Review Paper

Zeolite Synthesis, Characterization and Application Areas: A Review

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Abstract

This report reviews the researches that have been carried out on the synthesis, characterization and application of zeolite. The material zeolite is introduced by first defining what it is, how it is obtained, the classifications and the different nomenclatures used. The many different methods through which zeolite are obtained has been explained. The different ways through which zeolite materials have been characterized have also been looked at in details. The different starting raw materials and the processing steps which have been used to synthesize zeolites have been given explained. The application areas have been presented with special emphasis on the current trends in the application of zeolites apart from its use in catalysis, detergents and ion exchange.

Keywords: Zeolite, Kaolin, Metakaolin, Catalyst, Pore Size, Absorption Agent.

Introduction

Zeolites can be described as materials made up of micro-porous, aluminosilicate crystals which are used as ion exchangers in the detergent industry, in radioactive waste storage, in the treatment of liquid waste, as separators in purification, drying, environmental treatment, in the catalytic cracking of petroleum and in refining petrochemical, coal and fine chemical industries[1-3]. The properties which enables them to perform all these functions in several industrial applications are their uniform pore size and shape, the mobility of their cations to act as catalysts and their hydrophilic and/or hydrophobic nature to some solutes[4]. Primarily, zeolites are built from $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral which are infinitely extended in a three dimensional network that is linked together by a shared oxygen atom[5,6]. This $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral can be represented by TO_4 which is often referred to as the primary building block (PBU), where **T** represents either the silicon (Si^{4+}) or Aluminium (Al^{3+}) ions while the **O$_4$** represents each of the oxygen atom that is shared by the two **T** atoms. This is shown in Figures-1 and 2.
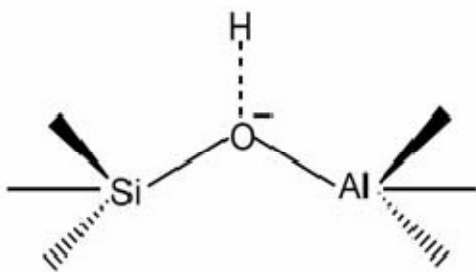

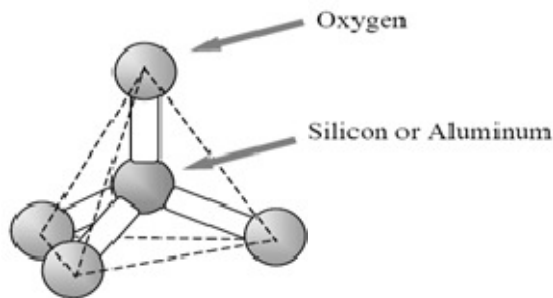**Figure-1:** Description of the Chemical Structure of Zeolite[7].

Figure-2: Schematic of the Building Unit of Zeolite Structur[6].

Zeolites are represented based on their crystallographic unit cell by the general formula in equation 1:

$$M_{a/b}\left[(AlO_2)_a (SiO_2)_y\right] cH_2O \qquad (1)$$

where M represents either an alkali metal or an alkaline earth metal cation, b represent the valency of the alkali or the alkaline earth metal cation, c is the amount of water of crystallization per unit cell of the zeolite while a and y represent the total number of the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral in a unit cell of the zeolite. The ratio y/a normally has a value that ranges from 1 to 5, but in the case of a silica based zeolites, the values of y/a can range from 10 to 100.

Currently there are more than 200 types of zeolites and they can be identified by their Silicon-Aluminium (Si/Al) ratio present in the atomic structure of the zeolite. The ratio can vary from 1 in type A zeolites to infinity in silicalite, which is an aluminum free crystalline silica modified zeolite[8]. When the Si/Al ratio of

zeolites increase, both their thermal stability and acid resistance also increase.

The secondary building unit (SBU) of a zeolite can be defined as an infinite lattice that has identical building blocks of repeating units and the relationship between the Tetrahedral, the PBU and SBU can be seen in Figure-3. The secondary building unit is the main unit that is used to describe the zeolite structure except for the water and cations present in the zeolite framework. There are nine known SBUs that describe all the known zeolite frameworks. Cations can be seen within zeolite pores and this is to make up for the residual negative charge resulting from the isomorphous substitution of a Si^{4+} ion by an Al^{3+} ion during the formation of a zeolite framework.

The frameworks of zeolite are generated from the SBUs and in some cases, combinations of SBUs are used to form zeolites. An example is Faujasite which is obtained from the frameworks of sodalite zeolite which are made up of either a single six member ring or a four member ring which is gotten from a double six ring building unit. The location of cations and water within the cavities and holes in the framework however cannot be explained by the SBU[9]. The molecular water and cations in the zeolite framework are highly mobile and the water molecules are capable of being removed in a reversible reaction at temperatures ranging from 100 to 500°C. Zeolite structures are often stable at temperatures between 700 to 800 °C.

The nomenclature of zeolite framework has also evolved over the years with the zeolites synthesized by D. W. Breck and his fellow researchers named using Arabic letters, like zeolite A, zeolite B, zeolite X, zeolite Y etc,. This Arabic letters has evolved into the use of Greek letters like α-zeolite, β-zeolite, Ω-zeolite, etc. to represent the zeolites produced by Mobil Oil Company researchers[9]. The naming of synthetic zeolites was later taken further by assigning the name of the parent zeolite mineral when the synthesized zeolite has the same topology as the parent mineral. Examples include synthetic Mordenite, Chabasite and Erionite[9]. The structural committee of International Zeolite Association (IZA) finally produced an atlas of zeolite structure in which each zeolite framework type is given a three letter code used in describing and defining the network of corner sharing tetrahedral of the atoms irrespective of its composition[3,10]. The three letter codes are usually derived from the name of the source material. There are about 194 different zeolite frameworks as at July 2010 and each with its individual code[11]. Example of some of the most important zeolite framework with their codes include zeolite A with a code of LTA meaning Linde type A, while zeolite X and Y are assigned the code FAU meaning zeolite with faujasite topology and finally ZSM-5 and silicalite with illustrative code as MFI. Today the name of zeolites follows the three major conventions and they are all accepted. For example, the polyhedron present in the zeolite LTA, which is normally referred to as a cage, is actually a cavity. Cages present in some zeolite frameworks are shown in Figure-4[12].

