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Catalytic Reforming of Iraqi Naphtha over Pt-Ti / HY Zeolite Catalyst

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Abstract

In the present work, zeolite Y has been synthesized successfully by sol-gel method.Zeolite was synthesized by crystallization of the final gel which consist from seeding and feed stock gels at 85 ^{o}C. HY zeolite was prepared by an ion exchange process with ammonium chloride solution and then loaded with different percentages of platinum and titanium by the wet - impregnation method.

X-ray Diffraction (XRD), X-ray Florescence (XRF), Scanning Electron Microscopy (SEM), BET surface area and, Crushing strength were used to characterize the synthesized and prepared catalysts . Results showed high crystallinity 90% with silica to alumina ratio 5 for HY, high surface area of 600 m^2/g and pore volume of 0.38 cm^3/g.

The activity of the prepared zeolite was investigated using a pilot plant unit for the catalytic reforming of Iraqi heavy naphtha. All prepared catalysts were investigated at temperatures of 490,500 and 510^{o}C ,pressure of 20 bar, H_2 /HC ratio 3 and LHSV 1.4.hr^{-1}.

Reformate was produced with 86 RON and 94% yield at 510ºC and 20 bar using 0.13 wt.% Pt - 0.75 wt.% Ti loaded on synthesized HY.

Keywords: Zeolite Y, Sol-gel method., Naphtha catalytic reforming.

Introduction

Catalytic reforming of naphtha is considered as a commercial process to produce high octane gasoline, and the main objective of this process is to transform paraffins and naphthenes of naphtha to aromatic rich product with a little ring opening or cracking as possible [1].

Commercial catalysts generally use platinum metal dispersed on porous promoted alumina or silica alumina base both metal and oxide components play an active role [2].

Zeolite encompassing mesoporosity and microporosity have many potential applications such as improved catalytic activity and stability in many catalytic reactions [3].

Typically, platinum catalysts are used in the reforming of naphtha and because of quick deactivation as a result of coke formation, high pressures processes and bimetallic catalysts are used to meet the increasing severity requirements such .metallic is rhenium, tin or iridium [1].

Catalytic reforming reactions proceed by bi-functional catalyst which include hydrogenation and dehydrogenation reactions are processed on the metallic site while isomerization, cracking and cyclization reactions on the acidic site [4].

As the catalyst should be able to convert the naphtha feed into more favorable products, therefore the catalyst should exhibit strong acidic properties.

Another support for platinum catalyst is the crystalline aluminosilicate (zeolite) which has specific properties such as ion-exchange ability ,high exchange capability , crystalline structure with regular pores and certain ratio of silica to alumina [5].

The bi or multi metallic compounds are usually introduced to the pores of zeolite and reduce to their elemental form with hydrogen under selective condition towards aromatic hydrocarbons, thus the metal is mainly atomically in the pores of zeolite lattice [6].

The objective of the present study is to prepare of Zeolite Y and converted to HY zeolite after that loading HY zeolite with Platinum (0.13 and 0.25 wt. %) and Titanium metals (0.75, 1 wt.%) by a co-impregnation method.

Testing of prepared samples for its activity and selectivity in reforming reactions and studying the effect of different metal loadings at pressure of 20 bar and temperature of (490, 500 and 510 °C) on octane number, reformate yield and percentages of the components in the product.

Experimental

Zeoilte Preparation

Sodium aluminate ($NaAlO_2$), sodium silicate solution (Na_2SiO_3) supplied by Sigma-Aldrich, sodium hydroxide (NaOH) by Merck were used. Zeolite Y was synthesized according to sol-gel method. Seeding gel is prepared by adding 19.95 gm of deionized water to 4.07 gm of sodium hydroxide and 2.09 gm sodium aluminate [7]. The mixture was stirred in a plastic bottle until dissolved then 28.3gm of sodium silicate solution was added and stirred moderately for at least 10 min. Then the seed gel was aged for aging time of 48 hr at room temperature. The feed stock gel was prepared by mixing 131 gm of deionized water, 0.14 gm sodium hydroxide and 13 gm sodium aluminate. Stirring was continued in 500 ml plastic beaker until the constituents were completely dissolved, then 178 gm of sodium silicate solution was added with stirring vigorously at 1600 rpm until smooth gel was obtained.

The final gel is prepared by adding 16.5 gm of aged seed gel to feed stock gel slowly with mixing up for 20 min. at 1600 rpm. After that the final gel was transferred to a poly propylene bottle and heated in an oven at 85 ^{o}C overnight. Precipitation occurred until a clear solution was observed indicating complete crystallization. The bottle was opened and left to cool then the wet solid product was set to filtration, washing with distilled water several times until the pH of the filtrate was 9. The product was dried at 110 ^{o}C for 24 hr. and then calcined at 500^{o}C at a rate of 2 ^{o}C /min. for 3 hr.

