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RESEARCH ARTICLE

STUDY THE PHYSICAL PROPERTIES OF SUDAN NATURAL AND SYNTHETIC ZEOLITES MODIFICATION BY PT ELEMENT.

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Key words:-

zeolite , DSC , TGA ,TPR and BET.
List of Abbreviations
BET : Brunauer , Emmet , and Teller
TPR : Temperature Program Redecution
TPD : Temperature Program
Determination
TGA : Thermogravimetric Analysis

Abstract

Zeolites is one of very important elements that for several application in various technologies, Zeolite material, dependence on their extremely high frame work ,extended interactive surface , ability to interact with molecules and cations . Show a wide variety of interesting properties which result in remarkable applications in the fields of catalysts, gas separation, selective adsorption and water softening. The natural zeolites are materials with their properties (that in some cases are even unique) or super than those obtained by synthetic .

The zeolite catalyst loaded with finely dispersed noble metal (Pt) have been used in hydrogenation, hydrocracking, hydroisomerization and the oxidation of hydrocarbons .

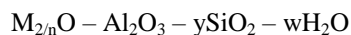
In this study the natural zeolite collected from north of Sudan and prepared it to determination the physical properties . And the other one is Synthetic zeolites (Y) . The natural zeolite (scolecite) and synthetic zeolite (Y) are modification by two methods impregnation and ion exchange using ammonium chloride and platinum hydrochloride H_2PtCl_6 to upgrade their properties . The study characterized , the natural zeolite (Scolecite) and Synthetic zeolites (Y) and their modification using different techniques as follow : Thermal analysis by two methods DSC , TGA ,TPR and measured surface area of zeolite Yby BET. The result show good characterization of two types of zeolites specially after modification with Pt element and it be ready to use in application .

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Introduction:-

Zeolites definition:-

Zeolites are crystalline aluminosilicates of group IA and IIA elements such as sodium, potassium, magnesium, and calcium. Chemically, they are represented by the empirical formula.



Where y is 2 to 10, n is the cation valence, and w represents the number of water molecules contained in the voids of the zeolite. Structurally, zeolites are complex, crystalline inorganic polymers based on an infinitely extending three- dimensional, four- connected framework of AlO_4 and SiO_4 tetrahedra linked to each other by the sharing of

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oxygen ions. Each AlO_4 tetrahedron in the framework bears in Figure (1-2) Pore size distribution of representative adsorbent. A) 5A (CaA) zeolite; B) X or Y zeolite; C) Carbon molecular sieve; D) Activated Carbon; E) porous alumina.

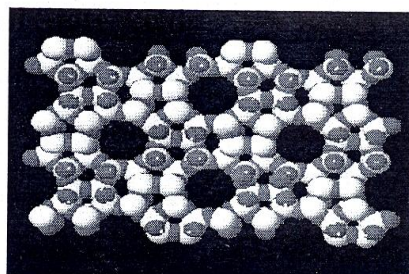
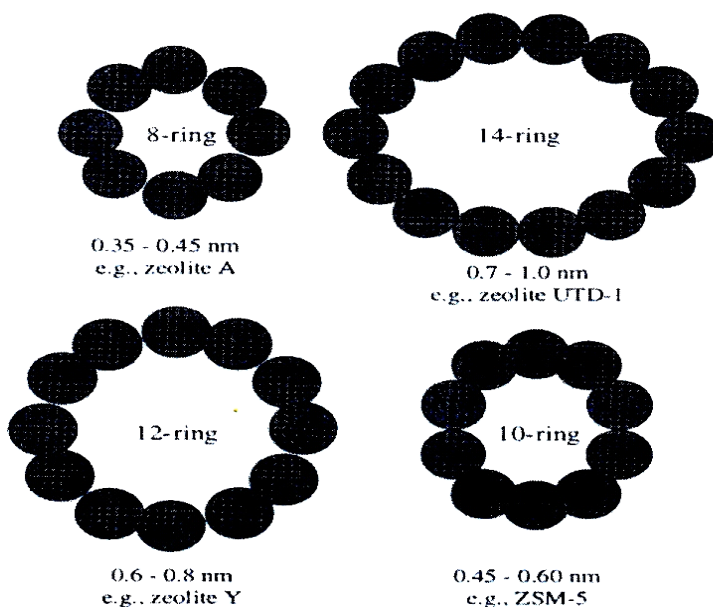


Fig. 1. Zeolite.

A net negative charge which balanced by an extra – framework cation. The framework structure contains channels or interconnected voids; the second provides a system of uniform channels which, in some instances, are one-dimensional channel systems. The preferred type has two- or three – dimensional channels to provide rapid intracrystalline diffusion in adsorption and catalytic applications.



Figure(2): Typical zeolite pore size illustrated with oxygen packing models.

In most zeolite structures the primary structural units, the AlO_4 or SiO_4 tetrahedra, are assembled into secondary building units which may be simple polyhedral such as cubes, hexagonal prisms, or Cubo- octahedral. The final framework structure consists of assemblages of the secondary units.

More than 70 novel distinct framework structures of zeolites are known. They exhibit pore size from 0.3 – 1.0 nm, and pore volumes from about 0.10 to 0.35cc/g. typical zeolite pore size using oxygen- packing models are shown in figure 2. They include small pore zeolites with eight – ring pore with free diameters of 0.30 – 0.45nm, e.g., zeolite A; medium pore zeolites formed by a ten ring, 0.45 – 0.60nm in free diameter, e.g., ZSM-5 large pore zeolites with 12- ring pore, 0.6 – 0.8nm, e.g., zeolites X and Y; and extra large pore zeolites.

The zeolite framework should be viewed as somewhat flexible, with the size and shape in fig (2).

The illustration of the molecular sieve effect, is such that the straight chain molecular normal octane (left) passes through the eight- ring aperture of 5A (Ca A) zeolites; while the branched molecule iso- octane (right) cannot.

Zeolite are crystalline aluminosilicate with an open, three dimensional frameworks consisting of tetrahedral SiO_4^{4-} and AlO_4^{5-} units linked through shared oxygen as continuous array. They were discovered by a Swedish mineralogist, constant in the eighteenth country. The SiO_4^{4-} and AlO_4^{5-} units are illustrated in Figure (3).

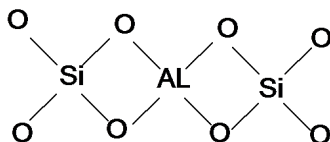


Figure 3:- SiO_4^{4-} and AlO_4^{5-} units in zeolite. Zeolites are micro porous crystals of alkali or alkali earth aluminosilicates with the following stoichiometry:

$\text{M}_x/\text{n} (\text{AlO}_2)_x (\text{SiO}_2)_y, \text{wH}_2\text{O}:-$

With being the valence of the cation M, x and y integers with y/x equal to greater than, and number of molecules of water per cell.

The crystal lattice is built of a three dimensional arrangement of tetrahedrons $[\text{SiO}_4]$ and $[\text{AlO}_4]$ connected by their apexes. These sequences form polyhedrons that are arranged according to a given symmetry to make the crystal. The void delimited by the aluminosilicate skeleton is organized into a network of cavities connected by pores of uniform size. The effective pore diameter, variable depending on the type of zeolite, is of the same order of magnitude (3 to 10 Å) as that of most organic molecules. This explains the name “molecular sieve” given to these adsorbents. The M cations and the water molecules make up the extra-skeletal species. The cation offsets the negative charges generated by the aluminum atoms of the skeleton and can be involved in exchanges to adjust adsorption properties.