Structure of zeolites

Zeolites have many different structures and its basic unit is the SO^{4-} and AlO^{4-} tetrahedral, linked together by the sharing of an oxygen atom. Zeolites A, zeolites X and zeolite Y consist of a cubo-octahedral (i.e. p-cages) having the SO^{4-} and AlO^{4-} tetrahedral at each corners of the framework. The structures of zeolites A are often as a result of the linkage between the P-cages through the quadratic surfaces which has a cubic shape. The linkage between the over six cornered surfaces and the hexagonal prisms leads to the formation of zeolite X and zeolite Y which correspond to faujasite zeolite. The ZSM 5 zeolite systems have a complicated structure and this is due to the presence of a system having two crossing channels, one linear one zigzag.
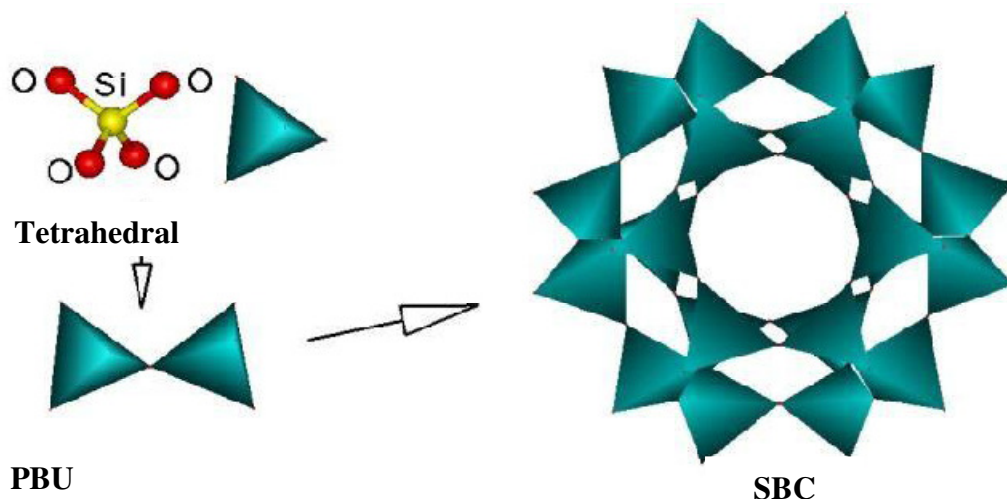

Figure-3: Diagram showing the relationship between the Tetrahedral, the PBU and the SBU[3].

Pore Structure: In other to have a better knowledge of the Zeolite structure, first we need to understand the pore structure. Zeolites have pore structures that are characterized by cavities or channels present in the lattice of each zeolite and the pore has volume and diameter that are typical for each zeolite. The cavities are interconnected with one another by pores that also have specific diameter for each zeolite. Among these zeolites that have channels, there are those zeolites that have channels which run parallel to one another exhibiting a multidimensional and/or non-multidimensional crossing channel system.

Table-1 shows the diameters (in m) of the pores for zeolite A, X and Y as well as the pore volumes (in %).

Table-1: The Diameter of the Pore in 10^{-10} m and pore volumes (in %) of low silica zeolite[8]

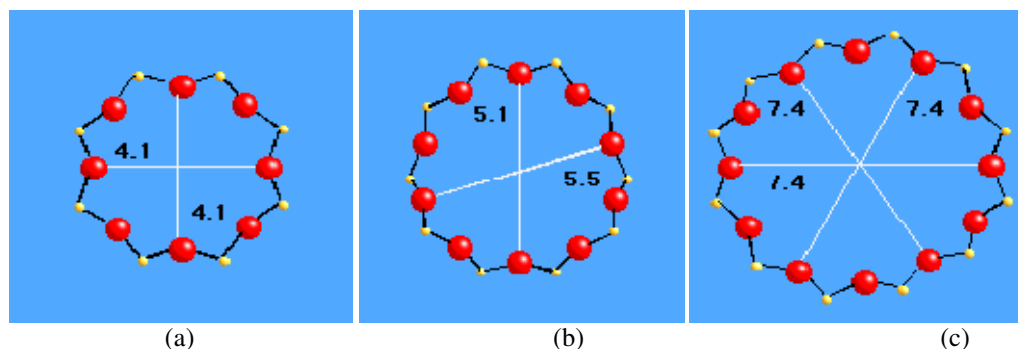| Zeolites	A	X	Y
Pore Diameter (10^{-10} m)	4.1	7.4	7.4
Pore Volume (%)	47	50	48

Table-1, shows values of zeolites made up of sodium cations, these cations are mobile and can be exchanged in the zeolite lattice. When these sodium cations present in the zeolite lattices are exchanged by a potassium cations, the pore diameter is reduced to 0.3 nm. Properties like the adsorption and catalytic capacity of zeolite are affected by the right cation exchange[8].

The pore size and shape present in a zeolite framework affect the adsorption properties of a zeolite and its ability to act as a molecular sieve. Zeolites classification can be done base on the pore size present in the zeolite framework and this can be defined by the number of T atoms present in the framework where T = Silicon or Aluminium ion. The type of pore opening system present in the zeolite framework is known to affect their catalytic and adsorptive processes and presently we have: i. 8 member rings (often referred to as small pore size zeolite). An example is the zeolite A. ii. 10 member rings (often referred to as medium pore size zeolite). Example is ZSM-5 zeolite. iii. 12 member ring (often referred to as the large pore size zeolite) with zeolites X and Y as examples.

Figure-5 below shows examples of the three main pore systems found in zeolite:

3^4 4^8(D4R) $4^5 5^2$ $3^1 4^5 5^3$ $4^6 6^2$

$4^4 5^4$ $4^3 5^6$ $4^8 6^3$ $4^8 8^2$(op) $4^2 4^4 6^4$
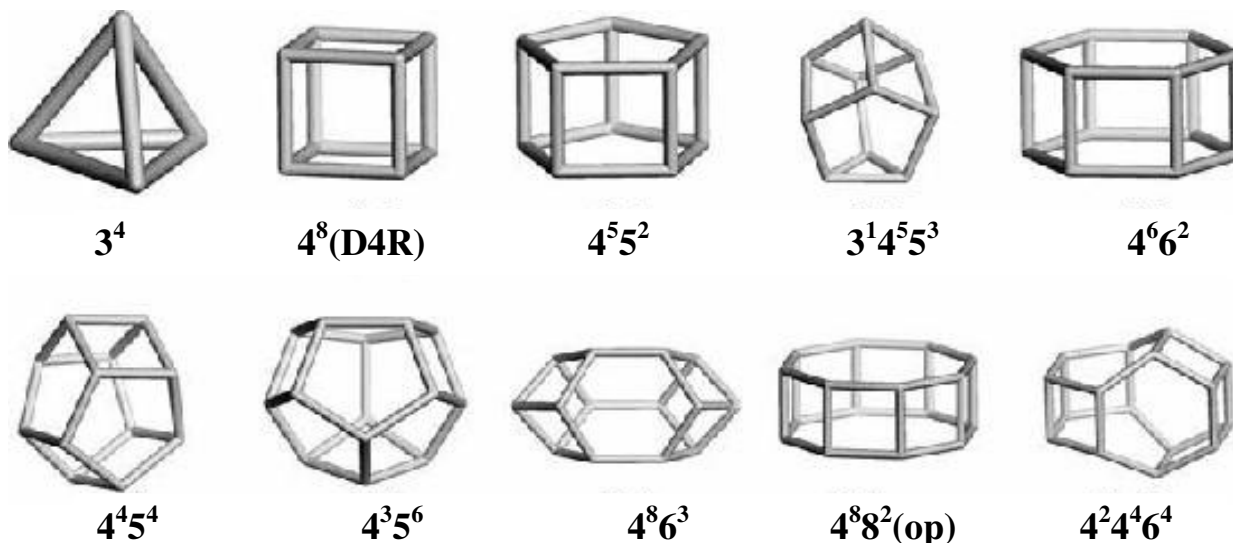
Figure-4: Some of the cage building units in zeolites[12].