Ion Exchange

The acid form of zeolite Y was obtained by ion exchange process. 10 gm of zeolite NaY was slurried in 200 ml of ammonium chloride solutions with mixing at 70 °C for 2 hr and then left at room temperature overnight. After that the exchanged zeolite was filtered off, washed with deionized water, dried at 110 °C overnight, and then calcined at 525 °C for 3 hr [8], [9].

Preparation of Pt-Ti/HY Catalyst

A 100 g of prepared HY-zeolite powder was used for preparation of 0.13 and 0.25 wt.% Pt and different concentration of Ti 0.75,1 by co-impregnation method over HY zeolite. 1.256 g of chloroplatinic acid with 50 ml deionized water and 8.3 ml of Titanum butoxide solution after that the HY zeolite was placed under vacuumed condition then the solution was added drop by drop under magnetic stirring until it finished and the vacuum was cut off and the sample was left under mixing for about 2 hr to have a homogenous distribution of metal precursors. Then the slurry was filtered, washed with distilled water, dried at 110°C overnight and calcined for 3 hr at 260°C at a rate of 2 °C /min [10], [4].

The catalysts powder were formulated by using granulator machine (Multi Bowl Spheronizer, Calvea, England), so 100 g of catalyst was mixed with 15 wt.% of montmorillonite clay as a binder and appropriate amount of water to form a paste which put in the granulator ,then drying overnight at 110 °C and calcination at 500 °C for 3 hr. at a rate of 2 °C / min.

The prepared zeolite and catalysts were characterized by different techniques and compared with the commercial type. These techniques include (XRD), (XRF), (SEM), (BET).

The XRD pattern for powder product was measured using Philips Diffractometer with Cu target at 2 theta value from 5- 60° at scanning speed of 5 deg / min using Cu-Kα radiation source of wave length λ=1.5406A°.

The chemical composition of zeolite and the metallic loaded weight percent were determined via (XRF) Spectro Xeros, Germany. The morphology was analyzed using SEM at different magnification by oxford instrument. BET surface area and pore volume were performed using a micrometrics ASAP 2020. The samples were degassed for 2 hr under vacuum at 250 °C.

Catalytic Reforming Pilot Plant Unit

Catalytic activity of Pt-Ti/HY prepared catalyst was carried out by using catalytic reforming pilot plant unit manufactured by VINCI Technology / France at Petroleum Research & Development Center (PRDC) laboratory/ Ministry of Oil.

The unit consists of a fixed bed carbon steel reactor {1.5 m length, 2.5 cm O.D.} with control system and all specifications as shown in Figure 1 (A and B).

The reactor was charged with 60 g of catalyst and the upper and lower parts were filled with ceramic balls.

Before the reaction carried out the catalyst was reduced with hydrogen gas at 450 °C for 3 hr, after that heavy naphtha was pumped and mixed with hydrogen then passed through the catalyst bed to carry out the reaction.

Feed stock properties are shown in Table 1.

The product was cooled and separated in a separator to product. The "reformate was collected and analyzed using GC analysis(Type, 3300 Varian) for Paraffin ,Aromatic, Naphthene concentrations, and for Research

Octane number "RON" which was measured using portable octane analyzer.

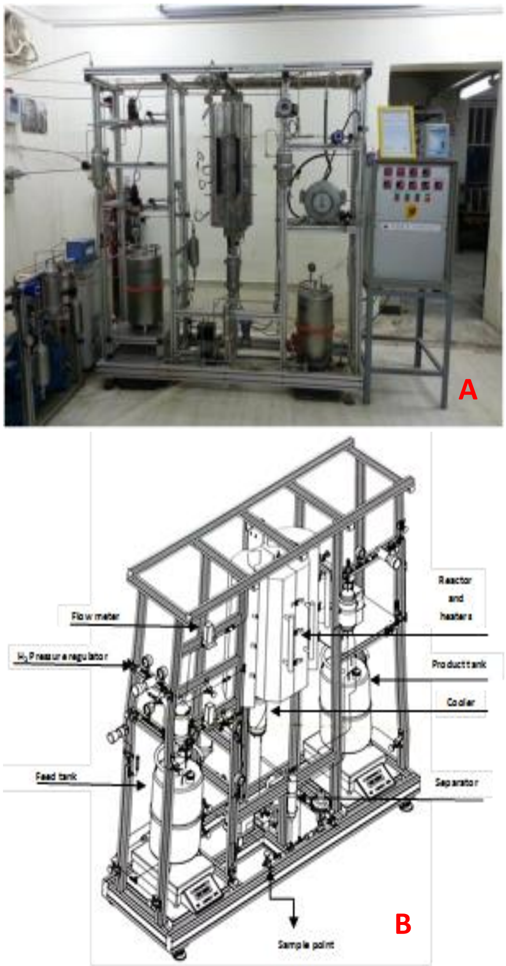

Fig. 1: A. Catalytic reforming Unit. (PRDC), B. Diagram of reforming Unit

Table 1: Properties of Heavy naphtha

Properties	
Sulfur content, ppm	1.3
Density, g/cm^3	0.74
Chemical Composition wt.%	
Paraffins	71
Aromatics	11
Naphthenes	18
RON	57

Results and Discussion

1. XRD

The powder diffraction patterns of zeolite samples confirms the formation of zeolite Y phase. Figure 2 shows that the characteristic maximum peak of zeolite Y at 2 theta of 6.181 is properly distinguished [11]. All other peaks which belong to zeolite Y are found in their particular regions, and the crystallinity for the prepared zeolite was 95% as calculated with the reference to the commercial type. Comparison indicates that the preparation method result is compatible with crystal structure of zeolite Y to conclude that the preparation method gives a good synthesized indigenousness of zeolite Y as shown in Figure 2 [12].

