The use of Prepared Zeolite Y from Iraqi kaolin for Fluid Catalytic Cracking of Vacuum Gas Oil

Abdul Halim Abdul Karim Mohammed **Ibtehal Kareem Shakir** **Karim Khalifa Esgair**[*]
imahalim2005@yahoo.com ibtehal_27@yahoo.com karimkhalifa70@yahoo.com
Chemical Engineering Department, College of Engineering, Baghdad University
[*]Foundation of Technical Education.

ABSTRACT

The faujasite type Y zeolite catalyst was prepared from locally available kaolin. For prepared faujasite type NaY zeolite X-ray, FT-IR, BET pore volume and surface area, and silica/ alumina were determined. The X-ray and FT-IR show the compatibility of prepared catalyst with the general structure of standard zeolite Y. BET test shows that the surface area and pore volume of prepared catalyst were 360 m^2/g and 0.39 cm^3/g respectively.

The prepared faujasite type NaY zeolite modified by exchanging sodium ion with ammonium ion using ammonium nitrate and then ammonium ion converted to hydrogen ion. The maximum sodium ion exchange with ammonium ion was 53.6%.

The catalytic activity of prepared faujasite type NaY, $NaNH_4Y$ and NaHY zeolites was investigated by using the experimental laboratory plant scale of fluidized bed reactor. The cracking process was carried out in the temperature range 440 to 500 ^oC, weight hourly space velocity (WHSV) range 10 to 25 h^{-1} ,and atmospheric pressure . The catalytic activities of the prepared faujasite type NaY , $NaNH_4Y$ and NaHY zeolites were determined in terms of vacuum gas oil (VGO) conversion, and gasoline yield . The conversion at 500^{o}C and WHSV10 hr^{-1} by using faujasite type NaY, $NaNH_4Y$ and NaHY zeolite were 50.2%, 64.1% and 69.5wt% respectively. The gasoline yield using the same operating conditions were 24.8%, 30.5% and 36.8wt% respectively.

Keywords : Fluid catalytic cracking ; gasoline production ; vacuum gasoil cracking

استخدام الزيولايت من نوع Y المحضر من الكاؤلين العراقي لعملية التكسير الحفازي المائع لمادة زيت الغاز الفراغي

د.عبدالحليم عبدالكريم محمد ، د.ابتهال كريم شاكر ، د.كريم خليفة أزغير

الخلاصه

تم تحضيرالعامل المساعد الفيوجيسايت نوع Y زيولايت من الكاؤلين المتوفر محليا. اجريت تحاليل الاشعة السينية ، والاشعة تحت الحمراء ، والمساحة السطحية و الحجم المسامي ، وتحليل نسبة السليكا الى الالومينا للعامل المساعد فيوجيسايت نوع NaY زيولايت.اظهرت تحليلي الاشعة السينية ، والاشعة تحت الحمراء توافق العامل المساعد المحضر مع التركيب العام للزيولايت القياسي و كانت المساحة السطحية 360م^2 /غم والحجم المسامي 0.39 سم^3 /غم .

طور العامل المساعد المحضر فيوجيسايت نوع NaY زيولايت و ذلك باستبدال ايون الصوديوم بايون الامونيوم باستعمال نترات الامونيوم ومن ثم جرى تحويل ايون الامونيوم الى ايون الهيدروجين .كانت اعلى نسبة استبدال لايون الصوديوم 53.6% .

درست الفعالية الحفازية للفيوجيسايت بصيغة الصوديوم NaY ، و صيغة الامونيوم $NaNH_4Y$ و صيغة الهيدروجين NaHY زيولايت باستخدام وحدة تجريبية بحدود درجات الحرارة بين 500 ^oC – 440 وسرعة فراغية بين 25 – 10 سا$^{-1}$.

تم تعيين الفعالية الحفازية للفيوجيسايت بصيغة الصوديوم NaY ، و صيغة الامونيوم $NaNH_4Y$ و صيغة الهيدروجين NaHY زيولايت بصيغة تحويل المتفاعلات الى مختلف النواتج ونسبة الكازولين الناتج .لقد كانت نسبة تحويل المتفاعلات الى نواتج عند درجة حرارة 500 ^oC وسرعة فراغية 10 سا$^{-1}$ 50.2% و 64.1% و 69.5% على التوالي. وان انتاجية الكازولين لنفس الظروف التشغيلية كانت 24.8% و 30.5% و 36.8% على التوالي .

الكلمات الرئيسية : التكسير الحفازي المائع ، انتاج الكازولين ، تكسير زيت الغاز الفراغي .

INTRODUCTION

Catalysis by zeolites—with focus on hydrocarbon conversion and formation—covers nowadays a broad range of processes related to the upgrading of crude oil and natural gas. This includes, among others, fluid catalytic cracking (FCC), hydrocracking, dewaxing, aliphate alkylation, isomerisation, oligomerisation, transformation of aromatics, transalkylation, hydrodecyclisation as well as the conversion of methanol to hydrocarbons.All these conversions are catalysed by zeolites or related microporous materials, based both on the acid properties and shape-selective behaviour of this type of materials (Michael Stocker,2005).

A number of different FCC catalysts exist and catalyst changes in the worldwide about 350 refinery FCC units are made often, depending on the feedstock type and quality available (Ballmoos, et al 1997)

.

The FCC process produces about 45% of the total gasoline pool either directly or indirectly (Reza Sadeghbeigi, 2000). With the introduction of zeolite (faujasite type) containing cracking catalysts in 1962, replacing the amorphous silica–alumina, a tremendous change concerning FCC technology took place. Zeolite containing catalysts are much more active, show higher gasoline yield performances and produce less coke than the amorphous silica–alumina based catalysts, resulting in higher feedstock conversions and severities as well as enhanced economic benefits of the process (Corma, et al 2002). The actual FCC technology involves the formulation of proprietary multifunctional cracking catalysts, consisting of different amorphous (catalytically active macroporous matrix, clay type binder) and crystalline acid functions zeolites like Y-type zeolite containing mesopores due to dealumination forming the ultra-stable Y zeolite—USY), and a series of additives for metal passivation (mainly V and Ni), sulfur removal, promoters for total combustion and octane enhancing additives (Corma, et 2002). The matrix plays a critical role in the selective cracking of the (high molecular) bottoms fractions when residue containing feedstocks are processed. the unique pore architecture of Y zeolite is ideal for cracking gas oil components into gasoline molecules. Moreover, it has been observed that the activity of the Y zeolite for gas oil cracking has a maximum for a Si/Al ratio of 5–8,corresponds to a unit cell size (UCS) 2.436– 2.440 nm. This clearly indicates that gas oil cracking requires the presenc**e** of strong Bŕonsted acid sites. Unfortunately, so far it has not been possible to prepare Y zeolite with a framework Si/Al ratio above 4 by direct synthesis. Therefore, highly dealuminated zeolites have to be prepared by dealumination of commercially prepared Y zeolite samples with Si/Al ratios in the range of 2.6.(Corma, et al 1988).