(a)   (b)   (c)

Figure-5: Structure of the pores in some zeolites showing (a) an 8-ring, zeolite A (b) a 10-ring, ZSM-5 (c) a 12-ring, zeolite Y[11].

To determine the nature of pore size in zeolites, a selection of molecular probes is used for adsorption process through the zeolite. For example cyclohexane with size 6.5 to 7.4Å cannot be absorbed into an 8-member ring pore system but can be readily absorbed into 12 member ring hence cyclohexane can be used as a probe for only large pore zeolite and not small pore zeolite. The classification of the pore structure in any zeolite is based on the dimensions and shape of the pore system[11].

There are two major types of zeolites namely; natural and synthetic zeolite. There are over 200 types of zeolites available and of these, 50 are naturally occurring while the remaining 150 are synthetic zeolite. Natural zeolites are as a result of indirect volcanic activities with the most common type of natural zeolite being Clinoptilolite, while synthetic zeolites are manufactured either from natural raw materials such as kaolin or from synthetic raw materials such as sodium aluminates and silica[13,14]. Natural zeolites were first discovered in cavities and vugs found in basalt rock and later they were seen in sedimentary rocks that are much closer to the earth crust. Natural zeolites were initially used in agriculture and as adsorbents[14]. The production of natural zeolite can be forecasted to exceed 50,000 metric tons per year while its sales is expected to reach 40,000 metric tons per year in a couple of years[15] but these natural zeolite has a problem of inconsistencies in their properties as those obtained from the different areas of the same mine can exhibit a variation in chemical composition, also a poor mineral deposit which may have as low as 15–20% zeolite content making mining from such site expensive[16-19], and finally there is a potential human health risk from the inhalation of fibrous Erionite and Mordenite present in these natural zeolite sites which discourage their use as adsorbents[20, 21].

It has been observed that natural zeolites have better resistance to acid environments and greater thermal stability compared to many common commercial synthetic adsorbents[22-24] while their thermal stability tends to increase with increasing Si/Al ratio and the presence of alkaline cations in the zeolite framework[25,26].

Properties of Zeolite: As Ion Exchangers: Most zeolites have a natural ion exchange ability making it to be commercially one of the most important properties of zeolite. The ability of zeolite to exchange ions allow for cation replacement in the zeolite structure by an outside ion from the solution[9]. This property of zeolite is as a result of the isomorphous substitution of the silica ion (Si^{4+}) by an aluminium ion (Al^{3+}) in the zeolite framework resulting in a negative charge. Different types of cations can be used to neutralize this negative charge given rise to a balanced or neutral ionic zeolite framework. Generally, zeolites are synthesized using the sodium (Na^+) ion as the balancing or neutralizing cation in the zeolite framework and in an ion exchanging reaction, other cations can easily replace the sodium (Na^+) ion.

In the example below, Mg^{2+} exchanges with Na^+ in zeolite framework as shown in equation 2

$$2NaZ + MgCl_2 \Leftrightarrow MgZ_2 + 2NaCl \qquad (2)$$
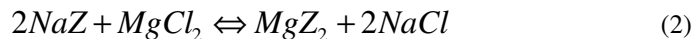
Where: the zeolite is represented by Z.

A similar reaction occurs when protons from mineral acid or ammonium hydroxide exchanges the cation present in the zeolite framework resulting in a protonated zeolite which is used as an acid catalyst. The ion exchange properties of zeolites are widely used in detergents, treatment of waste or hard water as well as in radionuclide separation[10].

As Catalysis: The use of zeolite as catalyst is another important aspect for which zeolites have been applied industrially. About 99% of the world's petroleum that are sourced from crude oil is dependent on the use of zeolite as catalyst, these catalytic property of zeolites is as a result of the combination of the intrinsic properties found in zeolite and these properties are responsible for its overall behavior. However the production of active sites also known as Bronsted sites as shown in Figure-4, which result from the exchange of cations with ammonium hydroxide and then calcination is regarded as one of the most important step in zeolite catalyst production. These sites are referred to as the bridging hydroxyl which is formed at each oxygen bridge site near the clustering of the Si-O-Al where the cation that neutralizes the negative charge is represented by protons. The Bronsted sites are the main reason zeolites are used as catalyst in industries and this is as a result of the formation the hydroxyl group inside the pore structure of the zeolite that has high electrostatic field attracting organic reactant molecules resulting in a rearrangement of bonds especially during reactions that involves cracking.
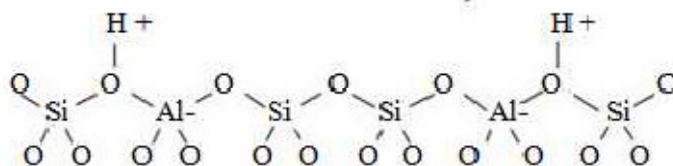
Figure-6: A schematic of the Bronsted acid Sites in Zeolite materials[27].

Some of the reactions that take place in the formation of Bronsted acid sites are represented using equations 3 and 4 respectively:

$$NaZ_{(s)} + NH^+_{4(aq)} \Leftrightarrow NH_4Z_{(s)} + Na^+ \qquad (3)$$

$$NH_4Z_{(s)} \rightarrow NH_3 + HZ_{(s)} \qquad (4)$$
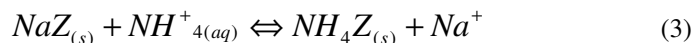
The above reactions are mostly associated with zeolite having low silica like zeolite X and zeolite Y, however for zeolites with high silica content such as ZSM-5, mineral acids such as Hydrochloric acid (HCl) or Tetraoxosulphate VI acid (H_2SO_4), can be used in the production of protonated zeolite by direct ion exchange resulting in the creation of the Bronsted site. Some

important industrial applications of zeolites as catalyst are in the areas of catalytic cracking, hydro-isomerization, reduction of NO_X and xylene isomerisation.

As Adsorption Agent: Adsorption is a process whereby gas or liquid molecules of a material adhere to a solid surface. This process can be used in the separation of a mixture of species and is dependent on the affinity of the mixture toward the solid surface, while the solid surface is called the adsorbent, the adhering molecule is referred to as adsorbate and the removal of the molecules that adhered to the solid surface is known as desorption, this can be achieved by altering the pressure and temperature of the system, allowing for the adsorbent to be reused. The mechanism for adsorption in zeolite system depends on factors such as, pore size of the zeolite as well as the physical and chemical makeup of the zeolite, other mechanisms are: i. The adsorption selective equilibrium. ii. The rate of adsorption selectivity, iii. The adsorption selective shape, iv. The ion exchange of the adsorption. v. The reactivity of the adsorption.