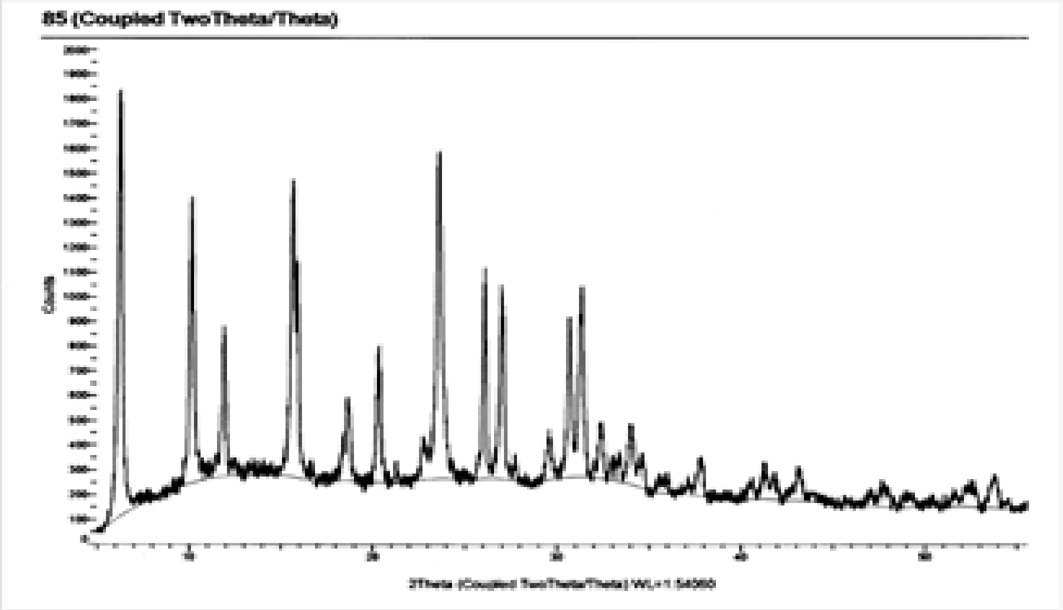

Fig. 2: XRD pattern of Synthesized NaY zeolite

2. XRF

XRF technique was used to determine the chemical and structural formula of prepared samples and silica to alumina ratio was also calculated from the results of this analysis.

The exchange technique was used in this process in one step at constant temperature and the mechanism of ion exchange is shown in Figure 3.

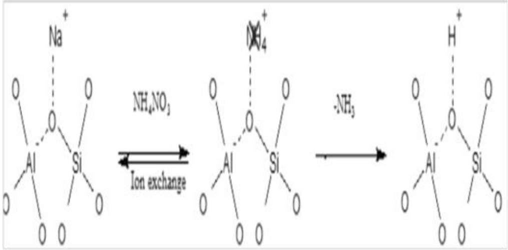

Fig. 3: Ion Exchange Mechanism

The degree of ion exchange, silica to alumina ratio and concentration of sodium ion before and after protonation were listed in Table 2.

Table 2: Chemical composition of zeolite

Zeolite	**NaY**	**HY**
Chemical Composition , wt.%		
SiO_2	59.17	57.96
Al_2O_3	20.1	19.01
Na_2O	9.3	1.95
SiO_2/Al_2O_3 Molar ratio	5.005	5.183
Ion Exchange %		79

Silica to alumina molar ratio for the prepared zeolite is found equals to 5 and is within the range of type Y zeolite [12]. Also, the degree of ion exchange was calculated with reference to the percentages of sodium oxide before and after the ion exchange step and was 79 %.

3. Surface Area and Pore Volume

Nitrogen adsorption –desorption were carried out using Micromeritics ASAP 2020 instrument to determine the BET (Brunaure Emmett Teller) surface area and pore volume.

After degassing the isotherms is investigated at relative pressure P/Po from 0 to 1. Surface area and pore volume are also measured. BET surface area is calculated according to this equation:

$$S_A = \frac{V_m}{22400} * a_m * N * 10^{-20} \qquad \ldots(1)$$

Where S_A: surface area m^2 /gm, V_m: volume of monolayer m^3, a_m: area occupied by one molecular of nitrogen in monolayer is 0.162 $nm^{2,}$ N: Avogadro's number $6.02*10^{23}$ molecules /mole.

