



Sudan University of Science and Technology

College of Graduate studies



Thermal Conversion of Kaolin to Zeolite

التحويل الحراري للكاولين الى زيوليت

A Thesis Submitted in Partial Fulfilment for the Requirements for the
Degree of Master of Science in Chemistry

BY

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إِسْتِفْتَا ح

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قَالَ تَعَالَى:

﴿ وَإِذِ اسْتَسْقَى مُوسَى لِقَوْمِهِ فَقُلْنَا اضْرِبْ بِعَصَاكَ الْحَجَرَ فَانْفَجَرَتْ مِنْهُ اثْنَتَا عَشْرَةَ عَيْنًا قَدْ عَلِمَ كُلُّ أُنَاسٍ مَشْرِبَهُمْ كُلُوا وَاشْرَبُوا مِنْ رِزْقِ اللَّهِ وَلَا تَعَثُوا فِي الْأَرْضِ مُمْسِدِينَ ﴿٦٠﴾ ﴾

سورة البقرة الآية (60)

صدق الله العظيم

Dedication

To my Parents

To my brothers and sisters.

Acknowledgement

Firstly I would to thank Allah, the most Merciful, Gracious, for giving me the strength and good health to complete this research.

Secondly thanks are due to my supervisor Dr. Mohammed Suleiman Ali Eltoum, for suggesting the idea of this work and guidance during all stages of the research.

I am also grateful to any person who worked with me in any way in this research such as technical staff of the chemistry department, Sudan university of science and technology for their help and finally thanks are due to my family for their constant support.

Abstract

In this research preparation of zeolite from a locally available kaolin has been studied. Two steps were involved in the conversion of kaolin to zeolite (1) thermal activation of the kaolin to get a dehydroxylated product called metakaolin (metakaolinisation) and (2) hydrothermal reaction (zeolitisation) of metakaolin in alkaline medium in the presence of additional silica to crystallise the zeolite. The metakaolinisation temperature (800°C) is found to have an important role in determining the type of zeolite formed during the hydrothermal reaction. Zeolite was obtained from kaolin under hydrothermal preparation. The obtained products were characterized using different analytical techniques x-ray fluorescence (XRF), x-ray diffraction (XRD), IR spectrometry. XRF was used to estimate the percentage or content of silica and alumina in the kaolin before use in the preparation of zeolite, the obtained data from XRD and IR spectrum agreed well with expected characteristic peaks of zeolite.

المستخلص

في هذا البحث تم تحضير الزيوليت من خام الكاولين المحلي وذلك من خلال التفاعل الذي يتضمن خطوتين (1) تنشيط حراري للكاولين لينتج ميتا كاولين (الكاولين المنشط). (2) التفاعل الثيرموحراري (الزيوليت) للميتا كاولين المنشط عند 800 درجة مئوية ووجوده الذي يلعب دور مهم في تحديد نوع الزيوليت من خلال التفاعل الثيرمو حراري، فتم الحصول على الزيوليت من التفاعل الثيرمو حراري. وتم تحليل المركبات الناتجة باستخدام تقنيات مختلفة شملت الأشعة السينية الفلورنس و الأشعة السينية نظام الحيود والأشعة تحت الحمراء وتم استخدام الأشعة السينية الفلورنس لمعرفة نسبة السيلكا والألومينا في الكاولين قبل استخدامه في تحضير الزيوليت. والأطياف الناتجة من المركبات المحضرة باستخدام الأشعة السينية نظام الحيود والأشعة تحت الحمراء أعطت الإمتصاصات المتوقعة للزيوليت.

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Chapter one

1- Introduction and literature review

1.1- Kaolin:

Kaolin is a soft, white plastic clay consisting mainly of the mineral kaolinite, which is a hydrated aluminum silicate $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is formed by the alteration of feldspar and muscovite. It is an important industrial mineral, which is used in many industrial applications. Kaolin (china clay) is a hydrated aluminum silicate crystalline mineral (kaolinite), formed from weathered granite that once sat below the earth's surface. It is one of the most common minerals on earth and can be easily identified by its fine particle size and plate-like structure. The world's largest reserves of premium kaolin are located in the United States and Brazil. Seventy million years ago, in the United States, the Atlantic coastline stretched from Columbus to Augusta, and the southern part of Georgia was covered by the sea. Weathered crystalline rocks from the Piedmont Plateau (now the foothills of the Smoky Mountains) began to break down and rushing streams carried the tiny feldspar and kaolinite crystals seaward to form large sedimentary deposits in what we refer to today as Georgia's fall line. These reserves are world renowned for their brightness, purity and fine particle structure. Banks of the Jari River in the Amazon region in the northeastern section of Brazil ⁽¹⁾. Are much like Georgia kaolin, these deposits are known for their brightness, purity and fine particle size, while delivering unique rheological properties in customer formulations . identifying the actual crude reserves. After mining, clays are further cleaned and purified through a series of processing technologies to ensure the quality and consistency of products. See info graphic for a look at all of our different processing steps ⁽²⁾.

1.1.1- View Kaolin Processing Info graphic:

kaolin will found in paper, paint, rubber, plastic, ink ,adhesives, sealants and many other products ⁽³⁾.