The ability of zeolite to act as an adsorption agent irrespective of the controlling mechanism is broadly influenced by some specific properties of the zeolites. This property is a very important characteristic of zeolites because it directly influences the application of the zeolite as catalyst as well as a separator. The use of zeolite as adsorption agent also has both economic and environmental benefit because of their application in oil refining and petrochemical industries.

Some important applications of the adsorption and molecular sieve properties of zeolite include their use as drying agent as seen in the gas drying column of the Gieger Mueller Counter, gas separation and separation of mixture, other applications are: i. Aromatic bonds removal from linear paraffin. ii. Removal of nitrogen, iii. Removal of oxygen, iv. Removal of sulphur.

Methods Used in Zeolites Synthesis

Crystalline solid state materials production can be classified into two groups. There are those whose reaction occurs in solid state and those where it occurs in liquid state. This solid state reactions often occurs at temperatures above 300°C to overcome the difficulties that arises from the transportation of the reactants to the sites where this reaction takes place, while in the other group the reactions occurs in the liquid phase, in the presence of a solvent[28] and since the transportation of molecules is much easier in the liquid phase than in the solid phase, these syntheses are carried out at a relatively lower temperature, much lower than 300°C. Hence, the syntheses of zeolites are carried out in the liquid phase and there are three methods used in the synthesis of zeolites and they include:

Hydrothermal method: Hydrothermal method is the earliest method of synthesis of zeolite in which synthesis is carried out in the presence of water as solvent, base solution as mineralizer and at temperature range of 90–180°C. The reactants are usually put inside a Teflon-lined Autoclave with hydrothermal synthesis pressure (up to 15 bars) for optimum zeolite production. Since the temperatures required for the hydrothermal synthesis of zeolite is much lower, this method is much easier and cheaper than other methods[28]. Nucleation and crystallization of the crystals do not necessarily occur in solution but can take place at the gels present in the mixtures.

Solvothermal method: Solvothermal method of zeolite synthesis involves the use of a solvent to produce the zeolite. Based on this broad description, the hydrothermal method can also be said to be a member under this classification, since water is by far the most common solvent. There are however other solvents such as alcohols, hydrocarbons, pyridine etc. that had been used successfully for zeolite synthesis. The solvents used in the solvothermal method of zeolite synthesis varies from nonpolar and hydrophobic to polar and hydrophilic[28].

Ionothermal method: Ionothermal is another special category of solvothermal synthesis method in which the solvent used are mainly ionic compounds and are not molecular in nature as in the case of the solvothermal solvents. The solvents used in the ionothermal method of zeolite synthesis are called ionic liquids and their ionic nature has an effect on some particular properties such as low vapor pressures[28].

Materials for Zeolite Synthesis: The synthesis of zeolites are usually carried out using the hydrothermal synthesis method using commercial chemicals as the primary source of SiO_2 and Al_2O_3[29]. The production process of these chemicals is expensive leading to complications and high cost of zeolite synthesis, resulting in a limitation in commercialization and uses of these zeolites in many industrial applications[13], from the above mention disadvantages, the use of cheap and relatively abundant raw materials which serve as combined sources of silica and alumina for the synthesis of zeolite is highly desirable[30-32].

As an example, the cost comparison of obtaining a silica and alumina source from a chemical feedstock and kaolin/metakaolin has been carried out[33], and the result shows that clay as a precursor to zeolite A synthesis has a comparative cost advantage of 15% over a commercial chemical such as sodium silicate.

Synthetic zeolites made from natural or synthetic raw materials having wide range of chemical properties, pore size and better thermal stability are commercially widely used compared to natural zeolites because they are of higher purity and have a more uniform particle size[5,6,8].

The preparation of synthetic zeolite from silica and alumina chemical sources are expensive, yet cheaper raw materials such as clay minerals, natural zeolite, municipal solid waste, coal ashes, industrial slag, incineration ashes etc. are being used as starting materials for zeolite synthesis[6]. Presently a lot of researches are ongoing with respect to the use of clay and other

raw materials in zeolite synthesis, which has the advantage of being relatively cheaper, readily available and more abundant[34,35].

Table-2: A tabular representation of cheap, abundant and readily available raw materials that has been used to synthesize zeolite and the type of zeolite synthesized:

Name of Raw Material	Type of Zeolite Synthesized	Reference
Kaolin	NaX, NaA, Y, ZSM-5, RHA, Hydroxysodalite, β	36-49
Rich Husk ash	Analcime, Y	50-53
Fly Ash	X-type Zeolite	54
Waste Perlite	Na-P1	55
SiO_2 Sinter and Perlite glass.	Zeolite Y, P and gmelinite	56
Template-free batches of macro-porous α-alumina disks	ZSM-5	57
Halloysite mineral	NaA	58
Lithium Slag	NaX-1	59
Brazilian chrysotile and rice husk.	NaA	60
Coal Fly Ash	Hydroxysodalite or Na-P1	61
Silicic acid and Sodium aluminate	ZSM-5	62

From Kaolin: Faujasite zeolites has been synthesized using kaolin samples from Kankara Nigeria by Atta *et al.*[36]. Sodium hydroxide was fused into the kaolin and the resulting mixture was allowed to age for 3 days and subsequently crystallized at 100˚C for 24 hours. The resulting product was a zeolite having mixed phase of zeolite X and zeolite Y.

Christidis *et al.*[56] synthesized faujasite type zeolite from silica and pearlite. Both the silica and the pearlite were mixed in sodium hydroxide solution and commercial form of aluminium hydroxide was dissolved in the sodium hydroxide to produce the synthesized gel. Crystallization of the gel to produce zeolite was done at a temperature of 90˚C for 120 hours and mixed phases of zeolite Y, zeolite P and gmelinite were produced.

Htay and Oo[37] produced zeolite Y from kaolin by fusing kaolin with sodium hydroxide at a temperature of 850˚C for 3 hour. The fused mixture was hydrothermally crystallized at 100˚C for 16 hours and the product was mixed phases of zeolite Y and zeolite P.

Mezni *et al.*[63] used Tunisian illite clay to produce a mixed phases of zeolite X and RHA. This was made possible by the fusion of the Tunisian illite clay with sodium hydroxide solutions and heating the mixture hydrothermally at 110˚C for 96 hours.

Atta *et al.*[50] used Kankara kaolin and rice husk ash mixture to produce zeolite P and Analcime with the conventional hydrothermal method of zeolite synthesis in the presence of sodium hydroxide solution. The aging process lasted 72 hours and the subsequent crystallization of the mixture was done at a temperature of 80˚C and a time of 24 hours.