It can be seen from the isotherms in Figure 4 (A, B) that the sample exhibited behavior of type two according to the classification of BET and this type shows large deviation from Langmuir model of adsorption and the intermediate flat region in the isotherm correspond to the formation of monolayer. Surface area and pore volume were obtained as shown in Table 3.

Table 3: Surface area and Pore volume of synthesized zeolite

Surface area m^2/g	**Langmuir surface area, m^2/g**	**Pore volume cm^3/g**
641.87	925.63	0.379

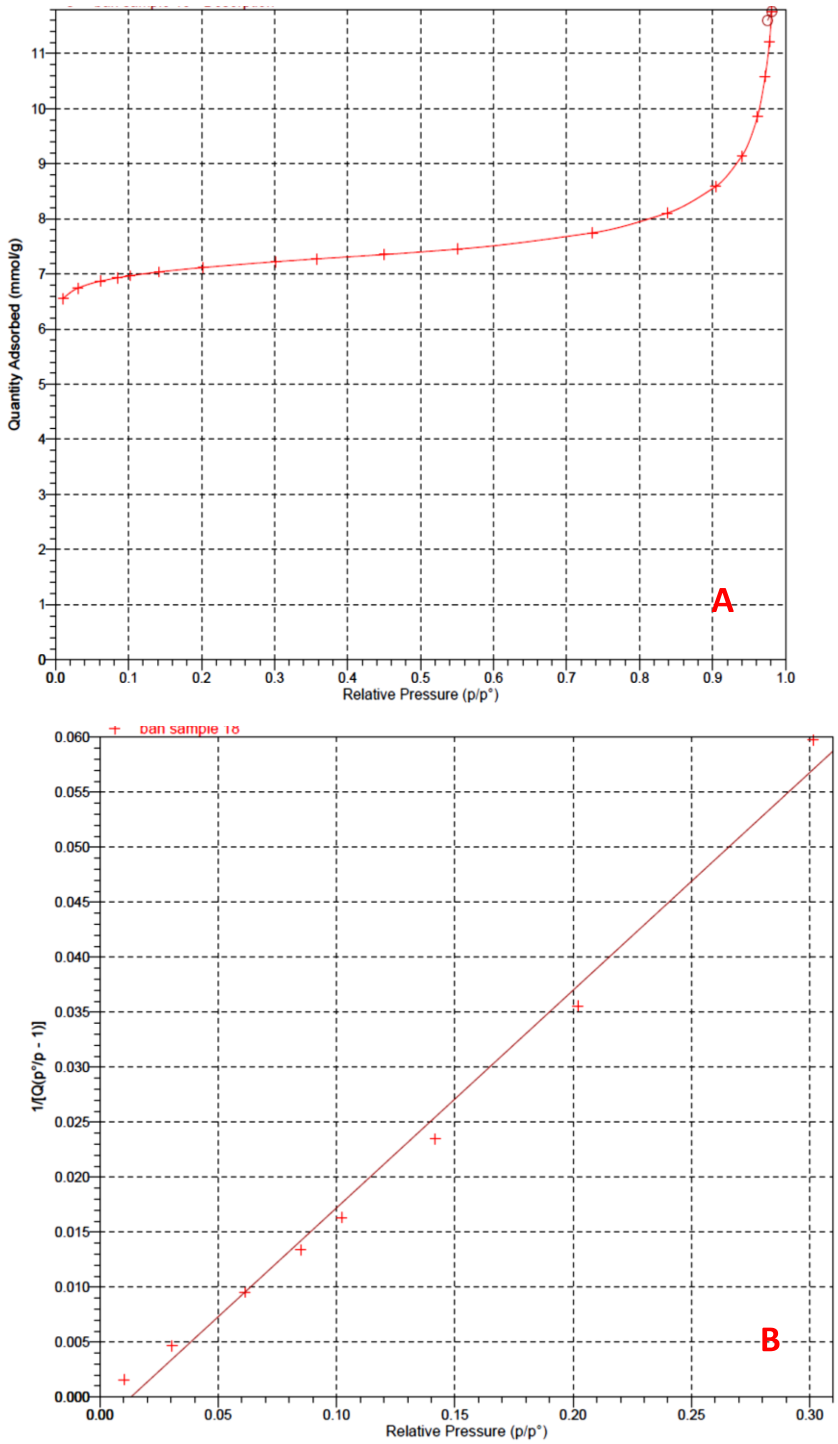

Fig. 4: A. Adsorption isotherm of synthesized NaY ., B. BET Plot

4. SEM

Na-Y zeolite crystal size and morphology were observed by SEM. Figures 5 to 7 show that the crystalline micrographs of the synthesized zeolite having small average size because of nano sized particles as compared with commercial one and the images show a good agreement with that shown in literature revealing a uniform particle size with regular shape and uniform particle size distribution [13], [14].

AFM technique is used to measure the particle size and Figures 8 to 10 shows that the average particles size were the nano size of prepared NaY zeolite is about 80 nm and for HY zeolite is 71 nm while for commercial one is about 91nm [10], [15].

