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RESEARCH ARTICLE

DETERMINATION OF THE NATURAL ZEOLIES CHARACTERISTICS IN SUDAN COUNTRY

Ardelshifa Mohammed Elhassan

King Saudi Arabia Quassim University, College of Science and Art OyunAljwa

A R T I C L E I N F O

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A B S T R A C T

This work aims to Knowledge of the characteristics of natural zeolites because it is essential for multiple applications.
Nearly 200 years the geologists discovery zeolite, we considered the zeolite mineral to occurs as large crystals in the vugs and cavities of basalts and other traprock formation. Natural zeolites found in volcanogenic sedimentary rocks. They are many area in Sudan have very much of natural zeolites in different areas and it many types of natural zeolite. In this work selected one type of natural zeolite (ZK-5) and determined the characters. Whenthe properties of natural zeolites compare with synthetic one it low cost natural material, and it no less mportant in terms of its application than industrial zeolite. Natural zeolites have been used as building stone, as lightweight aggregate and pozzolans in cements, sofling nuclear waste and fallout, in the removal of ammonia from municipal industrial, and soften drinking water, Absorbent carbon", which is actually an adsorber, also has an affinity for water at some sites, which decreases its capacity to adsorb organic molecules from streams containing water molecules. This can be either true or false for zeolite depending on the type of zeolite that you select. Generally, the higher the silicon to aluminum ratio, the more hydrophobic the zeolite.
zeolites demonstrate higher thermal stability and also selectivity with respect to the most hazardous toxic expands the area of their application for treatment of radioactively contaminated aqueous solutions [2]. For those properties now it be fledged mineral commodities. In this context for the study we selected Zk-5 zeolite natural.
Natural zeolite samples were collected from different areas in Sudan.from Wad Kawly in Gadarief region eastern of Sudan Second sample was collected from Bayouda desert in the Northern region). Samples were characterized by X-ray diffraction analysis (XRD) showed these samples to be composed Thomsonite, Scolecite and ZK-5 as Natural zeolites.
And choice one (ZK-5) to determined its properties .In this work we illustrates some properties of natural zeolite using multiple techniques like , IR ,TPR, DSC.And atomic Absorption Spectrophotometer (AAS) used to determined chemical composition (other elements content). Scanning Electron Microscopy (SEM) used to determined internal structure and Infra Red Spectroscopy (IR). Also the characters determination relying on the thermal stability etc.
The results show in figures bellow good properties for Sudan natural zeolite zk-5 and it be comfortable to use in many application.

INTRODUCTION

Zeolite is a rock composed of aluminum, silicon, and oxygen. It occurs naturally inseveralregions of the world where prehistoric volcanic activity has happened near water, or the water has been present for millennia since the eruption. In 1756, the Swedish mineralogist Baron Axel Fredrick Cronstedt discovered zeolite. One account has his dog digging up the stone and him naming it zeolite from a word which means "dog" in Swedish. In another account, he found that when the zeolite (it was actually Stilbite) was heated it gave off steam. Zeolite means "boiling stone" in Greek. Since I do not know either Swedish or Greek, you will have to judge whether either or both of these stories are correct. We do know for sure that zeolite was discovered.

Natural zeolites are environmentally and economically acceptable hydrated aluminosilicate materials with exceptional ion-exchange and sorption properties. Their effectiveness in different technological processes depends on their physical-chemical properties that are tightly connected to their geological deposits. The unique three dimensional porous structure gives natural zeolites various application possibilities.

Because of the excess of the negative charge on the surface of zeolite, which results from isomorphic replacement of silicon by aluminum in the primary structural units, natural zeolites belong to the group of cationic exchangers. Numerous studies so far have confirmed their excellent performance on the removal of metal cations from wastewaters.

However, zeolites can be chemically modified by inorganic salts or organic surfactants, which are adsorbed on the surface and lead to the generation of positively charged oxihydroxides or surfactant micelles, and which enables the zeolite to bind also anions, like arsenates or chromates, in stable or less stable complexes.

