Chapter 3

**RESULTS AND DISCUSSION**

The results and discussion of our experiments were separated into 4 parts as the following.

1. The synthesis of NaY zeolite.

2. The preparation of USY, REHY and REY zeolite.

3. The preparation of FCC catalysts.

4. Evaluation of the performance of catalysts.

3.1 NaY zeolite

The synthesis of NaY zeolite from sodium silicate involves the use of aluminium sulfate, sodium aluminate and initiator (seeds). Initiator was prepared by slowly mixing sodium aluminate solution into a solution of sodium silicate under conditions of high agitation and controlled temperature. The resulted molar composition of sodium aluminosilicate gel obtained from experiment is:

$$4.58 \text{ Na}_2\text{O} : \text{Al}_2\text{O}_3 : 8.96 \text{ SiO}_2 : 180.76 \text{ H}_2\text{O}$$
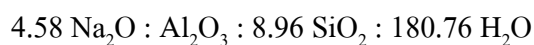
After crystallization process, the physical and chemical properties of synthesized NaY zeolite were shown in table 3-1.

Table 3-1 Physical and chemical properties of synthesized NaY zeolite.

zeolite	% crystallinity	UCS (Å)	Thermal stability ($^{\circ}C$)	Surface area (m^2/g)	Na_2O (%wt)	SiO_2/Al_2O_3 (mole ratio)
NaY	102.2	24.72	937.18	653	8.97	4.32
NaY[*]	98.0	24.65	939.19	652	nd	nd
NaY[**]	96.3	24.70	nd	nd	8.70	4.55

(*) = NaY prepared by Jukkrit Tuntragul

(**) = NaY prepared by Kritsana Kritsanaphak, nd = not determined

Figure 3-1 X-ray patterns of NaY zeolite

3.2 Preparation of USY, REHY and REY zeolites

Removing of the sodium from the zeolite is necessary in FCC catalysts because the sodium has poisons active sites zeolite. In commercial FCC catalysts, the sodium content of zeolite is minimized, usually below 1 percent Na_2O. This is accomplished by ionic exchange of the zeolites with solution of ammonium and/or rare earth salts.

3.2.1 Preparation of USY zeolite

In this experiment, the sodium ion was exchanged with ammonium chloride, since direct exchange with an acid destroys the crystallinity framework of the zeolite. Once the ammonium ions are placed inside the cages and the sodium ions are removed. The zeolites are calcined at a high temperature to decompose ammonium ions, drive off ammonia and leave protons in the place of the original sodium ions.

The hydrothermal approach to dealumination involved treating the zeolite with steam temperature at $600^{\circ}C$. Aluminium-oxygen bonds are broken by the steam and the aluminium atom is expelled from the zeolite framework.

The fully exchanged Y zeolite contained 0.73 %wt of sodium oxide and the other properties are shown in Table 3-2.

Table 3-2 Physical and chemical properties of USY zeolite.

zeolite	% crystallinity	UCS (Å)	Thermal stability ($^{\circ}C$)	Surface area (m^2/g)	Na_2O (%wt)
USY	63.7	24.37	1011.52	480	0.73
USY[*]	65.5	24.37	1015.20	462	0.90

(*) = USY prepared by Wachira Ritthichai

Calcination of an ammonium-exchanged Y zeolite in the presence of steam results in the expulsion of tetrahedral aluminium from the framework into nonframework positions. This process, which consists essentially in a high-temperature hydrolysis of Si-O-Al bonds, leads to the formation of nonframework aluminium species, while increasing the framework silica to alumina ratio and decreasing the zeolite unit cell size (Figure 3-2 (A)). In addition to amorphous alumina, amorphous silica-alumina is also formed. The progress of framework dealumination can be observed from the x-ray diffraction scan, since the diffraction peaks are shifted to higher 2θ values (lower d-spacings) with progressive dealumination. It was show that the defect site left by dealumination are filled to a large extent by silica, which leads to a very stable, highly siliceous framework (Figure 3-2 (B)). (Scherzer, 1990)
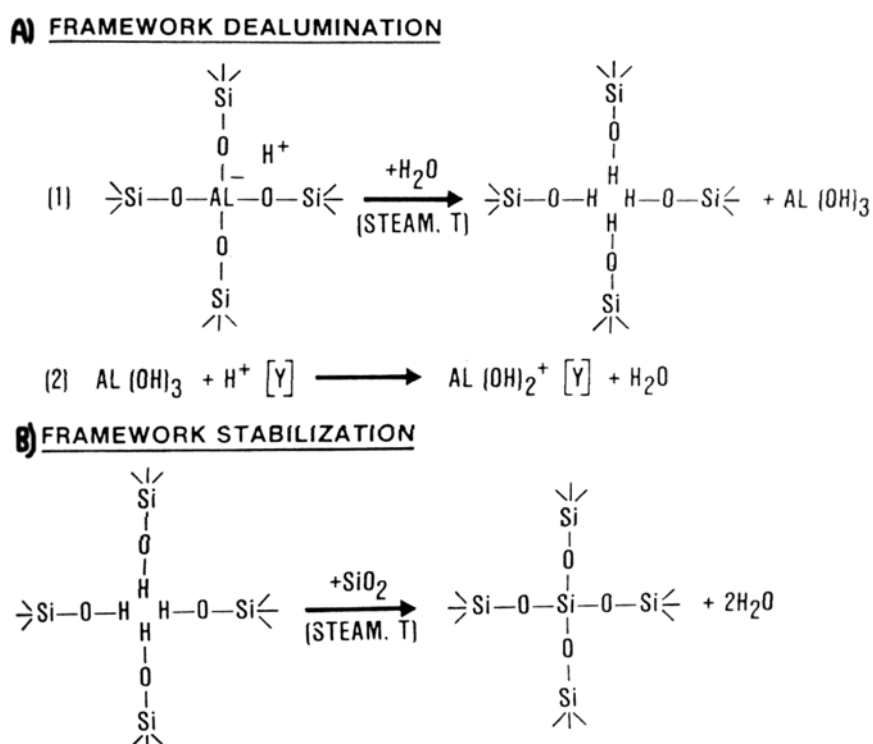
Figure 3-2 Reaction mechanism for hydrothermal dealumination and stabilization of Y zeolite (Scherzer, 1990 : 25).

3.2.2 Preparation of REHY

REHY zeolites are prepared from NaY zeolite by ion exchange with rare earth and ammonium salts in solution. The rare earth salts are a mixture of lanthanum and praseodymium, with smaller amounts of cerium and neodymium. The present of rare earth in the Y zeolite increases its stability and catalyst activity.

The ionic exchange occurs primarily with supercage sodium ions, due to the inability of hydrated rare earth ions ($\phi \approx 7.9$ Å) to penetrate the 6- membered ring of the sodalite cage ($\phi \approx 2.4$ Å). Some of the zeolite sodium ions are exchanged by hydrogen ions present in the acidic rare earth salt solution. Calcination of the primary rare earth exchanges zeolite results in stripping of the hydration shell from the rare earth ions and migration of the dehydrated ions into the sodalite cages. At the same time, most of the remaining sodium ions move into supercage positions and are subsequently removed by ammonium exchange. During calcination, some the cerium ions present in the rare earth mixture are oxidized to the tetravalent state. Furthermore, the rare earth ions that migrate into the sodalite cages form cationic polynuclear hydroxy complexes (Scherzer, 1993). Upon calcination, RE-NH_4Y is converted into RE-HY zeolite.