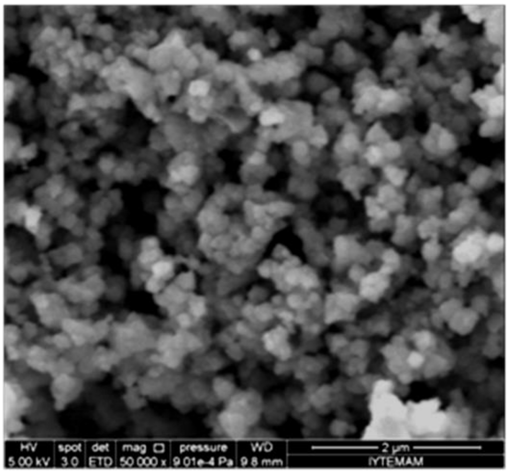

Fig. 5: SEM images of Synthesized NaY zeolite

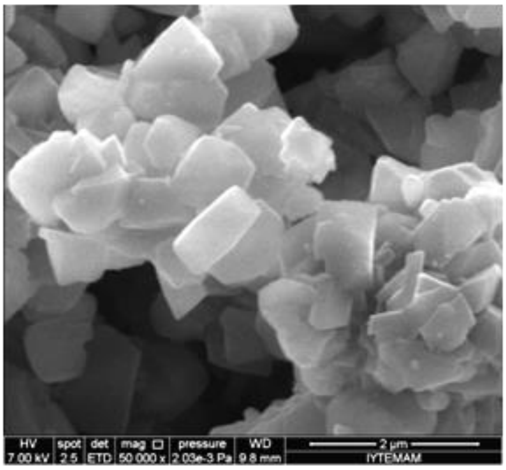

Fig. 6: SEM images of Commercial NaY zeolite

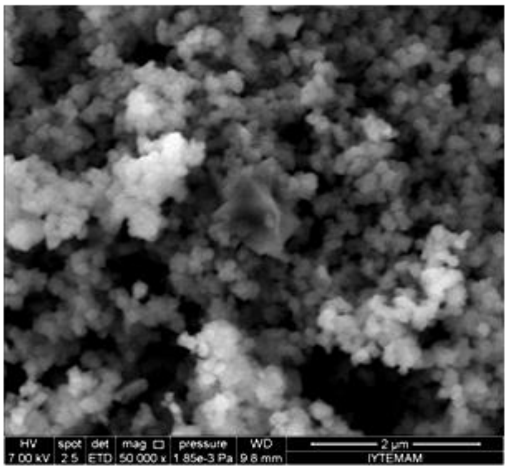

Fig. 7: SEM images of Pt / HY catalysts

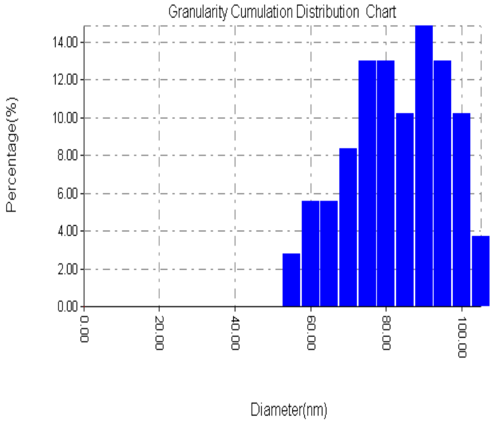

Fig. 8: Particle size distribution of synthesized Y zeolite with average diameter of 81nm

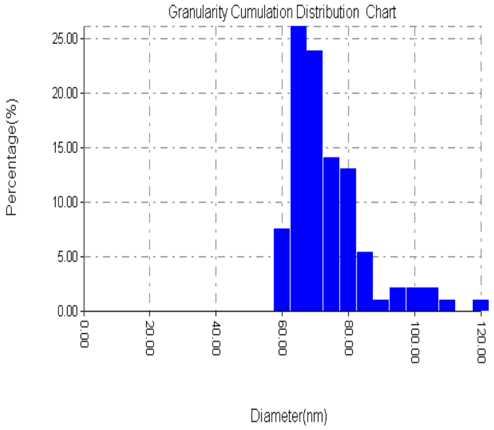

Fig. 9: Particle size distribution of HY zeolite with average diameter of 72nm

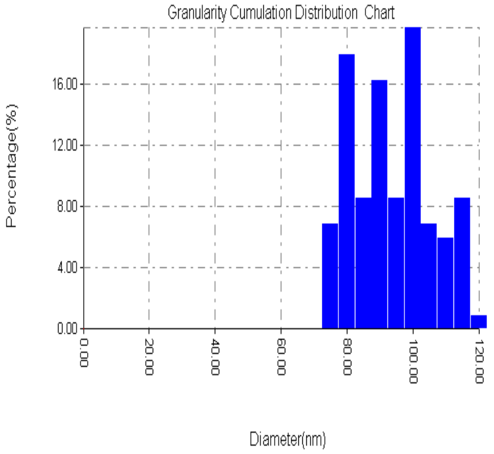

Fig. 10: Particle size distribution of Commercial HY zeolite with average diameter of 91nm

Activity Testing

The activity of all prepared of catalyst samples were investigated for naphtha reforming reaction and all properties and the crushing strength which gives a good withstanding through operation were listed in Table 4.