In this respect, Y zeolites dealuminated by steaming (USY) create a secondary porosity formed during the partial destruction of the zeolite framework and forming mesopores which facilitate diffusion of larger molecules into the zeolitic channels. The obtained USY type zeolites show, in addition, a much better hydrothermal stability, which is a pre-requisite of the application as FCC catalyst (Sie et al, 1994). Due to the pore architecture, ZSM-5 increases the octane number of the gasoline by selectively upgrading low octane gasoline components into lower molecular weight compounds with a higher octane number . The concept of using ZSM-5 as co-catalyst to modify the performance of a generic FCC catalyst system can significantly increase the product flexibility in the FCC unit (Ward, et al 1990).

The present work is aimed to prepare Y zeolite from Iraqi kaolin and study the characteristics and activity of prepared catalyst.

EXPERIMENTAL

Kaolin

The Kaolin used is available in Al-Dewekhala Quarry in Al-Enbar region. It is supplied from State Company of Geological Surveying and Mining. Table 1 shows the chemical analysis of this material as determined by State Company of Geological Surveying and Mining.

Table 1: Chemical analysis of local kaolin

Component	Weight %
SiO_2	53.21
Al_2O_3	32.13
Fe_2O_3	1.41
K_2O	0.35
Na_2O	0.21
MgO	0.13
CaO	0.15
TiO_2	0.41
L.O.I	12.00

LOI = Loss on Ignition

CATALYST PREPARATION

Preparation of faujasite type NaY zeolite catalyst

The catalyst is prepared by steps consisting of:

1. Kaolin was finely divided to a particle size < 75 µm
2. Sodium hydroxide solution was prepared at concentration 45% wt and mixed with kaolin at weight ratio $\left(\frac{Kaolin}{pureNaOH} = \frac{1}{1.5}\right)$.
3. The mixture in step 2 calcines at 850 °C for three hours in a programmable electrical furnace .The resultant from this step called fused kaolin
4. Fused kaolin was sieved to particle size < 75 µm.
5. Fifty grams of fused kaolin powder and 63.35 grams of sodium silicate were dispersed in 750 ml of deionized water in a 1000 ml flask with two necks, one neck connected with water cooling reflux condenser and the other neck with thermometer. Agitation speed and flask temperature were kept constant using regulator attached with electrical magnetic stirrer. The gel formation step was achieved at temperature 60 °C and atmospheric pressure during 1 hr .
6. The resultant slurry which has pH 13.6 was placed in 1000ml sealed glass jar, and subjected to aging at 50 °C for 24 hr in a programmable electrical furnace, then the gel slurry was subjected to hydrothermal crystallization at 100 °C for 48 hr in the same furnace .
7. The resultant precipitate was separated from the mother liquor by filtration using a Buckner funnel with the aid of a vacuum source. The crystalline mass is then washed with deionized water until a pH of 11.5. The drying of crystalline mass was achieved at 100 °C for 16 hr using a programmable electrical furnace The dried powder was activated by calcination in a programmable electrical furnace at 500 °C for 1hr.

Ammonium - Zeolite Preparation

Ammonium - form catalyst was prepared by ion exchange method of the prepared catalyst NaY zeolite with 1.0 M ammonium nitrite solution . Thus 100 g NaY zeolite was mixed with 600g of NH_4NO_3 solution at 80 °C for 6 hr under stirring. This operation was followed by filtration using a Buckner funnel and washing with deionized water until no nitrate ions were detected. The produced ammonium zeolite sample was dried at 90 °C for 2 hr then at 120 °C for 6 hr using a programmable electrical furnace .

HYDROGEN -ZEOLITE PREPARATION

Hydrogen -form catalyst prepared by calcinations NH_4-Y at 600 °C for 6 hr. During calcination ammonia and water are liberated and decationized H-form catalyst is formed.

ANALYSIS AND CHARACTERIZATION

X– Ray diffraction analysis was done in the Research Center of Chemistry and Petrochemical – Ministry of Science and Technology. Analysis was carried out using X– Ray diffractometer type Shimadzu SRD 6000.

The chemical analysis of silica and alumina of prepared calcined powdered faujasite type NaY zeolite was achieved in The State Company for Geological Survey and Mining.

The sodium content of prepared calcined powdered faujasite type NaY zeolite before and after ammonium ion exchange was determined using digital flame analyzer by flame photometer Gallen Kamp in The State Company for Geological Survey and Mining. Sodium is commonly reported as the weight percent of sodium oxide (Na_2O) on the catalyst.

The Infrared Fourier Transform Spectroscopy (FT-IR) test was done to investigate the synthesized zeolite structure. This test was achieved at University of Baghdad/ College of Science/ Chemical Laboratory, by the device of Shimadzu FTIR 8400S type.

Catalyst surface area was determined using BET method by Thermo Finnegan type, apparatus located at Oil Development and Research Center, Ministry of Oil .

CATALYTIC ACTIVITIES TEST

The catalytic activities of prepared zeolites NaY, NH4Y and HY were investigated by using experimental laboratory plant scale of fluidized bed reactor shown in figure 1. The FCC experiments were carried out at temperature range 440 to 500 ^oC, WHSV range 10 to $25h^{-1}$, and atmospheric pressure using prepared catalyst NaY form, NH_4Y form, and NaH form with particle size between75 to 150 micrometer.

The effect of catalyst regeneration temperature at temperature 600, 650, 700, and 750^oC on equilibrium catalyst activity was carried out at 500 ^oC, $WHSV=10h^{-1}$, and atmospheric pressure using NaH form catalyst.