Zeolite has a natural porosity because it has a crystal structure with windows, cages, and supercages. The natural zeolites are limited in their window size ("pore size") and are all hydrophilic (having an affinity for water). Some synthetic zeolites are similar to an absorbent carbon, since both can be considered hydrophobic (having an affinity for organics, with lack of or a decreased affinity for water), and can adsorb organic vapors with molecules smaller than their "pore size." With both carbon and zeolite you can adsorb water and organic molecules; however, that for which it has affinity will displace the other molecules. Zeolite has a uniform "pore size" which leads to it being referred to as a "molecular sieve," while carbons appear to have pores leading to smaller pores leading to still smaller pores ad infinitum.

Zeolite-like crystal structures have even been created by substituting other elements for either the aluminum or the silicon in the synthesis, but the zeolite that we will discuss here is purely an alumino-silicate.

There have been 40 natural zeolites discovered; 118 zeolites have been cataloged by the Structure Committee of the International Zeolite Association; more than 600 zeolites have been identified, and, if you were to include zeolite-like crystal structures using other elements, the number would be increasing daily. One zeolite is not exactly like any other.

Zeolites are a well-established technology used in a range of processes and industries. Zeolites are not new materials—they have been investigated for over two and a half centuries, with stilbite and natrolite both being identified in the 1750s. Industrial applications include catalysis in the petroleum industry, various uses in agriculture, horticulture, gas separations, domestic water treatment and nuclear waste processing. The value of zeolite catalysis to petroleum cracking is well in excess of $200 billion. About 50 naturally occurring zeolites have been identified; over 150 synthetic zeolites have been prepared and characterized; and further thousands of combinations of framework and composition are available. Zeolites have long been used in the nuclear industry owing to their properties as ion exchangers. The planned siting of the United States' first deep geologicradioactive waste repository at Yucca Mountain in Nevada, where design philosophycalled for both engineered and natural barriers to inhibit the transport of any potentially leaking radionuclides, was influenced considerably by the localabundance of the natural zeolites mordenite and clinoptilolite, both of which have largecationic exchange capacities.

Description

Zeolites are crystalline aluminosilicates, compositionally similar to clay minerals, but differing in their well-defined three-dimensional nano- and micro-porous structure. Aluminum, silicon, and oxygen are arranged in a regular structure of [SiO4]- and [AlO4]- tetrahedral units that form a framework with small pores (also called tunnels, channels, or cavities) of about 0.1-2 nm diameter running through the material. Figure 1 shows a representation of a typical zeolite framework. It should be clearly noted that this is just one of a large and growing number of types of zeolite framework. In 1970, the Atlas of Zeolite Framework Types listed 27 known frameworks, but by 2003, the number had grown to 145. The variety of size and shape available for the pore structure is the source of zeolites' catalytic activity that is so important to the petrochemical industry.

A second consequence of the framework being built from negatively charged units is that it possesses a net negative charge that must be balanced by the presence of positively charged cations. Most naturally occurring zeolites have the environmentally predominant sodium ion as a loosely bound counter ion. These can be readily displaced by other ions for which a particular framework has a much greater affinity, thus giving zeolites significant ion exchange properties.

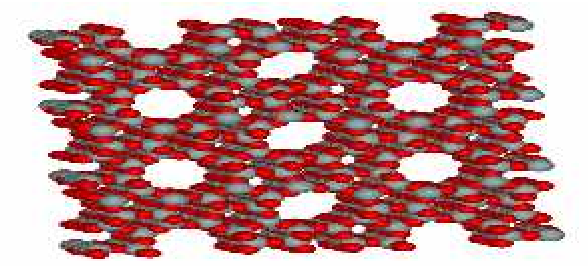


Figure1 zeoliteframework

Natural zeolite exists as a natural rock, and these can reach boulder size. However, synthesized zeolite crystals are always less than a millimeter in size -- because the crystals grow slowly, and we usually want the zeolite in this century or millennium. These small grains can rapidly transport the adsorbed molecule to the adsorption area. Air flow through a bed of zeolite powder creates a large pressure drop. Granular zeolites have now been developed in which grains are bonded together to create larger air flow channels, and hence have lower resistance to air flow.