Table .4 Properties of prepared catalysts

Catalyst	Surface area m^2/g	pore volume cm^3/g	Bulk density g/cm^3	Crushing strength kg
(0.13 wt.% pt, 1wt.% Ti)/HY	357	0.38	0.701	1.93
(0.25 wt.% pt, 1wt.% Ti)/HY	402	0.209	0.649	0.62
(0.25 wt.% pt, 0.75 wt.% Ti)/HY	550	0.392	0.695	1.24
(0.25 wt.% pt, 0.75 wt.% Ti)/HY*	575	0.831	0.601	0.82

* Commercial zeolite HY

1. Effect of Temperature and Bimetallic Loading on RON of Reformate

Reaction temperature is one of the critical operating parameters on catalytic naphtha reforming and by reducing or rising the temperature the octane number (RON) of reformate will be changed.

It can be observed from Figures 11 to 14 that by increasing the reaction temperature from 490 to 510 ºC the octane number of reformate will be increased from 79 to 86.

Catalyst with 0.13 Pt wt.% & 0.75 Ti wt.% gives high RON of 86 at temperature of 510 ºC as compared with RON of 83 for same metallic loading but for commercial HY zeolite at same temperature as shown in Figures 13 and 14.

This increase in octane number is attributed to increase in aromatics compounds due to dehydrogenation reaction of naphthenes [16], [17].

Titanium bounds directly to the surface of zeolite and during calcination of TiO_2^+ reacted with lattice oxygen to give TiO_2 or TiO^+ in the framework through Ti-O-Si bonds forming a strong electrostatic fields with polar adsorbate giving a good catalytic activity of zeolite [18].

TiO_2 contains isolated and tetrahydrally coordinate titanium oxide species in the frame work of zeolite giving more stable catalyst and much higher selectivity towards isomerization and aromatization reactions because Ti modified and enhance the hydrogenation-dehydrogenation metallic function of pt active site also balancing the total acidity of HY zeolite resulting in an efficient balancing between metallic and acidic function of catalyst. [19].

It can be deduced that Ti shows a good activity for all catalyst and the optimum or best results obtained for 0.75 wt% which gives a good sharing active site to Pt towards the hydrogenation and dehydrogenation giving high reformate quality.

The titanium activity improved the performance of the catalyst and the interesting point that it lowers the need of the typical platinum loading of 0.3% in the commercial type.

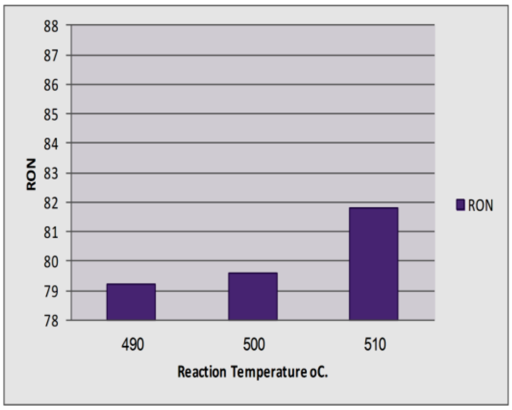

Fig. 11: Research octane number for product Reformate for catalyst 0.13 Pt wt.%- 1 Ti wt.% /HY

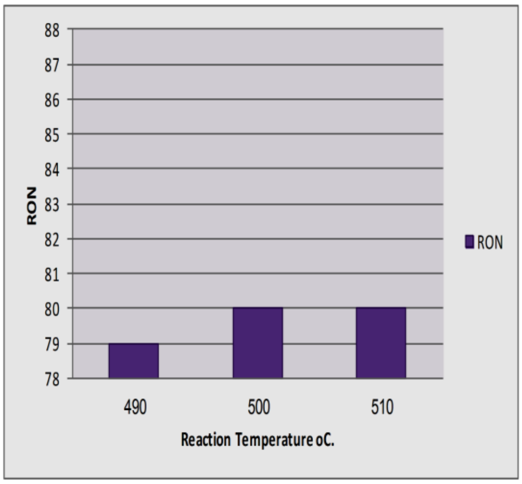

Fig. 12: Research octane number of product reformate for (0.25 Pt wt.% -1 Ti wt.%) / HY