Saceda *et al.*[53] synthesized Zeolite Y by partially substituting rice husk ash with chemicals of high purity and crystallization of the zeolite was done at 100˚C.

Ma *et al.*[38] synthesized zeolite type X using kaolin as the precusor material and the conventional method of zeolite synthesis by the fusion of the kaolin with sodium hydroxide at a temperature of 90˚C for 8 hours.

D. Georgiev *et al.*[39] studied the most important stage during the synthesis of zeolite NaX from Bulgarian clay as the basic raw material. The use of additives such as sodium hydroxide and lithium hydroxide helps the crystallization optimization and to achieve a high pure phase of the synthesized zeolite which took place after 36 hours at a temperature of 95ºC.

S. Chandrasekhar[30], investigated the effect of calcination temperature on the synthesis of zeolite 4A from kaolin. The clay used was gotten from Thiruvananthapuram district of Kerala, India with a fairly good crystallinity, having a Hinckley Index = 0.79. It was concluded that, the optimum temperature of dehydroxylation was 900ºC for a period of 1 hour, also zeolite 4A with 80% crystallinity and good brightness was formed at a metakaolin temperature of 900ºC and a holding time of 4 to 5 hours. Zeolite with similar crystallinity has been successfully synthesized using other metakaolinzation temperature when the reaction is carried out for a longer period of 8 hours.

Ugal *et al.*[64] prepared zeolite 4A from Iraqi clay. This was carried out by first exposing the clay to a high temperature of about 550ºC for 1.5 h where it was converted to metakaolin. They came to the conclusion that it is possible to use Iraqi kaolinite clay to prepare type 4A zeolite by converting it to metakaolinite via the calcination of the kaolin at a temperature of 550ºC and then using sodium hydroxide for ion exchange to insert the sodium ion into its structure. The structure was characterized by XRD spectroscopy and water adsorption capacity of 92% efficiency was obtained.

Omoleye *et al.*[43] compared the zeolite obtained from Nigerian clay (Elefun in Ogun State) and that obtained from a commercial zeolite Y. The process involves the bounding of sodium hydroxide with dealurninated kaolinite clay in a ratio of

2.5: 1 by weight and molar composition of $6SiO_2$: Al_2O_3 : $9Na_2O$: $24H_2O$ [44]. They concluded that the comparison of the X-ray diffraction, Lattice spacing and SEM results for prepared zeolite Y catalyst with that of Standard zeolite Y shows that the developed catalyst is approximately the same with the standard.

Atta *et al.*[36] studied the synthesis of Faujasite Zeolites from Kankara kaolin Clay. The clay being unreactive was transformed to a more reactive (amorphous) form by subjecting it to heating at 600^oC before using it as a reactant. Dealumination of metakaolin was effected by leaching out the structural alumina with sulphuric acid, to meet the silica–alumina mole ratio[65, 66] required for the targeted zeolite.

Kovo *et al.*[45] investigated the synthesis and characterization of zeolite Y and ZSM-5 from Nigerian Ahoko Kaolin using a novel, lower temperature, metakaolinization technique. In their study, 30 kg of raw representative sample of kaolin clay was used along with sodium hydroxide which was obtained from Sigma-Aldrich (99% analytical grade). From the study it was concluded that reactive metakaolin can be produced at very short exposure times, of the order of 10 minutes, to a temperature of 600^oC. This is a significant reduction in both time and temperature on previous studies and represents both a reduced energy requirement and the potential for a continuous production process.

Farag and Zhang[46], simulated the synthesis of zeolite 4A and 5A by calcining kaolin at temperatures between 500 and 600^oC to form metakaolin. The metakaolin is then mixed with caustic soda and water in a gel make-up tank to produce zeolite 4A gel. To obtain zeolite 5A, zeolite 4A gel is fed to an ion exchanger, where it is mixed with calcium chloride and water. In this process some of Na^+ ions in zeolite 4A gel are replaced by calcium ions, Ca^{2+}. The wet zeolite 5A was then allowed to pass through a dryer to remove part of the water and form the dry zeolite at 1000 F. It was observed that, in the kaolin conversion process to produce Zeolites 5A, hydrogen and oxygen utilization efficiency can be improved via water and steam recycling while Oxygen and Sodium utilization efficiency can be improved through Na_2O recycling. Also, in the hydrogel process that produces Zeolite 4A water recycling can improve Hydrogen and Oxygen utilization efficiency.

From Rice Husk: Khabuanchalad *et al.*[67] synthesized zeolite Y using rice husk ash as the source of alumina and silica. The rice husk ash was then fused in sodium hydroxide solution. The synthetic gel was gotten by mixing the fused ash with a commercial sodium aluminate. Hydrothermally crystallization of the synthetic gel was carried out at a temperature of $100^\circ C$ for 24 h and zeolite Y and zeolite P were obtained.

Rahman *et al.*[52] synthesize Faujasite zeolite with rice husk ash as the precursor material. The synthetic gel was produce by mixing the rice husk ash and sodium hydroxide solution with commercial sodium aluminate and the synthetic gel produced

was aged for 24 h and then crystallized at a temperature of $90^\circ C$ for 22 hours.

Petkowicz *et al.*[60] studied the synthesis of zeolite NaA from Brazilian chrysotile and rice husk. Chrysotile was used in its natural form and after leaching in a typical acid leaching treatment, 30 g of chrysotile were refluxed with a HCl solution (5 mol L^{-1}) for 2 days at 80^oC, according to procedure described in the literature[68]. The resulting chrysotile was thoroughly washed with distilled water and then dried in an oven at a temperature of100^oC. The resulting leached material was labeled an LChr. It was concluded that Zeolite NaA can be synthesized by a direct hydrothermal route, using silica from Chrysotile and rice husk as a silica source. Brazilian Chrysotile and rice husk seems to be good alternative silica sources for zeolite NaA synthesis. In the case of Chrysotile, in its natural form, no zeolitic material could be obtained, demanding a leaching procedure before its use. Even then, traces of non-reacted Chrysotile could be detected in the resulting zeolites. Except in the use of natural Chrysotile, all the other investigated possibilities afford highly crystalline zeolite NaA.

Dalai *et al.*[41] synthesized and characterization NaX and Cu-exchanged NaX zeolite from silica obtained using rice husk ash. Rice husk ash, sodium hydroxide, Aluminium hydroxide and silica gel were used as the starting materials. The silica solution was first prepared by treating the rice husk ash with 2.5 molar aqueous sodium hydroxide solution at a temperature of 80^0C for a period of 5 h with continues shaking. They concluded that a number of zeolite types such as NaX, P_C, analcime and hydroxysodalite were synthesized using silica obtained from rice husk ash. A series of NaCuX zeolite were also prepared by exchanging Na of the synthesized NaX with copper.