Zeolites occurring:-

The zeolites form a large family of aluminosilicates which has been studied by mineralogists. For more than 200 years. This is illustrated by the dates discovery of individual members of the group, recorded by break fire crystals are often found lining cavities and cracks in basaltic rocks of volcanic origin. The cavities are considered to be formed by bubbles of fluids in the parent magma, and the zeolite crystals grow as a result of the chemical action on the magma of these fluids or of fluids which have subsequently displaced them.

In general the bulk compositions of the zeolites tend to correlate with those of the parent rock—more aluminous zeolites are associated with rocks deficient in silica and more siliceous zeolites with rocks high in silica. There may be more than one zeolite species present and evidence is sometimes found of slow replacement of one zeolite by another rather than of co-crystallization. Zeolite of this volcanic origin is usually dispersed in occurrence and is not there for suitable for industrial purposes.

More massive deposit occurs as very small crystal grains in certain sediments and grade metamorphic rocks. Some of these deposits are extremely large. Aqueous and normally alkaline solutions acting upon volcanic ash deposited in lakes account for much of the zeolitization of this kind. Phillipsite and clinoptilolite are found in ocean sediments and are again thought to have formed from volcanic debris. Zeolites are sometimes found in arid alkaline soils which may also be rich in salts. Beds rich in zeolites may be hundreds of meters thick; indeed beds of tuff converted largely or in part to zeolites can reach thicknesses of several kilometers. Some deposits can be primarily of one zeolite species and the deposits may contain little else than zeolite.

Zeolites occur in nature and have been known for almost 350 years as aluminosilicate minerals. Example is faujasite, mordenite, offretite, ferrierite, erionite and chabazite.

Zeolites are a large class of highly crystalline aluminosilicate materials, defined by a network of linked cavities or pores of molecular dimensions that gives rise to their molecular sieving properties.

Zeolites are also known as molecular sieves. Molecular sieves, zeolites are a class of stable mineral and synthetic crystalline inorganic compounds characterized by the presence of an open three dimensional oxide framework structure. This open structure leads to a regular network of uniform pores of specific molecular dimensions. The porous structure enables the zeolite to selectively admit some molecules while excluding those that are too large to fit into the pores. This leads to its molecular sieve properties.

Zeolites are a large class of highly crystalline aluminosilicate materials, defined by a network of linked cavities or pores of molecular dimensions that gives rise to their molecular sieving properties.

Zeolites properties:-

The tetrahedral coordination of the aluminum atoms in the framework generates charge deficiency, which is balanced by cations, which are not an integral part of the framework. Water in zeolites can be removed thermally at around 400 to 500°C and this leaves the zeolite in its active state when the zeolite is dehydrated, the cations become highly mobile and can be replaced by ion exchange to varying degree depending on the particular zeolite structure and the exchanging cation. The type and number of cations present affects the catalytic, adsorptive and ion-exchange properties of the zeolites. It should be noted that the zeolites available are cations and not anion exchangers and zeolites. Silica-alumina ratio too has a bearing on the above mentioned properties.

The aluminum containing materials exhibit characteristic zeolite exchange properties and therefore, should be regarded as a molecular sieve and not a zeolite.

Besides, zeolites are also regarded as shape selective catalysts. It is based on the formation of active catalyst sites inside the zeolite pore system, which is very uniform in one or more discrete sizes.

Molecules with dimensions similar to or slightly larger than zeolite pores can usually diffuse through the pore structure due to the molecular vibration or breathing of the zeolite pore and the vibration of the loaming atoms on the diffusing molecule or perturbations of its structure. Bond cleavage, followed by reconstruction of the bond has been suggested for the diffusion of some in organic materials. In this case, the rate of diffusion controls the rate of reaction rather than by any catalytic phenomenon. Shape selectivity catalysis involves the reactivity of primary, secondary and tertiary carbon atoms, which can be classified into three major classes. They are reactant selectivity, product selectivity and restricted transition state selectivity.

Zeolite is an active catalyst. Hydrogen exchanged zeolites give rise to high acidity selective reactions can occur over zeolites. They can also serve as oxidation or reduction catalysts. It happens often after a metal has been introduced into the framework.

The following is a summary of some catalytic elements of the zeolites:

- defined micro pore system
- crystal size and morphology can be manipulated
- Thermo stability
- Bronsted and Lewis acidity
- Cations at choice
- Dispersion of cations adjustable
- Metal incorporation possible
- Hydrophilicity or hydrophobicity spectrum.

Structures and classification of zeolites:-

There are hundreds of zeolite species occurring naturally or synthetically, and millions more have been hypothetically proposed. Zeolite crystals are constructed from an underlying three-dimensional network of TO_4 building block units. Within this network there are loosely bonded exchangeable cations, adsorbent phases and the building block central atom is tetrahedral coordinated with four oxygen atoms. Predominantly, Si, Al or P is the element in the center of the tetrahedral building blocks and is referred as the t-atom. Zeolite networks are constructed by specially accommodating the To_4 building blocks by corner sharing the oxygen located at their crystal. Thus, these underlying networks depend directly on the connectivity of TO_4 units. Other zeolite crystal components such as cations, adsorbents' phase chemical composition, and observed crystallography properties are irrelevant in the determination of underlying network. There are topological differences between networks in different crystals. The question, what makes zeolites so special when compared to other crystalline inorganic oxide materials, can be answered by mentioning a combination of properties:

The microspores character with uniform pore dimensions, allowing certain hydrocarbon molecules to enter the crystals while rejecting other based on too large a molecular size, the ion-exchange properties which allow to perform all sorts of ion exchange reactions, the ability to develop internal acidity which makes the zeolites interesting materials for catalyzing organic reactions and the high thermal stability of the zeolites.

Zeolites can be classified as natural or synthetic zeolite. Natural zeolites are formed through a chemical reaction between volcanic glass and saline water for over 50,000 years. Most natural zeolites are homogeneous and contaminated. Synthetic zeolites whereas are free of contamination.

Table 1:-Classification of zeolites based on framework topology.-

Groups	Secondary Building Units (SBU)
1	Single, 4- ring, S4R
2	Single, 6- ring, S6R
3	Double, 4- ring, D4R
4	Double, 6- ring, D6R
5	Complex 4-1, T_5O_{10} unit
6	Complex 5-1, T_8O_{16} unit
7	Complex 4-4-1, $\text{T}_{10}\text{O}_{20}$ unit

The relatively simple configurations resulting from their linkages are called secondary building units. Some of the more common secondary building units found in zeolite framework is illustrated in figure (4).

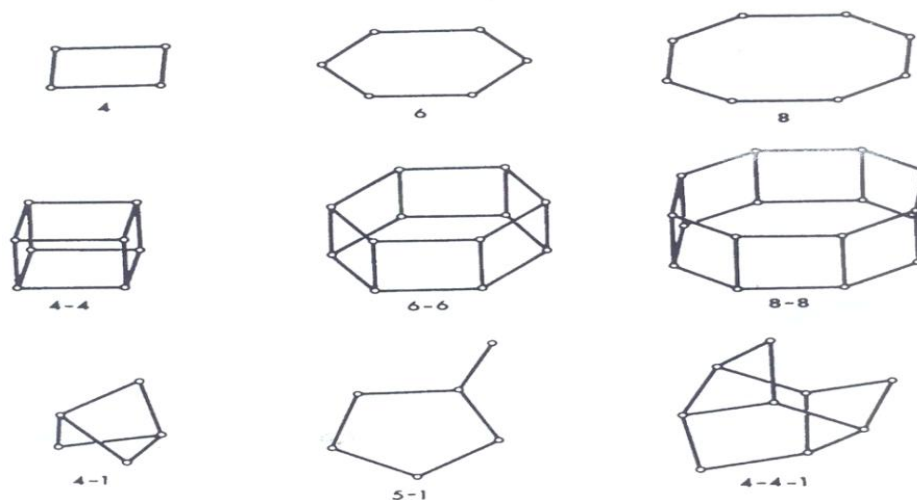


Figure 4.2. Secondary building units of zeolite framework

Figure (4) Secondary building units of zeolite framework:-

There are over 45 known different framework topologies for natural zeolites, and nearly 150 synthetic type have been reported.

