

## Characterization and Cracking Activity of Zeolite Prepared from Local Kaolin

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### Abstract

The synthesis of zeolite NaX from locally available kaolin has been studied. The operating conditions for zeolite NaX production from kaolin with good crystallinity were as follows; a gel formation step of metakaolin in alkaline medium in presence of additional silica to crystallize the zeolite was achieved at 60 oC for 1 hr, and with stirring. In ageing step of the reactants at room temperature for 5 days and crystallization step at 87±2 oC for 24 hr. The catalytic activity of catalyst prepared from local kaolin was studied by using cumene cracking as a model for catalytic cracking and compared with standard HY zeolite and HX zeolite catalysts. The activity test was carried out in a laboratory continuous flow unit with fixed bed reactor at duration time in the range 10-240 minutes, temperature 823 K, and LHSV 1 h<sup>-1</sup>. The prepared and the standard catalysts were characterized by atomic absorption, X-Ray Diffraction Analysis, Fourier Transform Infrared Spectroscopy, surface area and pore volume.

### Introduction

Most catalysts used in commercial catalytic cracking units today are either amorphous synthetic silica-alumina combinations or mixtures of amorphous synthetic silica-alumina and crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves [1]. The advantages of the zeolite catalysts over the natural and synthetic amorphous catalysts are: higher activity, higher gasoline yields at a given conversion, production of gasoline containing a larger percentage of paraffinic and aromatic hydrocarbons, lower coke yield (and therefore usually a larger throughput at a given conversion level), increased isobutane production, and ability to go to higher conversions per pass without overcracking [1,2].

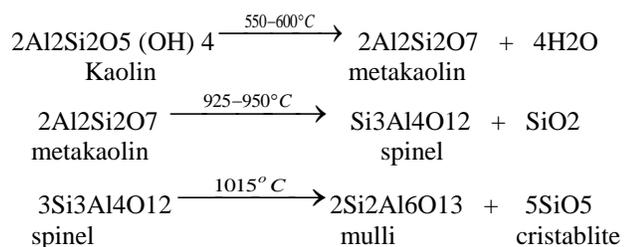
Despite the fact that activated natural clays have not been used as cracking catalysts for a long time, awareness of their characteristics is important since natural clays continue to be included in the composition of synthetic catalysts in order to reduce their cost. This technique, initially used in the production of silica alumina catalysts, is used today on a large scale in the production of zeolitic catalysts [3].

Clay minerals of the kaolin group are convenient starting materials for the synthesis of zeolites. Kaolin clay must be sufficient plastic so that it can be molded and remain strong in the green and dry state, must not be so plastic that it shrinks and distorts on drying [4]. Kaolin type clays or clay minerals have the general composition  $Al_2O_3 \cdot 2SiO_2 \cdot 2-4H_2O$ , which makes such clays preferred for synthesis of zeolite types [5]. Kaolin is inexpensive, naturally occurring, abundant material and was employed as the sole source of silica and alumina [6]. It is largely available in Iraq; particularly in Al-Ga'ara areas of western Iraq that have four regions (Dewkkla, Samhat, Tel-Afef and Bir Mlusi) [4]. Kaolinite is the major mineral component of kaolin, which may contain impurities such as quartz, illites, smectites, and feldspars [7].

When kaolin-type clay is heated, it will undergo several transitions. The first of these takes place at about (550-600°C), and produces the disordered metakaolin phase (metastable phase) by an endothermic dehydroxylation

reaction [8], and it has been reported that metakaolin is more reactive under chemical treatments, this transformation occurs with the loss of structural water with a reorganization of the structure; only a small part of AlO<sub>6</sub> octahedral is maintained, while the rest are transformed into much more reactive tetra- and penta coordinated units [7].

The metakaolin is then stable to about 935-950°C where it rearranges to give a defect aluminum-silicon spinel, which is also referred to as a  $\gamma$ -alumina type structure. The so called  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase converts to mullite 3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> at 1050°C, as shown in the following equations [9]:



Metakaolin is believed to be a defect phase in which the tetrahedral silica layers of the original clay structure are largely retained. It is known to be more reactive, therefore it is used as a starting material for the synthesis of zeolite [9].

Zeolites (aluminosilicates) are crystalline clays that can be either natural minerals or prepared synthetically by crystallizing silica and alumina solutions [10].