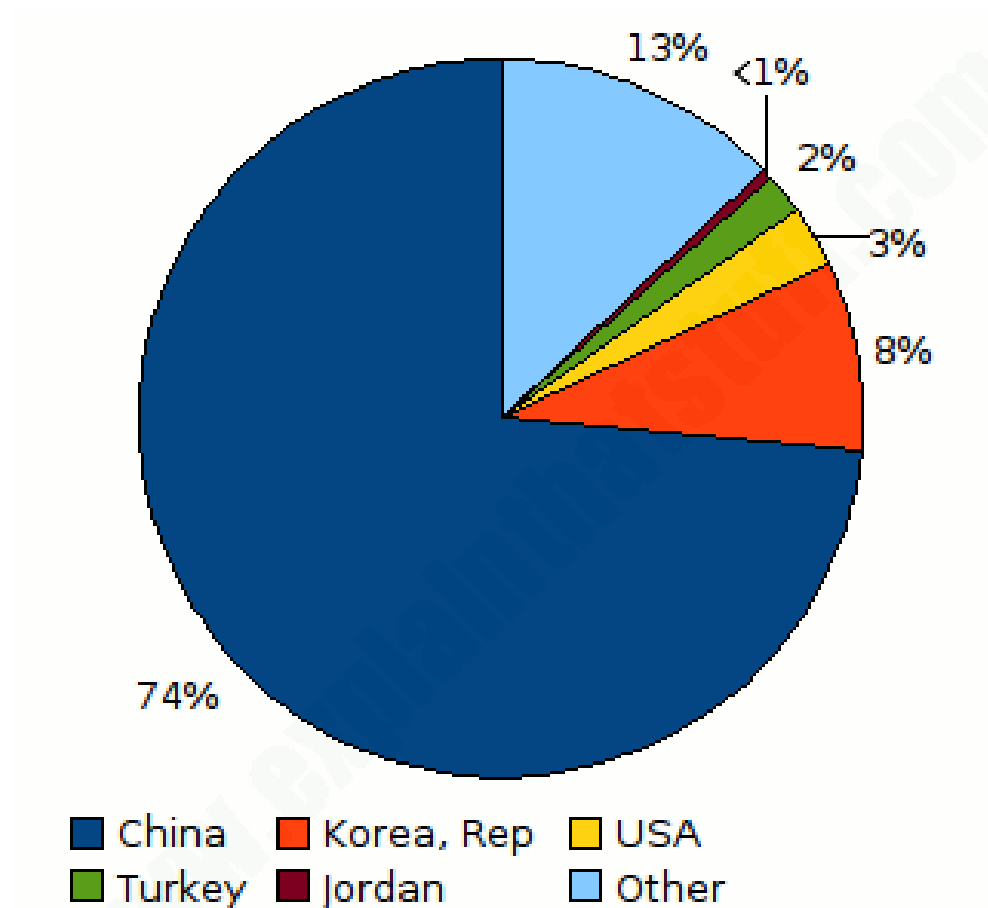


Figure (1.1) : Elemental Composition and kaolin graphic

1.1.2- Kaolin is used:-

- In ceramics (it is the component of porcelain).
- In toothpaste.
- As a light diffusing material in white incandescent light bulbs.
- In cosmetics.
- In pre-work skin protection and barrier creams.
- In paint extend the titanium dioxide white pigment and modify gloss levels.
- For modifying the properties of rubber upon vulcanization.
- In adhesives to modify archeology.
- In organic farming as a spray applied to crops to deter insect damage, and in the case of apples prevent sun scald.
- For facial masks or soap.
- As adsorbents in water and wastewater treatment.
- As an indicator in radiological dating since kaolinite can contain very small traces of uranium thorium.

1.2- Zeolite:



Figure(1.2) :- The Zeolite production⁽⁴⁾

zeolites are hydrated alumina silicate minerals made from interlinked tetra hydra of alumina (AlO_4) and silica (SiO_4). In simpler words, they're solids with a relatively open, three-dimensional crystal structure built from the elements aluminum, oxygen, and silicon, with alkali or alkaline-Earth metals (such as sodium, potassium, and magnesium) plus water molecules trapped in the gaps between them. Zeolites form with many different crystalline structures, which have large open pores (sometimes referred to as cavities) in a very regular arrangement and roughly the same size as small molecules. There are about 40

naturally occurring zeolites, forming in both volcanic and sedimentary rocks; according to the US Geological Survey, the most commonly mined forms include chabazite, clinoptilolite, and mordenite. Dozens more artificial, synthetic zeolites (around 150) have been designed for specific purposes, the best known of which are zeolite A (commonly used as a laundry detergent), zeolites X and Y (two different types of faujasites, used for catalytic cracking), and the petroleum catalyst ZSM-5 (a branded name for pentasil-zeolite). Where do natural zeolites come from? Estimated world mine production for 2013. China produced almost three quarters of all natural zeolites (2 million tons). Source: US Geological Survey: Mineral Commodity Summaries: Zeolites (Natural). According to the USGS, total world reserves of zeolites are unknown "but are estimated to be large."⁽⁴⁾

Zeolites were first recognized as a new type of minerals in 1756 by a Swedish reek word: meaning boiling stone) as it seemed to boil at high temperature due to high water content ⁽⁵⁾. Since then, many types of naturally occurring zeolites have been found, such as: chabazite, erionite, faujasite, mordenite, etc. ⁽⁵⁾. Zeolites consist of microporous crystalline aluminosilicates and possess properties of adsorption, reaction, and ion-exchange. The first industrially important zeolite was produced in 1942. Since then, more than 150 synthetic zeolites have been reported. At present, over 130 types of zeolite structures are approved by the International Zeolite Association (IZA). Currently only a few are of commercial importance such as, type A, X, Y, Z, L, ZSM-5, etc. ⁽⁵⁾. The primary building block of all zeolites is a tetrahedron of four oxygen anions that surround a silicon or aluminum ion, as shown in Figure 1.3(a). These tetrahedra are arranged in such a way that each of the four oxygen anions is further shared by another silica or alumina tetrahedron. The crystalline framework extends in three dimensions, therefore the 2 oxidation state of each oxygen is accounted for. The +4 charge on each silicon ion is balanced by the four tetrahedral

oxygen making the silica tetrahedral electrostatically neutral. On the other hand, the +3 charge on aluminum is not balanced by the surrounding four tetrahedral oxygens, leaving a residual charge of 1 on each alumina tetrahedron. Thus each alumina tetrahedron requires a +1 charge from a cation in the structure to be electrostatically neutral, as shown in **Figure(1.3)**. The cations providing electric stability to alumina tetrahedron are generally sodium in the zeolite where they occupy non-framework positions⁽⁶⁾.