The fully rare earth exchanged Y zeolite contained 10.17 %wt of rare earth oxide and 0.89 %wt of sodium oxide. According to Scherzer (1993), REHY zeolites with over 10 % wt RE_2O_3 are highly active and are used primarilly in gasoline FCC catalysts. The other properties are shown in Table 3-3.

Table 3-3 Physical and chemical properties of REHY zeolite.

zeolite	% crystallinity	UCS (Å)	Thermal stability ($^\circ$C)	Surface area (m^2/g)	Na_2O (%wt)	RE_2O_3 (%wt)
REHY	27.06	24.63	1014.86	572	0.89	10.17
REHY[*]	26.76	nd	1018.00	nd	0.94	11.85

(*) = REHY prepared by Rattana Liangsagul, nd = not determined

3.2.3 Preparation of REY

Generally, the level of RE_2O_3 content in REY zeolite, which fully exchanged is about 16 %wt or higher. The ion exchange process must be carried out for two times to get a desired level of rare earth and decrease the level of sodium content to be lower than 1%wt. In the research of Kritsanaphak (2001), the first rare earth exchanged (REY‑1) zeolite still contained high sodium content (6.64 %wt of Na_2O). So that, to remove the remaining sodium ions and increase the level of rare earth, the zeolite was carried out for the second exchange. The fully rare earth exchanged Y zeolite contained 23.81 %wt of rare earth oxide and 0.60 %wt of sodium oxide. The other properties are shown in Table 3-4.

Table 3-4 Physical and chemical properties of synthesized REY zeolite.

zeolite	% crystallinity	UCS (Å)	Thermal stability ($^{\circ}$C)	Surface area (m^2/g)	Na_2O (%wt)	RE_2O_3 (%wt)
REY	29.3	24.68	998.38	575	0.60	23.81
REY[*]	33.4	nd	1001.32	nd	0.63	22.41
REY[**]	43.8	24.67	nd	nd	0.38	22.31

(*) = REY prepared by Sutha Onkham

(**) = REY prepared by Kritsana Kritsanaphak, nd = not determined

3.2.4 Comparison of silica to alumina ratios of USY, REHY and REY zeolites

All cracking catalyst share one property, a surface that contain an acid site of sufficient strength to cause the formation of a carbenium ion when a hydrocarbon molecule interacts with the surface. Active sites in cracking catalysts are acid sites, i.e., they are proton donor (Bronsted acid sites) or electron pair (Lewis acid sites). Acid sites in all conventional cracking catalysts are formed by interactions of silica and alumina (SiO_2 and Al_2O_3). Under appropriate reaction conditions, these two materials interact to form a solid acid of the following simplified structure.
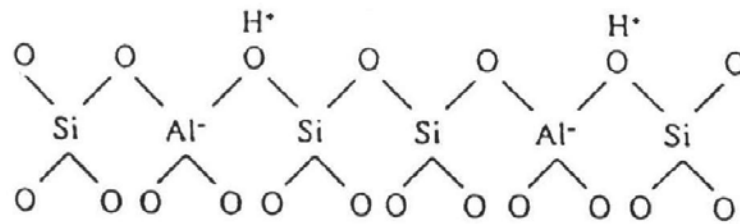
Alumina in this structure has a negative charge. The balancing positive charge lies on a proton, the H^{+} of the composite acid.

In the Y type zeolites, silica/alumina linkages were shown in Figure 1-5 in chapter 1. At each intersection there is either silicon or an aluminium atom, and between each intersection there is an oxygen atom connecting the silicon or aluminium. Silicon may be connected through oxygen to other silicon or aluminium, but aluminium can only be connected through oxygen to silicon. No Al-O-Al connections are allowed in this structure.

In general, as the zeolite framework is dealuminated, the unit cell size (A_0) decreases. The number of aluminum atoms per unit cell (N_{Al}) can be estimated from the unit cell size according to the Breck-Flanigan relationship (Dai, 1996):

$$A_0 = 24.191 + 0.00868(N_{Al}) \tag{3.1}$$

Because the total number of aluminum and silicon atoms ($N_{Al} + N_{Si}$) is constant, according to:

$$N_{Al} + N_{Si} = 192 \tag{3.2}$$

then, the framework Silica to Alumina mole ratio can be expressed as:

$$SiO_2/Al_2O_3 = 2\,[(1.6704/(UCS-24.19))-1] \tag{3.3}$$

where UCS is the unit cell size in Angstroms equivalent to A_0 (in Angstroms) of equation 3.1.

A unit cell has 192 silicon or aluminium atom. The starting type Y zeolite will contain 48 aluminium and (consequently) 144 silicon. The number, then, of potential acid sites is 48, equivalent to the number of Al atom present in the structure.

X-ray diffraction unit cell size measurements can therefore be used to estimate the framework silica to alumina mole ratios (see Table3-5). The unit cell size of the zeolite may also predict zeolite properties such as hydrothermal stability, total acidity, and acid strength.

Table 3-5 Silica to alumina ratios of prepared zeilites according to the Breck-Flanigan relationship.

Zeolites	UCS (Å)	N_{Si}	N_{Al}	SiO_2/Al_2O_3
USY	24.37	171.38	20.62	16.56
REHY	24.63	141.42	50.58	5.59
REY	24.68	135.66	56.34	4.82

This dealumination, when controlled, simply removes aluminium from the structure lose one active sites, since each active site is associated with a tetrahedrally coordinated Al. The tetrahedrally coordinated Al needs a nearby proton (the acid of the active site) to balance its negative charge. RE stabilizes the structure, giving the highest number of active sites but of relatively low acid strength. USY stabilizes the structure at the lowest number of active sites, but of relatively higher acid strength.

Figure 1-6 in chapter 1, illustrates what the Y structure looks like for a highly dealuminated structure (USY) compared to a slightly dealuminated structure (REY). Intermediate levels of dealumination can be prepared by partially RE exchanged USY and by using combination RE/NH_4^+ exchanges to form RE/NH_4Y materials. Upon combination these give REHY does not undergo as extensive dealumination as USY, and REHY dealuminates more severely than REY.

All three types are commonly used in cracking catalysts because of their differences in the number of acid sites, the strength of sites and the difference in site separation. When incorporated in an active matrix, very different cracking selectivities are observed.

3.3 Catalyst Preparation

Modern FCC catalysts consist of two major components: zeolite and matrix. Some catalysts also contain a third components: one or several additives. Most commercial FCC catalysts contain between 15-40 percent zeolites, which is the major contributor the catalytic activity and selectivity of the FCC catalyst (Scherzer, 1993). Catalytic matrices can be catalytically inactive or active. Inactive matrices often consist of amorpous silica and clay. For active matrices, the catalytically active component is usually alumina, silica-alumina or modified clay.

For catalysts with active matrices, the activity and selectivity of the catalyst is determined by both zeolite and matrix. The active matrix contains acid sites usually associated with alumina atoms. Catalysts with active matrices are often used in FCC units where higher conversion and improved gasoline octane cannot be achieved by operating at higher severity due to unit limitations.