At present some 39 naturally occurring zeolite species have been recorded and their structures determined. In addition more than 100 synthetic species with no known natural counterparts have been confirmed as new zeolite and the majority await full structural determination [11].

Cumene (isopropyl-benzene) is a typical aromatic compound in the gasoline pool. Thus the reactions of these important aromatics are quite significant for refiners [12].

The chemistry and kinetics of cumene cracking have been received the largest attraction from researchers due to its simplicity. Corma and Wojciechowski have reviewed this reaction in detail [13]. Long-chain aromatics also draw the attention of researchers because they represent the aromatics in gas oil. Corma and co-workers [14,15] reported that these compounds crack by a number of competing reaction pathways including dealkylation, side chain cracking, and self alkylation.

Thus, although cumene cracking has been used extensively as a test reaction to investigate the characteristics of newly developed cracking catalysts [12], locally limited research has developed on the cracking of cumene.

Frillete et al. [16] studied the cumene cracking and found that the conversion was low at 510°C over NaX-zeolite (6 mole%), more extensive over CaX-zeolite (59 mole% at 470°C), but not so extensive over amorphous aluminosilicate.

Kazuo and Hiroshi [17] examined the effects of the degree of ion exchange and the silica to alumina mole ratio on the cumene cracking activity of faujasite-type zeolite. When they studied the activity of five different faujasite-type zeolites with different silica /alumina mole ratio; (Na-X2.5, Na-Y5, Na-Y3.25, Na-Y3.85, and Na-Y4.6) by cumene cracking, and treated the Zeolites under the same conditions, they found that when the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio was 5.1 and the reaction temperatures 300, 350, 400, and 450°C the cumene conversion (mole%) would be 0.5, 10.8, 35.2, and 62.5, respectively.

And they found that when sodium ions in Na-form zeolite are replaced with polyvalent metal ions or NH<sub>4</sub> ions, the order of activity is La>NH<sub>4</sub>>Ca>Na; where the activity would be determined by both the acidity and the acid strength. The catalytic activity of La-Na-Y at 350°C becomes notable after the cation exchange exceeds 50%, and reached the maximum value 100mol% cumene conversion at 87% exchange. The same phenomenon was observed by James [18] who examined the cumene cracking for a series of faujasites ion-exchange with alkali and alkaline earth elements (K, Na, Li, Ba, Sr, Ca, and Mg) using micro-reactor. The order of cumene conversion is Mg>Ca>Sr>Ba>Li>Na>K.

Peter et al. [19] studied dealkylation of cumene over Zeolite Y in hydrogen form pretreated at temperatures between 500 and 800°C and they found that the main products were benzene and propylene and they calculated the conversion data from the concentration of benzene in the product.

Donald and Wojciechowski [20] used cumene cracking reaction to evaluate the activity of 100/140 mesh of LaY zeolite catalyst. Cumene accumulative conversion increases as the temperature increases from 360 to 500°C and increasing catalyst/oil (wt/wt) ratio from 0.004 – 0.016 at the same time on stream. Also it was observed that the accumulative conversion increases and reaches a stable value at 200 sec time on stream at the same above conditions.

Lin et al. [21] studied the cumene fractional conversion over LaY zeolite vs. time on stream at several reaction temperatures (360-500°C), several space times (2.5- 10 ×10<sup>-3</sup> gs/mol), and two particle sizes (-20 + 40 mesh) and (-60+80 mesh). A 10.8 mol% initial cumene conversion was observed at 360°C and 5.2×10<sup>-3</sup> gs/mol. during the first 5 min and the rate of reaction declines as the time on stream increases at the same conditions, the conversion reaches 7.5 mol% at 141 min time on stream.

This work deal with the production of HX zeolite from locally kaolin and test it is cracking activity by cumene cracking.