The remaining 113 zeolites span ranges pore widths which coincides with the range of dimensions of a very large number of molecules. It is furthermore seen from Fig. 4 that zeolite with eight ten and 12-membered ring pores for which, respectively, the terms small-pore, medium-pore and large-pore zeolites are customary, strongly predominate with a total of LOH structures, whereas the super-large-pore materials with pores formed by more than 12 TO_4 -tetrahedra and materials with pores formed by an odd number of TO_4 -tetrahedra are still scant.

One advantage of zeolites is their regular intracrystalline pore system, formed a three dimensional network of corner sharing TO_4 -tetrahedra ($\text{T}=\text{Si}, \text{Al}$). This creates the high surface area of zeolites, with over 9970 (depending on the crystalline size) inside the bulk. The space of these molecular scale microspores, which depends upon the precise architecture, is responsible for the shape selective properties of the zeolitic catalysts. Until now more than 30 different natural and over 50 synthetic zeolite structures are known.

The availability of new zeolite structures yearly increase, reading the impressive number of 179 different framework types known today. Each of them is characterized by a peculiar porous structure and may differ from the others in terms of free dimension of the pore openings, dimensionality of the pore system (1D, 2D or 3D), presence or absence of cages. Since the diffusivity and reactivity of the organic species involved in a catalytic process i.e. reactants, intermediates, products) strongly depend on their interaction with the inorganic framework, it is clear that a deeper insight into these phenomena is necessary not only for an accurate interpretation of the catalytic data but even for prediction. The behavior of a given zeolite.

Today, these and other zeolite structures are of great interest in catalysis, yet their naturally occurring forms are of limited value, because (i) they almost always contain undesired impurity phases, (ii) their chemical composition varies from one deposit to another and even from one stratum to another in the same deposit, and (iii) nature did not optimize their properties for catalytic applications.

It was only with the advent of synthetic zeolites from catalyst that this class of porous material began to play a role in catalysis.

The terms zeolites, micro porous material and molecular sieve are there form of ten used as synonyms indicating that the regular array of micro pores with well-defined dimensions is the unifying principle which renders this wealth of materials attractive for catalysis (and other application).

Applications:-

Zeolites are crystalline material with regular structures consisting of molecular sized pores and channels. These crystals are widely used in the field of adsorption, ion-exchange, heterogeneous catalysis (basically all gasoline

production employs zeolite catalysts), as well as health applications, sensors energy conversion. The dimensions of zeolites channels and their ability to adsorb gases and water have made zeolite molecular sieves suitable for a number of applications such as in the areas of refinery fuel processing, production of chemicals and environmental pollution control.

A wide variety of industrial applications of zeolites, mainly catalysis and separations, exist. Development of the methanol to gasoline (MTG) process by Mobil in the 1970's (increased gasoline yield from each barrel of crude oil by 50 percent and improved octane number) and development of methanol to olefins (MTO) process by UOP/ hydro in 1996 (UOP/ hydro 2007) spurred petrochemical zeolite applications. Heterogeneous catalysts have an edge over liquid – phase processes waste minimization, wide range of possible process operating conditions, and ease of product separation are some advantages.

However, solid- acid catalysts cannot replace all industrial homogeneous catalysts. Difficulties in reactant and product diffusion to and from the zeolite surface in the absence of solvent are major obstacle.

There are three main zeolites industrial application: catalysis, gas separation and ion exchange (Lentech 2007). A more detailed description is available elsewhere .

Porous inorganic materials such as zeolites and zeolite like crystalline molecular sieves are of great interest because of their range of commercial applications such as catalysis, adsorption/separation, and ion exchange, the term zeolite refers to the specific class of aluminosilicate molecular sieves, although the term is frequently used more loosely to describe compounds other than aluminosilicates that have frameworks similar to known zeolites.

Physical and Chemical properties of zeolites:-

Before a zeolite can be used for a certain application it's necessary to characterize this zeolite, to see if it has the desired properties for that application. If not, another synthesis method should be used or the zeolite must be modified, to meet the specific cations. Zeolite synthesis; modification, characterization and application .

Of course not all zeolite properties are of the same importance every application. This aspect is illustrated in fig (4) in which is indicated, which characteristics are of special importance for the main application of three different zeolite A in detergents particle size and morphology are extremely important while acidity and stability play a minor role.

These characterizations, however, are just of crucial importance for the application of zeolite y in cracking catalysts for this reason we will discuss the different characterization methods in relation to the application for which the specific property is important .


















Important characteristic	Type of Zeolite		
	Zeolite A	Zeolite y	ZSM-5
Structure defects			
Pore-Size			
Chemical composition			
Framework Si/Al Ratio			
Acidity			
Stability			
Morphology particle size			
Important application	Absorbent ion exchanger in detergents	Cracking catalyst	Shape selective catalyst

Fig. (4) Most important characteristics for three well-known zeolites and their major .

Table 2:- The physical and chemical properties of zeolites as the framework $\frac{Si}{Al}$ ratio is increased:-

$\frac{SiO_2}{Al_2O_3}$	From 0 – 5 infinity
Stability	From 700°C to 1300°C
Surface selectivity	From hydrophilic to hydrophobic
Acid site density	Decreasing
Acid strength per site	Increasing
Cation concentration	Decreasing
structure	From 4 – 6 – and 8 – membered rings to 5 – membered ring

The reactivity and the selectivity of molecular sieve zeolites as catalysts are determined by active sites. The active sites are provided by an imbalance in charge between the silicon and the aluminum ions in the framework. Each aluminum atom contained within the framework structure induces a potential active acid site. The replacement of SiO_4 tetrahedra by the $(AlO_4)^{-1}$ tetrahedra in the zeolite framework causes excess negative charges and protons are needed to neutralize them. Compensation the negative charge by an associated cations, e.g. H^+ , Na^+ , K^+ , Ca^{2+} , NH_4 generate the acid sites.

If the charge compensating cation associated with the tetrahedral aluminum is hydrogen, the zeolite surface obtains the capacity to act as a proton donor and therefore can serve as a Brønsted acid that is proton – donor acidity,

When hydrogen for zeolite is heated to a temperature than 550°C, lewis acid site and water occur. Lewis acidity is electron acceptor acidity. One Lewis acid site is formed from two Bronsted acid sites. Formation of lewis acid site. If transition metals are introduced into the zeolite by conventional ion exchange techniques, a third type of active site can be generated.

Material and methods:-

Natural zeolite collected from 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 upgrade their properties. 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 hydrogenolysis.

On other hand, the ion exchange technique normally brings about a strong metal –support interaction. The physical properties were characterized by the Analysis used, the thermal analysis (DSC, TPD, TPR), surface area BET, scan electron, atomic absorption were done also. All this techniques was implicated to synthetic zeolite Y also.

Catalyst Preparation:-

Various techniques 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 hydrogenolysis.

On other hand, the ion exchange technique normally brings about a strong metal –support interaction.

Impregnation:-

Impregnation is the simplest and most direct method. The objective is to fill the pores with solution of a metal salt of sufficient concentration to give the loading.

The impregnation method involves three steps:

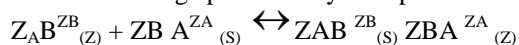
- With excess of solution. The support is placed on a screen and dipped into an excess quantity of solution for the time necessary for total impregnation the solid is then drained and dried
- With repeated application of solution. A more precision control is achieved by this technique termed dry impregnation or impregnation to incipient wetness. The support is contacted with a solution of appropriate concentration, corresponding in quantity to the total known pore volume or slightly less. The catalysis is kept in motion in rotated cylinder or a drum, and sprinkled as required with a solution of salt by sprayer.

