Enhancement of Sudan Gasoline Octane Number by Natural and Synthetic Zeolites

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ABSTRACT

The sample of natural zeolite is collected from the Sudan area, (scolecite) from Buda desert. And the other one is synthetic zeolite (Y). The study characterized the natural zeolite (scolecite) and synthetic (Y). Using thin sections for natural zeolite to recognize it. Beside different techniques as follow: Atomic absorption, x- ray diffraction (XRD), inferared spectroscopy (FTIR), acidity measured by pyridine FTIR, scanning electron microscopy (SEM). The study was carried out for selected natural zeolite (scolecite) and synthetic zeolite (Y) they are modification by two methods impregnation and ion exchange using ammonium chloride and platinum hydrochloride H_2PtCl_6 The Naphtha was obtained from the refinery of Khartoum Company (it has octane number40). Piona of naphtha was studied by GC. The natural and synthetic zeolites modification was applied on reforming process to increase the gasoline octane number. The study carried out fourteen experiments for each kind of zeolite with a variety of reactions conditions like liquid hour space velocity (LHSV), pressure and temperature, the optimal experiments with suitable conditions gave good results. Octane number increased in pressure rang 8-12 bar, liquid hour space velocity 2 and temperature 480- 500^0C .

The synthetic zeolite (Y) raised the octane number from (40 to 93.5). The natural zeolite (scolecite) also showed good properties and increased the octane number from (40 to 87.9). It needs more purification and modification to reach the synthetic. The study explained that the two zeolites (natural, synthetic) are successful for application in reforming process.

Keywords: zeolite, XRD, FTIR, LHSV, GC

1. INTRODUCTION

Zeolites are used in several technological applications and also comprise and important rock - forming mineral group. Zeolites are used as catalysts for example, in the cracking of hydrocarbons, in molecular sieving and for used in action exchange process. In nature, they can found in sedimentary rocks, in low grade metamorphic assemblages and in various hydrothermal deposits. The chemistry of zeolites with a single cation in the channels (we use here the terminology based on the I U P A C recommendations out lined by MC Cusker et al -2001) can be represented by the general formula M $_{x/n}$ (Al O₂) $_{x}$ (SOi₂) $_{x}$. m H₂O where m is action of valence n and m is the number of water molecules in the unit cell. In terms of their Crystal structure Zeolites are classified as frame work silicates consisting of corner – linked AlO $_4$ and SiO₄ tetrahedral. To balance the negative charge in the farm work, resulting form the person of the Al cation s, M cation s are located in structural channel. The m cation is typicically monovalent such as \hat{h}^+ and Na⁺, or divalent such as Mg²⁺ or Ca^{2+,} for example. H₂O molecules are also found in the structural channels and are present in different concentration. The natural Zeolite scolecite, Ca8 (A l $_{16}$ Si $_{24}$ O₈₀). 24 H₂O are classified as small pore Zeolites consisting of eight membered rings having channels around 2.5 x 4 A^0 in size that are parallel to the Crystallographic C – axis surprisingly in as much as it is the presence of molecules in small channels and their effect on the physical behavior that make the Zeolites so interesting and a useful class of silicates, relatively little research has been directed toward to enhance the gasoline octane number (1).

A primary object is to increase the gasoline yield and raise the octane number. The source of the large hydrocarbon molecules is often the naphtha fraction or the gas oil fraction from the fractional distillation of crude oil (petroleum) (2).

The increasing interest in improving environmental protection and promoting efficiency of auto – motive motors encourages the formulation of new catalyst and development of new processes for gasoline production. Considering branched chain alkane have higher octane numbers than linear alkenes the use of gasoline that contains higher proportions of these compounds is an alternative to obtaining fuel with the required characteristics. These compounds are and alternative to replace some additives normally used in gasoline to increase the octane number, for example, MT B E, whose use is considerably criticized by environmental protection agency (E P A). The traditional isomerization catalyst is Pt – loaded chloride alumina, which is very active and can be operated at low temperature, but will cause corrosion and pollution problem, (4).