## Experimental work

### Materials

Materials	Properties
<b>Cumene</b>	
Supplied by	BDH with 98% purity
Molecular weight	120.20 g/mol
Density	0.860 g/cm <sup>3</sup>
Boiling point	423K
<b>HY-Zeolite(CBV600)</b>	Zeolyst International (UWE
Supplied by	Ohlrogge (VF) as a powder .
	0.2
Na <sub>2</sub> O(wt %)	5
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio	24.3 Å
Unit cell	0.92
pore volume	660 m <sup>2</sup> /g.
surface area	Linde company as pellets
<b>Synthetic Zeolite type 13X</b>	(3*5)mm .
Supplied by	14
Na <sub>2</sub> O(wt%)	2.2
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> mole ratio	24.9 Å
Unit cell	0.35
pore volume	340 (m <sup>2</sup> /g)
surface area	Al-Dewekhala Quarry in Al-
<b>Kaolin(locally)</b>	Enbar region.
The used kaolin is available in	53.49
SiO <sub>2</sub> (wt%)	30.83
Al <sub>2</sub> O <sub>3</sub> (wt%)	0.22
Na <sub>2</sub> O(wt%)	2.15
Fe <sub>2</sub> O <sub>3</sub> (wt%)	2.82
TiO <sub>2</sub> (wt%)	0.056
CaO(wt%)	0.056
MgO(wt%)	0.422
K <sub>2</sub> O(wt%)	9.956
L.O.I(wt%)	
<b>Colloidal sodium silicate</b>	
<b>Ammonium Nitrate</b>	BDH limited Poole England
Supplied by	.80.04 g/mole .
molecular weight	BDH limited Poole England
<b>Sodium Hydroxide</b>	40 g/mole .
Supplied by	High grade quality (purity 99.9
molecular weight	%) of nitrogen obtained from
<b>Nitrogen</b>	Al-Mansor factory

### Preparation of H-X zeolite from kaolin

**H-X zeolite is prepared by steps consisting essentially of:**

1. Calcination of the raw kaolin at 550°C for 1 hr in a programmable electrical furnace (Model N<sub>2</sub>O/H,Max. Temp. 1340°C), after that, the kaolinite can be transformed to metakaolinite.

2. Sieving the metakaolinite to a particle size ≤75 μm.

3. The gel was prepared by mixing 5 ml of NaOH solution (10 wt% NaOH) with 1g colloidal sodium silicate. At low alkali concentration the reaction did not take place, because the crystallization speed was so low that no crystalline species were obtained as observed by Caballero et al. [22], and De Lucas et al. [23, 24]. So, at sodium hydroxide concentrations below 10%, the desired zeolite may not form [25].

The resulting solution was mixed with 1 g of metakaolinite in a 1000 ml round –bottom flask with two necks: one neck fitted with water –cooling reflux condenser, and the other neck with thermometer to measure the temperature, where the reaction was carried at atmospheric pressure. Agitation and heating of the flask were done by oil bath on magnetic heater stirrer, where the temperature of the mixture in the heated flask was kept constant by using voltage regulator .

The gel formation step was achieved at 60°C, for 1 hr. Caballero et al. [22] found that the stirring speed does not exert a strong influence on the zeolite relative crystallinity value, and it was only necessary to guarantee good gel homogeneity.

4.The aging step was done at room temperature and for 5 days [26] without agitation. The product will be more crystalline when aging the gel at low temperature before carrying out the high temperature crystallization [26].

5.Crystallization step was done at temperature 87±2°C [27] for 24 hours without agitation. At the end, the flask was quenching in cold water. 6.The next steps were decantation and washing several times with deionized water until the PH value equal to 10 [28] then the powder was filtered in Buckner funnel with the aid of a vacuum pump. The drying was achieved at 120°C for 12 hr using a programmable electrical furnace(Model N<sub>2</sub>O/H,Max. Temp. 1340°C). After that, the product was milled to convert it to a fine powder, which was sieved to a particles size ≤ 75μm.

7. A 100 g of catalyst powder was prepared by mixing 25 g [4,29] of the binding material which is kaolin with 75g of catalyst powder.The resulted dry powder was mixed with deionized water manually using spatula to form a paste.

8. The paste was placed in a cylindrical cavity of 2 cm inside diameter, and 10 cm long. Extrudates shapes were obtained when the paste was compressed manually. Very uniform spaghetti shaped paste was ejected and put in a porcelain crucible at room temperature overnight.

9. Extrudates were dried in a programmable electrical furnace at 120°C for 2 hr [4, 30]. The calcination was done at 550°C for 2 hr [4, 31]. Then the calcined extrudates were cut into 4-8 mm long.