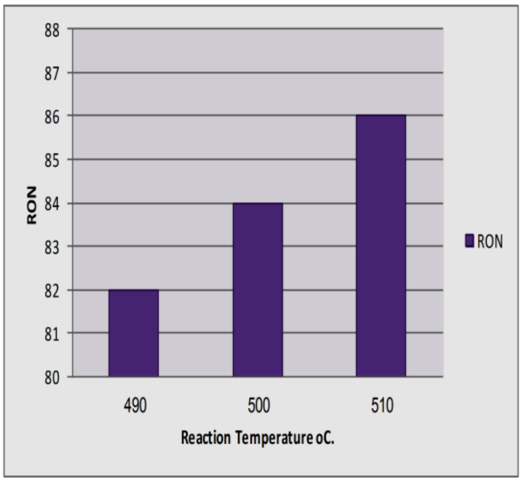

Fig. 13: Research octane number of product reformate for (0.13 Pt wt.% , 0.75 Ti wt.%) / HY

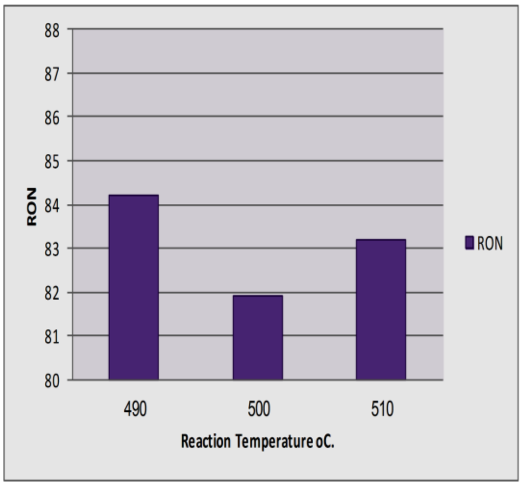

Fig. 14: Research octane number of product reformate for (0.13 Pt wt.% , 0.75 Ti wt.%) / commercial HY

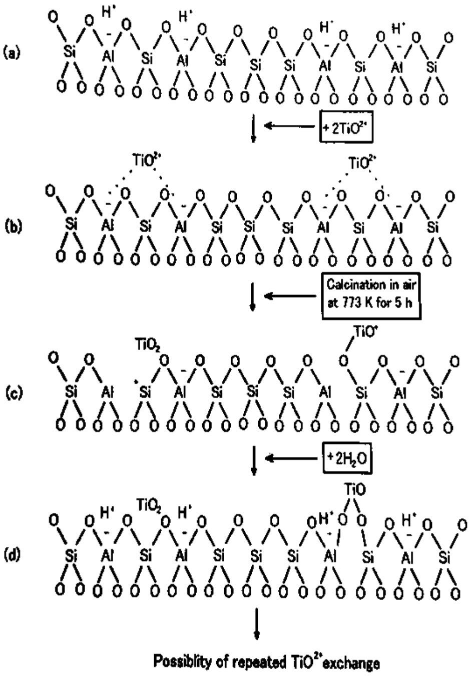

Fig. 15: TiO_2 incorporation into the framework structure of zeolite [18]

2. Effect of Temperature and Bimetallic Loading on Distribution of Reformate Hydrocarbons

Catalytic naphtha reforming showed to proceed a typical bifunctional reactions occurred on both metallic site represented by Pt and Ti and the acidic site represented by HY zeolite. Figure 16 shows a possible mechanism [20].

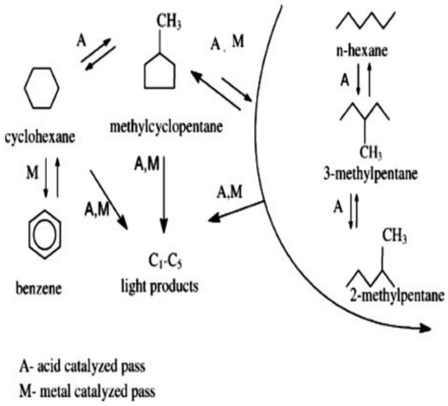

Fig. 16: Mechanism on Metalic and Acidic Sites of Bifunctional catalysts [20]

As in this research although HY zeolite catalyst exhibited a hydrophobic properties derived from high SiO_2 / Al_2O_3 ratio, the TiO_2 loading on pt /

HY result a higher hydrophobicity leading to achieve efficient activity.

For all tested catalyst it can be observed that at high temperature the selectivity towards aromatics increases and also a better performance was obtained at low level of metal loading as shown in Figures 19 and 20. The same conclusions were found from the study of Regali, (2014) [21].

Another advantage of the bimetallic loading in the composite catalyst could be related to that Titanium may form an alloy with platinum preventing the increase in platinum crystallites size and keeping it well dispersed (prevent sintering) also preventing of coke precursors to deposit onto the surface of catalyst [22].

Finally from all results it can be deduced that Ti shows a good activity for all catalyst and the optimum or best results obtained for 0.75 wt% which gives a good sharing active site to Pt towards the hydrogenation and dehydrogenation giving high reformate quality.

The titanium activity improved the performance of the catalyst and the interesting point that it lowers the need of the typical platinum loading of 0.3% in the commercial type.