Zeolite structure

The structure of a zeolite crystal is based on a tetrahedron formed by four oxygen atoms joined to a silicon atom by its four valence electrons. These tetrahedrons are joined at the oxygen "corners" to make crystals. When aluminum is present while the crystals form, the silicon is replaced by aluminum atoms which have only three valence electrons. The remaining valence electron is usually provided by either hydrogen or sodium because they are commonly found in the hydrating water. This distorts the tetrahedron and makes an "acid site" for exchange of other ions. This also makes the structure hydrophilic. If the zeolite is formed in a mix that contains an organic cation (i.e., a cation having a carbon backbone), the structure can be formed around the organic cation, using it as a template. This has led to silicon-rich hydrophobic zeolites with large enough "pore size" (or window size) to admit all but the largest petroleum molecules. The crystal structure of a zeolite consists of windows, cages, and super cages. The windows are how the molecules reach the cages and super cages to be adsorbed or catalyzed. The cages are the smaller cells in the crystal structure. The super cages are cells in the crystal structure that are larger than cages and may even contain cages.

The Chemical Structure In general formula, $M_xD_y[Al_{x+2y}Si_{n-(x+2y)}O_{2n}]$. mH_2O.Where: M, are monovalent and D, are divalent cations.

The portion in square brackets represents tetrahedral framework and is characterized by overall negative charge which increases as the Si/Al ratio decreases. The exchangeable cations which neutralize framework negative charge. Where (m) water molecules.

Structures of ZK-5 zeolite

The basic structural element of the zeolite ZK-5 crystal lattice is the 26-hedron (icosihexahedron) (or-cage), which is geometrically identical to the largest cage of zeolite A [1]. The icosihexahedrons are interconnected by 6-membered double rings consisting of tetrahedrons (hexagonal prisms) to form several smaller 18-hedrons, decaoctahedrons, (3,-cages). The access to each of the ~- or 3,-cage is encircled with six 8-membered oxygen rings. In or-cages all the rings are identical and only slightly deformed. Each v-cage consists of two 8-membered rings, with two a-cages. The other four 8-membered rings are highly deformed and connect the 3,w, age with the four neighboring ones.

The Si/A1 ratio in zeolite ZK-5 is usually 2.0-3.5 [2, 3]. However, a low-silica zeolite ZK-5 (Si/A1 = 1.5-1.7) was obtained from a Li20-Na20-AI203 -SiO2-H20 system, and described in [4]. It was shown that the smaller Si/AI ratio has a substantial effect on the properties of the molecular sieve: The intracrystalline volume of the low-silica zeolite (in contrast to high-silica) is impenetrable by hexane molecules at 291 K and by nitrogen molecules at 77 K.

ZK-5 structure: $Na_{24}Al_{24}Si_{72}O_{192}.H_2O$ $=12\ Na_2O\ .\ Al_2O_3+72\ SiO_2+90\ H_2O$

Zeolites properties and uses:-

Zeolites are important industrial materials used in the separation and catalytic transformation of organic molecules.

- The unique adsorption and catalytic properties of zeolites are a consequence of the zeolite micro pores' dimensions being the same magnitude as the small organic
- Molecules occluded in them. As a result, subtle changes in the framework geometry, composition, and number and identity of extra framework cations often lead to large differences in the diffusivity and reactivity of molecules occluded in zeolites. The catalytic properties and diffusivity of these occluded molecules are determined in general terms by the forces between the organic molecules and the zeolite structure. These organic–inorganic interactions are also important in the context of zeolite synthesis and structure-direction

While a fundamental understanding of the mechanisms of structure-direction is still incomplete, the interactions between the organic structure-directing agent (SDA) and the inorganic phase play a crucial role in determining what material is obtained from synthesis. The forces experienced by occluded molecules can range from weak dispersive van der Waal interactions with the zeolite framework and quadrupolar interactions with extra-framework cations, to strong hydrogen-bonding or electrostatic interactions between the organic molecule and inorganic framework.
These forces are difficult to predict quantitatively apriority, but can often be deduced from knowledge of the rotational modes of motion (frequently anisotropic) exhibited by the occluded organic molecule. Over the past few years a variety of investigations have studied the motion of occluded organic molecules in zeolites.