10. Hydrogen-form catalysts were prepared by ion exchange method of the original catalyst with 3 N ammonium nitrite solution [32, 33]. Thus 120 g of ammonium nitrite in 500 ml deionized water was contacted with 50 g of catalyst in a continuous stirring for 2 hr at 90°C [28]. The pH of the solution was held constant at 7.5, and soaking this catalyst in a fresh solution of ammonium nitrite with pH 7.5 at room temperature overnight. The extrudates were washed, filtered, and dried at 120°C for 2 hours [28]. The dried extrudates were calcined at 550°C for 4 hr. During calcination ammonia and water are liberated and decationized H-form zeolite is formed.

#### Preparation of H-X zeolite from Na-X standard zeolite

Hydrogen-form standard Na- X zeolite was prepared by ion exchange method of the original Na-X catalyst with 3 N ammonium nitrite solution [32,33]. Thus ,120 g of ammonium nitrite in 500 ml deionized water was contacted with 50 g of catalyst in a continuous stirring for 2 hr at 90°C [28]. The pH of the solution was held constant at 7.5, and soaking this catalyst in a fresh solution of ammonium nitrite with pH 7.5 at room temperature overnight. This procedure repeated twice. The extrudates were washed , filtered, and dried at 120°C for 2 hours [28]. The dried extrudates were calcined at 550°C for 4 hr. During calcination ammonia and water are liberated and decationized H-form is formed.

#### HY-Zeolite Shaping

1. A 70 g of HY-zeolite as a powder was mixed with 30 g montmorillonite clay as binder. The preferred binder content percent of mixing is between 15-30% as noticed by Allain et al. [34], Martens et al. [35]. The chemical composition of montmorillonite is: 51.3% SiO<sub>2</sub>, 28.73% Al<sub>2</sub>O<sub>3</sub>, 1.3% Na<sub>2</sub>O, 3.4% CaO, and 3.3 % MgO. The resulting mixture was mixed with water to form a paste.
2. Steps 8 and 9 used for prepared NaX zeolite were repeated to finalize HY-zeolite preparation.

#### Activity test

The cracking activity tests were performed in a continuous laboratory unit. The unit consists of feed tank, flow meter , feed pump, evaporator , reactor, separator , collector and cooler with appropriate control system for heating. The reactor was a carbon steel tube with an outside diameter of 1.9 cm, 2 mm thick and 80 cm length .A fresh catalyst was charged to the reactor between two layers of inert materials (glass balls).The activity was

carried out at 823K, LHSV 1 h<sup>-1</sup> , atmospheric pressure and at duration time ranging from 10-240 minutes.

#### Test method for liquid product analysis

Liquid products were trapped by condenser at -5C, collected periodically and analyzed by using gas chromatography. The gas chromatography model Packard 438A was used for the analysis .This device equipped with column of 0.25mm diameter ,50 m length and FID detector.

## Results and Discussion

### X-Ray Diffraction

The XRD test was used in the present work to study the crystal structure of the prepared catalysts.

Figure1. represent the X-ray pattern of the prepared Na - X zeolite. This pattern was compared with X-ray data of standard zeolites reported by [9] ,X-ray pattern of standard zeolite for HY (Figure 1) and HX (Figure 2). It was found that prepared NaX zeolite has a 52.17% crystallinity at D spacing  $14.64e^{-8} \pm 0.1$  , and has approximately the same crystal structure as the standard type NaX-zeolite .

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

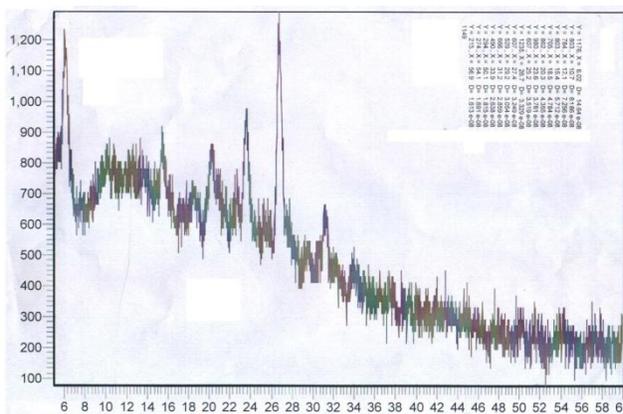


Fig. 1 X-Ray Diffraction Spectrum for the Prepared Na-X zeolite Catalyst After Adding the Binder .