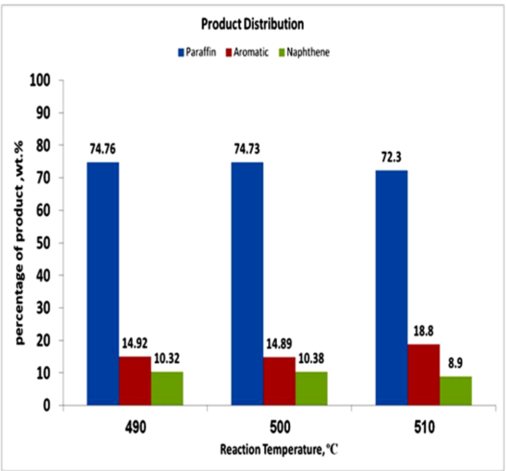

Fig. 17: Product distribution for (0.13 Pt wt.% - 1 Ti wt.%) / HY at different temperatures

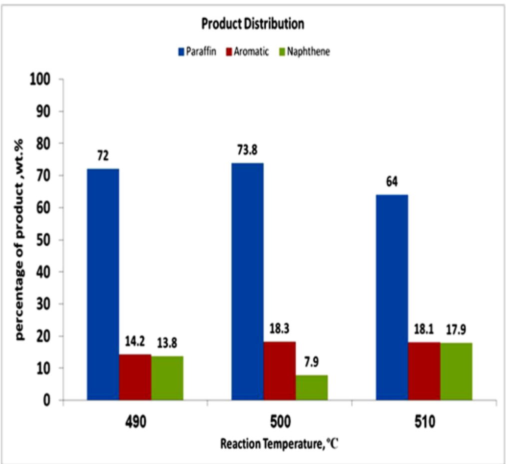

Fig. 18: Product distribution for (0.25 Pt wt.% - 1 Ti wt.%) / HY at different temperatures

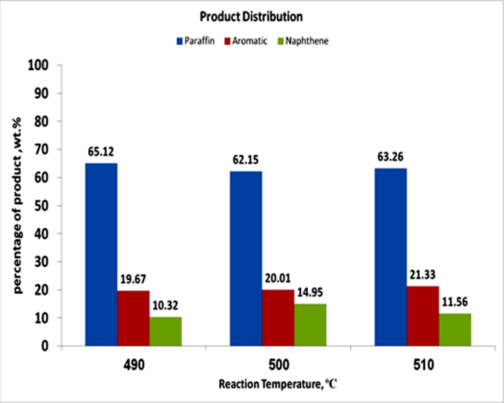

Fig. 19: Product distribution for (0.13 Pt wt.% - 0.75 Ti wt.%) / HY at different temperatures

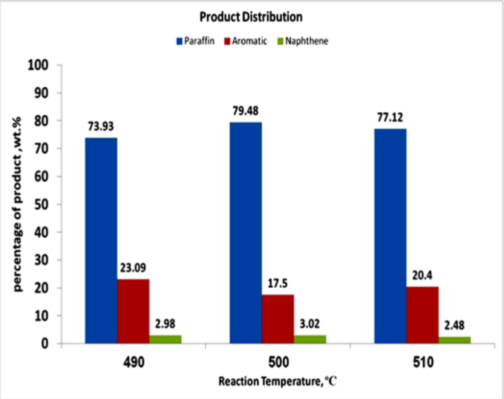

Fig. 20: Product distribution for (0.13 Pt wt.% - 0.75 Ti wt.%) / commercial HY at different temperatures

3. Effect of Reforming Conditions on Reformate Yield

In catalytic reforming the yield of reformate is defined as the volume of product reformate to the volume of heavy naphtha feed and the results showed high reformate yield obtained ranges from 91 to 95 for all catalyst investigated as shown in Figure 21.

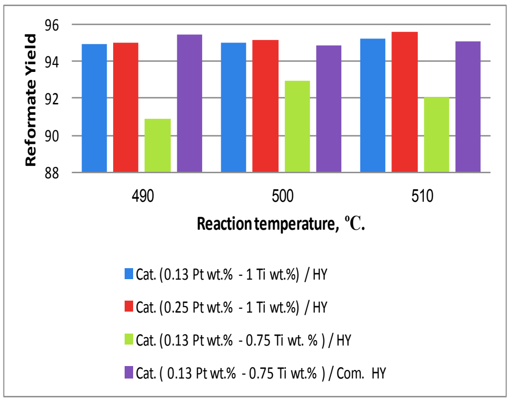

Fig. 21: Yield of product reformate for different catalyst

Conclusions

As a result of this work these conclusions have been made:-

- a very good crystallinity of 90% ,silica to alumina molar ratio of 5 and BET surface area of 600 m^2/g has been obtained for synthezied zeolite .
- high octane number of 86 is obtained at temperature of 510 °C for 0.13wt.% Pt and 0.75wt.% Ti /HY catalyst.
- Titanium loading on zeolite was found to give a good activity with loading 0.75 wt.% Ti which also has an important results from economic point of view in reducing the percentage of platinum loading to 0.13 wt.% Pt compared with commercial type of 0.3 wt.%Pt.

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