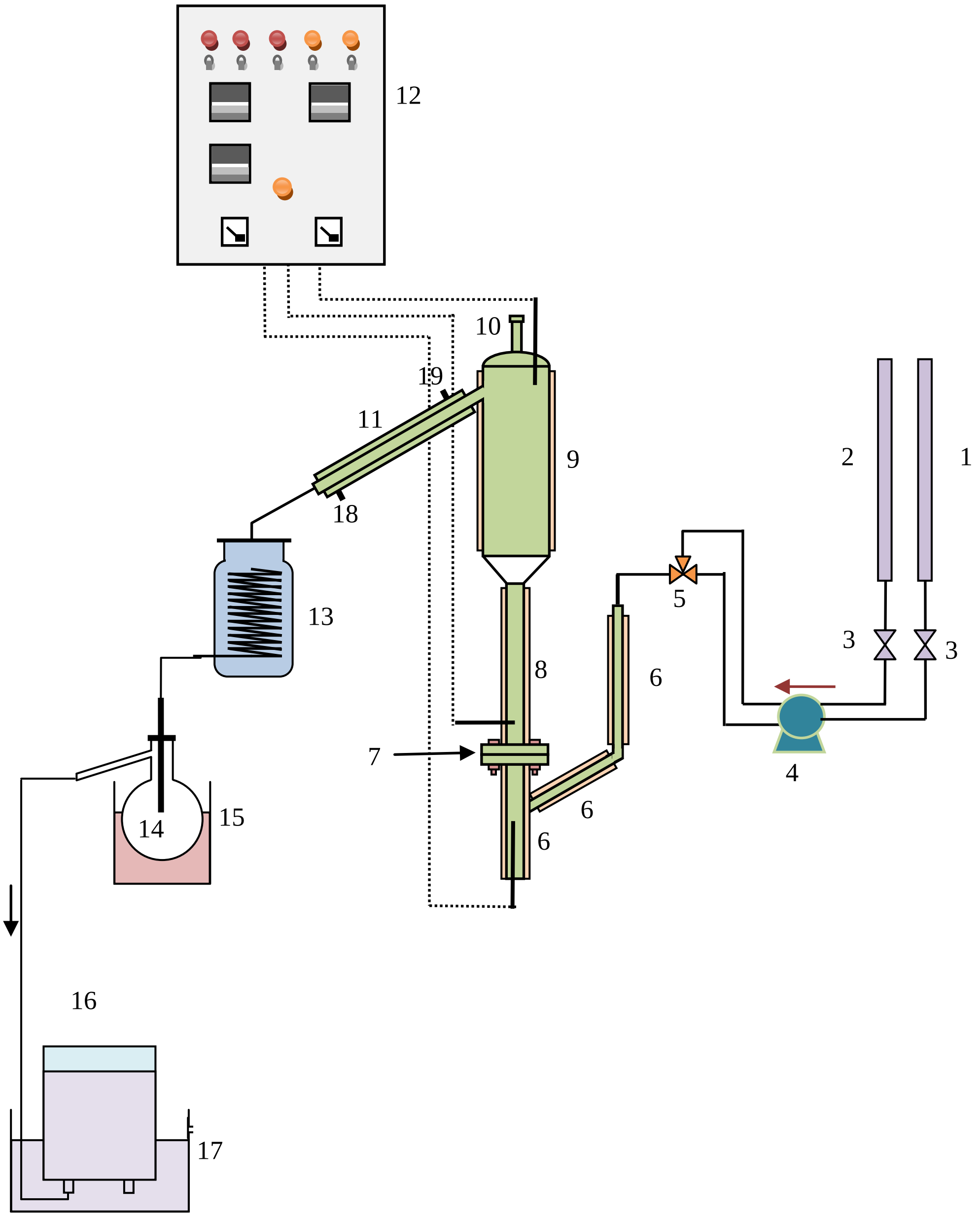


Fig. 1 Schematic flow diagram of the fluidized catalytic cracking system:

(1) Burette VGO feeding; (2) Burette water feeding; (3) Valve; (4) Dosing pump; (5) Three way valve; (6) Preheated section; (7)Distributor (8)Fluidized bed reactor section; (9)Reactor separation section; (10) Catalyst charge inlet; (11) Double pipe heat exchanger; (12) Control panel; (13) Internal tube ice water bath; (14) Separation and collection flask; (15) Ice water bath ; (16) Gas collection ; (17) Water tank; (18) Chilled water in; (19) Chilled water out.

RESULTS AND DISCUSSION

Characterization of Prepared Catalysts

1. X–ray Powder Diffraction (XRD)

X-ray Powder Diffraction technique is the best method to define the crystallographic structure of zeolite. Each zeolite has their own specific pattern that can be used as references for the determination of solid crystal phase and it is used as fingerprint for every zeolite. This technique can signify whether the solid sample is amorphous or crystalline phase, the degree of crystallinity and identification of phase present. The purity of solid crystal will be measured by comparing the X-ray diffractogram pattern of sample with X-ray diffractogram pattern of standard that can be obtained from International Zeolite Association (West, 1988). The powder X-ray diffraction pattern of the prepared calcined powdered faujasite type NaY zeolite is shown in Figure 2, while Figure 3 shows the standard zeolite Y X-ray analysis with silica to alumina ratio of five. From these Figures, it can be seen that the prepared zeolite in the present work, is approximately comparable with the standard.

The presence or absence of some peaks of the diffractogram indicates the existence of other crystal phase or zeolite contaminated with other phases. The size and shape of unit cell for any crystal are easily determined by using the diffraction of the X-rays.

Some differences are found among the X-ray diffraction data which can be attributed to the distribution of sodium cation, different in silica to alumina mole ratio, and different in a mode of preparation.

A comparison between lattice spacing of prepared calcined powdered faujasite type NaY zeolite with standard synthesis faujasite –Na is illustrated in table 2. It can be noted from this table that the lattice spacing of prepared faujasite-Na sample gave similar lattice spacing of standard synthesis faujasite –Na.

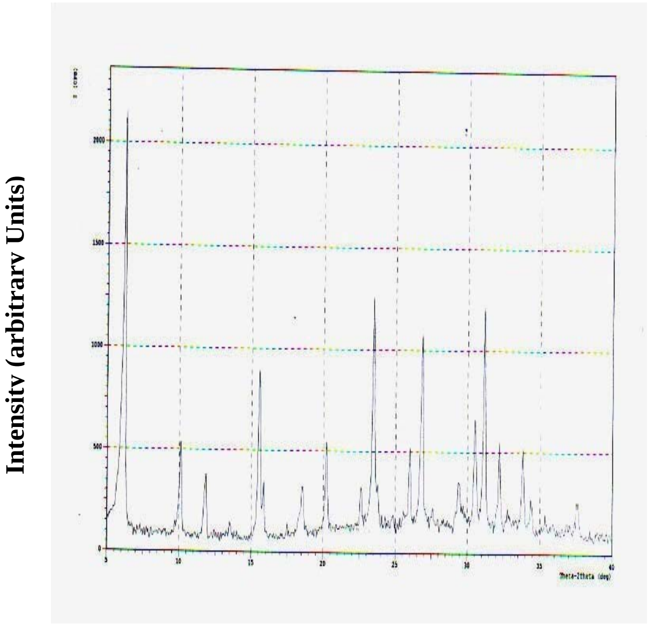


Fig. 2 X – Ray diffraction Spectrum for the Prepared faujasite type Y zeolite Catalysts