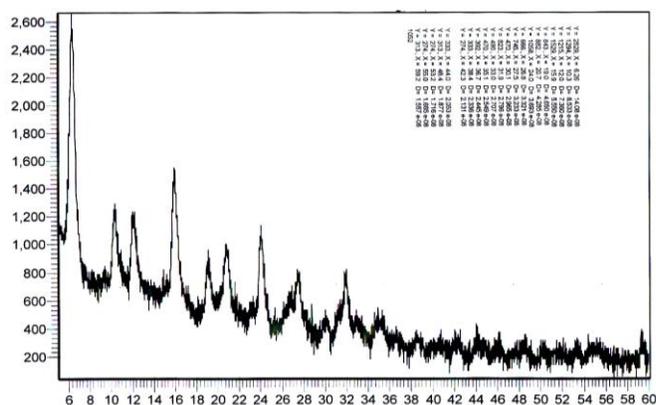


Fig. 2 X-Ray Diffraction Spectrum for the standard H-Y zeolite Catalyst After Adding the Binder .

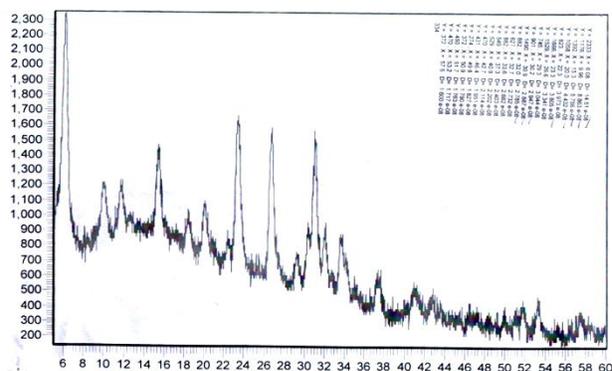


Fig. 3 X-Ray Diffraction Spectrum for the standard Na-X zeolite Catalyst After Adding the Binder.

#### Fourier Transforms Infra Red Spectroscopy (FTIR)

FTIR was used in this study to identify the structural properties of the catalysts HX-zeolite and prepared NaX zeolite before ion exchange, which contains fundamentals vibrations of the framework of silica-alumina tetrahedral, can be used in characterization of zeolite type. These vibrations include symmetric and asymmetric stretching and bending mode of Si (Al)<sub>4</sub> tetrahedral, and double ring vibration. Figures 4 and 5 show the spectrum of HX-zeolite and prepared Na X zeolite (before ion exchanges).

It was observed that the characteristic bands for the vibrations of HX-zeolite (fig.4) and FTIR data from Breack [9] and Chandrasekhar et al. [27], are symmetric due to asymmetric stretch at 970 and 1100 cm<sup>-1</sup> and symmetric stretch at 750, 670, and 690 cm<sup>-1</sup>, double ring 560 cm<sup>-1</sup> and Si(Al)-O bands 455 cm<sup>-1</sup> are clearly found in the prepared NaX zeolite. So, the FTIR spectral analysis results support the XRD inferences.

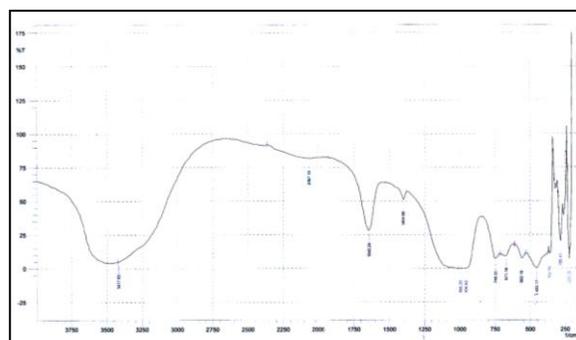


Figure 4 FTIR Spectrum of standard Na-X zeolite Before Ion Exchange.

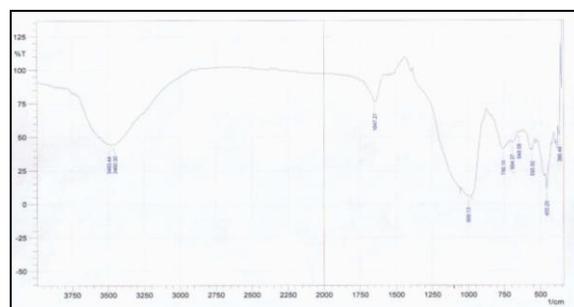


Figure 5 FTIR Spectrum of prepared Na-X zeolite Before Ion Exchange.