For both techniques the main operating variable is the temperature which affects both the precursor solubility and the solution viscosity and as a consequence, the wetting time.

Ion Exchange Method:-

Ion Exchange is the reversible interchange of ions between a solid and a liquid in which there is no permanent change in the structure of the solid that is the ion-exchange material usually contacting the zeolite with a salt solution of different cation performs ion exchange reaction one type of cation is replaced with another.

The ion exchange process may be represented as follows



Where ZA, ZB are the charges of the exchange cation A and B, the subscripts z and s refer to the zeolite and solution, respectively the ion exchange behavior of the zeolite depends upon:

- The nature of the cation specie, the cation size both anhydrous and hydrated and the cation charge
- The charge temperature
- The concentration of the cation specious in solution
- The anion specious associated with the cation in the solution
- Solvent
- The structure characteristics of the particular zeolite.

Plating method :

This method was done by used the plating instrument to preparing zeolites to be ready to use in catalysis application.

Commercial (Na Y) Zeolite and Scolecite preparation:-

The NaY zeolite was supplied by union carbide corporation with an atomic ratio of Si/Al = 2.36 and was highly crystalline.

The acid form of this zeolite was obtained by ion exchange 200g zeolite y are mixed careful, continue the mixed from period to period with NH₄ solution NH₄ < 99%) with aqueous ammonia access aqueous ammonia was added slowly to the 200 g of Zeolite (NaY) with vigorous stirring at 70° C then the PH was increased up to 7 by drop wise addition of aqueous ammonia with stirring after stirring at 70° C for 24 h, the precipitated gel (H/Y) was filtrated

and washed thoroughly by distillation water until the PH becomes less than 7, dried at 110 °C for 12 h, and subsequent calcination in air atmosphere at 530 °C for 4 h, resulting in acid form (H/Y).

The supported metallic catalyst was prepared by incipient wetness impregnation using 0.35 mass% metal from H₂ PtCl₆ added 200 ml from H₂ PtCl₆ solution to the zeolite H/Y, heated in temperature 110 °C min⁻¹ for 12 hours in dynamic air flow at a rate of 50 cm³ min⁻¹ and calcinated in 530 °C for 4 hours.

The Pt/H/Y and H/Y the properties determined by instrument surface area BET and, thermal analysis (DSC,TPD ,TPR were done also.

2- All the experiments before was do to the natural zeolite scolecite and the characteristics were studied too by Thermal Analysis by TPR and TPD, , DSC, and surface area. The Zeolite were characterized by Thermo analytical measurement were carried out on a perkin Elmer Ta A-7 instrument and on a perkin Elmer Data -17000 instrument with 1 m% of purity the acid properties of pt/H/Y and Pt/H/Scolecite zeolite were investigated to upgrading the product properties.



Figure 2-1:a shows the zeolite Y plating.



Figure 2-2:- b shows zeolite scolecite plating.

Characterization:-

In general, the characterization of a zeolite has to provide information about, the ability to sorb and retain molecules and the ability to chemically convert these molecules. Information on the structural, chemical and catalytic

characteristics of zeolites is essential for deriving relations between their chemical and physicochemical properties on the one side and the sorptive and catalytic properties on the other side. Such relations are of high importance, as they allow the rational development of sorbents, catalyst and advanced structural materials. In this study, the zeolite was synthesized from rice husk ash and the main uses are as cation exchangers and sorbent, thus only characterizations with respect to these applications are being dealt with in depth. There are many characterization techniques but the important physical ones in this study are studied. Each of the characterization techniques will be described below.

Analysis by temperature programmed reduction (TPR):-

(TPR) measurement were carried out in amicomeritics (chemisorb 2705) system provided by a thermal conductivity detector (TCD)

to monitor the H_2 consumption. A quarter U-tube was packed with a small amount (0-1g) of calcined sample. Before the measurement, the sample was gradually heated up to $200^\circ C$ at $10^\circ C/min$, held for 1 h, and then cooled down to $25^\circ C$ under argon atmosphere. Afterwards, the reduction carrier gas of 5% H_2 / N_2 was flowed through the reactor at rate of 40 ml/min. The TPR was taken by heating the reactor up to $1000^\circ C$ at a constant rate of $10^\circ C/min$. The water product was trapped by passing the effluent gas plus liquid nitrogen ¹³⁰.

Thermal Analysis of Zeolites Y (Synthesis) and Scolecite (Natural):-

Zeolite are framework aluminosilicates with open channels containing molecular water and extra framework cations. Their distinctive crystal structures endow them with high cation-exchange capacities and molecular sieve capabilities, which are widely applied in water softening, catalysis and waste water treatment. Thermodynamic data are essential to determine the stability of zeolites and evaluate their Paragenesis.

Reversible dehydration of intracrystalline water in zeolites is an important consideration for assessing their stability particularly at elevated temperatures and pressures.

In this study, we have directly measured heat or temperature of zeolites by simultaneous differential scanning calorimetric (DSC), and thermo gravimetric analysis (TGA) system and used the TPD, TPR also. The temperature dependence of enthalpies of hydration H_{hyd} in zeolite and scolecite. The temperature dependence of H_{hydro} provides an alternative means of assessing C_p .

In addition, the stability of zeolites with respect to other aluminosilicates is dependent on their hydration state as hydrated zeolites are often stable at earth surface conditions with respect to dense aluminosilicate assemblages and free water, but their dehydration are not. In fact, accurate prediction of the partial dehydration of zeolites can be key to understanding their stability in geologic environments – Dehydration also has a dramatic effect on the ion-exchange properties of zeolites.

Hydrothermal systems often produce zeolites as well with complex Parageneses caused by overprinting of diagenetic and metamorphic occurrences. Zeolite stability is sensitive function of pressure, temperature and fluid composition, making them useful indicators of the physical and chemical conditions associated with petroleum resources, geothermal resources and basalt-hosted ore deposits in earth's crust. Zeolites and associated authigenic clay minerals can significantly reduce the porosity and permeability of hydrocarbon reservoir rocks, and their presence is often regarded as an economic basement of exploration for oil and gas.

In addition, they are frequently considered as passive barriers in radioactive waste repositories both as sorptive barriers radionuclide migration and consumption of thermal energy.

The response of zeolites to changes in temperature and water vapor pressure is a very important aspect of their behavior and structural change. Detailed studies of the structural effects accompanying dehydration processes allow evaluation of the changes in environmental conditions that ultimately lead to structural modification or breakdown.

Zeolites are divided into three categories according to their thermal stabilities. Those with:-

1. Reverse rearrangement of the extra framework cations and residual water molecules.
2. complete or nearly complete reversible dehydration accompanied by a large distortion of the framework and significant decrease in unit-cell volume and
3. irreversible dehydration accompanied by irreversible change in the framework.

Equilibrium between a zeolite and water vapor can be represented by a reaction of the form.

$ZnH_2O = Z + nH_2O$ vapor, where ZnH_2O and Z are homologous hydrated (water sites occupied) and dehydrated (water sites vacant) components of a zeolite and n is the number of moles of H_2O in the fully hydrated zeolite. The one approach to determine thermal of zeolite is transposed temperature drop calorimetry in which H_r is determined via thermochemical cycle involving dehydration of the zeolite at high temperatures (usually and heat content of the hydrated 973) zeolite and water.

Determination of the temperature dependence of C_p of hydrous mineral at super ambient conditions, particularly those that dehydrate continuously with temperature such as zeolite presents considerable experimental obstacles.