Pseudoboehmite alumina (PBA) has a high surface area (327.04 m^2/g). The present of pseudoboehmite derived alumina in the catalyst not only increase its catalytic activity and stability, but also improves its attrition resistance. The surface area, pore structure, and hydrothermal stability of the alumina are critical in FCC operations. In general, the function of the active alumina is to crack large, heavy molecules boiling typically above 650 $^\circ$F into a material with a lower molecular weight. Alumina is to absorb condensed aromatics, which are not crackable. The absorption prevents the molecules from blocking access to the zeolite and decreasing catalyst activity.

Clays are used in almost all commercial catalyst formulations. Clays used in FCC catalyst formulations are kaolinite and halloysite. They have a two-layer structure, consisting of alternating sheets of SiO_4 tetrahedral and AlO_6 octahedral, as shown in Figure

3-3. The ideal composition corresponds to the formula $2SiO_2.Al_2O_3.2H_2O$. However, natural clays frequently contain impurities, such as iron, magnesium, calcium, etc., as well as different mineral impurities (eg., quartz). The clays used in FCC formulations are usually purified and have small average particle size (high percentage of particles less than 2μ in size). The small particle size and a high degree of dispersion improve the attrition resistance of the catalyst.
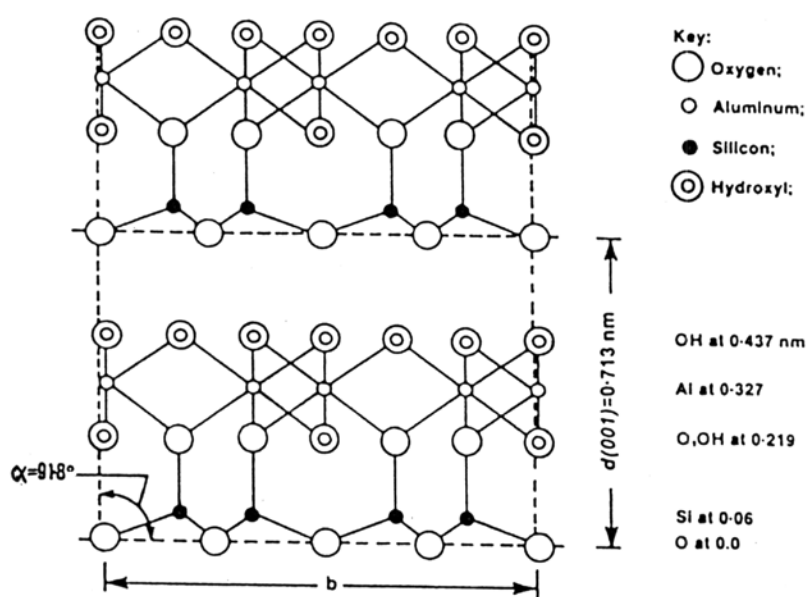
Figure 3-3 Kaolinite layer viewed along the α axis.

Source: Scherzer, 1990: 60

The catalyst were prepared with varying matrix (PBA and RIPP clay) and zeolite contents (USY, REHY and REY) to demonstrate how matrix and zeolite interact for cracking of gas oil, and their activity were measured by using micro-activity test.

3.4 Evaluation of the catalysts performance

Microactivity test condition of this work was performed at standard conditions, as seen in section 3.1.1.

Definition

1. %Conversion (MAT) = 100-{[(100-A)*B]/C}

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

B = Liquid product from MAT, g

C = Weight feed oil, g

2. %Coke (Feed Basis) = A*{B/[C*(1-(B/100))]}

Where: A = Weight of fresh catalyst used in MAT unit, g

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

C = Weight of feed oil, g

3. %Gas (Feed Basis) = 100 - %Coke - [(A/B)*100]

Where: A = Weight of liquid product, g

B = Weight of feed oil, g

4. Gasoline selectivity = %Gasoline / % Conversion

5. Coke selectivity = %Coke / % Conversion

6. Gas selectivity = %Gas / % Conversion

3.4.1 Effect of REY, REHY and USY on products yield.
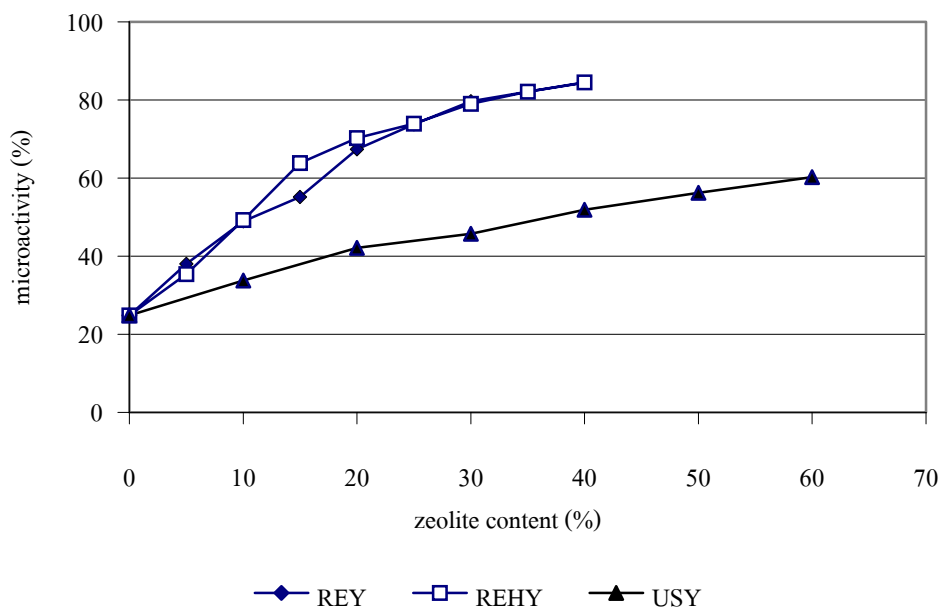
Figure 3-4 Effect of zeolite content on activity
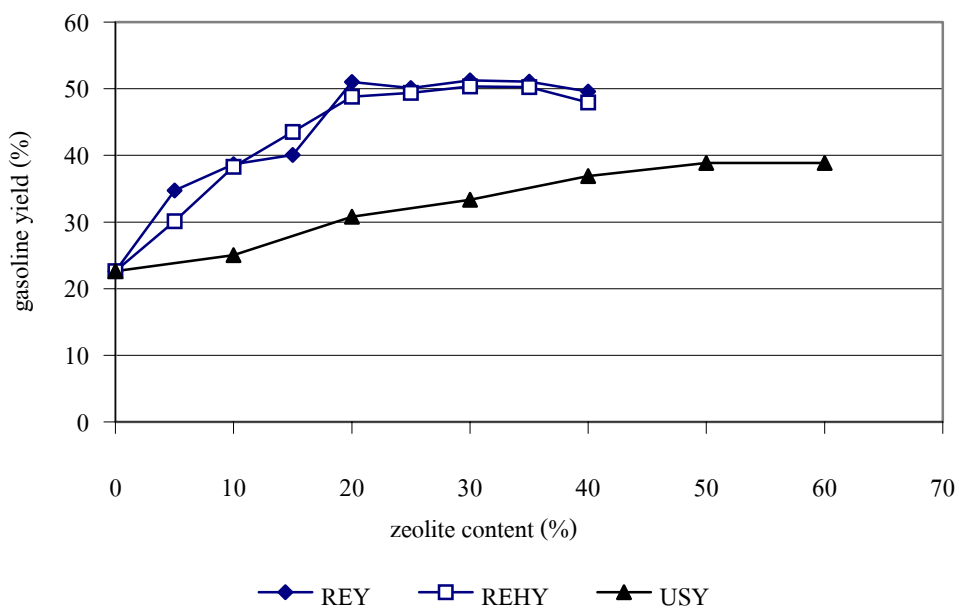
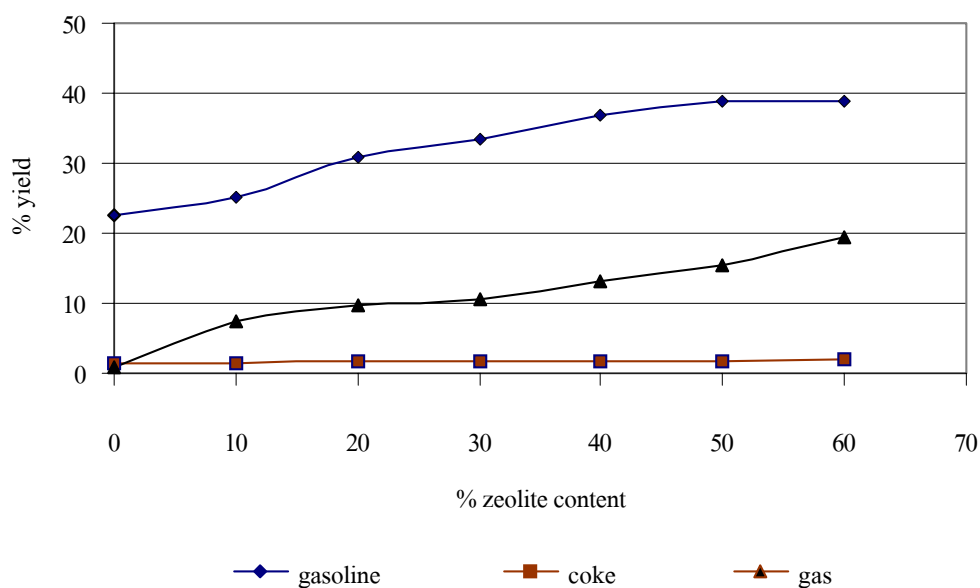**Figure 3-5** Effect of zeolite content on gasoline yield