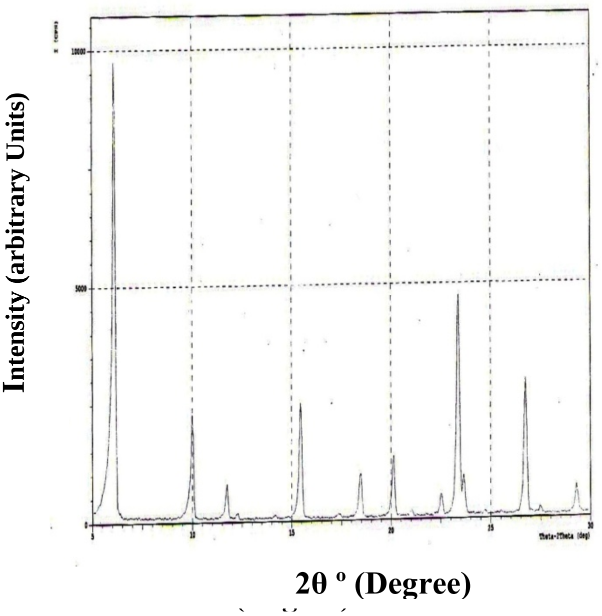


Fig. 3. X – Ray diffraction Spectrum for the standard zeolite Y (Treacy et al, 1996).

Table.2: Comparison of lattice spacing, between prepared faujasite -Na and standard synthesis faujasite –Na.

prepared faujasite-Na		Standard synthesis faujasite –Na(ICDD, 2009)	
Angle(2-Theta)deg.	d,spacing (Å)	Angle (2-Theta)deg.	d,spacing (Å)
6.1042	14.46736	6.181	14.3000
18.5855	4.77028	18.562	4.78000
26.8497	3.31783	26.845	3.32100
32.7971	2.72849	32.817	2.72900
37.5824	2.39134	37.618	2.39100

2.FOURIER TRANSFORMS INFRA RED SPECTROSCOPY (FTIR)

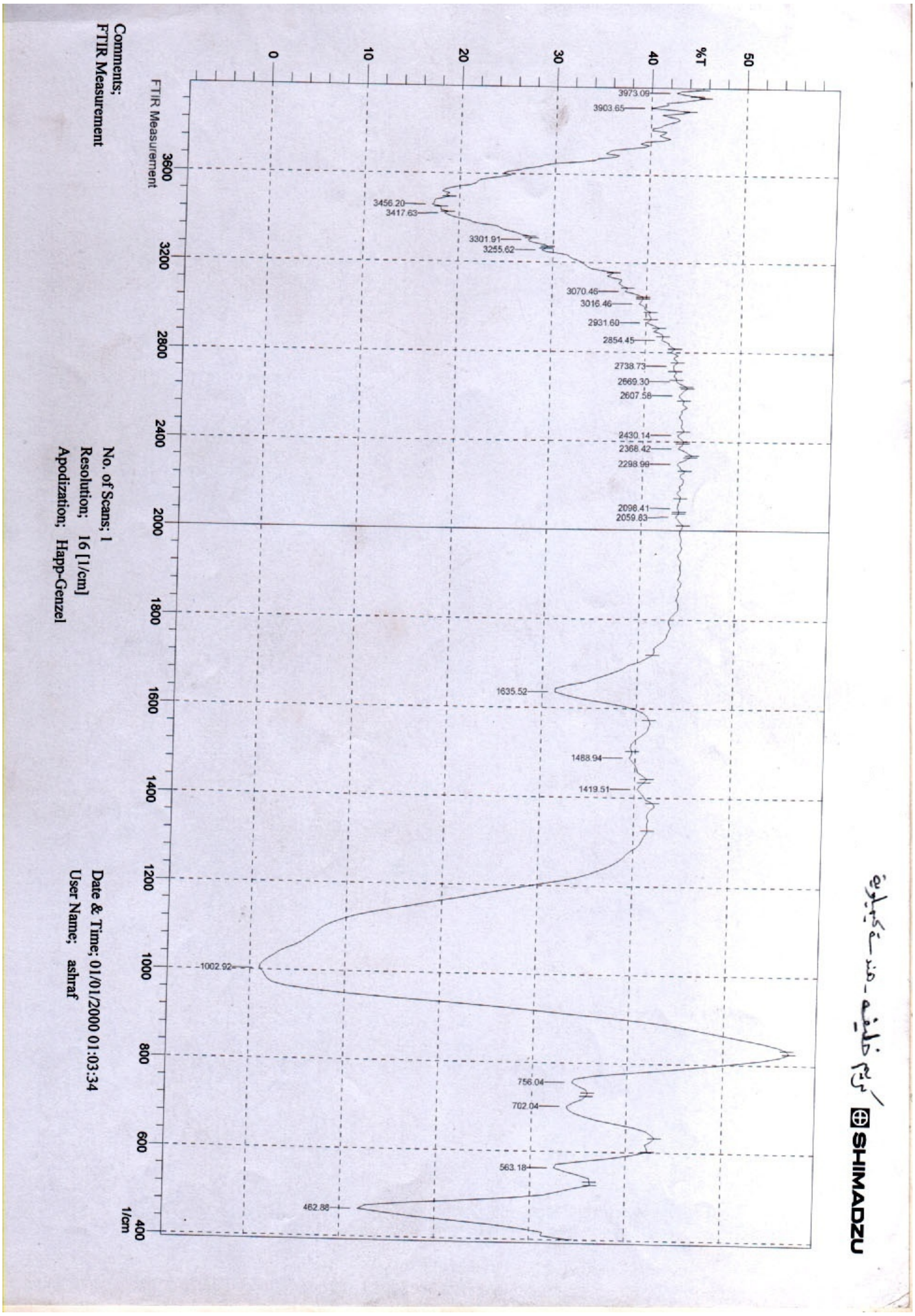
FT-IR spectroscopy is used to probe the structure of zeolites and monitor reactions in zeolite pores. Figure 4 shows the FT-IR spectra of prepared calcined powdered faujasite type NaY zeolite. This figure shows that the FT-IR spectra are compatible with categories of zeolites. The double ring opening vibration at 566 cm^{-1} in the FT-IR spectrum of NaY zeolite is characteristic of faujasite zeolites (Zhan et al,2002)

The T-O bending vibrations of internal tetrahedra in NaY can be identified by absorption bands around 500, 466 and 450 cm^{-1} (Karge,1998). These absorption bands characterizing T-O bending vibrations can be shifted to lower frequencies with decreasing Si/Al ratio in the internal linkages due to the different length of the Al-O (1.73 Å) and Si-O (1.62 Å) bonds. Three absorptions are observed in the spectral region between 3765 and 3630 cm^{-1}. The most intense and highest frequency band at 3744 cm^{-1} is assigned to terminal silanol groups that are on the external surface of the zeolite crystals (Jentys et al, 2001).