Calorimetric measurements of C_p by adiabatic, drop, or differential scanning Calorimetry (DSC) on these materials will inevitably include contribution not only from C_p but also the heat of dehydration.

Calorimetric technique:-

All the calorimetric measurement were performed on the net zseh STA49C Jupiter simultaneous thermal analysis system at of Florida. A schematic depication this system is shown in fig 1-3.

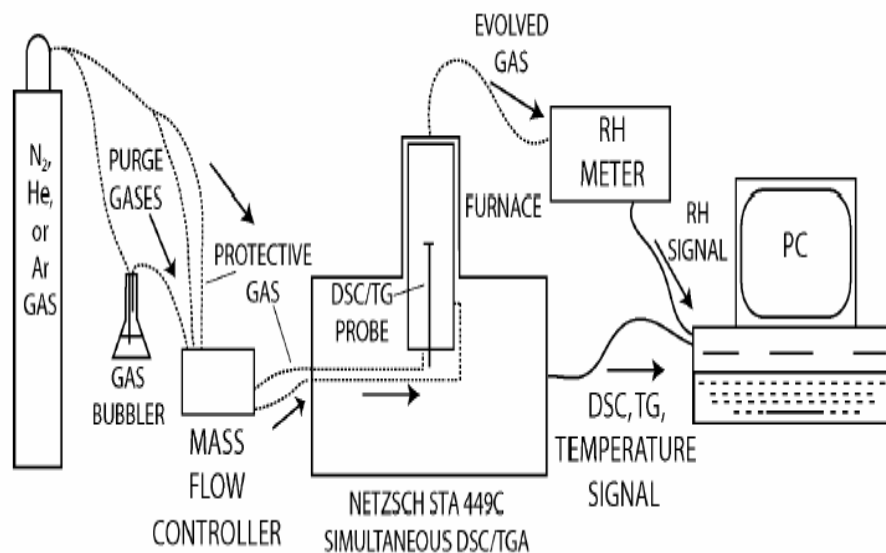


Figure 2-3:- Schematic representation of the simultaneous DSC/TGA system. Dashed

Curves represent gas lines; solid curves represent data transfer cables between the instruments and the computer.

The core component is a vacuum – tight, liquid nitrogen cooled furnace enclosing a sample carrier housing and electrode for measurement of temperature differences between the sample and reference pan, generating a heat flux DSC signal and thermo gravimetric analysis. With respect to setup is that the DSC and TGA signals are signal to be interpreted directly in terms of water loss or gain to the sample as measured by TGA. The temperature range for the furnace is 120 to 1050 K; temperature can be maintained within this range to a precision of better than 1K and for dynamic analysis can be run at controlled heating or cooling rates of up to 50K/minute. Samples as large as 5 gr and as small as 1 mg can be investigated, although sample sizes of the order of a few 10's of mg are optimal. Mass changes as small as 0.1 μ g can be detected. Calorimetric precision varies with experimental conditions and the amount of heat involved; instrument specification call C_p precision on the order of 2.5% and heat of reaction precision on the order of 3%.

Temperature and caloric calibration is performed by measuring the melting temperatures and heats of fusion high purity metal standards and C_p of sapphire disks. Temperature, DSC, and TGA signals are sent via data analysis.

Experimental conditions can be controlled with respect to not only temperature but also pressure. Experiments can be run under closed system conditions at total pressures ranging from atmospheric to vacuums of 10⁻⁴ torr, although typical operation involves a flowing gas atmosphere at atmospheric pressure – gas composition and flow rate are controlled externally via mass flow controllers, gases used in the experiments are ultra high purity He (for sub ambient temperatures) and N₂ (for C_p measurement and measurements under controlled humidity conditions). Humidity is a constant temperature, with water vapor pressure (P_{H₂O}) varied by mixing H₂O – saturated and dry N₂ gas in proportions. Humidity on the out and recorded by a sample systems RH-100 flow – through view point/relative humidity analyzer (1% accuracy in P_{H₂O} down to 1 pa).

Heat Capacity Measurements:-

The heat capacities of hydrated and dehydrated scolecite and zeolite Y were also determined by DSC also on the simultaneous DSC-TGA system. Each experiment consisted of four separate runs: 1) determination of background and baseline by measurement of an empty crucible; 2) DSC measurement of a standard (sapphire); 3) scanning heating of hydrated

scolecite and 4) scanning heating of dehydrated analcime. A sample of approximately 1.0 mg was packed into a covered Pt-Rh crucible before step 3 and kept to the end of the experiment. Data were collected in the range of 298 to 873 K at a scanning rate of 15 to 19 K/min. A purge of dry N₂ was used during the experiment to keep the relative humidity below 1%, and the gas flow was maintained at ~30 ml/min using mass flow controllers.

The furnace was heated to 873 K in each run and then cooled back to room temperature by liquid N₂ before the next step. During heating, hydrated zeolite lost mass with increasing temperature and finally became completely dehydrated. The resulting dehydrated analcime was kept in an environment of dry N₂ to avoid rehydration during cooling to room temperature and then measured by scanning heating again. Heat capacity of the sample as a function of temperature was calculated by

$$C_p = \frac{m_{std}}{m_s} \times \frac{DSC_s - DSC_b}{DSC_{std} - DSC_b} \times C_{p,std}$$

where m_s is the mass of sample, m_{std} is the mass of standard (27.314 mg), DSC_s , DSC_{std} and DSC_b are for sample, standard and baseline respectively. Triplicate calorimetric measurements were conducted and averaged. Based on previous measurements in this lab the precision was taken to be 1% of average value.

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 to determine the characterization shown in figure below.

Thermal analysis of scolecite:-

TPR and TPD analysis:-

Figures (2-4), (2-5 and (2-6) below show the temperature reduction and thermal determination programs of zeolite scolecite, and scolecite after treatment with ammonia and after treatment with platinum hydrochloride (H_2PtCl_6). The figures illustrated increase in zeolite stability temperature after treatment with ammonia and platinum.

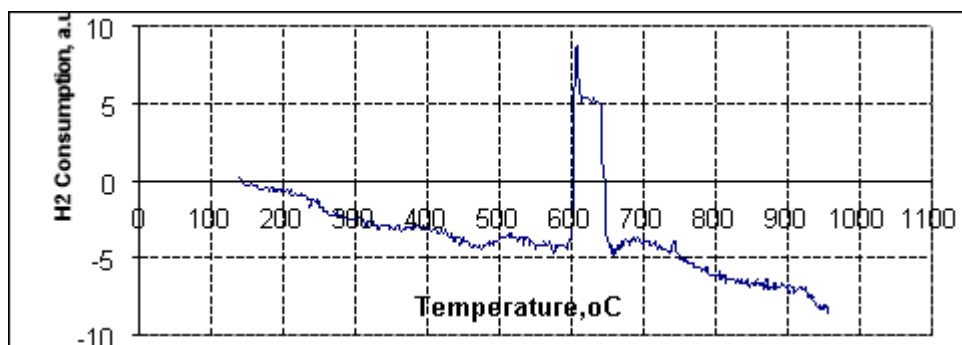
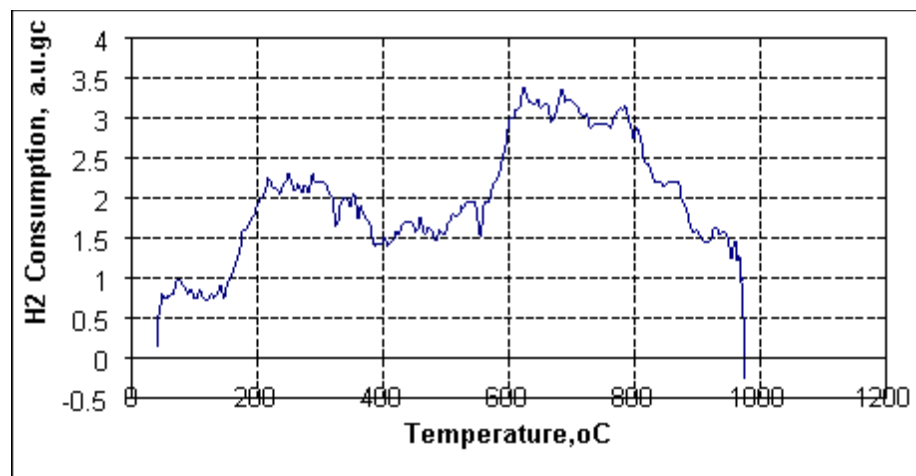