These days Zeolites are desired catalyst. Zeolites are natural minerals that are mined in many part of the world. Most Zeolite used commercially is synthetically produced (2). The use of Zeolits as support can eliminate such problems (4). In this study there are probably to modification the natural Zeolite of from the Sudan and used it in reforming process to enhancement the Sudan gasoline octane number. Today Zeolite Y is used commercially as catalyst in petroleum refinery because of its high concentration of active acid sites, its high thermal stability and high size selectivity. Zeolite Y is synthetic analog to the mineral faujasite and crystallizes with cubic symmetry. It has crystal sizes in the approximate range of 0. 2 – 0. 5 m and pore diameter of 7. 4 A^0 . It thermally decomposes at 793C^o

(2). In this research the reforming of n – alkenes over Pt – loaded Y Zeolite Pt / H /Y and P t / H scolecite has been studied.

2. MATERIAL AND METHODS

Natural zeolite collected from Buda desert (in north of the Sudan). The zeolite crystals separated from rock sample were washed, dried, crushed and sieved to obtain fine powder. The powder was refluxed with doubly distilled water to remove soluble impurities. It was then decanted and dried in an oven for two hours. The fine powder of natural zeolite is used for further modification to enhance the activity. Various techniques (impregnation, ion exchange) are available to introduce metal-support integration is weaker and large metal particles are obtained which can affect secondary reaction, namely those which are structure sensitive an example being hydrogenoloysis. On other hand, the ion exchange technique normally brings about a strong metal –support interaction. The Zeolite were characterized by the elemental Analysis used Atomic Absorption, the X-ray diffraction patterms obtained were recorded by using Philip powder (shimadz 24×6000 RD) diffract meter,ceta- 2ceta scan. The radiation used was Cu-K Alfa. The 2 ceta scan was form 10- 90 Fourier transform infrared spectroscopy (ABB Bomen MB 104) and nitrogen adsorption (Quanta Chrome Nova 2000). Scan electron Philips XL – 30 ESEm), Acidity measurement to differentiate between Lewis and Bronsted acid sites typical pyridine adsorption experiment followed by (F T I R) measurement were carried out. After pyridine desorption at 200 0C , the total Bronsted and Lewis acidity can be calculated strong Bronsted and Lewis a acidity can be obtained.

The acid properties of pt/H/Y and Pt/H/Scolesite zeolite were investigated by heavy naphtha reforming process. To enhancement the Sudan gasoline octane number and to upgrading the product properties. And study the properties of gasoline. At the end the gasoline octane number was measured by research octane number method.

3. RESULTS AND DISCUSSION

In this study the characterization of zeolite Y synthetics and type of natural zeolite from the Sudan areas is collected (zeolite scolecite) indicated all of their properties, I choice zeolite scolecite and zeolite Y for application reforming process to enhance the Sudan gasoline octane number, all of this characterization shown in figure bellow.

3.1 *Thin section analysis light)*

Fig-3.1: Thin section of zeolite scolecite (cross polarized

Table.3.4. Kesults of atomic absorption analysis of natural and scolecite zeomes			
Sample	Natural		
$CaO\%$	30.8%		
$Al_2O_3\%$	11.4%		
SiO ₂ %	55.8%		
$Na2O\%$	-		
Moisture	4.3%		

Table.3.2: Results of atomic absorption analysis of natural and scolecite zeolites

3.3 *X ray analysis*

Catalysts were characterized by means of powder x.ray diffraction using ashimadzu model XRD-6000 diffracted with monochromatic CUK_X Radiation.

Fig-3.2: Thin section of zeolite scolecite (plain cross polarized light)

3.3.1 *Xrd Characterization Of Natural Occurring Scolecite Type Zeolite*

The natural occurring scolecite type zeolite was collected from the Buda was subsequently washed with distilled water and acetone for several times, dried and crushed into fine powder which was further washed with distilled water 3-4 time and dried at 110 °C in an oven. The resulting sample was impregnated with NH₃ solution and H₂ Pt Cl₂2H₂O dried at 110 $^{\circ}$ C and heated at 530 $^{\circ}$ C in high temperature muffle furnace (SONAR)

For four hour at rate 3° C per minute and naturally cooled. These materials were characterized by XRD using a model D8 Bruker AXS with mono chromo somatic Ca radiation (40 kV and 30 MA) at room temperature.