From Fly Ash: Ojha *et al.*[54] studied the synthesis and characterization of zeolite from fly ash. They concluded that X type zeolite can be synthesized from fly ash by alkali fusion followed by hydrothermal treatment and that the fly ash, could be converted to pure X-type zeolite using suitable treatment conditions, the properties of the zeolite formed strongly depend upon these treatment conditions and concentrations of the raw materials. Zeolites having varying surface area, silica/alumina ratio, and crystallinity were obtained when the reaction parameters are altered, the crystallinity of the synthesized zeolite was also found to change with fusion temperature and have a maximum value of 823 K, for best quality, in terms of surface area and crystallinity, X type zeolite can be obtained at the following conditions, NaOH/fly ash ratio of 1:3, fusion temperature, 823 K, aging time of 24 hours and 6 hours for the hydrothermal treatment.

Other Sources: D. Mravec *et al.*[62] investigated the synthesis of zeolite ZSM-5 in the presence of ethylamine in aqueous medium by adding drops of hydrosol of silicic acid into an aqueous solution of amine and sodium aluminate. The prepared mixture was homogenized for 20 minutes at laboratory

temperature and poured into an ampoule where it was kept at a given temperature for a certain time. After cooling, the crystalline portion was filtered off, thoroughly washed with distilled water, and dried for 4 h in a vacuum drier at a temperature of 110°C. They observed that well crystallized zeolite of the ZSM-5 type originated from the sol of silicic acid and sodium aluminate in the presence of aqueous solution of ethylamine at a temperature of 150°C in the course of seven days. If the ratio $_n$(ethylamine): $_n$(SiO$_2$) was equal to 1.7, the proposed procedure yields zeolites with high degree of crystallinity.

Barth-Wirshing *et al.*[55] used waste pearlite to synthesize zeolites at temperatures between 100 and140°C in sodium hydroxide solutions, aluminium was added to the solution and hydroxyl-sodalite was obtained as the end product.

Wajima *et al.*[69] synthesized zeolite Na-P1 from paper sludge ash and diatomite. Sodium hydroxide solution was used as the reacting medium and hydrothermal crystallization was carried out for 12 hours at a temperature of 90°C.

Douglas *et al.*[70] investigated the use of the by-product of aluminum etching process for the production of zeolite by hydrogel process. They observed that the analysis of the chemical composition of the raw materials and the products, demonstrates that the by-product can be used to produce high quality zeolite because, it carries a large amount of Al$_2$O$_3$ which is usable as raw materials for zeolites synthesis. The synthetic zeolites were prepared using hydrogel process at 60-90°C for 1 h and mole ratio of reactants is about two.

Halil Kalipcilar and Ali Culfaz[57], synthesized ZSM-5 crystals from template-free batches on macro-porous α-alumina disks and reported that: The SiO$_2$/Al$_2$O$_3$ ratio of the synthesis gel influenced the crystal morphology, surface coverage and intergrowth among the crystals. Prismatic ZSM-5 crystals covered the disk surface when the SiO$_2$/Al$_2$O$_3$ ratio of the batch was higher than 100, whereas spherical polycrystalline particles of ZSM-5 were obtained from batches with a SiO$_2$/Al$_2$O$_3$ ratio of 80.

Mordenite type zeolite was formed on the disk surface due to the incorporation of alumina dissolved from the disk when the time of crystallization was extended. The effects of silica source and seeding of the support surface with 0.3 and 2 μm ZSM-5 crystals on the morphology of zeolite layer were also investigated. The purity, surface coverage and SiO$_2$/Al$_2$O$_3$ ratio of ZSM-5 crystals increased in the order of silica sol containing methanol, silica sol and silicic acid. Seeding decreased the length of prismatic ZSM-5 crystals from 45 μm to 10 μm and increased the surface coverage.

Zhao *et al.*[71] studied the preparation of highly ordered cubic NaA zeolite from halloysite mineral for adsorption of ammonium ions. Halloysite mineral which serve as silicon and

aluminum source was used to synthesis the NaA zeolite this was done by using alkaline fusion followed by hydrothermal treatment method. The results show that, pure form, single phase and highly crystalline NaA zeolite can be successfully synthesized from halloysite mineral by hydro-thermal method.

Chen *et al.*[72] investigated the synthesis and characterization of zeolite NaX-1 from lithium slag. Sodium hydroxide and lithium slag was mixed in a 1.5 weight ratio then the mixture was milled and fusion of the mixture was carried out in a platinum crucible at a temperature of 600°C for 4 hours. The fused mixture was then cooled at room temperature, crushed and water was added to form slurry, the slurry was stirred mechanically for 30 minutes and aged in a Teflon beaker at room temperature for 12 hours, and kept at 95°C for 8 hours without stirring. The resulting precipitate was then repeatedly washed with distilled water to remove excess sodium hydroxide, filtered and dried. The synthesized zeolite was called "NaX-1".

Applications of Zeolites

Since the introduction of zeolite into the market in the 1950's, zeolite consumption and its application in industrial processes has steadily increased. This increase has accelerated in recent years due to their utilization in detergents as shown in Table-3.

Table-3: Manufacturing Capacity and Consumption of Zeolite A in Detergent Industry in 1995 (in 10^3 tons per annum)[8].

	Western Europe	Northern Europe	Far East
Consumption	600	317	248
Capacity	1077	453	522

Natural and synthetic zeolite has played an important and integral part of many industrial processes. The world demand for zeolite has continued to increase with the world demand for synthetic zeolite estimated to be approximately 1.8 million metric tons while the demand for natural zeolite was projected to hit 5.5 metric tons by 2010[73]. Both types of zeolite are important in modern day industry. 90% of natural zeolites are mainly used in the construction with the remaining used in animal feeding, horticulture, treatment of hard water, in odor control and etc.

Synthesized zeolites are applied chiefly in process industries. A data obtained in 2001 shows that about 81% of synthetic zeolite is used in the detergent industry while others find application as catalysis, adsorption. Zeolites utilize the ion exchanging characteristic to function as an additive in detergents. In detergency zeolites, typically zeolite A (LTA), act as a water softener preventing carbonate precipitation through the exchange of calcium and magnesium ions with the highly mobile sodium ion present in the zeolite framework[74]. The increased application of zeolites in the detergent industry can be

attributed to environmental concern. The use of phosphate builder has been banned in most countries because it causes eutrophication and is difficult to degrade when placed in water bodies, hence zeolites i.e. zeolite A and zeolite X offer a good replacement because of their high ion exchanging capacities.

The application of zeolites has its largest economic impact in the fuel catalytic cracking (FCC) processes. Zeolites give an increased yield over amorphous catalyst to the tune of around 1 billion US dollars a year[75]. Zeolite Y and ZSM-5 are two of the most important zeolites used in FCC catalysis. In fact ZSM-5 zeolite is regarded as a good octane booster. Other octane booster zeolites in FCC operation include mordenite, silicalites, MCM-20 and zeolite beta.