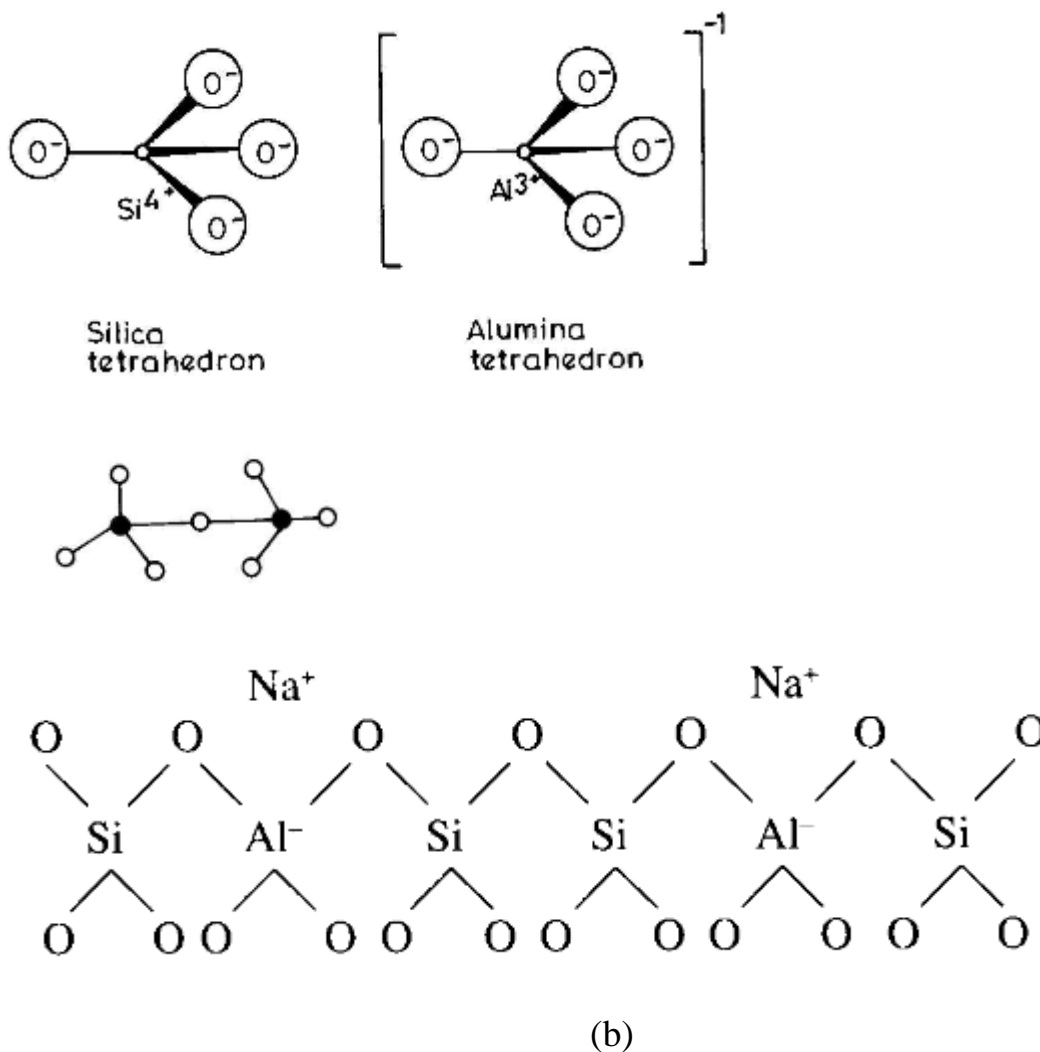
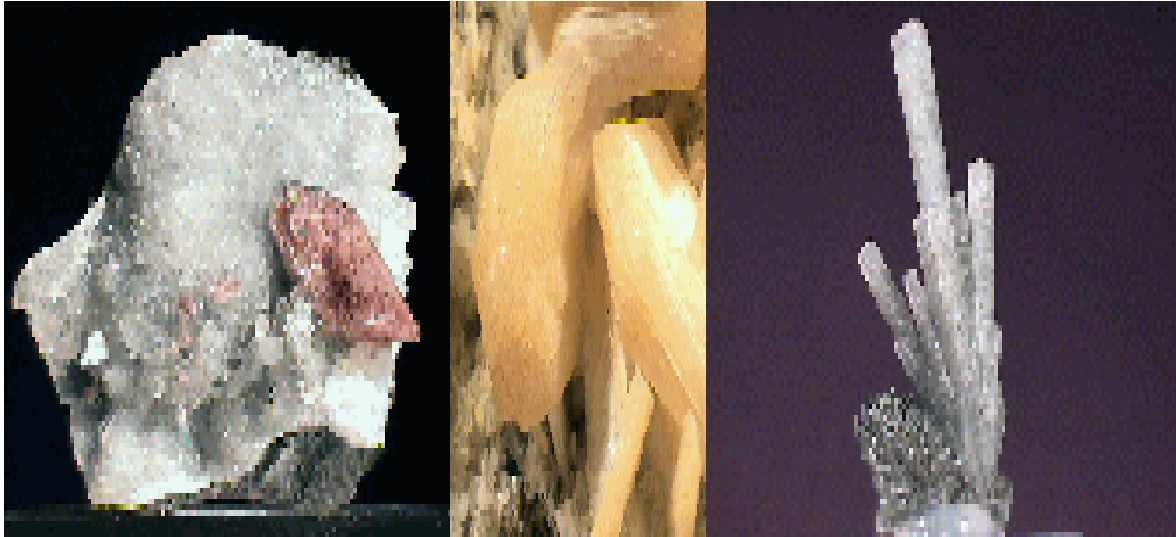


Figure (1.3): (a) Primary building blocks of zeolites, (b) Simplified surface structure of zeolite For any specific application, the cations can be replaced by ion exchange, which is the most direct and useful method to change the properties of zeolite. The building block of the zeolite crystal structure is

formed by the combination of silica and alumina tetrahedra into more complicated secondary units. The silica and alumina tetrahedral are geometrically arranged with the exception of Al-O-Al bonds. The unit cell formula is generally written as: $M^{2/n} OAl_2 O_3 xSiO_2 YH_2 O$ (3) where M represents the exchangeable cations, generally from group I or II ions, although other metallic, non-metallic, or organic cations may be used to balance the charge on framework; n represents the cation valence. These cations are present either during the synthesis or through post-synthesis ion-exchange. The value of x is equal to or greater than 2, as alumina tetrahedron does not occupy adjacent tetrahedral sites. Y value represents the degree of hydration. The tetrahedral are arranged in such a way that the zeolites have an open framework structure with a large surface area. The pore structure varies from zeolite to zeolite all zeolites are determined by the free aperture resulting from 4-, 6-, 8-, 10- or 12-membered rings of oxygen atoms, and their maximum values are calculated to be 2.6, 3.6, 4.2, 6.3, and 7.4 Å, respectively. As an example, Figure(1.3) depicts the structure and pore size of Y zeolite. However, due to some elongation of the oxygen ring or the presence of cations near or within the pore apertures, the Effective free aperture of the pore may be reduced, and the aperture may be Elliptical. The zeolites with 8- and 12-membered oxygen ring or more are used in major catalytic applications rather than small aperture size as it places unacceptable size limitations on the molecules to be adsorbed. Many of the zeolites formed are not in the equilibrium state but only in the metastable state, which in time may convert to other more stable zeolitic phases or other mineral phases. In principle, zeolites are prepared from alumina silicate gels, which in turn are prepared from aqueous solutions of sodium aluminate, sodium silicat.⁽⁶⁾

1.2.1- The Zeolite Group of Minerals:



Figure(1.4): The Zeolite Group.

The Zeolites are a popular group of minerals for collectors and an important group of minerals for industrial and other purposes. They combine rarity, beauty, complexity and unique crystal habits. Typically forming in the cavities (or vesicles) of volcanic rocks, zeolites are the result of very low grade metamorphism. Some form from just subtle amounts of heat and pressure and can just barely be called metamorphic while others are found in obviously metamorphic regimes. Zeolite crystals have been grown on board the space shuttle and are undergoing extensive research into their formation and unique properties⁽⁷⁾

The zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4 . In order to be a zeolite the ratio $(\text{Si} + \text{Al})/\text{O}$ must equal $1/2$ ⁽⁷⁾. The alumino-silicate structure is negatively charged and attracts the positive cations that reside within. Unlike most other **tectosilicates**, zeolites have large vacant spaces or cages in their structures that allow space for large cations such

as sodium, potassium, barium and calcium and even relatively large molecules and cation groups such as water, ammonia, carbonate ions and nitrate ions. In the more useful zeolites, the spaces are interconnected and form long wide channels of varying sizes depending on the mineral. These channels allow the easy movement of the resident ions and molecules into and out of the structure. Zeolites are characterized by their ability to lose and absorb water without damage to their crystal structures. The large channels explain the consistent low **specific gravity** of these minerals.⁽⁸⁾

Zeolites have many useful purposes. They can perform ion exchange, filtering, odor removal, chemical sieve and gas absorption tasks. The most well known use for zeolites is in water softeners. Calcium in water can cause it to be "hard" and capable of forming scale and other problems. Zeolites charged with the much less damaging sodium ions can allow the hard water to pass through its structure and exchange the calcium for the sodium ions. This process is reversible. In a similar way zeolites can absorb ions and molecules and thus act as a filter for odor control, toxin removal and as a chemical sieve.⁽⁹⁾