#### Surface Area

The physical properties of different catalyst were presented in Table 1 shows that commercial Y-zeolite powder has 660 m<sup>2</sup>/g surface area and the surface area decreases to 546 m<sup>2</sup>/g after adding a binder and shaped from a powder to extrudite form. The surface area depends on many parameters such as type of binder used during shaping process and Si/Al ratio. As Si/Al increases the surface area decreases as noted for HY zeolite after adding binder. Bokhoven et al. [36] observed that the external surface area and pore volume for HMOR-26 significantly higher than that of HMOR-57 and found that increase in surface area and pore volume related to lower content of silica. Thus after adding a binder, Si/Al mol ratio increases from 5 to 6 and that surface area and pore volume decrease also because of applying pressure throughout the extrusion to form zeolite extrudites was low. This is in agreement with the results published by Gates et al. [37].

Table 2, Physical Characteristics of the Catalysts.

Catalyst	HY Zeolite powder	HY Zeolite + binder	HX Zeolite	Prepared HX zeolite
Pore volume cm <sup>3</sup> /gm	0.92	0.850	0.320	0.318
Bulk density g/cm <sup>3</sup>		0.356	0.596	0.602
Porosity (%)		88.01	46.03	45.58
Surface area m <sup>2</sup> /g	660.0	546.00	299.70	290.20
Si <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> mole ratio	5.0	6.0	2.2	2.8

### Catalyst Activity

Cumene cracking was chosen as a model to evaluate the activity of the prepared HX zeolite and to compare the results with the activity of the standard catalysts HY and HX catalysts.

Cumene conversions over the prepared and standard catalysts were determined at different duration times (time on stream).

Figure 6 represents the activity comparison of prepared and standard catalysts at temperature 823 K and LHSV 1 h<sup>-1</sup>. As shown in this figure that the activity of cracking catalysts take the following order ; standard HY zeolite > prepared HX zeolite > standard HX zeolite . At 10 min, the cumene conversions were 52.38, 33.54 and 49.14 mol% for HY, HX and prepared HX zeolite, respectively . It was observed from this figure as the time on stream increases the cumene conversion decreases. Cumene conversions at 240 min decreased to 33.19, 21.2 and 20 mol%, respectively.

Usually the activity of cracking catalysts declines rapidly because of the accumulation of carbonaceous deposits on the catalyst surface at high time on stream values. The same phenomena was observed and reported in previous studies Donald and Wojciechowski [20], Lin et al. [21], William [38] and Yu Liu and Pinnavaia [39] .

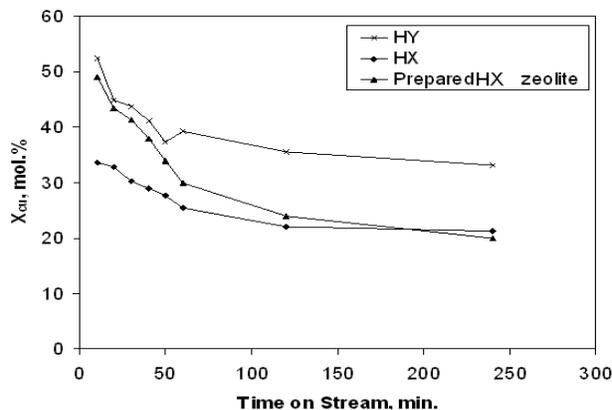


Fig. 6 The activity comparison of prepared and standard catalysts at temperature 823 K and LHSV 1 h<sup>-1</sup>.

### Conclusions:

According to the results obtained from this study, the following conclusions are deduced:

1. It was found from X-ray and FTIR tests that prepared Na X zeolite has a crystallinity 52.17% and nearly has the same crystal structure as the standard type 13X-zeolite with silica to alumina molar ratio 2.8 , and catalyst A did not represented any type of zeolite and it has very low activity.
2. It was observed that the activity of cracking catalysts take the following order ; standard HY zeolite > prepared HX zeolite > standard HX zeolite . At temperature 823 K , LHSV 1 h<sup>-1</sup>, and 10 min, the cumene conversions were 52.38, 33.54 and 49.14 mol% for HY, HX and prepared HX zeolite, respectively .