The XRD spectra are shown in Fig. (3.3) it seen that the sample are crystalline

It is seen that the sample are crystalline in nature due to calcinations, the high intensity peak has been shifted at 2Θ = 38.29 $^{\circ}$ and broad hump were observed in fig (3.4) the region of 2 Θ 25-35 $^{\circ}$. It shows that the crystal structure collapse at high temperature which was not seen in Fig. (3.5).

The XRD data leads to the following cell dimension a = 4.817416 A \degree , c = 34.11858 A \degree the high values of unit cell dimension are also reported for Edingtonite type zeolite. The average particle size found to be 1.9915 A^o and hexagonal crystal system. Characterization of the zeolite sample before and after treatment was performed by x.ray FTIR powder x.ray diffraction (XRD pallerns were recorded by Bruker 8D advance x.ray diffractometer using monochromator Cu –K q radiation (40 kv dn 30 mv) of wave length =1.5405 A°

X. Ray powder diffraction data suggest that natural Zeolite is mono clinic in type.

Preliminary indexing of the powder data gave a unit cell with a =9.5669, b= 8.1136, c=6.7945^o and α = 90.00°, B = 93.57°, \bar{X} = 90.00° and particle size = 0.3705 A° volume = 526.38A°.

The x.ray patterns for the sample before and after treatment of chloroplatinic acid (H₂ptcl₆) and NH₃ solution are presented in Fig(3-4) and (3-5) respectively. The x.ray diffraction data were optain in the 2theata range of 10-90 and are represented in (4) respectively. X-ray diffraction (XRD) to confirm of zeolite Y. powder XRD (Siemens -500 diffractometer using Cuka radiation) was used to determine sample structure and crystallinity. The formation of zeolite y phase was confirmed by comparing the diffractograms of all synthesized sample to the differactogram of the reference zeolite Y. according to Treacy and Higgins {m}, the XRD first peak will appear in the range ($2 \theta = 2-50^{\circ}$) 6-10° for the zeolite Y,

Fig-3.4: X- ray diffraction of H/ scolecite

Fig-3.5: X-ray diffraction of Pt/ H/ solicited

Fig-3.8: X ray of Pt/ H / Y zeolite

Diffraction data were obtained in the 2θ range of 10-90° and are represented in table respectively.

The small zig-zag peak refer to presence of some amorphous material in fig (3-7) Pt/H/y. in Fig (3-8) the first XRD peak is observed at exactly 6° and other peaks are also very sharp. It is shown to be fully crystalline. Crystallization of pure zeolite x using silica is favored at temperature lower that 100 c° , with less Na₂O or greater SiO₂ content in the initial mixture. This is because zeolite y is highly reactive. (Fig (3-6).

3.4 *Scan Electron Microscopy*

Scan electron microscopy of scolecite zeolite shows tow kind of twining one is (100) twining caused by an symmetric arrangement of cations and H2O molecules in the channel and the other is sectoral twining owing to a party ordered(Al, Si) arrangement (100) twining,although the from work of scolecite has aglide plane parallel to (100). the distribution of water molecules an Ca ions are asymmetric with respect to the plane in figure (3-4-1), and the fore(100) twining is allowed in scolecite. The three dimensional structure develops on the twined nucleus. Sectoral twining of scolecite are explained by the following idea suggested by the AKIZUKI (1987), THE Ca ions are bonded directly to the oxygen's of T2 tetrahedral. But not to be those of tetrahedral. Because of electrostatic charge balance and the Al, there for (100) twining is allowed in scolecite. The scan electron microscopy show n in figures (3-4-1, 3-4-2, 3-4-3) respectively

Fig-3.4.1: Scan electron of scolecite zeolite

Fig-3.4.2: Scan electron of/ H/Scolecite

Fig-3.4.3: Scan electron of Pt/ H/Scolecite

3.4.4 *Scan electron of zeolite Y*

The commercial zealite Y show similar scan electron microscopy (SEM) morphology to that of the reference sample zeolite Y. morphology of the zeolite Y mode faction with pt and without pt are given in figure(26), and (24), respectively. The SEM morphology in figure (24) show Avery clear and sharp crystal linty SEM analyses of the sample are figure (3-4-4) the influence of the impregnation of platinum of the H/y zeolite structure can also is confermed from SEM image.