The importantcharacteristicsof Zeolite their uses

- Zeolite is capable of selective ion exchange.
- Zeolite can adsorb molecules on its large internal area, provided they can pass through the windows. Zeolite and carbon are both the same in this respect, just differing in the adsorption area that can be reached by a given molecule passing through their "pores."
- Zeolite can be a solid acid catalyst. It can function as a strong acid (though it remains solid) when the hydration has substituted a hydrogen for the additional valence electron, or isoelectronic exchange with the aluminum occurs.
- Zeolite can be used as a molecular sieve because it has a uniform window (or pore) size.
- Zeolite is metastable; i.e., it is stable as long as it is at a suitable temperature and pH. Within this range, it is unaffected by wide swings in temperature, pressure, and ionizing radiation.
- Zeolites beused to control air pollution
- Zeolites can be used over a wider temperature range than carbon, and are generally superior to carbon as an adsorber, Separation of carbon dioxide from flue gas.
- Zeolite has been used as a molecular sieve to remove sulfur dioxide from flue gas. Sulfur oxides are also a product of processing some ores. Sulfur oxides are constituents of acid rain. Reducing the emissions of them could have a profoundly beneficial effect on the environment.
- A natural zeolite) can remove ammonia from wastewater. It has been used to control ammonia from urine in both "kitty litter" and horse stables. It is also used to adsorb VOC that cause odors from mildew, foot fungus, and carpets. It regenerates in sunlight and clean air.
- It is noteworthy that zeolite can even be used to catalyze oxidation of hydrocarbons in the presence of light. However, it can be very selective in these reactions according to CHEMTECH, 1996, 26(6), 24-30 American Chemical Society.
- Zeolite has been used in water softening. Passing hard water through a bed of zeolite to exchange the calcium and magnesium ions prevents them from forming insoluble soaps which we see as "soap scum." The zeolite can be regenerated by passing salt brine through it. The chlorides of the exchanged ions are water-soluble and therefore disposal is easy. Because natural zeolites are attacked by acidic tap water, more resistant materials are now used, although hydrophilic zeolite was used for decades.
- *Zeolite have use out side of controlling air pollution.* In treatment of radioactive wastes, zeolite is used to remove radioactive cesium and strontium from wastewater. Since zeolite is impervious to even high doses of radiation, it is used to exchange and trap these ions. It is capable of removing radioactive strontium at a concentration of 1 microgram per liter while sodium is present at 150,000 times that concentration. The zeolite is in powder or sand-size grains which are then

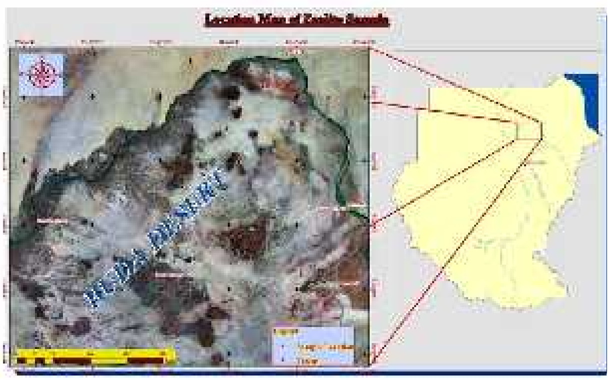
used as a filler in concrete. The concrete is then cast in drums for disposal. This method of disposal is deemed impervious to salt water leaching, and the radioactive waste can be disposed of either in a landfill or by ocean dumping.

- Zeolites are used only once, are "builders" in detergents. Zeolite is used as a "builder" and replaces most of the sodium tripolyphosphate which was formerly used and found to be environmentally harmful. Here again the zeolite removes calcium and magnesium ions from the water.
- The use of zeolite catalysts in "catalytic crackers" in oil refineries was dependent upon discovery of a large window zeolite that was hydrophobic. Zeolite catalysts now reduce our consumption of petroleum imports by $8 to $16 billion dollars per year. Added to that savings is the reduced carbon dioxide emissions from reduced energy requirements of refineries.
- Zeolite is used as a dryer for compressed air. Its acts as a desiccant to adsorb moisture. It can hold up to one-fourth of its weight in water without an appreciable rise in vapor pressure.
- Zeolite is also used in refrigerators to dry out the refrigerant. This prevents the formation of ice crystals which could clog the flow passages and valves.
- Slow release fertilizers use zeolite to control their release to the soil. Urea is converted to ammonia by soil bacteria. Clintoptilolite adsorbs the ammonia, and prevents the soil bacteria from converting it to nitrate. Subsequent slow leaching of the ammonia allows this nitrification to occur over a period of months. Otherwise, the surge of nitrates would wash out of the soil and pollute both groundwater and streams.
- Zeolite is used to separate nitrogen from oxygen in air. The small difference in size between a nitrogen molecule and an oxygen molecule, along with polarization and a suitable zeolite, allows oxygen to be adsorbed selectively from air. The nitrogen is vented, and the oxygen is then desorbed. This is used to generate oxygen for aircraft crews, industrial processes, and aquariums.