Zeolites can have the water in their structures driven off by heat with the basic structure left intact. Then other solutions can be pushed through the structure. The zeolites can then act as a delivery system for the new fluid. This process has applications in medicine, livestock feeds and other types of research. Zeolites added to livestock feed have been shown to absorb toxins that are damaging and even fatal to the growth of the animals, while the basic structure of the zeolite is bio biologically neutral⁽⁹⁾. Aquarium hobbyists are seeing more zeolite products in pet stores as zeolites make excellent removers of ammonia and other toxins. Most municipal water supplies are processed through zeolites before public consumption. These uses of zeolites are extremely important for industry, although synthetic zeolites are now doing the bulk of the work. Zeolites have basically three different structural variations. There are chain-like

structures whose minerals form acicular or needle-like prismatic crystals, ie **natrolite**. Sheet-like structures where the crystals are flattened platy or tabular with usually good basal cleavages, ie **heulandite**. And framework structures where the crystals are more equant in dimensions, ie **Chabazite**.⁽¹⁰⁾

A zeolite can be thought of in terms of a house, where the structure of the house (the doors, windows, walls and roof) is really the zeolite while the furniture and people are the water, ammonia and other molecules and ions that can pass in and out of the structure. The chain-like structures can be thought of like towers or high wire pylons. The sheet-like structures can be thought of like large office buildings with the sheets analogous to the floors and very few walls between the floors. And the framework structures like houses with equally solid walls and floors. All these structures are still frameworks (like the true tectosilicates that zeolites are). These variations make the zeolite group very diverse, crystal habit-wise. Otherwise zeolites are typically soft to moderately hard, light in density, transparent to translucent and have similar origins. There are about 45 natural minerals that are recognized members of the Zeolite Group⁽¹⁰⁾. Industrially speaking, the term zeolite includes natural silicate zeolites, synthetic materials and phosphate minerals that have a zeolite like structure. The complexity of this combined group is extensive with over 120 structural variations and more are being discovered *or made* every year. Collecting zeolites can be very enjoyable and fulfilling.⁽¹⁰⁾

1.2.2- These are the members of the Zeolite Group:

- **The Analcime Family:**
 - **Analcime** (Hydrated Sodium Aluminum Silicate)
 - **Pollucite** (Hydrated Cesium Sodium Aluminum Silicate)
 - **Wairakite** (Hydrated Calcium Sodium Aluminum Silicate)

- **Bellbergite** (Hydrated Potassium Barium Strontium Sodium Aluminum Silicate)
- **Bikitaite** (Hydrated Lithium Aluminum Silicate)
- **Boggsite** (Hydrated calcium Sodium Aluminum Silicate)
- **Brewsterite** (Hydrated Strontium Barium Sodium Calcium Aluminum Silicate)
- The Chabazite Family:
 - **Chabazite** (Hydrated Calcium Aluminum Silicate)
 - **Willhendersonite** (Hydrated Potassium Calcium Aluminum Silicate)
- **Cowlesite** (Hydrated Calcium Aluminum Silicate)
- **Dachiardite** (Hydrated calcium Sodium Potassium Aluminum Silicate)
- **Edingtonite** (Hydrated Barium Calcium Aluminum Silicate)
- **Epistilbite** (Hydrated Calcium Aluminum Silicate)
- **Erionite** (Hydrated Sodium Potassium Calcium Aluminum Silicate)
- **Faujasite** (Hydrated Sodium Calcium Magnesium Aluminum Silicate)
- **Ferrierite** (Hydrated Sodium Potassium Magnesium Calcium Aluminum Silicate)
- The Gismondine Family:
 - **Amicite** (Hydrated Potassium Sodium Aluminum Silicate)
 - **Garronite** (Hydrated Calcium Aluminum Silicate)
 - **Gismondine** (Hydrated Barium Calcium Aluminum Silicate)
 - **Gobbinsite** (Hydrated Sodium Potassium Calcium Aluminum Silicate)
- **Gmelinite** (Hydrated Sodium Calcium Aluminum Silicate)
- **Gonnardite** (Hydrated Sodium Calcium Aluminum Silicate)
- **Goosecreekite** (Hydrated Calcium Aluminum Silicate)
- The Harmotome Family:
 - **Harmotome** (Hydrated Barium Potassium Aluminum Silicate)

- **Phillipsite** (Hydrated Potassium Sodium Calcium Aluminum Silicate) **Wellsite** (Hydrated Barium Calcium Potassium Aluminum Silicate)
- The Heulandite Family:
 - **Clinoptilolite** (Hydrated Sodium Potassium Calcium Aluminum Silicate)
 - **Heulandite** (Hydrated Sodium Calcium Aluminum Silicate)
- **Laumontite** (Hydrated Calcium Aluminum Silicate)
- **Levyne** (Hydrated Calcium Sodium Potassium Aluminum Silicate)
- **Mazzite** (Hydrated Potassium Sodium Magnesium Calcium Aluminum Silicate)
- **Merlinoite** (Hydrated Potassium Sodium Calcium Barium Aluminum Silicate)⁽¹¹⁾
- **Montesommaite** (Hydrated Potassium Sodium Aluminum Silicate)
- **Mordenite** (Hydrated Sodium Potassium Calcium Aluminum Silicate)
- **The Natrolite Family:**
 - **Mesolite** (Hydrated Sodium Calcium Aluminum Silicate)
 - **Natrolite** (Hydrated Sodium Aluminum Silicate)
 - **Scolecite** (Hydrated Calcium Aluminum Silicate)
- **Offretite** (Hydrated Calcium Potassium Magnesium Aluminum Silicate)
- **Paranatrolite** (Hydrated Sodium Aluminum Silicate)
- **Paulingite** (Hydrated Potassium Calcium Sodium Barium Aluminum Silicate)
- **Perliaite** (Hydrated Potassium Sodium Calcium Strontium Aluminum Silicate)
- **The Stilbite Family:**
 - **Barrerite** (Hydrated Sodium Potassium Calcium Aluminum Silicate)
 - **Stilbite** (Hydrated Sodium Calcium Aluminum Silicate)

- **Stellerite** (Hydrated Calcium Aluminum Silicate)
- **Thomsonite** (Hydrated Sodium Calcium Aluminum Silicate)
- **Tschernichite** (Hydrated Calcium Aluminum Silicate)
- **Yugawaralite** (Hydrated Calcium Aluminum Silicate)

Zeolites have many "cousins" or minerals that have similar cage-like framework structures or have similar properties and/or are associated with zeolites; but are not zeolites, at least as defined mineralogically. These include the phosphates: kehoeite, pahasapaite and tiptopite; and the silicates: hsianghualite, lovdarite, viseite, partheite, prehnite, roggianite, apophyllite, gyrolite, maricopaite, okenite, tacharanite and tobermorite. It is interesting to compare these minerals to the zeolites⁽¹¹⁾