The macrographs showed the presence of small crystallites of platinum uniformly distributed along some intergrowth. SEM demonstrated that the morphology and particle size of pt / HY catalyst did not change with respect to those of HY zeolite – indication that on crystalline transformation occurred during the impregnation of pl platinum) on to HY zeolite. pt is finely dispersed as their presence in zeolite surface for that the impregnation of pt on H/Y zeolite result in as male change on microspore structure. This can be verified by the decrease of micro pore area and volume of all materials after impregnation. This effect may be attributed to the presence of metallic and extra frame work aluminum species in the interior of the zeolite pores and channels. The decrease in microspore area was pronounced for pt / H/Y catalyst, probably due to the formation of large partials inside the microspores. the synthesized zeolite Y genre similar scanning electron microscopy (SEM) morphology and FTIR spectrum pattern to that of the reference of sample zeolite Y (2009) M. M. Rahman, N. Hasnidb and W. B. Wan Nik Morphologies zeolite with H/Y and pt / H/Y in figure (3-4-6),(3-4-5) respectively. The SEM morphology in (H/Y) shows a very clear and sharp crystalline with some dirt.

Result of Scan electron microscopy of zeolite Y

Fig-3.4.4: Scan electron of zeolite y

Fig-3.4.5: Scan electron of zeolite H/y

Fig-3.4.6: Scan electron of zeolite Pt/ H/Y

3.5 *Infrared Spectroscopy (FTIR) of zeolite Scolecite*

FT-IR Spectra of natural zeolite samples are presented in fig (3-5-1) and fig (3-5-2) and fig (11) the results show that the band at 504 cm⁻¹ character of the presence of double four member ring (17). The broad band near 3558 cm⁻¹ is due to the presence of water molecules in the matrix of natural zeolite (17) and partial dehydration (17) band at 1655 cm⁻¹ $(H - 0 - H)$ deformation band, Band appears due to T-O-T (T – Si and /or Al) stretching at 1097 cm⁻¹ After modification of natural zeolite by H₂ Ptcl₆ the band 3558 cm⁻¹ are broaden and shifted towards higher wave number = 1097 cm^{-1} , the stronger band at 624cm^{-1} , is the characteristic of Si-O-Al deformation band and shifted towards higher wave number 761 cm⁻¹. The band 504 and 432 cm⁻¹ disappeared and new band is appeared at 572 cm⁻¹.

Fig-3.5.2: Infrared spectroscopy of H/scolecite (treated with ammonia)

Fig-3.5.3: Infrared spectroscopy of Pt/ H/scolecite

Table-3.5: Peak of Scolecite position of Infrared spectroscopy at temperature 300,500k and their assignment (Sh = shoulder).

	Measured Peak Position in cm ⁻¹		Assignment	
At 300k				
3589				
3507				
3409				
3327	334(sh)		V(OH)	
3232	3212			
3140 (sh)				
1665	1658			
1591			S(OH)	
1099	1101			
1068	1049	1035		
1047				
1034				
1020			$V[$ Si (Al)-O	
988	978	970		
		939		
931	929			
721	703	668		
692	673			
671				
632	610	610	σ [O – Si (Al)- O+ Si –O – Al	
604				
497	501	501		
422	422	422		

3.5.4 *FTIR of zeolite y*

The product was characterized by Fourier transform Infra Red (FTIR). Vibrational spectroscopy, of Zeolite show strong IR absorption in the spectral region below 1500 c m vibration frequencies of the Zeolite lattice which results from stretching and bending modes of the $T - O$ units which is observed in the range 300 to 1300 c m -1 indicates that $SiO₄$ or A $1O₄$ are linked.

