-5 Temperature profile during catalytic cracking of sample 2nd conventional exchange

3. Calculate gasoline yield from the integration of the area under the resulted chromatogram with retention time from initial to 9.4 minutes (C_{12} below).
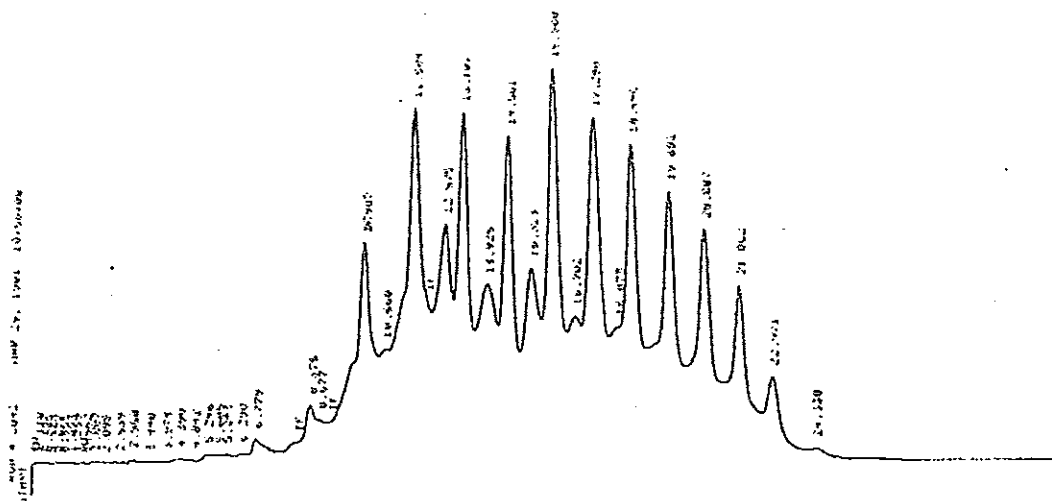

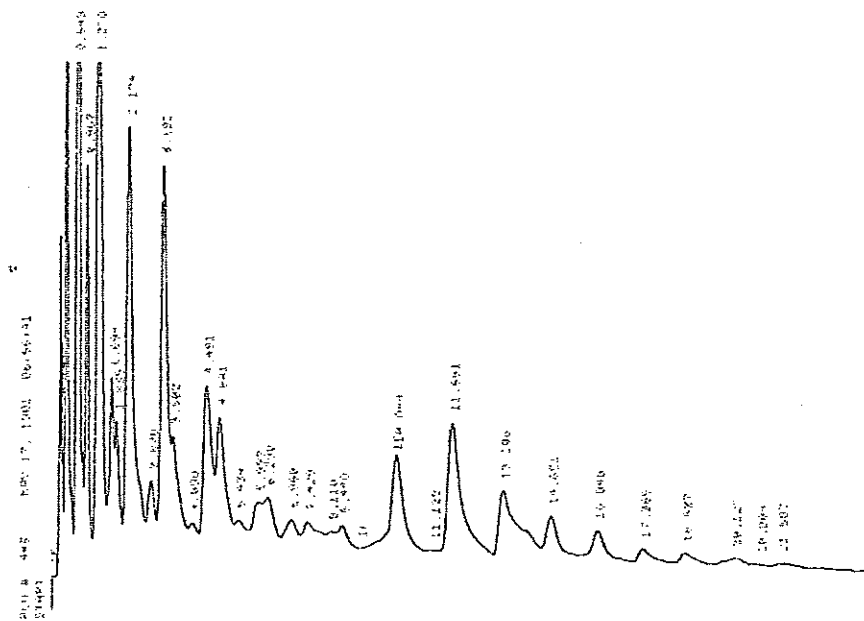Figure B-6 Chromatogram of gas oil (LCO) before reaction with catalyst.

Figure B-7 Chromatogram of liquid after reaction with catalyst sample 2nd conventional exchange

4. Put the gasoline yield (gasoline area, %wt), liquid products yield in program WSF-1D to calculate the microactivity.

Table B-3 MAT operation report

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

B-2 Hydrothermal Deactivation (by CLY-1 Hydrothermal Aging Unit)

B-2.1 Installation and Preparation

B-2.1.1 Power Supply

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

B-2.1.2 Air Supply

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

B-2.1.3 Water

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

B-2.1.4 Temperature Adjustment

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

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

B-2.2 Aging Procedure

B-2.2.1 Load Catalyst

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

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

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

3) Better to fill 40 ml. Catalyst inside the tube.

4) Put a quartz cotton layer of about 1-2 cm. Thick on the top of the catalyst bed.

5) Put some broken porcelain chips in.

6) Put in the tube with porcelain rings.

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

B-2.2.2 Pre Air Stripping and Start Heating

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

2) Turn the "power" switch on.

3) Set the heating time for 2 hrs.

4) Set the aging time for 4, 6, 8, 12, 17, (16) hrs. respectively.

5) Set the alarm time at aging time minus 1 min.

6) Push the button "heat" to start heating.

7) Turn on pump power and set pump rate at 0.41 ml/min.

B-2.2.3 Start Hydrothermal Aging

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

B-2.2.4 Post Air Stripping

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

B-2.2.5 Finish

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

Figure B-8 Hydrothermal aging unit

Vitae

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