Catalytic activities of prepared catalysts were performed by micro-activity testing (MAT) unit at standard conditions (460°C, cat/oil ratio 3.2, WHSV 16 hr^{-1}) using Fang gas oil (boiling point range 260-340°C) as a feed stock. Figure 3-4 shows microactivity of REY, REHY and USY catalysts which contain different zeolite contents. USY catalyst gives lower value of activities than REY and REHY catalysts which are in the same values. The activity increases with zeolite content containing in the catalyst. Figure 3-5 shows gasoline yield obtained from catalytic cracking of these catalyst. Gasoline yield from REY and REHY catalysts are also in the same values and they have the maximum yield when catalyst contain zeolite between 20-35 percent. It seems that at 40 percent of zeolite content gasoline yield is slightly decrease. This may come from the overcracking that transfer gasoline to gas by secondary reaction. USY catalyst gives an increasing gasoline yield with increasing zeolite content as same as activity to zeolite content of 60 percent. The overcracking phenomena does not exist to USY catalyst because of its very low activity.
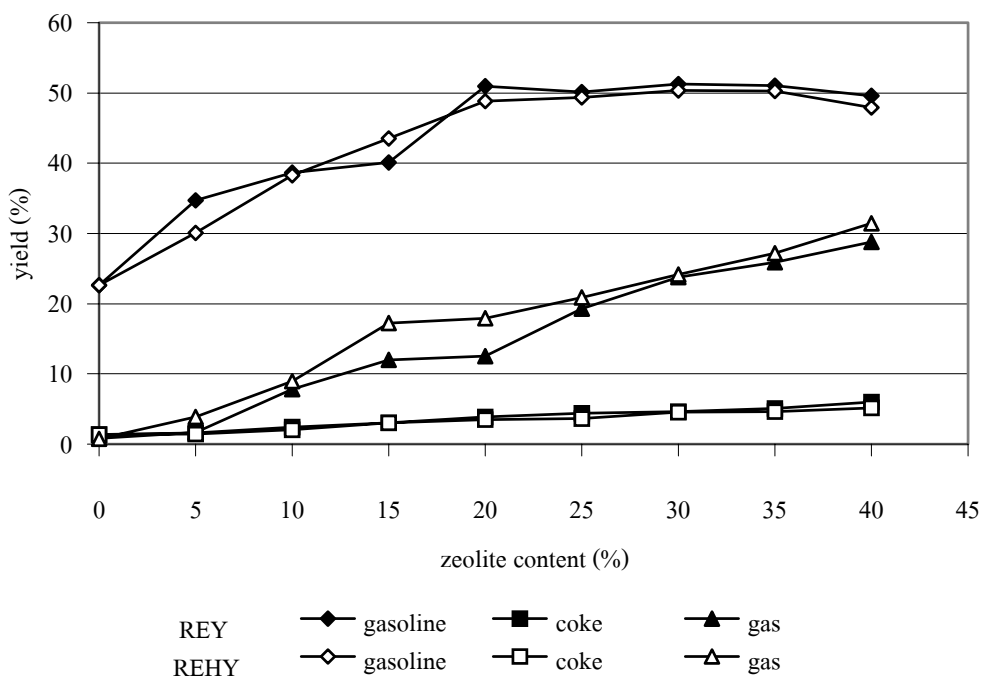
Figure 3-6 Effect of REY and REHY zeolites content on yields

The selected catalyst depends on feedstock, operating conditions and desired product. The REY or REHY zeolite can contain different levels of rare earth, which will have different activities and selectivities to the catalyst. In general, a higher rare earth content in zeolites results in higher activity, gasoline selectivity and also in higher coke formation.

Selectivity is the measure of a catalyst's ability to yield desired product. For example, a catalyst has good gasoline selectivity when it produces high yield of gasoline. For the REY and REHY catalysts (Figures 3-6), at the presence of 20-35% zeolite in catalyst is possible to be an optimum zeolite level for gasoline catalyst in the catalytic cracking process of Fang gas oil. Because at this level, it has a high gasoline yield and low coke and gas yield. This means that at 20-35% REY and REHY containing catalysts will have high desired product (gasoline) and low undesired product (gas and coke).

**Figure 3-7** Effect of USY zeolite content on yields

In the case of USY zeolite containing catalyst, at the zeolite content of 50-60 percent, the gasoline yield is slightly increase (see Figure 3-7). Generally, zeolite is not contained in catalyst more than 50 percent. Because the presence of clay is necessary to provide physical integrity (density, attrition resistance, particle size distribution, etc.), heat transfer medium, and fluidizing medium.