The absorption band at 3695 cm^{-1} is assigned to hydroxyl groups attached to Na^+ [15](Fritz et al,1989). An absorption band at 3656 cm^{-1}, associated with hydroxyl groups attached to extra framework alumina (EFAL) species. In the O-H stretching region, infrared spectra of zeolites provide a wealth of information on hydroxyl groups attached to zeolite structures. The hydroxyl groups are important for the chemistry of zeolite materials (Khabtou et al,1994).

At least five types of hydroxyl groups are present in zeolite Y, including (i) lattice termination silanol groups (~3745 cm^{-1}), (ii) hydroxyl groups occurring at defect sites, i.e. hydroxyl nests (~3720 cm^{-1}), (iii) OH groups attached to cations which compensate the negative charge of the framework (~3695 cm^{-1}), (iv) OH groups attached to extra framework aluminum (EFAL) species (~3655 cm^{-1}), and (v) for zeolite Y in the H-form, the bridging OH groups with Bronsted acidity (~3630 and 3560 cm^{-1}) .

The bands at 1135 and 725 cm^{-1} assigned to the asymmetric and symmetric stretching modes of internal tetrahedra, respectively. The bands at 1020 and 792 cm^{-1} are associated with the asymmetric and symmetric stretching modes of external linkages (Szostak, 2001).



Wavenumber cm^{-1}

Fig. 4. FT-IR spectra of faujasite type Y zeolite

The catalytic performance of the zeolite is strongly affected by its composition and structural characteristics, such as framework $SiO_2/A1_2O_3$ ratio and unit cell size.

Table 3 shows the effect of additional silica source on the silica to alumina mole ratio of prepared zeolite

Table 3: Silica / alumina Ratio of prepared zeolite

No.	Additional source	SiO_2 (wt%)	Al_2O_3 (wt%)	SiO_2/Al_2O_3 mole ratio
1	Na meta silicate	45.96	23.93	3.27
2	Sodium silicate	55.14	24.35	3.85

The above results show that the silica to alumina ratio of prepared samples was affected by type of additional silica source in the mixing step, when using sodium metasilicate as additional silica source gave silica to alumina ratio 3.27 sample 1. While Sample 2 shows higher ratio than sample 1, this may be due to using sodium silicate as additional silica source. One of the important zeolite characterizing items is the silica to alumina ratio, and according to this ratio sodium silicate which gives silica to alumina 3.85 was selected as additional silica source for further preparation of catalyst used in this investigation.

The obtained silica-to-alumina ratio 3.85 (Si/Al=1.925) of prepared calcined powdered faujasite type NaY zeolite was in a good agreement with those results obtained by Break (Break,1974). Chandrasekhar et al, (Chandrasekhar, 1999), and Zhu et al (Zhu et al, 1999). They recorded that the silica to alumina ratio of zeolite X is 2 to 3 (Si/Al=1 to 1.5) , while for zeolite Y this ratio higher than 3 to 6 (Si/Al=1.5 to 3) .

Zeolite silica-to-alumina ratio and cationic exchange form have the most significant influence on its thermal and hydrothermal stability. An increase in framework $SiO_2/A1_2O_3$, ratio increases zeolite stability, provided a minimum number of vacancies left in the framework as a result of dealumination. It is for that reason the thermal and hydrothermal stability increase in the order X < Y < HSY zeolites. Since an increase in framework $SiO_2/A1_2O_3$ ratio is associated with a corresponding decrease in unit cell size, zeolite stability increases with decreasing unit cell size (Scherzer, 1991) .

4. UNIT CELL SIZE (UCS).

The elementary building block of the zeolite crystal is a unit cell. The UCS is the distance between the repeating cells in the zeolite structure.

The UCS of the prepared calcined powdered faujasite type NaY zeolite was calculated from figure 5,and the result was 24.73 Å.

This result is in agreement with results published by Beck (Break,1974),who recorded that for synthesized powdered zeolite Y in sodium form has a unit cell size from 24.6 to 25 Å .Also this result is in agreement with those results published by Reza (Reza Sadeghbeigi, 2000), who recorded that freshly manufactured NaY zeolite has a UCS in the range of 24.50 Å to 24.75 Å.

The UCS is an indicator of zeolite acidity. The decrease in UCS causes farther apart of acid sites. The strength of the acid sites is determined by the extent of their isolation from the neighboring acid sites.

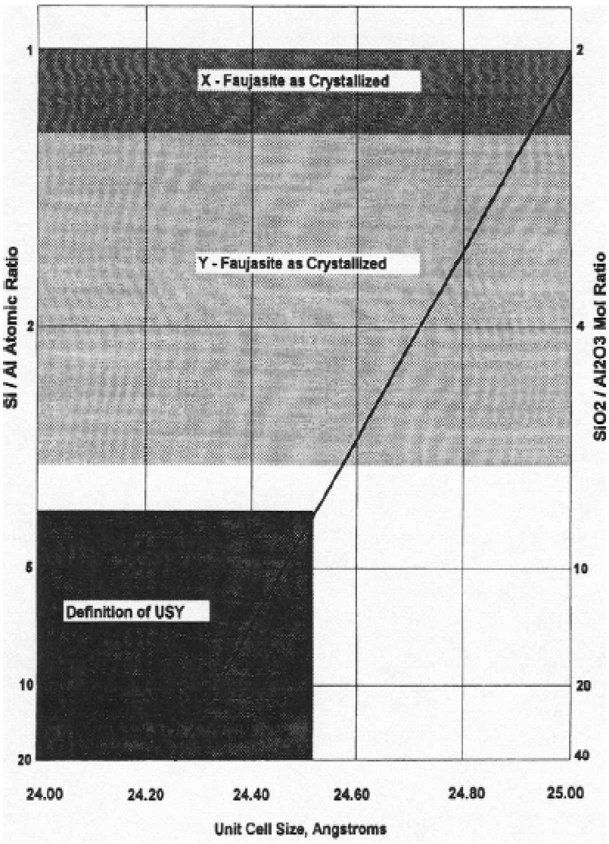


Fig. 5 Silica-alumina ratio versus zeolite unit cell size (Reza Sadeghbeigi, 2000).