The Zeolite y gave similar spectrum pattern to that of the reference sample Zeolite y figure (3-5-4), (84) an the FTIR of Zeolite H /Y (zeolite Y after treated with ammonia) figure (3-5-5) show strong IR absorption in the spectral but the Zeolite Y after treated with platinum figure (3-5-6) Pt / H / Y show strong IR absorption 1041.

Fig-3.5.4: FTIR analysis of zeolite Y

Fig-3.5.5: FTIR analysis of zeolite H /Y

Fig-3.6.3: Acidity of zeolite scolecite

Figures above (3-6-3) show the acidity of zeolite scolecite, zeolite scolecite treated with ammonia H/scolecite and zeolite scolecite treated with platinum hydrochloride Pt/H/scolecite measured by pyridine FTIR, the figure show clearly increase of acidity in figure 3-6-3) and (3-6-4) after zeolite treatment.

Acidity of zeolite Y

Figures (3-6-4) of zeolite Y before treatment, figure (3-6-5) of zeoilte after treated with ammonia, and figure (3-6-6) of zeolite after treated with platinum hydrochloride are show acidity of zeolite Y respectively measurement by FTIR after treated by pyridine acid. Figure (3-6-5) and (3-6-6) illustrated the increasing of zeolite acidity after treatment.

4. SAMPLE OF NAPHTHA

Fig-4(45): Piona analysis of naphtha by GC

5. DISCUSSION OF REFORMING AND HOW TO ENHANCE OCTANE NUMBER

In the catalytic reforming process the seven types of reactions are taken place as the following: -

1- dehydrogenation,2- isomerization, 3- cyclization, 4-Aromatization, 5- Hydro cracking, 6- Hydrogenolysis, 7- Coke formation.

Some of these reaction are desired because of increasing octane number of gasoline and some of them are undesired because of decreasing it. For paraffin's, increase of octane number is the result of increasing the number of branches such cyclization and aromatization. Therefore normal paraffin's conversion to isoparaffins, naphthenes and aromatics result in increasing octane number. On other hand, coke formation and coke deposition, causing the deactivation of the catalyst are undesired reactions. There are three kinds of this process in use today: semi – regenerative, Continuously catalyst regenerative, (C C R) and cyclic (6). Recently there has been renewed interest in the reforming process first because reformate is a major source of aromatic in gasoline, and second, because of the new legislation of benzene and aromatics content in commercial gasoline (5).

6. CONDITIONS EFFECT IN OCTANE NUMBER INCREASE

6.1 Reactor temperature:

Once a process unit has been installed, the primary mechanism to adjust product octane number is that of adjusting reactor operating temperatures. Typical reactor inlet temperatures range from 490°C to 550°C. With the other

operating conditions held constant, a higher reactor inlet temperature results in a higher product octane number. Higher temperatures also increase operating severity and cause more rapid catalyst deactivation,

Fig-3.7: Effect of temperature (8 bar, 4 LHSV)

6.2 *Reactor Pressure*

Reactor operating pressure can practically vary from 3.5 to 30 bars, although there are no theoretical limits. As a consequence of the typical catalyst distribution between the reactors, the last reactor inlet pressure provides a close approximation of the average pressure in the overall catalyst bed. The lower the operating pressure, the higher the reformate and H yields. Low operating pressure results in more severe conditions, causing higher catalyst deactivation rates. The lowest operating pressures are typically only practiced in continuous reforming units.

Fig.3.8.1: Effect of Pressure, bar (480 oC, 4 LHSV)

Fig.3.8.2: Effect of Pressure, bar (480 oC, 3 LHSV)

 2 4 6 8 10 12 14 **P Ressure, bar**

F

Fig-3.8.3: Effect of Pressure, bar (480 oC, 2 LHSV)

Space velocity:

Space velocity is the ratio of the feed rate to the amount of catalyst. It is typically measured in volumetric terms as Liquid Hourly Space Velocity (LHSV) in units of h Space velocity affects the temperature required to achieve a desired product quality. Lower space velocity entails larger catalyst volumes, signifying that lower temperatures are required to achieve the same product quality. High space velocity, a more severe condition, results in higher temperature requirements for the same product quality. Following the construction of a reforming unit, the LHSV can only be adjusted by varying the naphtha charge rate.