MATERIAL AND METHODS

Sample preparation

Samples of zeolite deposits Natural zeolite, were collected from north and east 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.

Experimental s and Characterization

Various techniques used to determined the properties by Analysis .There are many characterization techniques but the important ones in this study are X-ray diffractogram (XRD)), Powder XRD patterns of the resultant products were measured with an X-ray diffractometer (Rigaku, Miniflex) system using a Cu-Ka radiation at 40 kV and 20 mA.): Philips, Model: X\-pert PRO stress XRD analyzer Cu-target radiation is used to illisturate the crystallization of sample**.** It used for identification zeolite deposits by powder method analysis. Atomic Absorption spectrophotometer (A.A.S); Perkin Elemr Model; 2380, flame doube beam systems. It was used to determined chemical composition reported as oxides.
Sample is characterized by scanning electron microscopy (SEM) to observed the morphologies of dry gels and products were by using SEM (Hitachi, S-4500S, 13C analysisScanning Electron Microscopy (SEM): Model; TESCAN. Oxford industrial company, using energy dispersive spectrometry (EDS) system. It used for characterization by high magnification micrographs to show internal structures (pores). infrared spectroscopy (IR) andThermal 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 measured temperature of zeolites by simultaneous differential scanning calorimetric (DSC), and thermo gravimetric analysis (TGA) system and used the TPD, TPR also done to indicated the sample thermal stability . Each of the characterization techniques will be described below.

RESULTS AND DISCUSSIONS

In this research natural zeolites selected from the Sudan were characterized. Zeolite zk-5 was collected from east of Sudan, and after assigning all properties of zeolite zk-5 was done in figures bellow:

Properties of Zeolite Zk-5

Figure (2) shows thin section of zeolite zk-5 (crosspolaized light), while figure (2,3) shows the same section (pliancrosspolarized).

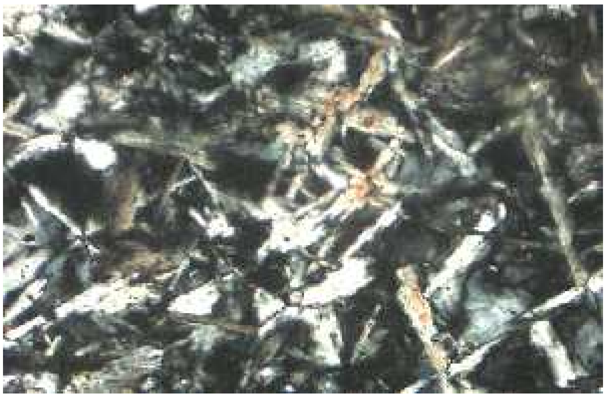


Figure 2 Thin section of zeolite zk-5 (crosspolaized light)

Figure3 Thin section of zeolite zk-5 (plain crosspolarized light)

Table 1 atomic absorption analysis of natural zeolite zk-5

Sample	Natural zeolite
CaO%	-
Al2O3%	24.1%
SiO2%	57.5%
Na2O%	24.8%
Moisture	4.6%

XRD Diffraction for ZK-5 Zeolite

The crystallization as demonstrated by XRD patterns shown in Figure 4powder XRD (Siemens D-500 diffractometer using Cuka radiation) was used to determine sample structure and crystallinity. The formation of zk-5Zeolitephase was confirmed by comparing the diffractograms of all natural sample with differactograms of the reference ZK-5 Zeolite. According to Treacy and Higgins {m}, the XRD first peak will appear in the range ($2\ \theta = 2-^{o}$) $6-10^{o}$for the zeolite zk-5, see Figure (4).