### References:

- (1) Thomas, C. L. , " *Catalytic Processes and Proven Catalyst*", Academic Press Inc. Publishers, New York, (1970).
- (2) Gary ,J. H. , " *Petroleum Refining-Technology and Economics*" ,4<sup>th</sup> Ed. , Marcel Dekker, Inc., New York, (2001) .
- (3) Serge Raseev , " *Thermal and Catalytic processes in petroleum Refining*" ,Marcel Dekker, Inc., New York, (2003).
- (4) Nada, A. Z., " *Preparation of Zeolites 3A and 5A from Locally Available Raw Materials and*

- Their Extrusion with Different Binders*", M.Sc. Thesis, University of Baghdad,(2002).
- (5) De Oliveira , F. M., and Ortiz, N. , "Process for whitening Kaolin",U.S. Patent ,5,242,874,(1993).
  - (6) Haden W. L. , Metuchen , and Dzierzanowski F. J. , "Method for Making Synthetic Zeolitic Material", U.S. ,Patent, 2,992,068,(1961).
  - (7) Belver,C. , Banares,M. A., and Vicentc,M. A., "Chemical Activation of a Kaolinite under Acid and Alkaline Conditions" , *Chemical Material*, Vol.14, 2033,(2002).
  - (8) Corma, A., "Inorganic Solid Acids and Their Use in Acid-Catalyzed Hydrocarbon Reactions", *Chem.Rev.* , Vol.95, 559-614, (1995).
  - (9) Break, D. W. , "Zeolite Molecular Sieves Structure Chemistry and Use", John Wiley and Sons , New York,(1974).
  - (10) Xiaobo Zheng , "A Computational Investigation of Hydrocarbon Cracking :Gas Phase and Heterogeneous Catalytic Reaction on Zeolites", Ph.D thesis, University of Arizona,(2006) .
  - (11) Suchuchchai Nuanklai , " Effects of Particle Size and Hydrothermal Treatment of Y-zeolite on Catalytic Cracking of n-Octane " , M.Sc. thesis, University of Chulalongkorn, (2004) .
  - (12)Al-Khattaf, S., " The Role of Temperature in 1,3-di-iso-propylbenzene Catalytic Reactions Using FCC Catalysts" ,*The Arabian Journal for Science and Engineering*, Vol.30, No.1B, 13,(2005).
  - (13) Corma, A., and Wojciechowski, B.W., "The Catalytic Cracking of Cumene", *Catal. Rev.-Sci. Eng.*,Vol. 24 , 1-65,(1982).
  - (14)Corma,A., Miguel,P.J., Orchilles,A.V., Koermer,G. and Madon,R., "Cracking of Long-Chain Alkyl Aromatics on USY Zeolite Catalysts", *J. Catal.*, Vol. 135, 35- 45,(1992).
  - (15)Corma,A. , Miguel,P.J., Orchilles,A.V. ,and Koermer,G., "Zeolite Effect on Cracking of Long-Chain Alkyl Aromatic", *J. Catal.*, Vol. 145,181-186,(1994).
  - (16) Frilette,V. J., Weisz,P. B., and Golden,R. L., " Catalysis by Crystalline Aluminosilicates I. Cracking of Hydrocarbon Types Over Sodium and Calcium "X" Zeolites" , *J. Catal.*, Vol. 1, Issue 4, 301-306,(1962).
  - (17) Kazuo, T., and Hiroshi ,T. , "Cumene-Cracking Acitivity of Zeolite Catalyst", *J. Catal.* , Vol. 24, 1, (1972).
  - (18)James, T. R. , "The Effect of Faujasite Cations on Acid Sites",*J. Catal.*,Vol. 9 , 182,(1967).
  - (19) Peter,A. J.,Hugo ,E.L., and Jan, B. U., "Active sites in Zeolites : I. Cumene Cracking Activity of NH<sub>4</sub>Y Zeolites After Different Reactor Prtreatments" , *J. Catal.* ,Vol. 33, 17-30,(1974).
  - (20) Donald, B. , and Wojciechowski , B. W., "The Catalytic Cracking of Cumene /The Kinetics of The Dealkylation Reaction", *J. Catal.* , Vol. 47, 343-357,(1977).
  - (21) Lin ,C. C., Park,S. W. and Hatcher,W.J. , "Zeolite Catalyst Deactivation by Coking", *Ind. Eng.Chem. Process Des. Dev.* , Vol. 22, 609,(1983).
  - (22)Caballero,I.,Colina, F. G., and Costa, J., " Synthesis of X-Type Zeolite From Dealuminated Kaolin by Reaction With Sulfuric Acid at High Temperature" , *Ind.Eng. Chm.Res.* , Vol. 46,1029,(2007).
  - (23) De Lucas, A. , Uguina , M. A. , Covian , I. , and Rodriguez, L., "Use of Spanish Natural Clays as Additional Silica Sources to Synthesize 13X Zeolite From Kaolin", *Ind. Eng. Chem. Res.* , Vol. 32, 1645,(1993).
  - (24) De Lucas, A. , Uguina , M. A. , Covian , I. , and Rodriguez, L., "Synthesis of 13X Zeolite From Calcined Kaolins and Sodium Silicate For Use in Detergents", *Ind. Eng. Chem. Res.* , Vol. 31, 2134,(1992).
  - (25) Haden , W. L., et al., "Synthetic Zeolite Contact Masses and Method for Making the Same", U.S. Patent, 3,367,886,(1968).
  - (26) Haden,W. L., et al., "Method For Making a Faujasite-Type Crystalline Zeolite", U.S. Patent, 3,338,672,(1967).
  - (27) Chandrasekhar, S.,and Pramada, P.N., "Investigation on The Synthesis of Zeolite NaX From Kerala Kaolin", *J. of porous materials*,Vol. 6, 283-297,(1999).
  - (28) Zhou, J., Min, E., Yang H., and Zong B., "Y-Zeolite Containing Composite Marerial and a Process for Preparing the Same", U.S. Patent, 7,067,449B2, (2006) .
  - (29) Ali, A. A. , "Preparation of Zeolite Type 13X from Locally Available Raw Materials", M.Sc. Thesis, University of Baghdad,(2001).
  - (30) Flank, W. H. ,et al. , "Process for Producing Molecular Sieve Bodies", U.S. Patent , 4,818,508,(1989).
  - (31) Bashir, B. N. , "Preparation of Zeolite-Binder Agglomerates from Locally Available Raw Materials as Cylindrical Pellets", M.Sc. Thesis , University of Baghdad,(1997).
  - (32) Khalid ,A. S., "Modification and Characterization of Platinum Supported