Figure (2-4) TPR/SCOLECITE



figure(2-5) TPR of H/SCOLECITE

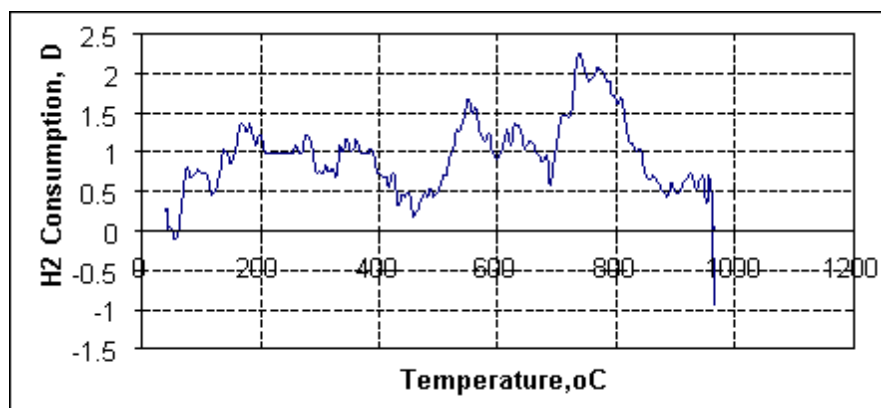


figure (2-6) TPR of Pt/ H/SCOLECITE

3-3-5- DSC and TGA analysis of scolecite zeolite:-

Figures (2-7), (2-8) and (2-9) show the temperature analysis of scolecite zeolite, scolecite treated with ammonia (H/ scolecite) and scolecite treated with platinum hydrochloride (Pt/H/scolecite) by DSC and TGA analysis.

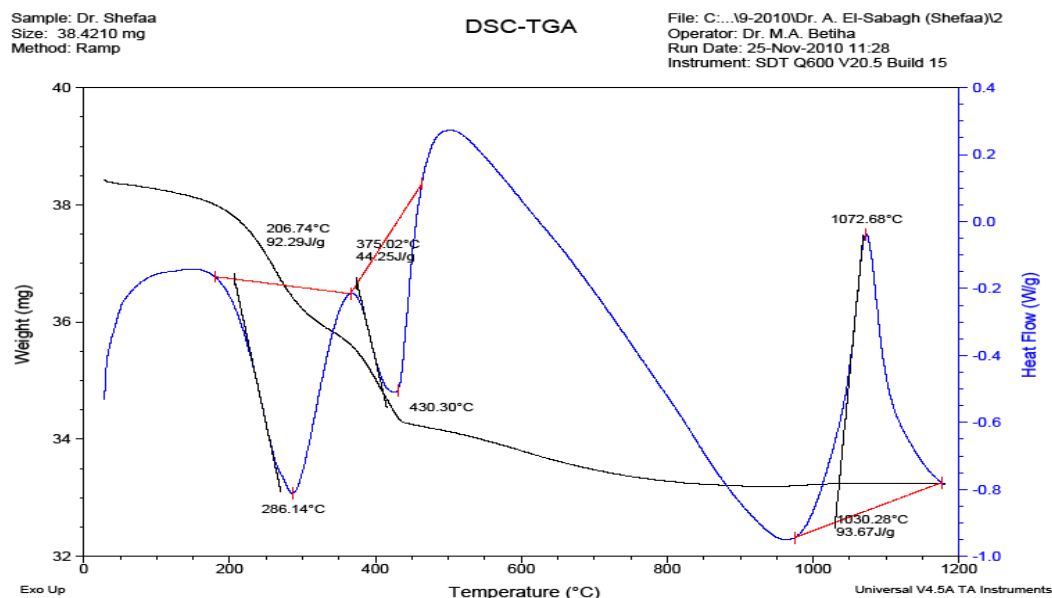


Figure 2-7:- DSC and TGA analysis of scolecite zeolite.

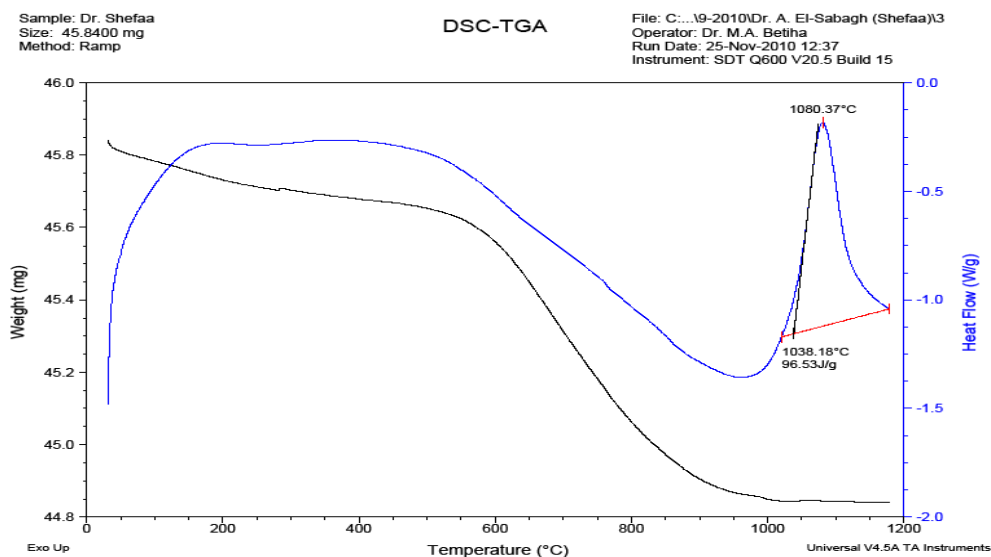


Figure 2-8:- shows DSC and TGA analysis of H/ scolecite zeolite(zeolite treated with ammonium)

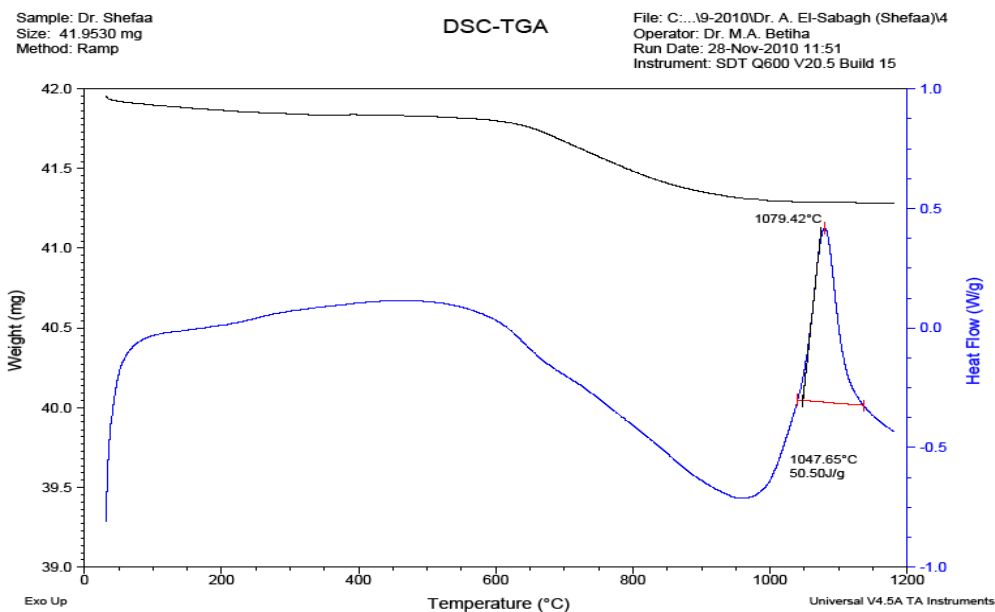


Figure 2-9 DSC and TGA analysis of Pt / H/ scolecite zeolite.