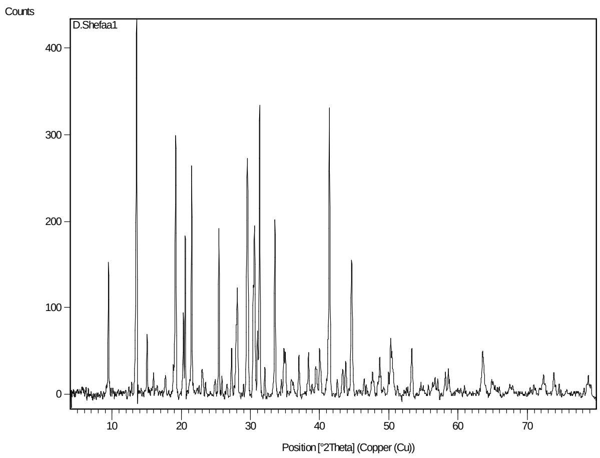


Fig 4 X-ray diffraction of zk-5 zeolite

IR characterization

Figure (5) demonstrates that the infrared spectrum of ZK-5 Zeolite without chemical processing but grinding as powder.It is reported the following positions of these bands:$634,54^{-1}$ bending [O-Si(Al)- O+ SiO- Al], 1411.80cm^{-1} stretching [Si(Al)- O], 1733.89cm^{-1} [O—O] bond of water molecules bending (OH), and around 3423.41 cm^{-1} region stretching (OH).The shifting of OH due to hydrogen bond.

Scan electron microscopy

Figures (3-5) and (3-6) shows the images and morphological of zeolite zk-5the result obsavred the smaller nano-particles in an amorphous of standard one.