Acid distribution of the zeolite is a fundamental factor affecting zeolite activity and selectivity. The UCS measurement can be used to indicate octane potential of the zeolite. A lower UCS presents fewer active sites per unit cell. The fewer acid sites are farther apart and, therefore, inhibit hydrogen transfer reactions, which in turn increase gasoline octane as well as the production of C_3 and lighter components. The octane increase is due to a higher concentration of olefins in the gasoline (Pine et al, 1984).

The number of aluminum atoms per unit cell (N_{Al}) can be calculated by equation (1) (Break,1974):

$$N_{Al}=192/(1+R) \qquad (1)$$

Where, $R = N_{Si}/ N_{Al}$

The number of aluminum atoms per unit cell of the prepared calcined powdered faujasite type NaY zeolite calculated from equation 2 was equal to 66. This value within the range given by Beck (Break,1974), where the number of aluminum atoms per unit cell for zeolite X vary from 96 to 77 and from 76 to 48 for zeolite Y.

5. SURFACE AREA

The measured specific surface area and pore volume of the prepared powdered faujasite type NaY zeolite were $360 m^2/g$ and $0.39 cm^3/g$ respectively. Such a high surface area is obvious due to the micro porosity of prepared powdered zeolite.

This result is in agreement with the results published by Auerbach et al. (Auerbach et al, 2003).

They recorded that the internal surface of zeolite is highly accessible and can compose more than 98% of the total surface area,and the surface areas are typically of the order of 300–700 m^2/g.

6. SODIUM CONTENT

The Sodium content of prepared calcined powdered faujasite type NaY zeolite was 12.5 wt%. This result is in agreement with the result published by *Reza* (Reza Sadeghbeigi, 2000). and Jones (Jones, et al 2006). They recorded that a typical NaY zeolite contain approximately 13wt% Na_2O . The sodium on the catalyst originates either from zeolite during its manufacture or from the FCC feedstock , and the sodium content of the zeolite should be minimized for two reasons . First high sodium content is detrimental to zeolite stability, and activity. Sodium decreases the hydrothermal stability of the zeolite. It also reacts with the zeolite acid sites to reduce catalyst activity (Suchuchchai Nuanklai , 2004). Second, high sodium content decreases the gasoline octane number, because the sodium is mobile in the regenerator. Sodium ions tend to neutralize the strongest acid sites, and can have an adverse effect on the gasoline octane. The loss of octane is attributed to the drop in the number of strong acid sites. (Hayward et al 1990).

Sodium content must be reduced. This is accomplished by ionic exchange of the zeolite with ammonium nitrate solutions.

Table 4 shows the effect of duration time of ion exchange on catalyst sodium content (Na_2O), from this table shows that the ionic exchange increases with increasing duration time ,after that the increasing of duration time lead to slightly increase of ionic exchange .This means that the ion exchange reaction not far form equilibrium, so the ion exchange process must be repeated for more than one time. The ion exchange process was repeated four times to reach the final result. The sodium content in the prepared calcined powdered faujasite after ionic exchange was reached to 5.8wt% Na_2O. This result represented 53.6 % ionic exchange . The diffusion difficulties during ion exchange inhibits a complete exchange of Na ion by NH_4 ion as mentioned by Plank(Plank, 1969).

This result of ion exchange is in a good agreement with that obtained by Mu et al (Mu et al, 2008). They reached to 44 percent ionic exchange for NaY Zeolite prepared from kaolin . Also, this result slightly differs from the result obtained by *Reza* (Reza Sadeghbeigi, 2000), and Jones et al(Jones et al, 2006). They recorded that the exchangeable sodium content is reduced to 3wt% Na_2O. Anyway the results of this work was in agreement with that obtained by Samar (Samar,2008) for zeolite X .The exchangeable sodium content is reduced to less than about 2%.

CATALYTIC ACTIVITIES OF PREPARED CATALYST

The activity of prepared catalyst on the VGO conversion and the yield of gasoline, gases, and coke was studied at reaction temperatures range 440 to 500 ^oC, and weight hour space velocity (WHSV) range 10 to $25h^{-1}$,

Figures 6, 7, and 8 show the effect of WHSV on the VGO conversion at different reaction temperature for Na form catalyst, $NaNH_4$ form catalyst, and NaH form catalyst, respectively. As shown from these figures, the VGO conversion increases with decreasing of WHSV at constant temperature. This means that the conversion of VGO is a function of reaction time for all catalysts, the increasing of the contact time of the feed molecules with the catalyst increases the VGO conversion in direct proportion to the amount of the catalyst and inversely proportional to the feed flow rate. The lower WHSV increases the contact time and favors VGO conversion. The results obtained for the effect of WHSV on the VGO conversion are in a good agreement with those obtained by Rawet et al(Rawet et al,2001) , and Ancheyta et al(Ancheyta et al 2002).

Table 4 The effect of duration time of ion exchange on catalyst sodium content.

Duration of ion exchange(hr)	Na_2O.(wt%)	Na_2O(wt%) exchanges
0.0	12.5	0.0
24	9.7	22.4
48	9.2	26.4
72	8.9	28.8
192	7.5	40
240	7.2	42.4
360	5.8	53.6

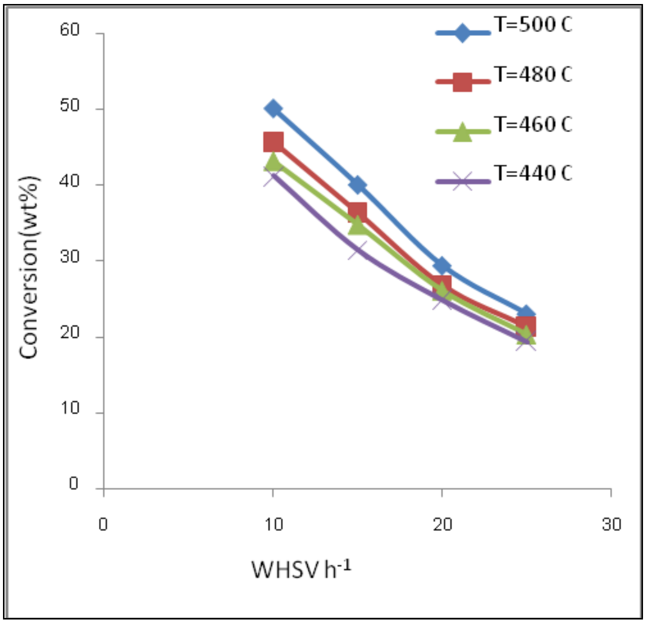


Fig.6 Effect of WHSV on the VGO conversion at different temperatures for Na –form zeolite catalyst