Characterization of Zeolite (y):-

TPR analysis of zeolite Y:-

figures (2-10) , (2-11) below show result of TPR of zeolite Y, zeolite Y treated with ammonia (H/Y) and zeolite (Pt/H/Y) treated with H_2PtCl_6 .

Evidently the thermal stability of zeolite was enhanced after treatment with Pt .

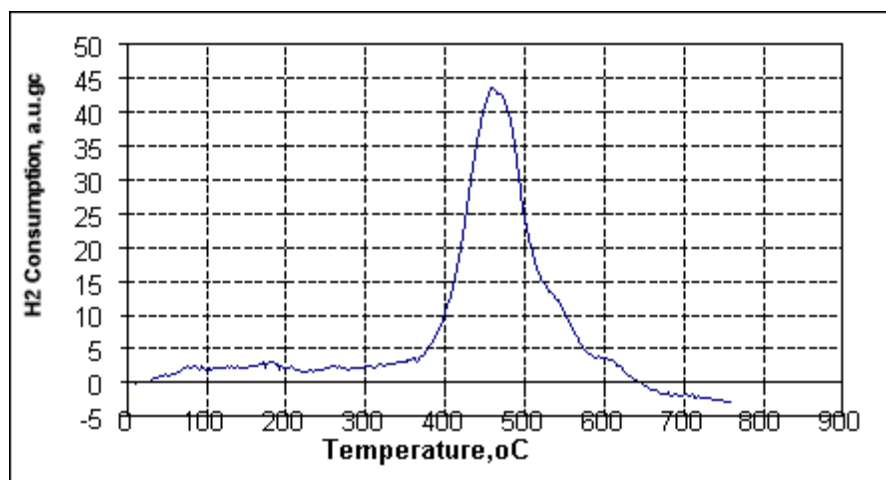
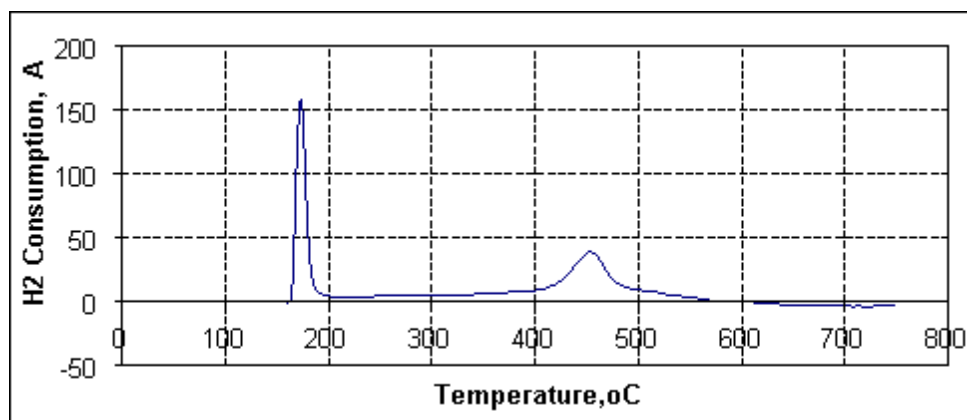


Figure (3-10) TPR analysis of H/Y



Figure(3-11) TPR analysis of Pt/H/Y

DSC and TGA analysis of zeolite Y:-

Figures(2-12 , (2-13) and (2-14) Show plots of thermal analysis of zeolite Y , zeolite H/Y treated with ammonia and zeolite H/Y treated with H_2PtCl_6 by differential scanning calorimetry and thermogravimetric analysis respectively . The temperature DCS of zeolite Y was increased in zeolite after treatment with ammonium ,and Pt . these results illustrated the enhance of thermal stability of zeolite Y .

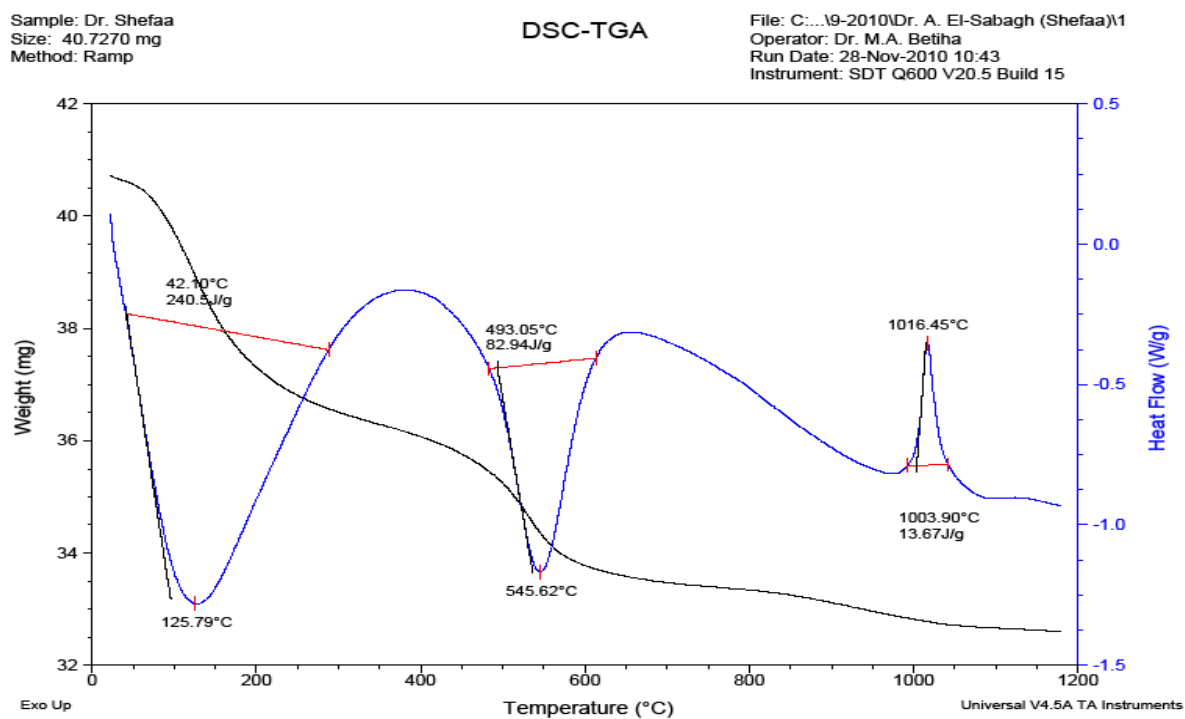


Figure 2-12:- DSC Analysis of Zeolite Y.