1.2.3- Special Properties Zeolites:-

Zeolites are very stable solids that resist the kinds of environmental conditions that challenge many other materials. High temperatures don't bother them because they have relatively high melting points (over 1000°C), and they don't burn. They also resist high pressures, don't dissolve in water or other inorganic solvents, and don't oxidize in the air⁽¹²⁾. They're not believed to cause health problems through, for example, skin contact or inhalation, though in fibrous form, they may have carcinogenic (cancer-causing) effects. Since they're unreactive and based on naturally occurring minerals, they're not believed to have any harmful environmental impacts. Although zeolites might sound incredibly boring, their stable and unreactive nature isn't what makes them useful. The most interesting thing about zeolites is their open, cage-like, "framework" structure and the way it can trap other molecules inside it⁽¹²⁾. This is how water molecules and alkali or alkaline-Earth metal ions (positively charged atoms with too few electrons, sometimes called cations) become a part of zeolite crystals—although they don't necessarily remain there permanently. Zeolites can exchange other positively charged ions for the metal ions originally trapped inside them (technically this is known as cation exchange) and, as Cronstedt found over 250 years ago, they can gain or lose their water molecules very easily too (this is called reversible dehydration). Zeolites have regular openings in them of fixed size, which let small molecules pass straight through but trap larger ones; that's why they're sometimes referred to as molecular sieves. Unlike natural zeolites, which occur in random forms and mixed sizes, synthetic zeolites are manufactured in very precise and uniform sizes (typically from about 1µm to 1mm) to suit a particular application; in other words, they're made a certain size to trap molecules of a certain (smaller) size inside them. Animat Animation (above): Ion exchange in zeolites: the zeolite "cage" (gray) traps incoming ions (red and orange) and releases others (yellow) in their place.

Although all zeolites are aluminosilicates, some contain more alumina, while others contain more silica. Alumina-rich zeolites are attracted to polar molecules such as water, while silica-rich zeolites work better with nonpolar molecules. ⁽¹²⁾

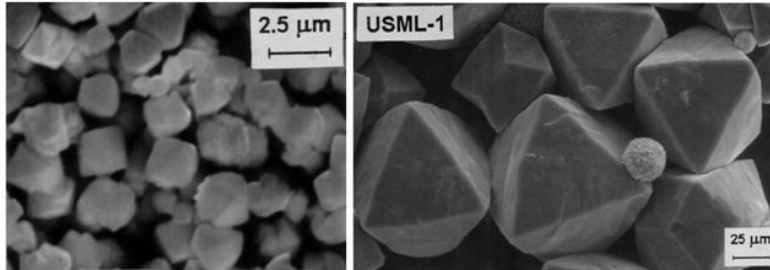


Photo: Synthetic zeolite crystals grown at CAMMP (Center for Advanced Microgravity Materials Processing), a NASA-sponsored Research Partnership Center. The ones on the right are about 10 times bigger (25 μ m) than the ones on the left (2.5 μ m). Photo courtesy of Dr. Albert Sacco and NASA Marshall Space Flight Center (NASA-MSFC).⁽¹³⁾

1.2.4- Uses of Zeolite:-

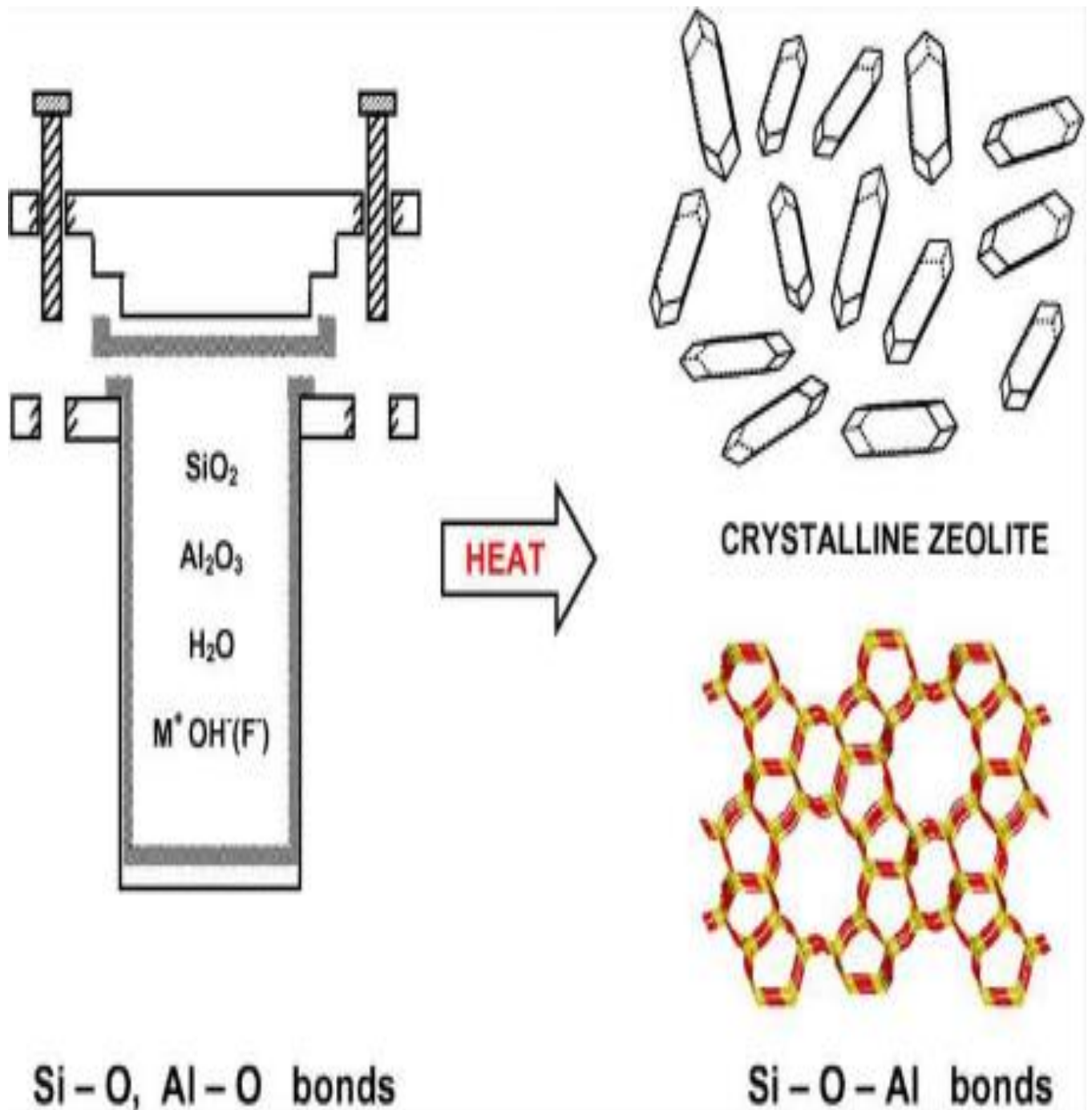
The cage-like structure of zeolites makes them useful in all sorts of ways. One of the biggest everyday uses for zeolites is in water softeners and water filters. In ion-exchange water softeners, for example, hard water (rich in calcium and magnesium ions) is piped through a column filled with sodium-containing zeolites. The zeolites trap the calcium and magnesium ions and release sodium ions in their place, so the water becomes softer but richer in sodium. Many everyday laundry and dishwasher detergents contain zeolites to remove calcium and magnesium and soften water so they work more effectively.⁽¹⁴⁾