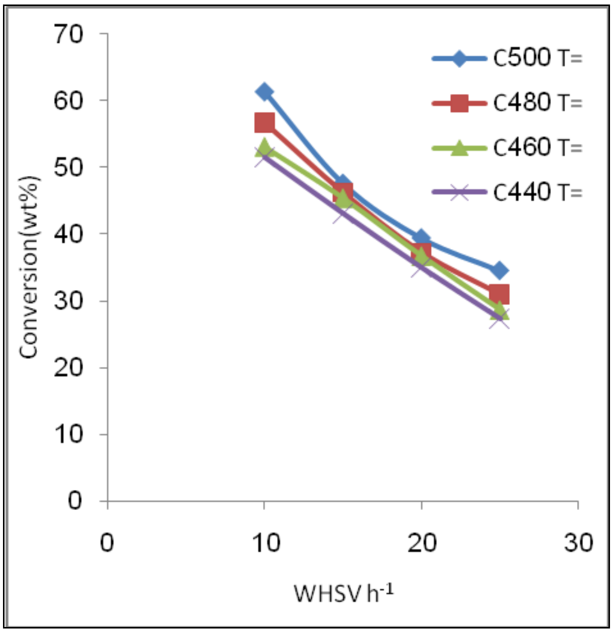


Fig 7 Effect of WHSV on the VGO conversion at different temperatures for $NaNH_4$ -form zeolite catalyst

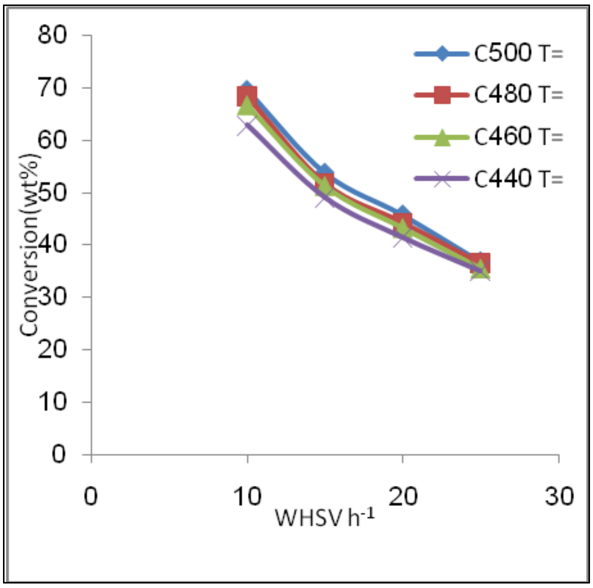


Fig. 8 Effect of WHSV on the VGO conversion at different temperatures for NaH

The selectivity of prepared catalyst to produce gasoline was calculated for Na form, $NaNH_4$ form, and NaH form at 10 WHSV and 500 ^{o}C and equals 37.3, 40, and 43.5% respectively. The selectivity increases with increasing conversion. These results agree with those obtained by Ravichander et. al(Ravichander, et al ,2009) and Al-Khattaf(Al-Khattaf 2002) .

Figure 9 shows the effect of regeneration temperature of prepared catalyst NaH form on the conversion and the gasoline yield. The experimental conditions of these tests are WHSV of 10 h^{-1}, reaction temperature of 500 ^{o}C,and atmospheric pressure.

As shown from this figure, the gasoline yield and the VGO conversion increases with increasing regeneration temperature to a certain limit, after that the gasoline yield and the VGO conversion decrease. The regeneration transformed the coke deposits into carbon monoxide, carbon dioxide, and steam, all of which are gaseous .Thus, the poisoning of catalyst by coke is a reversible process that can be effectively counteracted, when coke removing reach a maximum point, the surface area (active sites) and the activity reach a maximum level, thus leads to a maximum conversion (46.7wt%) and gasoline yield (22.5wt%). The excessive rise in regeneration temperature decreases the gasoline yield and the VGO conversion because the structure and texture of the catalyst may be irreversibly altered(Danial Decroocq 1984)

The activity of regenerated catalyst gives 61% of original activity. This result was far away from those obtained by Ravichander et al [29] (Ravichander, 2009) .They recorded that the activity of regenerated catalyst is 10% lower than that obtained with fresh catalyst.

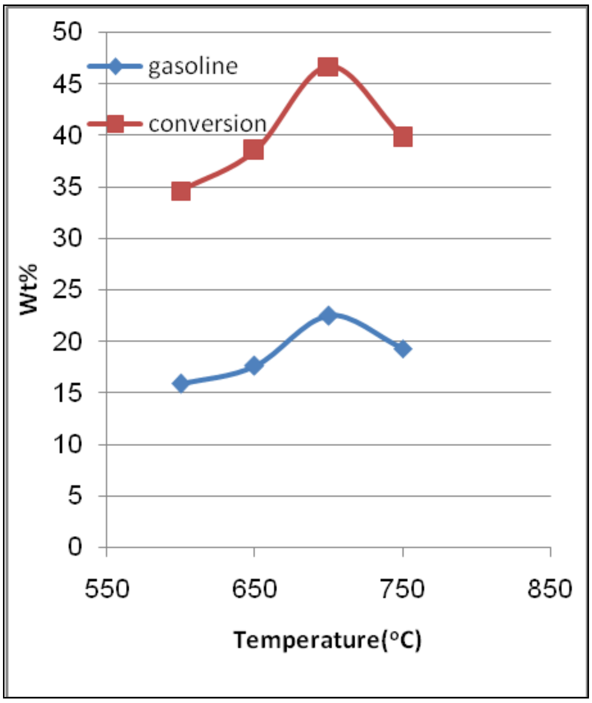


Fig. 9**:** Effect of regenerated temperature on the gasoline yield and VGO conversion

CONCLUSIONS

From the present work using kaolin (clay mineral locally found) as a raw material for preparation faujasite type Y zeolite and studying the performance of the prepared catalyst in fluidized bed reaction system the following conclusions are deduced:-

1- From the X-ray Powder Diffraction, FT-IR spectroscopy , silica-to-alumina mole ratio 3.85(Si/Al=1.925) , unit cell size (UCS) 24.73 Å ,surface area 360m^2/g , pore volume 0.39 and sodium content 12.5 wt%. for prepared catalyst and the comparison with the standard NaY zeolite ,it is possible to say that the prepared catalyst obtained from locally available kaolin in this work is NaY zeolite.