3.4.2 Comparison of the performance of REY, REHY and USY catalysts.
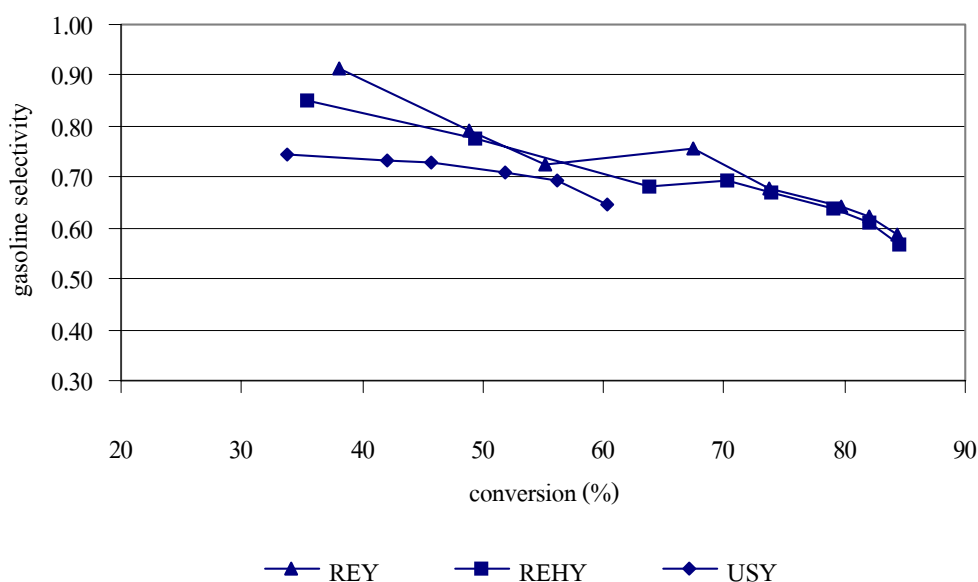
Figure 3-8 Correlation between gasoline selectivity and conversion

Catalyst selectivity is strongly affected by zeolite dealumination. According to the Breck-Flanigan relationship, USY zeolite has the highest silica to alumina ratio, also it has the lowest acid site density in the zeolite. Figure 3-8 shows data obtained from catalyst containing USY, REHY and REY zeolites. At equal conversion, REY catalyst give gasoline selectivity slightly higher than REHY, while gasoline selectivity of USY catalyst is lower than REY and REHY catalyst. As the unit cell size decreases and Si/Al ratio in the zeolite framework increases, catalytic conversion decreases.
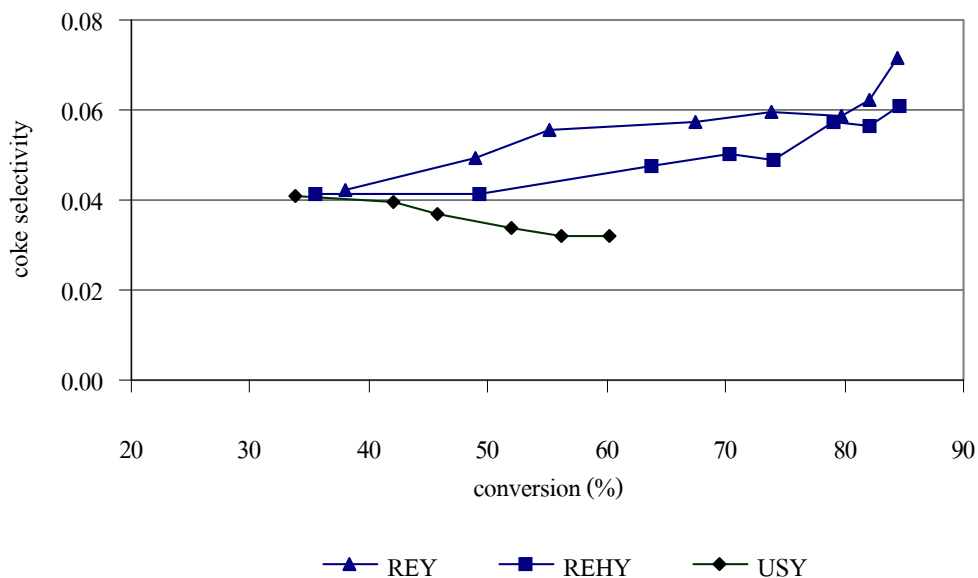
Figure 3-9 Correlation between coke selectivity and conversion

Pine et al.(1984, quoted in Scherzer, 1990: 99) have shown that a decrease in unit cell size results in a decrease acid site density and in the rate of hydrogen transfer reactions. There is also a correlation between zeolite unit cell size and framework silica to alumina ratio. A lower unit cell size corresponds to a higher Si/Al ratio in the zeolite framework.

Coke selectivity is the relative coke-making tendency of any given cracking catalyst. It is often defined by the ratio between coke yield (expressed in weight percent fresh feed) and conversion (Scherzer, 1990). Low coke selectivity is desirable in resid processing, since high coke yield cause high regenerator temperature which in the absence of heat removal, will limit the amount of resid that can be processed in the unit.

Figure 3-9 shows that REY has the highest (worst) coke yield and USY catalyst has the best coke selectivity. Usually, lower coke yield will permit a reduction of regenerator temperature, resulting in an increase in catalyst circulation rate and increased conversion (Young G.W., 1993). In addition to cracking activity, coke selectivity is also important for FCC catalysts, because FCC units are operated with a heat balance between the reactor and

the regenerator. The heat generated by coke burning is supplied for the endothermic cracking reaction. The coke selectivity of FCC catalysts is also affected by the unit cell size of the zeolite with the increase in the unit cell size, the coke formation is accelerated by the increased hydrogen transfer activity of the zeolite.