Two other very common, everyday uses of zeolites are in odor control and pet litter; in both, the porous crystalline structure of the zeolites helps by trapping unwanted liquids and odor molecules. This simple idea, so effective in our homes, has much more important uses outside them: zeolites have proved extremely effective at removing radioactive particles from nuclear waste and cleaning up soils contaminated with toxic heavy metals.⁽¹⁵⁾ The many other uses for zeolites including concrete production, soil-conditioners, and animal food.⁽¹⁵⁾

1.2.5-Synthesis of Zeolite:-

Zeolites are crystallized under mild temperature and pressure, by a hydrothermal synthesis process⁽¹⁶⁾. The nature of zeolite is determined by the specific synthesis conditions, i.e., reactant concentration, pH, reaction time, temperature, etc. The important factors affecting zeolite synthesis include: the nature of reactants chemical composition and pretreatment, the method of reactant mixture preparation, the overall, homogeneity or heterogeneity of the mixture, pH of the mixture, low temperature ageing of the gel, nucleation, seeding, addition of additives, temperature, pressure, and organic template. The amorphous reactants containing silica and alumina are mixed together in presence of a cation source, usually with a high pH. The reactants for the source of alumina are generally sodium aluminate, aluminum nitrate, or aluminum phosphate. For the source of silica, generally sodium silicate, amorphous silica, or silica sol are used⁽¹⁷⁾. Sodium hydroxide is normally used for the control of pH. The aqueous reaction mixture is heated to 100C .zeolite synthesis begins from the hydrous aluminosilicate amorphous gel. The carefully controlled conditions of the crystallization for the gel, gradually replaces all the amorphous phase into the desired zeolite phase. The resultant zeolite is then removed from the mother liquor, washed, and dried before any application⁽¹⁷⁾. The steps involved in zeolite synthesis are depicted in Figure(5). The key elements, i.e. Si

and Al, which make up the microporous framework of zeolite, are imported in an oxide form. These oxides and generally amorphous precursors contain Si-O and Al-O bonds. During the hydrothermal reaction in presence of a mineralizing agent, which is most likely an alkali metal hydroxide (e.g. NaOH), the crystalline zeolite product containing Si-O-Al linkages is created. Since the type of the bond of the product is very similar to that present in the precursor oxides, no considerable enthalpy change is anticipated. ⁽¹⁸⁾.



Figure(1.5): Hydrothermal zeolite synthesis. The starting materials (Si-O and Al-O bonds) are transformed by an aqueous mineralizing medium, such as OH- and/or F-, into the crystalline product (Si-O-Al bonds). ⁽¹⁹⁾ .

Another important use for zeolites is as catalysts in drug (pharmaceutical) production and in the petrochemical industry, where they're used in catalytic crackers to break large hydrocarbon molecules into gasoline, diesel, kerosene, waxes and all kinds of other byproducts of petroleum. Again, it's the porous structure of zeolites that proves important. The many pores in a zeolite's open structure are like millions of tiny test tubes where atoms and molecules become trapped and chemical reactions readily take place. Since the pores in a particular zeolite are of a fixed size and shape, zeolite catalysts can work selectively on certain molecules, which is why they're sometimes referred to as shape-selective catalysts (they can select the molecules they work on in other ways beside shape and size, however). Like all catalysts, zeolites are reusable over and over again.⁽²⁰⁾

Usually, zeolites are conventionally synthesized from aqueous basic aluminosilicate precursor gels under hydrothermal conditions at elevated temperatures in autoclave ⁽²¹⁾. Basic aluminosilicate precursor gels preferably prepared from pure solutions of sodium silicate and sodium aluminate. The use of kaolin to produce zeolites is lead by the fact that it provides a cheaper and easy means of silica and alumina source ⁽²²⁾. Utilizing the local kaolin from Sabah also enable the exploitation of the large sources of clay mineral deposit, consisting mainly of kaolinite in area of Sabah, which have been reported with an estimated value of 12.9 million tonnes (mt) ⁽²³⁾. A lot of researchers have worked on the synthesis of zeolites from different sources of kaolin around the world ⁽²⁴⁾.

1.2.6- Synthesized from kaolin:

One gram of metakaolin (MK) was mixed with 20 mL NaOH solution prepared from NaOH pellet (>99% w/w, Merck KGaA) to get the reaction mixture. Metakaolin was slowly added to the NaOH solution and a thorough mixing was done to get uniformity. Reaction mixture with different amount of NaOH (0.02, 0.04, 0.05, 0.06, 0.08 and 0.1 moles) prepared by adjusting the amount of NaOH in each sample to study the optimum alkalinity required to synthesis zeolite A. The reaction mixture was kept in the 250 mL Teflon bottle and capped tightly. This mixture was shook for 30 min using orbital shaker to get homogenous solution. The Teflon bottles was not filled more than 50% to avoid spillage. Samples were crystallized in the oven for 8 h at 100 °C. All samples were filtered then washed with 1 L of distilled water. Sample was dried overnight in the oven at 80 °C.⁽²⁵⁾

1.2.7- Application

Zeolites have basically found a wide array of applications due to their applicability in almost all fields of human life where chemical; biochemical and physicochemical processes are taking place. They can be used for purification of gaseous as well as liquid mixtures and solutions by sorption, for storing of molecules for sieving and filtering, for ion exchange purposes and also for catalysis under non-oxidizing and oxidizing environment. The uses for zeolites are generally categorized into three functional classifications, and within each function exists a broad range of applications as below.⁽²⁶⁾

1.2.7.1- Zeolite in adsorption and separation:

The basis for the usage of zeolite in gas adsorption is due to the shape-selectivity properties. The ability to preferentially adsorb certain molecules

while excluding others has opened up a wide range of molecular sieving applications.

Sometimes, it is simply matter of the size and shape of pores controlling access into the zeolite. In other cases, different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by silicalite⁽²⁶⁾.

Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also to find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with metal ions. Conversely, hydrophobic silica zeolites preferentially adsorb organic solvents. Thus, zeolites can be used to separate molecules based on the differences of size, shape and polarity. The use of zeolite in some application of adsorption and separation is stated as follows:

(a) Odour control

Zeolites are used in a wide range of consumer products to remove both moistures and odours. They have a large capacity for moisture absorption and can be re-used many times by simply heating to remove absorbed moisture. They also absorb undesirable odours and have many useful applications in the home. Some of the examples of zeolites usage in this case include fridge deodorizers, shoe cupboards, wardrobes, car and boat deodorizers, elimination of pet odours. In fact, zeolites can be used in almost any situation and problem where moisture and/or odours are involved. They are totally harmless to humans and animals, and can be re-used over and over agin.

(b) Industrial gas separation and purification

Synthetic zeolites have been used for many years in the petroleum industry, but natural zeolites are being increasingly used as a cost effective alternative in certain applications where there is no performance disadvantage. Natural zeolites are particularly effective in the following applications: Removal of water and carbon dioxide from gaseous hydrocarbons, removal of hydrochloric acid from gas streams, removal of hydrogen sulphide from gas streams and catalysis and natural gas separation ⁽²⁶⁾

(c) Water adsorption

Zeolite is a mineral which has a high affinity for water and has the capability of adsorbing and desorbing it without damage to the crystal structure. This property makes them useful in desiccation as well as other unique commercial application⁽²⁶⁾.