2- Activity of faujasite type Y zeolite NaH form is a highest among Na form, $NaNH_4$ form and NaH form.

3- The appropriate regeneration temperature for prepared catalyst was 700°C, which gives 61% from original activity.

4- The experimental results indicate that the effect of WHSV is higher than the effect of temperature on the VGO conversion and gasoline yield within the process variables.

REFERENCES

Al-Khattaf S.,"The influence of Y-zeolite unit cell size on the performance of FCC catalysts during gas oil catalytic cracking" Applied Catalysis A: General 231 (2002) 293–306.

Ancheyta , J.,and Sotelo, R., "kinetic modeling of vacuum gas oil catalytic cracking " J .Mexican,chem.society 46(2002)38-42

Auerbach ,Scott M. Kathleen A. Carrado, and Prabir K. Dutta "Handbook of zeolite science and Technology", Marceld Ekkeirnc Inc. (2003).

Ballmoos, R. von. D.H. Harris, J.S. Magee, in: G. Ertl, H. Kno¨ zinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, Wiley-VCH, Weinheim, 1997, p. 1955.

Break, D. W., "Zeolite Molecular Sieves Structure Chemistry and Use", John Wiley and Sons, New York, (1974).

Chandrasekhar,S., and, Pramada,P.N., " Investigation on the synthesis of zeolite NaX from Kerala kaolin" journal of porous material 6,(1999), 283-297.

Corma, A. Martinez, A.in: F. Schu¨ th, K.S.W. Sing, J. Weitkamp (Eds.), Handbook of Porous Solids, Wiley-VCH, Weinheim 2002, p. 2825

Corma, A. Martinez, A. in: M. Guisnet, J.-P. Gilson (Eds.), Zeolites for Cleaner Technologies, Imperial College Press, London, 2002, p. 29.

Corma, A.V. Forne´s, A. Martinez, F.V. Melo, O. Pallota, in: P. Grobet, W.J. Mortier, E.F. Vansant, G. Schulz-Ekloff (Eds.), Innovation in Zeolite Materials Science, Studies in Surface Science and Catalysis, vol. 37, Elsevier, Amsterdam, 1988, p. 495

Danial Decroocq ,"Catalytic Cracking of Heavy Petroleum Fractions", Imprimerir Louis-Jean, Paris,(1984)

Fritz , P.O., and Lunsford, J.H., J. Catal. (1989), 118, 85.

Hayward, C. M. and Winkler, W. S., "FCC: Matrix/Zeolite", Hydrocarbon Processing, February (1990), pp. 55-56.

International center for diffraction data (ICDD),12 campus boulevard ,Newtown square, PA 19073-3273,U.S.A,(2009)

Jentys, A., and Lercher, J.A., "Studies in Surface Science and Catalysis" (Vol. 137), Eds. H. van Bekkum, E.M. Flanigen, P.A. Jacobs and J.C. Jensen. Elsevier Science B.V., Amsterdam. (2001), p 345

Jones, D. S., and Pujad, P, R., "Handbook of Petroleum Processing", Published by Springer, (2006).

H.G. Karge, Microporous and Mesoporous Materials Micro. Meso. Mater. (1998), 22, 547.
Khabtou, S.T. Chevreau and Lavalley J.C., Microporous and Mesoporous Materials. 3(1994) , 133
.
Michael Stocker, " Gas phase catalysis by zeolites", Microporous and Mesoporous Materials, 82 (2005) 257–292
.
Mu Mu Htay, and Mya Mya Oo, "Preparation of Zeolite Y Catalyst for Petroleum Cracking", Pwaset Volume 36 ISSN 2070-3740, 2008, 859 – 865.

Pine,L.A.,Maher,P.J.,and Wachter,W.A.,"Prediction of cracking catalyst behavior by zeolite unit cell size model" Journal of catalyst 85,(1984), 466-476

Plank, C. J., "Conversion of clays to Crystalline Aluminosilicates and Catalysts There from" , U.S. Patent, 3,431,218,(1969).

Rawet , R ., Cerqueira , H. S.,and, Pinto, J. C.,"The influence of covariances during laboratory evaluation of FCC catalysts" Applied Catalysis A: General 207 (2001) 199–209

Ravichander, N., Chiranjeevi, T., Gokak, D.T., Voolapalli, R.K., Choudary, N.V. ,"FCC catalyst and additive evaluation—A case study" Catalysis

Today 141 (2009) 115–119.

Reza Sadeghbeigi, “Fluid Catalytic Cracking Handbook Design, Operation and Troubleshooting of FCC Facilities”, Elsevier Inc., (2000).

Samar.K.Dh,“Catalytic Dealkylation of Cumene”. M.Sc. Thesis, University of Baghdad,(2008).

Scherzer,J.,“ Designing FCC catalysts with high-silica Y zeolites” Applied catalysis, 75 (1991) 1 - 32.

S.T Sie, in: J.C. Jansen, M. Sto¨cker, H.G. Karge, J. Weitkamp (Eds.), Advanced Zeolite Science and Applications, Studies in Surface Science and Catalysis, vol. 85, Elsevier, Amsterdam, 1994, p. 587.

Suchuchchai Nuanklai ,“Effects of Particle Size and Hydrothermal Treatment of Y-zeolite on Catalytic Cracking of n-Octane” , M.Sc. , University of Chulalongkorn, (2004).

Szostak, R. “Studies in Surface Science and Catalysis” (Vol. 137), Eds. H. van Bekkum, E.M. Flanigen, P.A. Jacobs and J.C. Jensen. Elsevier Science B.V., Amsterdam. 2001, p 261.

Treacy, M.M.J., Higgins, J. B. and Von Bollmoos, R., ”Collection of Simulated XRD Powder Patterns for Zeolite.” 3rd ed. Amsterdam: Elsevier (1996).

Ward, W . D.L. Trimm, S. Akashah, M. Absi-Halabi, A Bishara (Eds.), Catalysis in PetroleumRefining 1989, Studies in Surface Science and Catalysis, vol. 53, Elsevier, Amsterdam, 1990, p. 417.

West, A.R., “Basic Solid State Chemistry”, New York: JohnWiley and Sons Inc., (1988).

B. Zhan, M.A. White, M. Lumsden, J. Mueller-Neuhaus, K.N. Robertson, T.S. Cameron and M. Gharghouri, Chem. Mater. (2002), 14, 3636.

Zhu, L., and Seff, K. “ Reinvestigation of the crystal structure of dehydrated sodium zeolite X” J. Phys. Chem.103(1999) 9512-9518.