- Zeolite Catalysts", M.Sc. Thesis , University of Al-Nahreen,(1996).
- (33) Anderson, R. B. ,*"Experimental Method in Catalytic Research"*, vol. II, Mc Graw Hill Inc., New York, (1979).
- (34)Alline, P.,Nagnoux Schulz, Ph.,and Guisnet, M., *"Hydroisomerization of n-Hexane Over Platinum Mazzit and Platinum Mordenite Catalysts Kinetics and Mechanism"*, *Appl. Catal. A :General*, Vol. 152, 227,(1997).
- (35)Martens , G. G. , Marin,G. B. , Martens ,J. A., Jacob, P. A., and Baron,G.U. , *"A Fundamental Kinetic Model for Hydrocracking of C<sub>8</sub> to C<sub>12</sub> Alkanes on Pt/US-Y Zeolites"*, *J. Catal.* , Vol. 195, 253-267, (2000).
- (36) Bokhoven, J.A.,Tramp, M., Koningsbarger, J.T., Miller and Pieters , J.A.Z., Lercher, J.A., Williams , Kung, *"An Explanation for the Enhanced Activity for Light Alkane Conversion in Mildly Steam Dealuminated Mordenite: The Dominant Role of Adsorption"*, *J. Catal.*, Vol. 202, 129-140,(2001).
- (37) Gates, B.C.,Katzner, J.R., and Schuit,G.C., *"Chemistry of catalytic process"* , Mc Graw Hill,(1979).
- (38) William , J. H., *" Cracking Catalyst Deactivation Models"* , *Ind. Eng.Chem. Res. Dev.* , Vol. 24, 10-15,(1985).
- (39) Yu Liu and Thomas J. Pinnavaia , *" Aluminosilicate Nanoparticles for Catalytic Hydrocarbon Cracking"*, *J.Am.Ch.Soc. Communications* , Vol.125, 2376-2377, (2003).