3.4.3 Zeolite mixtures in catalysts.

Zeolite mixtures in the catalyst formulation accomplished by changing the total amount and ratio among the zeolite used in the catalyst. From the previous results, we can conclude that the REY and REHY zeolites have the same catalytic performance, thus the zeolites were mixed between REY or REHY with USY. Scherzer (1990) reported that, mixtures of several zeolites can be used in the same catalyst particle, in order to obtain the desired activity and/or selectivity. FCC catalysts are formulated with mixtures of two or more zeolites, such as REHY+USY, REHY+RE-USY, REHY+acid-leached USY, REY+USY.
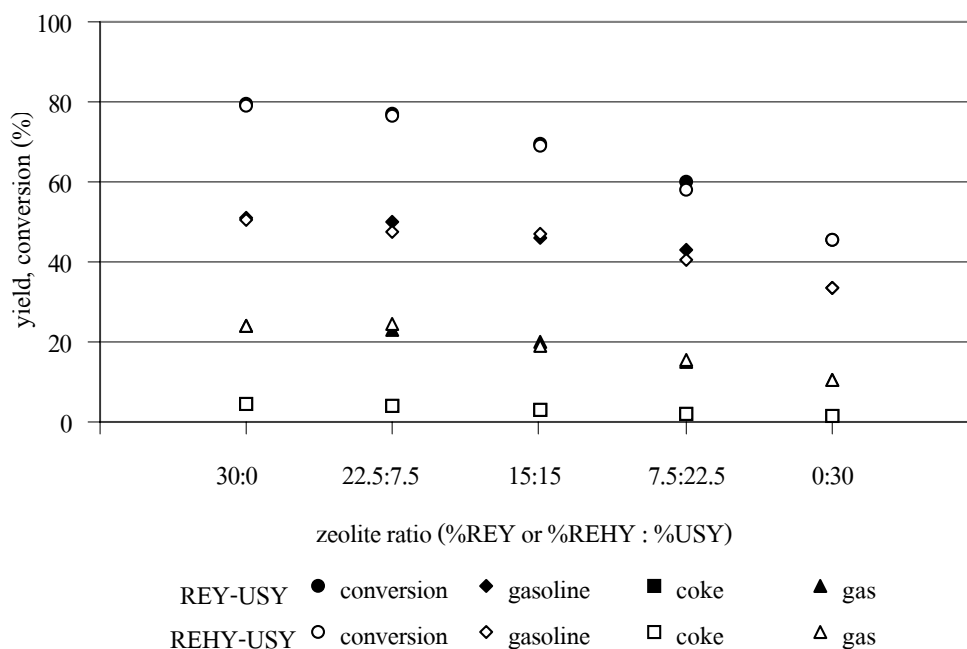
**Figure 3-10** Effect of REY-USY and REHY-USY zeolites combination of 30 %wt zeolite
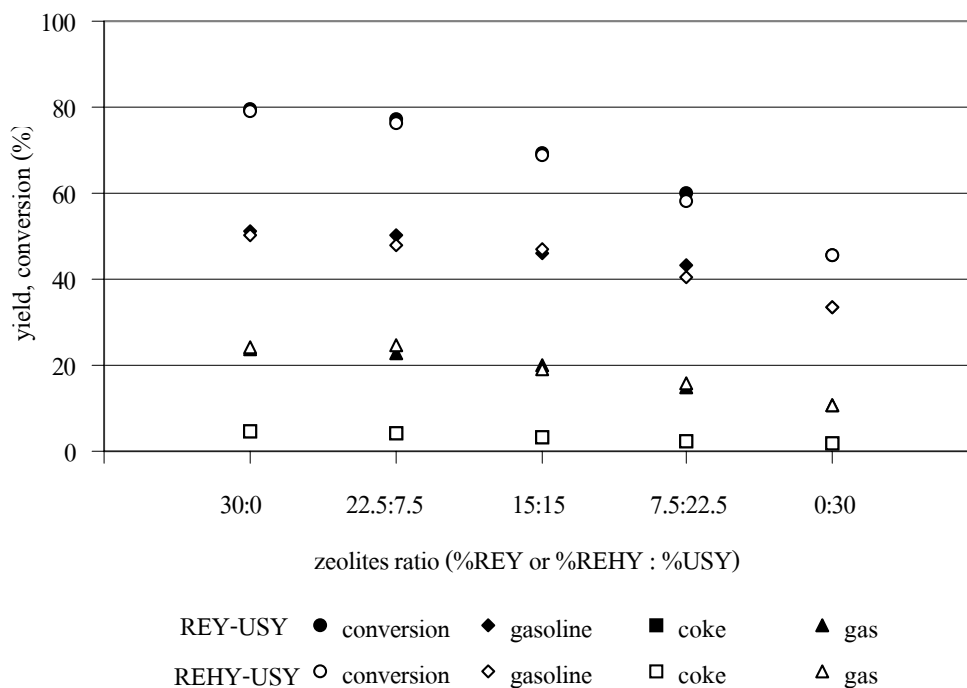
Figure 3-11 Effect of REY-USY and REHY-USY zeolites combination of 40 %wt zeolite

Figure 3-10 and 3-11 show that when REY or REHY zeolites in mixed catalyst decrease (or USY zeolite in mixed catalyst increase), the catalytic activity and product yield decrease. Therefore, the optimum ratio of zeolite content has been considered. The optimum ratio depends on feedstock, operating conditions and desired products. In this work feedstock and operating condition were controlled so that, the desired (gasoline) and undesired (gas and coke) were considered.

Figure 3-10 shows the conversion and product yields of total 30 %wt of mixed zeolite catalyst at different ratio of REY or REHY to USY zeolite. The catalyst of mixed zeolite 22.5% REY and 7.5% USY give gasoline yield slightly less than 30% REY catalyst. But coke and gas yields of mixed zeolite catalyst are smaller than. So, the mixed zeolite catalyst should be preferred to use. But for the mixed zeolite of REHY-USY catalyst, the

15% REHY and 15% USY catalyst is preferable because of the lower gas and coke yields but the same level of gasoline yield to higher content of REHY catalysts.

In the case of the catalyst based on total 40 %wt zeolites (Figure 3-11), the results indicate that the catalyst based on 20 %wt REY or REHY and 20 %wt USY zeolites give high gasoline yield and low coke yield. Therefore, catalyst based on 20 %wt REY or REHY and 20 %wt USY zeolites should be a preferable level of mixed catalyst for the catalytic cracking of Fang gas oil.
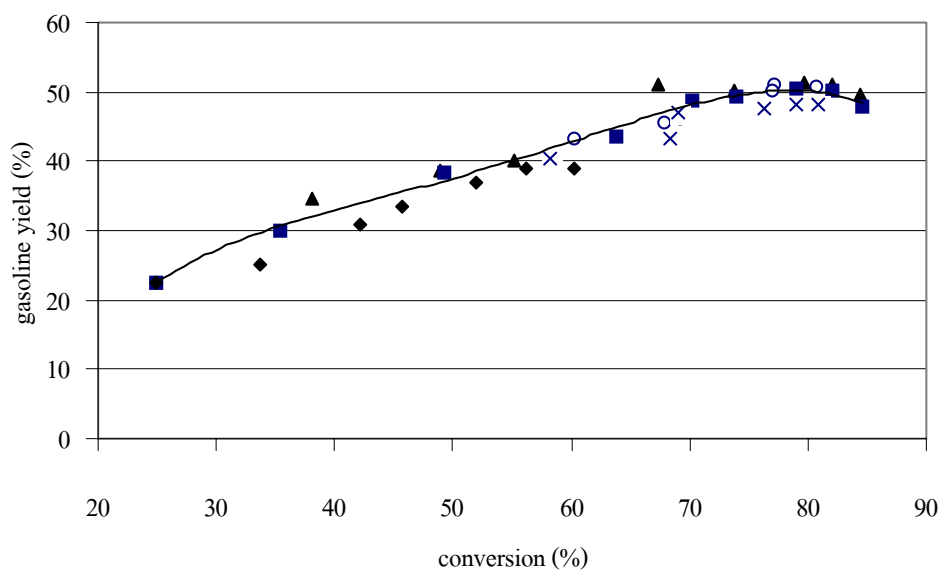
Figure 3-12 Correlation between gasoline yield and conversion of (▲)REY, (■)REHY, (◆)USY, (○)REY-USY and (x) REHY-USY catalyst
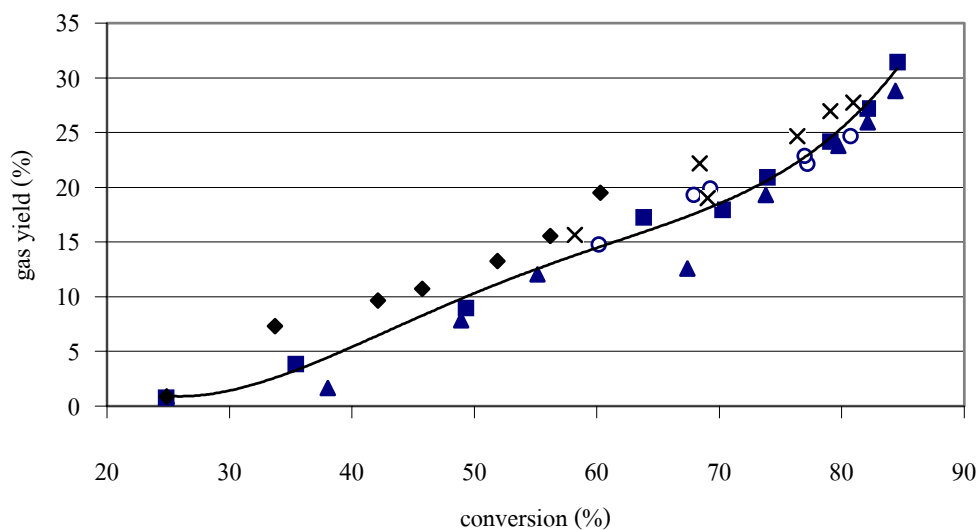
Figure 3-13 Correlation between gas yield and conversion of (▲)REY, (■)REHY,