Fig-3.8.4: Effect of LHSV (480 oC, 8 Pressure bar)

Hydrogen/hydrocarbon ratio or H is the measure of moles of hydrogen charged to the reactor as a ratio of the moles of feed naphtha. As mentioned earlier, hydrogen is recycled to the reactors to maintain catalyst stability. The amount of the hydrogen or H can be adjusted by the rate of recycled gas at a given operating pressure.

The hydrogen purity of the separator gas also has a direct effect on H a higher H results in a less severe operation and thus a lower catalyst deactivation rate. Operation at higher H must be balanced with the utility cost associated with recycling the separator gas. Feed stock. Feedstock can be characterized by the relative proportions of paraffin's, naphthenes and aromatics (PNA) in the feed along with its distillation range. The fastest reactions are those of naphthene dehydrogenation. Feedstock's rich in naphthenes require less severe conditions to reach a product octane number target or aromatic concentration. Feedstock's that are lean in naphthenes and correspondingly higher in paraffin's require more severe operating conditions.

To obtain specific quality product. A feedstock with a wide boiling range or one with a higher end point will also require more severe conditions to reach product targets. When reformate is produced for the purpose of feeding an aromatics complex, the boiling range of the feedstock tends to be more narrow, limited\ to the range that results in the desired aromatic species. Hydrogen/ hydrocarbon ratio. All these conditions are illustrated in figures above.

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All samples are tested to determine the octane number using the multi function portable fuel analyzer.

Table-3.4: Octaine Number For Naphta Samples Using Multi Function Portable Fuel Analyser

34.85 37.50 120 50 250 12 0.67 4 480 39.12 39.39 165 50 250 12 0.50 3 480

40.00 250 50 250 12 0.33 2 480

Table-3.5: Research octane number enhance by natural zeolite (scolecite)

7. DISCUSSION OF OCTANE NUMBER RESULT

87.9

The using of Zeolite in refinery is very important to solve many problem of fuel, and it had many uses in refinery processes to produce friendly product. In this study use tow kind of zeolite natural (scolecite) and synthetic (Y) in reforming process to increase gasoline octane number all these zeolites are get good probably for that purpose. The synthetic zeolite get very good result it rise the octane number from 40 in heavy naphtha to 93.5 this result in higher than the octane number can product by alumina loaded platinum in refinery of Khartoum company during the sample was omitted from. For that reason this study may success for increase gasoline octane number. The natural zeolite (scolecite) also get suitable result for increasing octane number from 40 in heavy naphtha to 87.9 but it not like synthetic one, for that natural zeolite used more purification and modification to do this work. Because it more enough, cheap and easy to collect than the synthesis zeolite. For that reason the researcher recommended to continuous more study in natural zeolite like use new methods, new elements to develop this work.

8. CONCLUSION AND RECOMMENDATION

Zeolite are stable, non toxic and preventing contamination of valuable feed stock's. Zeolite is used as heterogeneous catalyst due to stability to cavity,its thermal at high temperature and secretive even at unfavorable reactant ratio and the reaction is eco-friendly. Natural zeolites are having intercalated water molecules however after treatment of zeolite these molecules are removed and cavity which is responsible to the activity of zeolite.

The study identifies the main characteristics of zeolite Y and scolecite and the results show the most important of these types of zeolite in industrial uses. The researcher applied these zeolites in naphtha reforming process after modification and it get suitable results for increase the Sudan gasoline octane number. The researcher recommended that to continue this study to do more purification of natural zeolite.

Use of zeolite s as a catalyst in the manufacture of some fine chemicals should expand. New zeolite catalysts should be developed with improved application selectivity and new functionalities, perhaps for strong base and oxidation catalysis. New ion exchange of new micro porous oxide also may be expected. Experience has taught that the availability of new materials normally precedes by many years the discovery of all of their useful properties and the conception and development of new uses. The research should be continuing in the purification and modification of natural zeolite to be useful in many applications. Because it's economic and cheap.

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