1.3- Objectives of the research

The objectives of the present study, can be summarized as follows:-

- Firstly to preparation of zeolites from kaoline using hydrothermal process.
- Secondly to examination of the obtained product using different analytical techniques such as x-ray diffraction (XRD), x-ray fluorescence(XRF), IR spectroscopy.

Chapter two

2- Materials and Methods

2.1- Materials:-

2.1.1- Chemicals:-

- Sodium hydroxide (NaOH 5 M).
- Hydrochloric acid (HCL 11.8 M).
- Hydrochloric acid (HCL 2 M).

All Chemicals used in this research were of analytical type.

2.1.2- Apparatuses and Equipment :-

- Burrete (50 ml).
- Pipiette (10 ml).
- Beaker (500 ml ,50 ml, 100 ml).
- Voliometric flask (100 ml).
- Conical flask (250 ml).
- Porcelain crucible.
- Heating mantile (SHIMADZU) .
- pH papers.
- Glass watch.
- Balance (SHIMADZU JAPAN).
- Filter paper(what man 42).

2.3-sample:-

2.3.1 – kaolin sample:-

local Kaolin sample was obtained from International University of Africa , department of geology .

2.3.2 – sample preparation:-

The kaolin sample was crushed to finally grinding powder and was activated at 800 C° by oven to convert it to meta kaolin.

The composition and the different constituent of each sample were examined using x-ray flourcance (XRF):

Table(2.1): The x-ray flourcance (XRF) of the obtained product from kaolin sample:

Oxide	Content%
SiO ₂	69.943
Al ₂ O ₃	25.689
TiO ₂	1.391
CaO	0.776
Na ₂ O	0.298

2.4- Methods of preparation and characterization of Zeolite :-

2.4.1- Method of preparation Zeolite:

20 g meta kaolin (Activated before) were weighted in beaker(250 ml) , 15 ml of hydrochloric acid(HCL 11.8M) were added and settled to 6 hours ,the solution was flittered , the participate was dried, 50 ml of sodium hydroxide (NaOH 5M) was added and the solid was flittered (is SiO₂ participate was in soluble) , after that the solution was neutralized by hydrochloric acid till the medium was reached pH 10, the neutralization was carried out on heating mantle with stirring using magnetic rode ,the gel(were collected after evaporation) was dried in an air at room temperature .The obtained product was used in characterization⁽²⁷⁾.

2.4.1.1- Test of sample for silica content:-

0.8 g of the product was weighted in a test tube ,1 ml of distilled water was added, and finally 1 ml silver nitrate solution was added to examine the presence of silica⁽²⁷⁾ .

2.4.2- characterization Methods:-

2.4.2.1- XRD (X-ray diffraction):-

X-ray powder diffraction patterns was recorded at room temperature on adorn -2.0 equipment ,using Cu k radiation of ware lenght 0-15404 nm ,diffraction data was recorded form 0.5A to 50° 2-theta ,at an internal of 0-01° and scanning speed of 2°/ min.

2.4.2.2- IR Spectroscopy:-

IR measurement were performed on A jasco 5300 IR spectrometers with a resolution of 4 cm^{-1} and averaging over 250 scans, the potassium bromide [KBr] pellet technique was used to record the IR spectra in region $400\text{-}4000\text{ cm}^{-1}$ range. For the preparation of KBr pellets ,300 mg of previously dried KBr was mixed thoroughly with 0.5 mg of the sample and pressed into pellets of 13 mm diameter with pressure of 7 tons/ m^2

Chapter Three

3- Results and Discussion

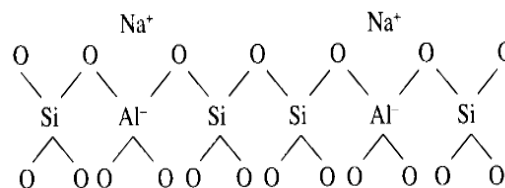
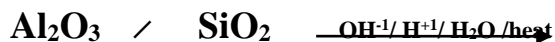
3.1- Results

.1.1- Results of preparation of Zeolite :-

Fig(6): below showed the crystal of the obtained product, its clear that the synthesis of Zeolite from kaolin involve the following stages:-



Figure (3.1): the formation of Zeolite from kaolin.



Si-O-Al bond

Zeolites are porous crystalline aluminosilicate, which have a highly regular and open structure formed by a three-dimensional network of SiO₄ and AlO₄ tetrahedra. Zeolite is one of the synthetic molecular sieves that has various applications in adsorption, separation, catalysis and detergents.

In simpler words, they're solids with a relatively open, three-dimensional crystal structure built from the elements aluminum, oxygen, and silicon, with alkali or alkaline-Earth metals (such as sodium, potassium), in figure (6) explain the synthesis of Zeolite from beginning local kaolin was activated to meta kaolin because it activity material, convert to Zeolite crystal this it finally product.

The equation was explained the bond from Si – O, Al– O to Si– O–Al– bond.

Table(3.2):

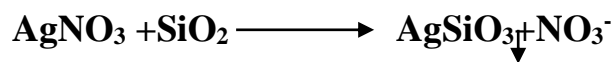
No a doubt that from the table below that the yield obtained using this methods of preparation was agreed with expected yield as found in the literature⁽²⁷⁾.

Weight of paper	Weight of paper and product	Weight of product
1.0980 g	16.987 g	15.889 g

The products obtained by thermal activation of kaolin is a white, soft powder consisting of roughly hexagonal, platy, crystals. kaolin is mixed with water in the range of 20 to 30 percent, kaolin is high melting point, and more resistant for heat, meta kaolin is dehydrated at 800 C° ,that meta kaolin is not simple mixture of amorphous silica (SiO₂) and alumina(Al₂O₃).but rather a complex amorphous structure that retains some longer-range order (but not strictly crystalline) due to stacking of its hexagonal layers. The addition of hydrochloric for 6 hours to the sample so that the meta kaolin was dissolved using sodium hydroxide and the product obtained using hydrothermal treatment to Zeolite.