Another example of the use of zeolites in catalysis is in hydrocracking which involves the conversion of higher paraffins over noble metal containing zeolite catalysts to yield distillate products. The description of the hydrocracking processes including all the mechanism are well documented[77] but the main point is the crucial role played by zeolite catalyst in the process in the replacement of old catalysts such as alumina.

Current Trends in Zeolite Application

Presently, some of the problems encountered in the synthesis of zeolites include the availability and high cost of obtaining the primary source of silica and alumina used in zeolite synthesis. Also both the reactivity and selectivity of commercial silica found in gels, sols, and in amorphous solids vary. Zeolites synthesized using chemicals as the primary source of aluminosilicate are expensive but alternatively cheap and readily available raw materials, like silica fume, kaolin, natural zeolites, fly ash, ashes from the incineration of municipal solid waste and industrial slags can be used to replace these expensive chemicals as the precusor materials for the synthesis of zeolites.

Using waste materials for the purpose of zeolite synthesis helps to mitigate environmental pollution.

Kaolin is also a good precusor material for zeolite synthesis because its structure is represented by a silica tetrahedral sheet linked to octahedral sheets of $Al(O,OH)_6$ by the sharing of an oxygen atom. Zeolites produced from natural kaolin have always been discovered to contain trace amount impurity elements, which were originally present in the kaolin. These elements affect their characteristic properties such as their catalytic activity, brightness, adsorption capability, electrical properties, etc. of the zeolite. Currently, lots of research work are ongoing in different areas of zeolite synthesis using kaolin[1,78,79], illite, smectite, interstratified illite-smectite[80], montmorillonite[81] and bentonite[78,82] as precursor materials, though the benefits of zeolite synthesis using kaolin as the primary source of aluminosilicate are widely known[34,35]. Many researchers have researched on the preparation of different types of zeolite using kaolin and other raw materials as the primary source of aluminosilicate and great progress has been made in synthesis of zeolite A, Mordenite type of, zeolite X, zeolite Y etc.

Calcination of the kaolin at temperatures ranging from 550°C and 950°C is usually done in order to convert the unreactive kaolin into a more reactive metakaolin. Only a little of the hydrated alumina octahedral is maintained and the rest is converted to a more reactive tetra- or penta- coordinated units[83]. The temperature and time at which the kaolin is calcined strongly influences the reactivity of the synthesized zeolite and to obtain a very reactive metakaolin, several researchers have suggested calcination temperatures between 600°C and 800°C and a calcination time of 30 min to 2 h[31, 82, 84].
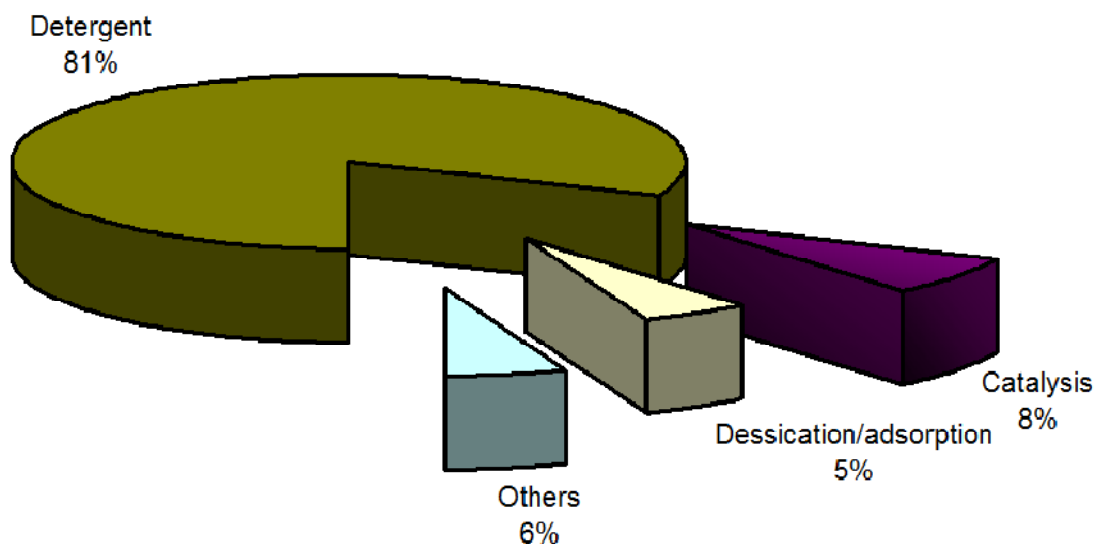

Figure-7: Chart showing the percentage utilization of synthetic zeolites in 2008[76].

Currently the use of zeolite has advanced in the following areas:

In Agriculture: Presently, zeolites are used in the food industry. Breweries use zeolites (NaA or/and LiX) to stabilize beer through the absorption of enzymes/proteins whose responsibility it is to further degrade the beer. Dealuminated zeolite Y helps in the removal of alcohol from beer while fatty acids present in edible oil can be eliminated using zeolite X. Zeolite are also used in the preparation of the formula for toothpaste production.

Zeolites have been used successfully as soil additives to improve the yield of agricultural products. The mercury adsorption by plants and its subsequent entry into the food chain can be restricted using natural zeolites[85]. For instance, considerable amounts of NH_4^+ can selectively be removed from wastewater using Italian chabazite-rich tuff zeolite. The zeolite also be reused in the correction of soil for the cultivation of common vegetables and flowers [85] while the wastewater can be treated with zeolite to strongly reduce the ammonia. After it has been used, the ammonia enriched zeolite acts like a fertilizer to give high efficiency in agriculture[86]. It has been reported that the reason for the successes that have been recorded regarding a well-known Hungarian wine called "Bull Blood" is related to the type of cellars the winemakers use in the Eger's mountains which are made from zeolite-rich soils. The zeolite helps the soil to maintain a constant level of atmospheric humidity during the wine maturation stages[87].

In Animal Production: The addition of clinoptilolite (a natural zeolite) to animal diet has been found to be of great benefits in the rearing of animals like pigs where pigs fed with diets containing clinoptilolite have shown significant gain in weight and high resistance to sickness than those fed with normal diets they also exhibited normal digestion, increased appetite for food, and increased meat content while the fat content reduces significantly. Zeolites such as clinoptilolite, chabazite, mordenite, erionite, and phillipsite have shown great ability to absorb hydrogen sulfide, carbon dioxide and ammonia as well as having deodorizing effect.

There is the possibility that zeolite has the ability to remove toxin and bring about changes in enzymes and immune system responses and all of these events have resulted from the addition of zeolites in animal feeds. In the production of eggs by hens also, 16-week-old pullets were divided into three strains, the first stain were given feeds with 135g protein/kg only the second were fed with 135g protein/kg mixed with 50g clinoptilolite/kg and the third were fed with 135g protein/kg and sterile river sand which act as control to maintain iso-energetic in the diets[87].