(◆)USY, (○)REY-USY and (x) REHY-USY catalyst
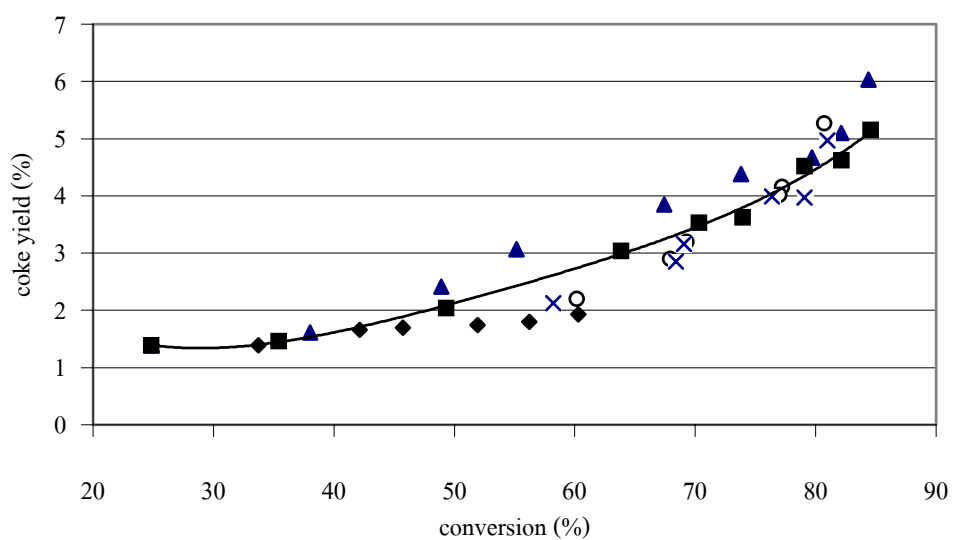
Figure 3-14 Correlation between coke yield and conversion of (▲)REY, (■)REHY,

(◆)USY, (○)REY-USY and (x)REHY-USY catalyst

The correlation between product yields and conversion obtained with the zeolite catalysts are shown in Figures 3-12, 3-13 and 3-14. As conversion increases, the gasoline yields go through a maximum and then decline due to overcracking (at the conversion higher than 78 percent). Coke and gas yields increase with increased conversion.

The concentration, strength and distribution of acid sites in the zeolite play a key role in determining its activity and selectivity. Although the reactions that take place during catalytic cracking of gas oil are rather complex and many of the primary products undergo secondary reaction (see Table 3-6), most of these reactions involve carbocations as intermediates (Scherzer, 1993). While cracking reactions of high input of zeolite contributes to high acid concentration, some primary products are converted to undesired product (e.g. gas and coke) by secondary reactions such as isomerization, cyclization, and intermolecular hydrogen transfer.

**Table 3-6** Main Reactions in FCC Catalysis (Scherzer, 1993: 154)
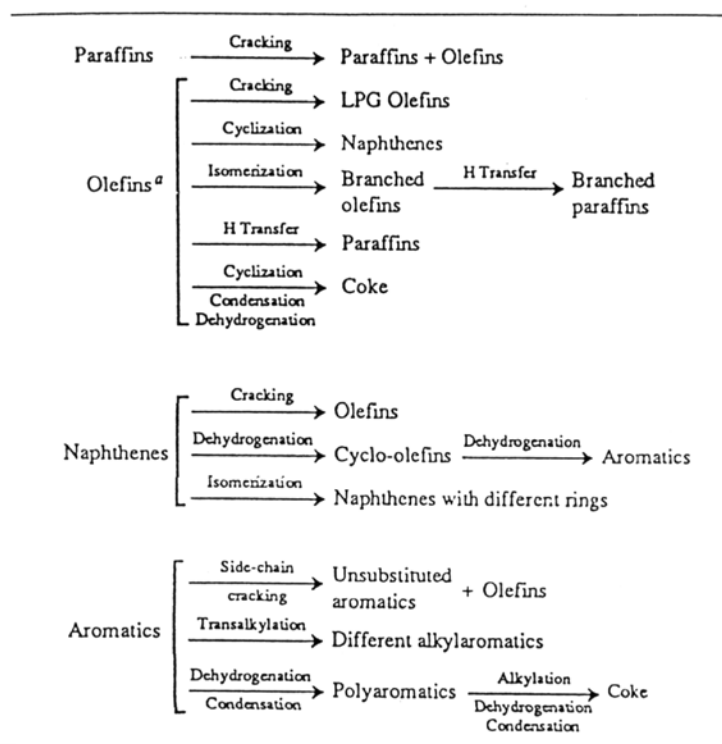
Hydrogen transfer plays an important role in the gas oil cracking process. It reduces the amount of olefins in the product through bimolecular hydrogen transfer, whereby reactive olefins and naphthenes are converted to more stable parafins and aromatics. Further hydrogen transfer from aromatics, coupled with condensation and polymeriztion, can lead to the formation of coke.

Yield ratio was used to illustrate the ability of USY zeolite in the mixed catalyst on the product yields (gasoline, gas and coke). Here it is defined by the ratio between product yields of mixed catalyst at the varied ratios of REY or REHY with USY and product yields of pure REY or REHY zeolites catalyst.
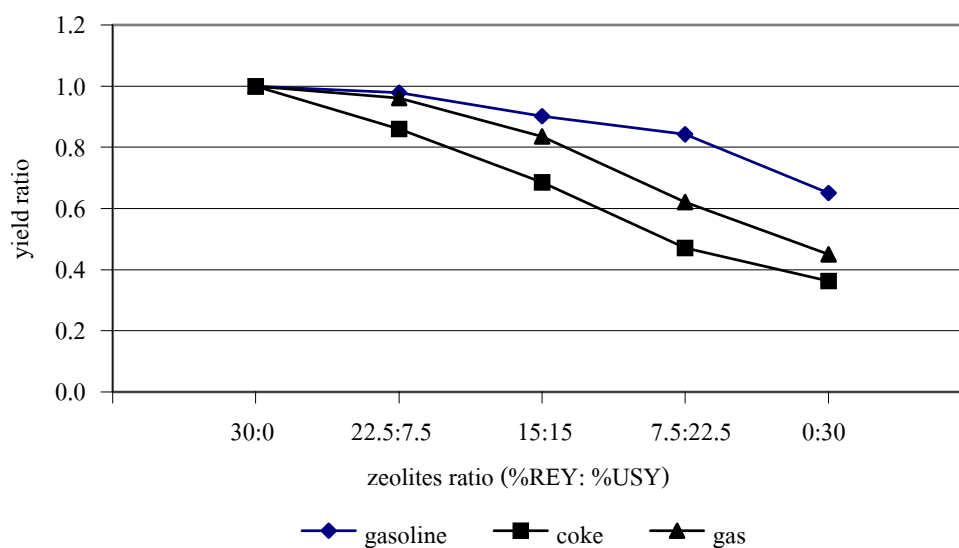
Figure 3-15 Yield ratio of REY-USY catalyst at total 30 %wt zeolites