3.1.2- Result of silica test:

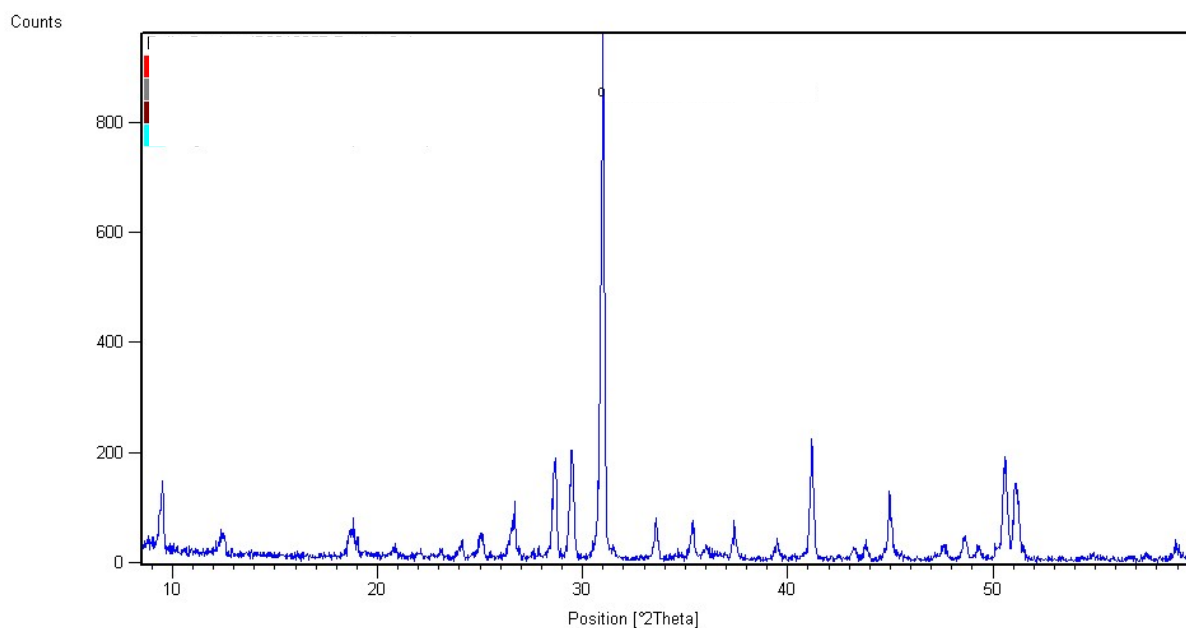
The test was produced precipitate in the test tube of silver silicate which was conformed by the XRF test and the content of silica in kaolin sample was 69.5%.⁽²⁸⁾



3.1.3- Results of characterization :-

3.1.4- Result of XRD:--

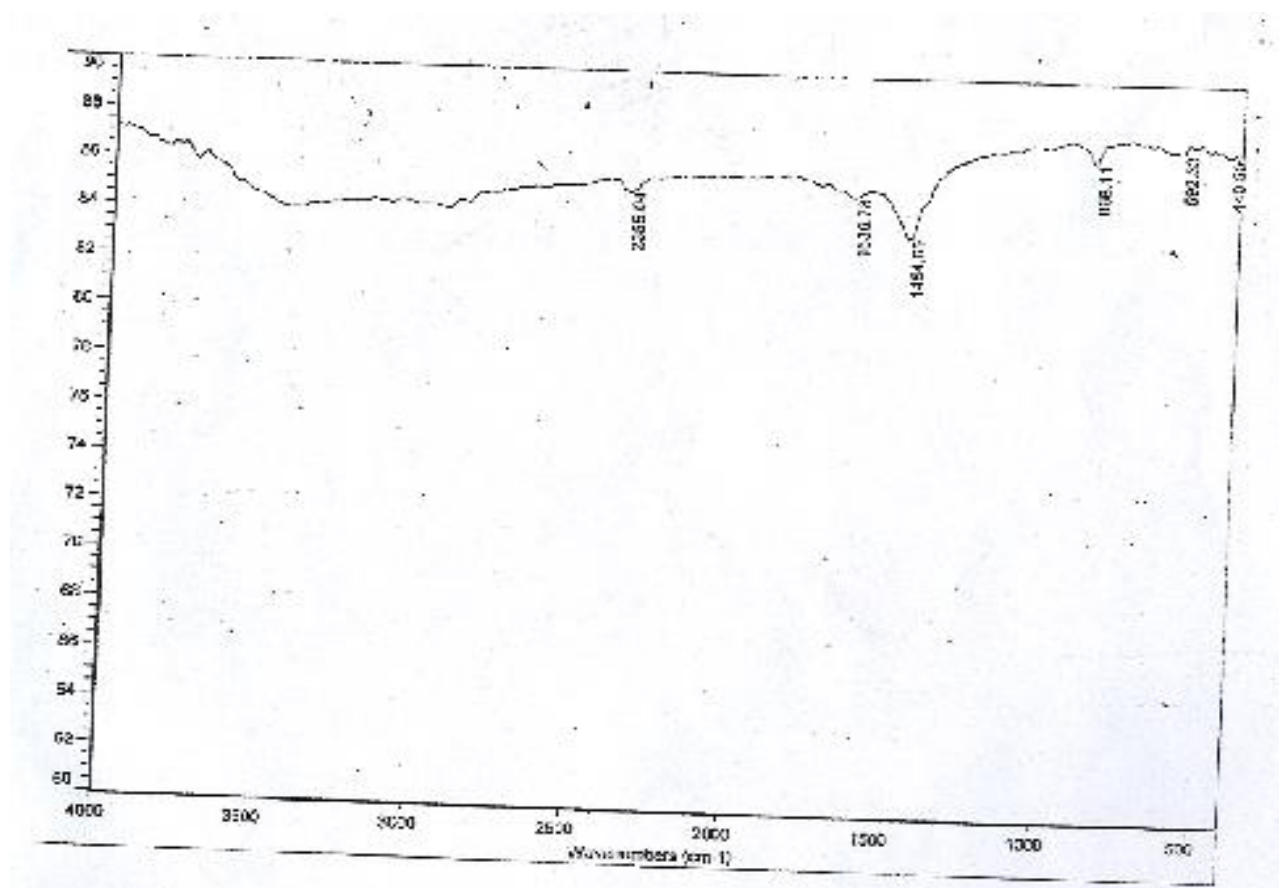
the result of x-ray diffraction was shown in figure(3.3) from the XRD patterns of synthesized products. One could say that a small amount of quartz was observed by a peak of low intensity at $2\theta = 20-31^\circ$. X-ray diffraction analysis also showed the presence of faujasite zeolite in the synthesized sample as evidenced from reflections of low intensity near $2\theta = 6.2^\circ, 18.6^\circ$ and 31.9° . peaks observed by XRD patterns of the synthesized product explain the formation of the crystalline structure of the zeolite as found in the literature. ⁽²⁹⁾



Figure(3.2): the XRD patterns of synthesized products

3.1.5- Result of IR:-

The vibrational spectra of Figure(3. 4) show the changes that occur from the starting material to the synthesis products stretch bands of OH group at 3597, 3653 and 3200 cm^{-1} characteristic of product. The bands with a maximum at 2355.04 and 1636.78 cm^{-1} are peculiar of vibrations of functional groups of OH type and are ascribed to water with zeolitic nature. Asymmetry stretching of bonds Si-O or Al-O vibration at 440.50 cm^{-1} , the peaks near 592.33-868.11 cm^{-1} are assigned to symmetric T-O-T vibration (T=Si,Al) of zeolite.



Figure(3.3): The IR Spectrum of synthesized product

Conclusion

At the present work Zeolite was prepared from local kaolin sample using hydrothermal treatment in aqueous sodium hydroxide medium .

The characterization test confirmed the formation of Zeolite using the above methods and this can be deduced from the characteristic of x-ray diffraction (XRD) and IR Spectroscopy .

Recommendations

- To enhance the studies and research in natural occurring minerals .
- Apply other method for synthesis of Zeolite.
- Transfer the result of this experiments to industries .

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