The diet of chicks containing Clinoptilolite greatly reduced the dangerous effects of aflatoxin because the presence of clinoptilotile strongly adsorbs aflatoxins and zearalenone which are responsible for this effect[88]. Mineral adsorbents such as natural zeolite and bentonite can be added to chick diets to prevent food poisoning resulting from the presence of mycotoxins in their diet.

Zeolites have been shown to affects the characteristics of eggs. In Greece it has been observed that clinoptilolite helps improves the weights of the albumen and yolk in egg. The benefits of Clinoptilolite in egg and albumen weight is not affected by how old the hen is and its diet the hen was subjected to[89,90].

Radionuclide Removal: Research has shown that several natural zeolites have the ability to accept some radionuclide such as 90Sr, 137Cs, 51Cr, 45Ca, and 60Co. Zeolites such as Mordenite, has effectively removed 137Cs and 90Sr found in contaminated soils[91]. Clinoptilolite also shows a significant protective effect in the reduction of 137Cs accumulation in male broiler that has come in contact with alimentary contamination.

Clinoptilolite supplement mixed with chicken feeds removed 137Cs deposited in some body parts of animals that has been exposed and contaminated after dietary administration of 2.5, 5 and 10% of clinoptilolite, zeolite results in radionuclide 137Cs elimination increases and the radioisotope deposit found inside some sensitive organs like the liver, muscles of the femur and kidneys decreased. The removal of radionuclide was experimented with preventive as well as corrective administration of clinoptilolite from 24 hours after the first contamination of brown rats[92,93]. Akyuz, *et al.* reported that clinoptilolite found in the deposit of these radioisotopes act as excellent absorber for ions of elements like Cs and Sr and can also be used in the treatment of wastewater from radioactive sites among its other uses in the de-contamination of other hazardous materials[94].

Heavy metals and organic poison removal: Waters contaminated with heavy metals are one of the pollution problems faced in the world because of its effect on the food chain. Natural zeolite is particularly applied in the removing of ammonia and heavy metals such as Cadmium ions, Lead ions, Zinc ions, Copper ions and partially Chromium ions. Generally, Clinoptilolite has high stability in acidic environment showing high ability to absorb many heavy metals.

Malion *et al.*[95] has proven that zeolite pore size have no effect on the actual absorption of metallic ion at the equilibrium point. However when the contact between the solid/liquid phase is little, the ability of the zeolite to remove heavy metallic ions from the liquid is adversely affected. This is an important parameter in the area of waste water treatment. A kinetic curves has been developed to show the selectivity of zeolite for Pb ions, and significant amounts of Cd ions that can be removed by zeolite[95].

Mercury which is known to be poisonous to humans on injection and have a negative impact on animal health is being used in a lot of industries as catalysts, pigments, batteries and in

agriculture such as in the manufacturing of antifungal insecticides, which has resulted in the pollution of the aquatic environment, which can lead to the presence of mercury in the biological and hydrological cycles, but the remarkable rate of mercury removal from aqueous solutions with the use of NaCl pretreated pure heulandite crystals and NaCl pretreated clinoptilolite found in rock samples have been observed and reported [96], hence, the chemically pretreated zeolite has a role to plays in heavy metal removal and it can be proposed that materials made of natural zeolite can be applied in the removal of heavy metals from solutions. The bonding of the metal to the zeolite can be attributed to ion exchange and surface absorption processes[97].

Hemodialysis, Anesthesiology and Hemoperfusion Application: Zeolite with the ability to remove impurities, have been used in hemodialysis processes[98]. The removal of NH_3 from a re-circulating dialysis stream is a major challenge among others in the development of a regenerable hemodialysis system that is very portable. Zeolites such as zeolite F, zeolite W and Clinoptilolite have been found to have high ammonia ion exchange capacity and thus can be used in hemodialysis application.

Zeolites with high ion exchange capability have been used to show high level of selective adsorption. This was achieved by the use of a high silica zeolite absorber that was placed in the outlet of an anesthesia machine[99]. Zeolites shows almost complete desorption which takes place at controlled temperature and condensation of the desflurane to a liquid state unlike charcoal filters and results prove that high percentage of the desflurane can be recovered having high purity through desorption process[100]. Some zeolites have also been used as cartridge in hemoperfusion. Clinoptilolite has serve as a light tight supply chamber used for hemoperfusion[101].

Cosmetic and Dermatological Application: Zeolites are currently being used in the protection of polymers from degradation resulting from exposure to ultraviolet radiation, other outward applications are in the areas of cosmetic and dermatology has been considered. Zeolites in powdery form have found application in the treatment of athletic foot and it has proven to be effective, it also shorten the time required for the healing of bruises and wounds from surgery[102]. The anecdotal information available indicates that injuries to workers in mines and factories that were exposed on the job to these zeolites have a remarkably quicker healing time. There are also some reports on mechanically micronized clinoptilolite has helped to heal the wound from ulcer and in the treatment of chronic skin diseases. The injuries sustained by horses and cows in places like Cuba for instance are routinely covered with clinoptilolite to make the healing process faster[102].

Bone Formation: Trace amount of silicon have shown to enhance bone formation in humans and zeolite A containing silicon has resulted in an increase in the thickness of egg shells in hen, these zeolites also have significant effects on the formation and structure of bones. Synthetic zeolite such as zeolite A has therapeutic ability in helping people suffering from abnormal loss of bony tissue resulting in fragile porous bones attributed to a lack of calcium, common in women who are postmenopausal and this is as a result of their ability to stimulate bone formation[103]. Zeolite A has also been reported to enhance the rapid multiplication and growth that occurs in older men or women[104].

Enzymes Encapsulation: Various techniques has been used to insert active sites like metallic cations into zeolite framwork and this has been used to develop a ship in a bottle system that allows for enzymes encapsulation[105-107]. This has also given birth to an exciting pharmacological application of zeolites and mesoporous silicate encapsulation of different ions and molecules having delayed release properties, giving rise to many enzymes being encapsulated and released with almost full activity. Also Clinoptilolite impregnated with Zn and Ag in its pore and salicylic acid on the zeolite surface has been applied for the treatment of skin diseases and as support materials for enzymes and antibodies[105,108].

Conclusion

Zeolite is an aluminosilicate mineral having tetrahedral building units made up of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$. Since its introduction in the 1960's, it has been applied in a wide range of areas starting from its use as catalysts in catalytic cracking, water softeners and molecular sieves. The current trend in its application is in agriculture, medicine etc. and the application areas keep increasing. Its versatility is based on the fact that many different raw materials can and have been successfully used in its synthesis. The use of readily available, cheap and abundant raw materials in the synthesis of zeolite has been proven to produce good quality zeolites compared to the use of rather expensive chemicals that are also in use to produce them.

Acknowledgement

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