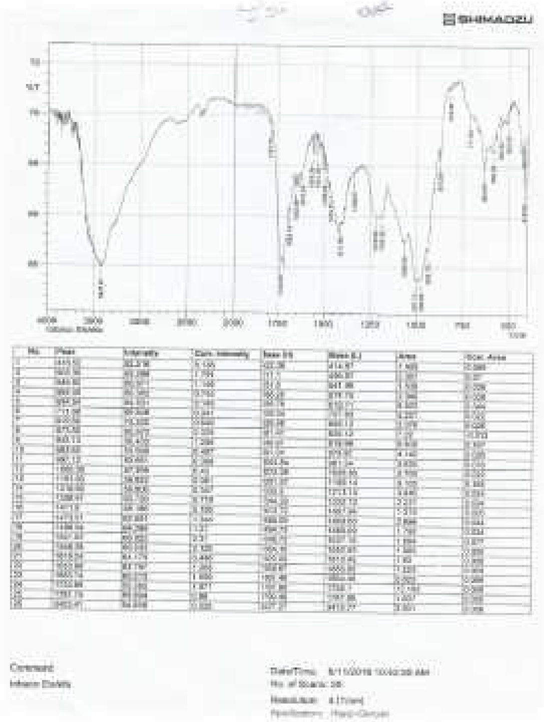


figure (3-4) IR of zeolite zk-5

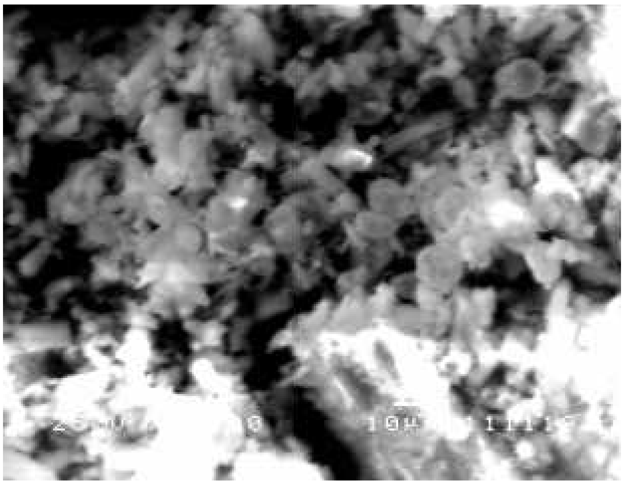


Figure (3-5) Scan electron of zk-5

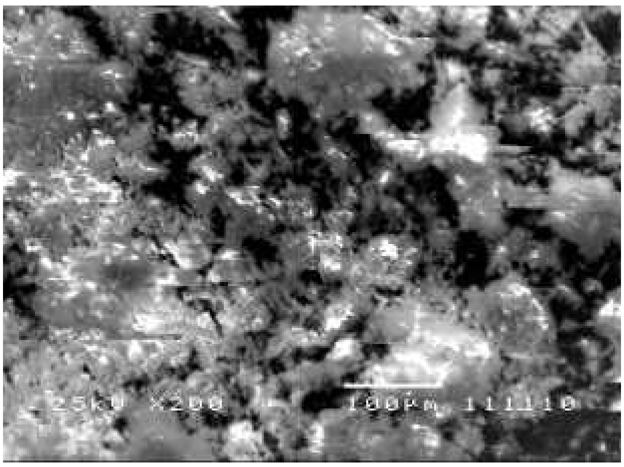


Fig. (3-6) SEM image of ZK-5 Zeolite

Thermal analysis

Figure (3-7) show thermal analysis by DSC andTGA:-

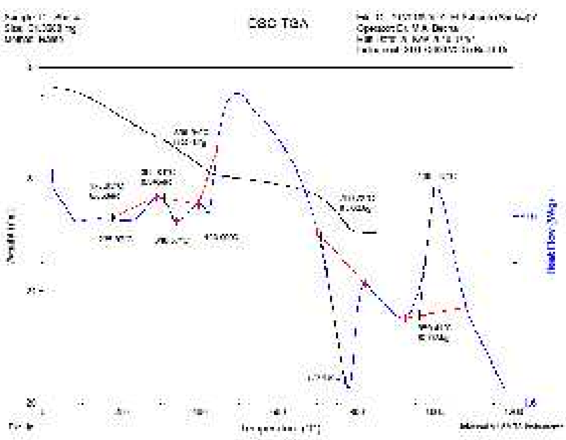


Figure (37) illustrat the DSC and TGA Analysis of Zk-5 zeolite

CONCLUSION AND RECOMMENDATION

Zeolites are important industrial materials used in the separation and catalytic transformation of organic molecules.

In general, it has been noted that the main research behind the use of natural zeolites as aremediation tool for contaminated soil has been conducted largely through laboratory andgreenhouse trials. There is very little evidence in the literature to support the long-termuse of natural zeolites in real remediation projects. It was also noted that the future potential of using zeolites has not been fully appreciated, and that there isan urgent need to undertake field trials and evaluate the in-situ efficiency for these remediation purposes.
Zeolites are a well-established technology with a variety of industrial uses ranging from construction materials and detergent builders, to catalysts and separation agents. They are one of the oldest separation technologies for the removal of radioactive components from aqueous waste streams. The flexible tectonic structure and ability to be chemically“tailored” to specific target species continues to stimulate their development. In additionto their use as an “end-of-pipe” treatment for aqueous streams, zeolites are one of the few materials offering the possibility of being an inexpensive amendment to soils contaminated with radioactive species, since extremely high species selectivity and binding strength can be designed into the material. Continued investigation of zeolites ingeneral is expected due to their catalytic properties; research in this area should support further developments, potentially leading to environmental applications.

Since zeolites are natural materials and are mainly used in industrial processes, little research is focused on their fate and transport, though an extensive volume of work existson their geological origin maintenance parameters. As would be expected, specific details are highly dependent onwaste streams involved. and behavior. Extensive data exists on operation and Seven hundred million tons of zeolite per year are used this way. Powdered zeolite has no harmful effect on the environment beyond sometimes being a nuisance dust.

Natural zeolites have advantages over other cation exchange materials such as commonly used organic resins, because they are cheap, they exhibit excellent selectivity for different cations at low temperatures, which is accompanied with a release of non-toxic exchangeable cations (K+,Na+, Ca2+ and Mg2+) to the environment, they are compact in size and they allow simple and cheap maintenance in the full-scale applications.

The results obtained in this research stage show the properties of natural zk –k zeolites from Sudan area is good and it ready to use in important applications.

For future research it is recommended to carry out an evaluation of the chemical composition of the preparation and its activity based on the weight ratio of manganese to oxygen in the preparation. Will do suitable modification and indicate another more properties of zeolite ZK-5. Based on the results of the following research, it will be possible to economically assess the whole technological process.

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