Figure 3-15 confirms that, the ratio of 22.5% REY: 7.5% USY catalyst should be the optimum ratio for REY and USY zeolites mixed catalyst base on total 30 %wt zeolite in catalyst. Because at this ratio coke yield reduction is high while gasoline yield is slightly reduced.
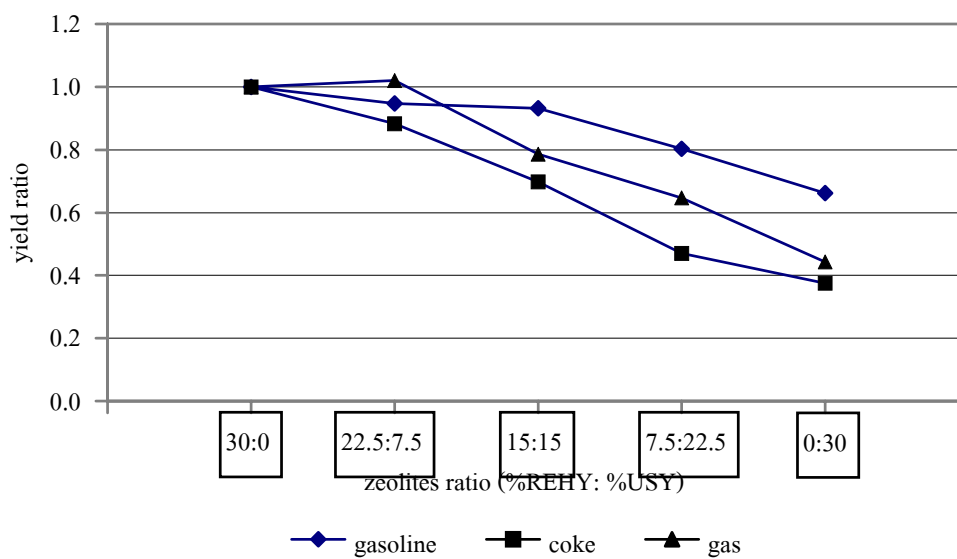
Figure 3-16 Yield ratio of REHY-USY catalyst at total 30 %wt zeolites

Figure 3-16 shows that, the ratio of 15% RHEY: 15% USY should be the optimum ratio for REHY and USY zeolites mixed catalyst base on total 30 %wt zeolite in catalyst. Because at this ratio coke yield reduction is high while gasoline yield reduction is small.
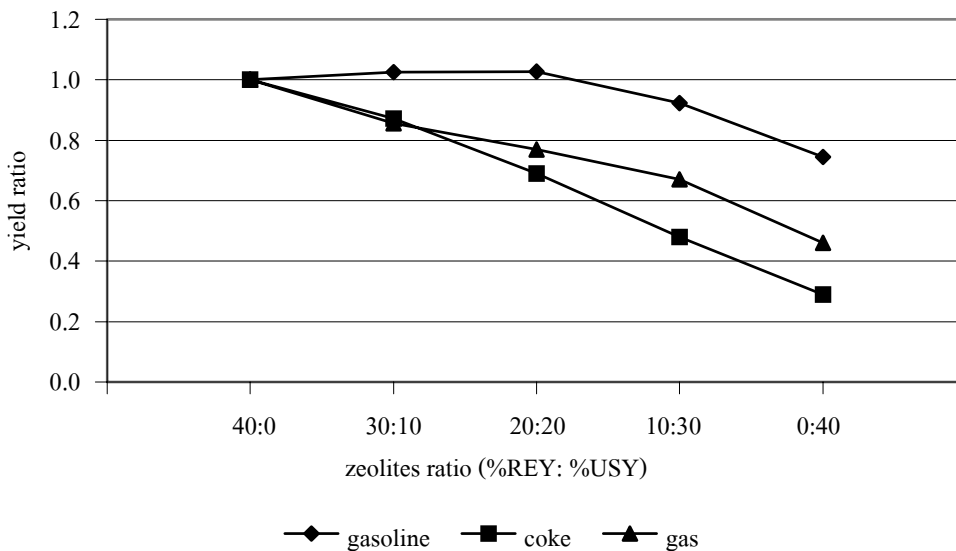
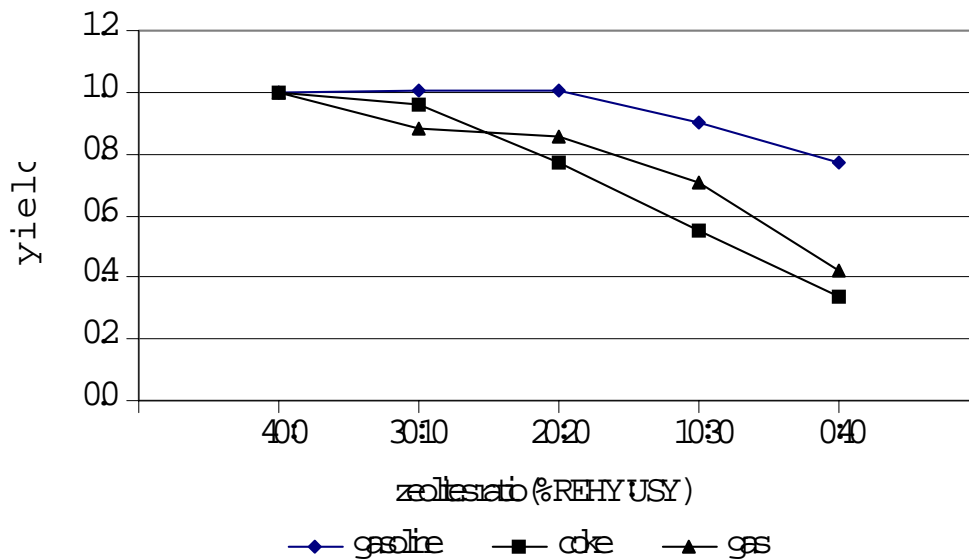**Figure 3-17** Yield ratio of REY-USY catalyst at total 40 %wt zeolites

Figure 3-18 Yield ratio of REHY-USY catalyst at total 40 %wt zeolites

Figures 3-17 and 3-18 indicate that, the ratio of 20% REY: 20% USY should be the optimum ratio for REY or REHY and USY zeolites mixed catalyst base on total 40 %wt zeolite in catalyst. These results indicate that the USY zeolite can be added to REY or REHY zeolite catalyst to lower coke yield while conversion and gasoline yield are at the satisfied level.

It was well known that, coke selectivity is also important for FCC catalysts, because FCC units are operated with a heat balance between the reactor and the regenerator. So, lower coke selectivity is desirable in the FCC process.