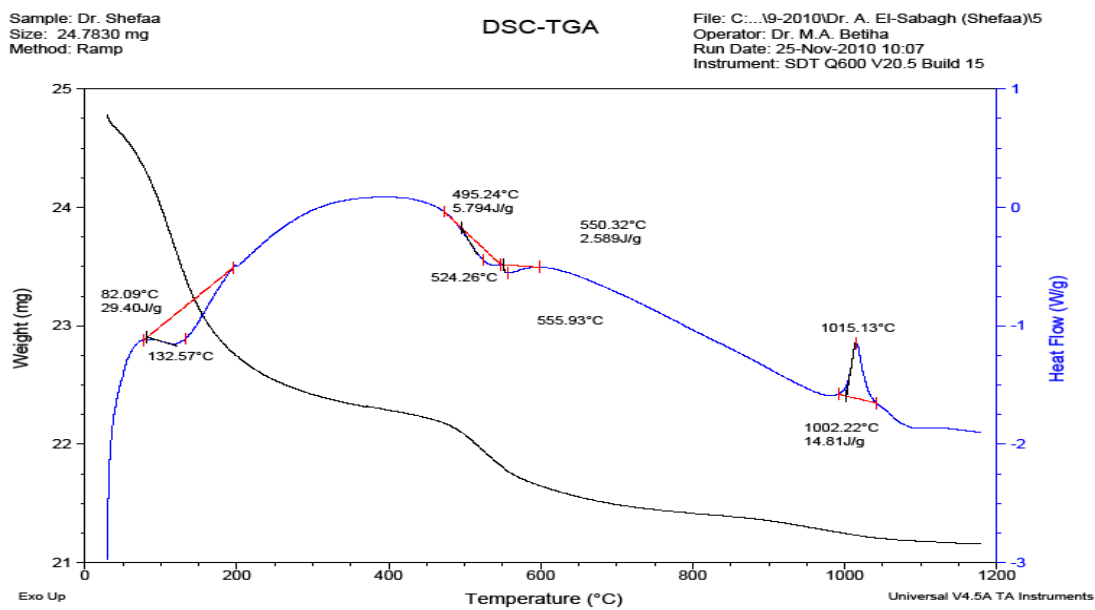


Figure 2-13:- DSC Analysis of Zeolite H/Y.

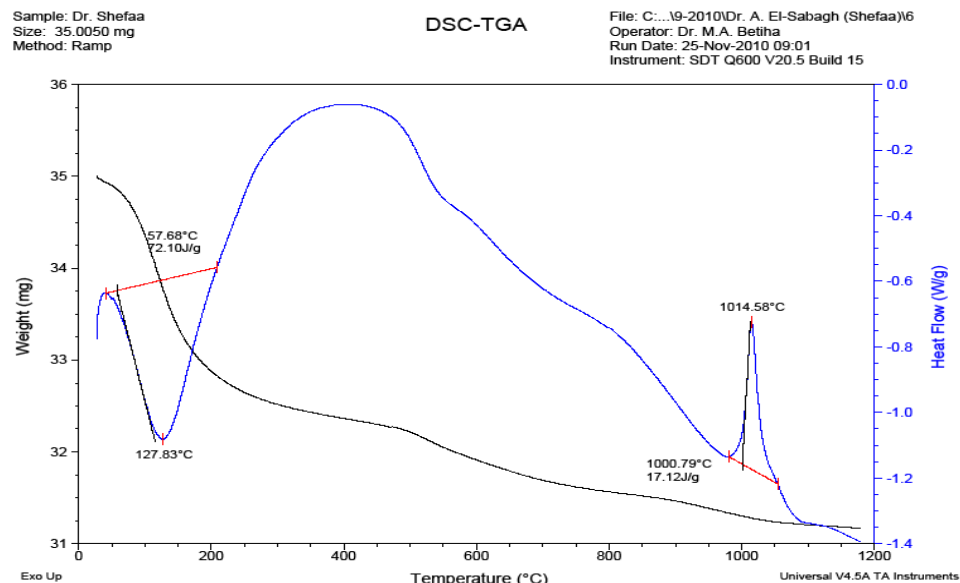


Figure 2-14:- DSC Analysis of Zeolite Pt/H/Y.

Surface area of zeolite Y:-

Figure (2-11) , (2-12) and (2-13) show plots of surface area of zeolite Y , zeolite Y treated with ammonia and zeolite Y treated with platinum hydrochloride respectively . Figure (3-46) gave the surface area of 350, while the surface area of zeolite after treated with ammonia and Pt increased to 340 and 370 respectively

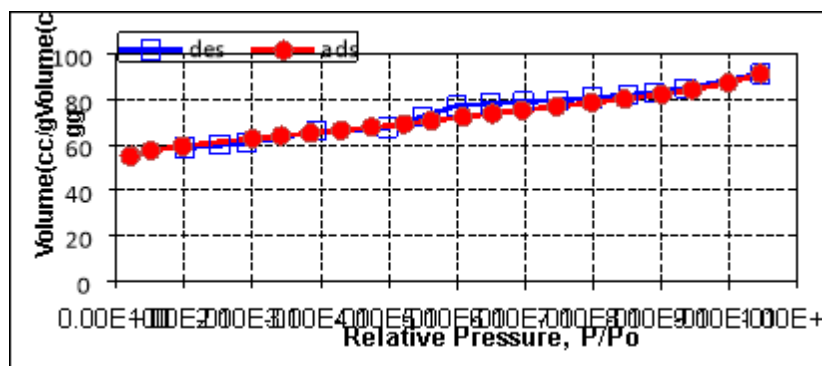


Figure (2-15) Surface area of zeolite (Y)

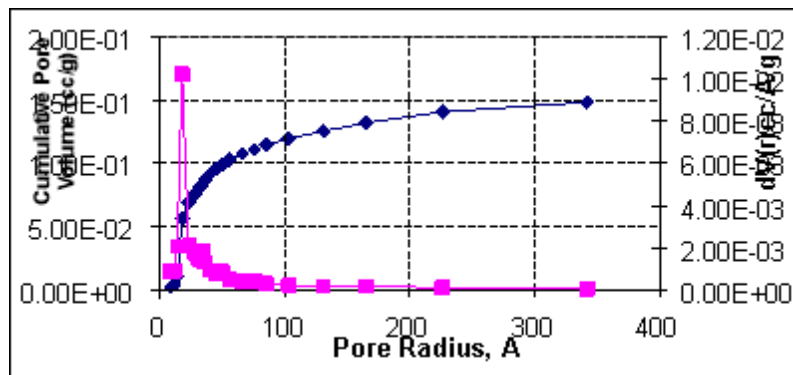


Figure (2-16) Surface area of zeolite (H/Y)

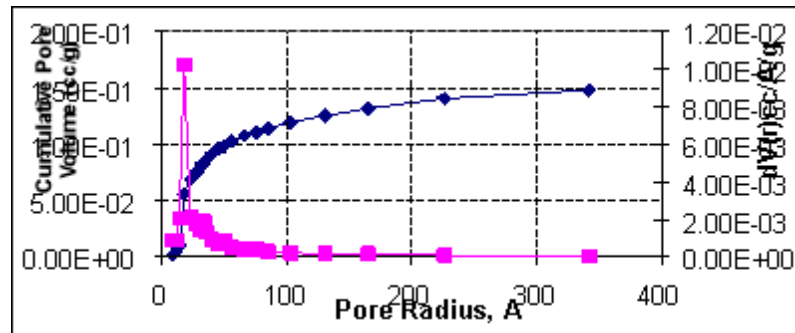


Figure (2-17) Surface area of zeolite (Pt/H/Y)

Conclusion and Recommendation:-

Zeolite are stable, nontoxic 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 selective 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 characterization after modification and it gets suitable results. The researcher recommended that to continue this study to do more purification of natural zeolite.

Use of zeolites 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 microporous 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 continued in the purification and modification of natural zeolite to be useful in many applications. Because its economic and cheap.

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