

Zeolites are just like
clay minerals
because both are
composed of
aluminosilicate...

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INTRODUCTIONS:

Zeolites are just like clay minerals because both are composed of aluminosilicates, although they differ in their crystal structure in that clay minerals deform in water showing expansion and contraction while zeolites are stable and rigid in water [8]. Both natural and synthetic zeolites are basically composed of aluminosilicates they may differ in the Si/Al ratio and pore sizes. Zeolites as defined by the mineralogist community ?? is a crystalline aluminosilicate with a 4-connected tetrahedral framework structure enclosing cavities occupied by large ions and water molecules both of which have considerable freedom of movement permitting ion exchange and reversible dehydration. ??[6]. Fig1

The tetrahedral structure of these micro porous aluminosilicates is of the form where T can be either Al or Si. The silicon based framework () structure is uncharged or neutral but when Al is introduced into this structure () a negative charge is induced due to shortage of electron from the Al with valence of taking the place of Si with . This has to be neutralized by extra cations attaching themselves to the structure [5]. In summary one can say the stability of the zeolite structure depends on the ratio of Si/Al. with higher ratio of these elements the zeolites have better stability for example in acidic environments. For Si/Al ratio > 10 the framework may be considered as having high silica. Zeolites may have the following structural formula. ..[5] . Where the first part represent extra framework cations, the middle term is the framework and the last part is the sorbed phase. Zeolites are unique considering their inherent physicochemical properties and a lot of

researchers and scientists worldwide have developed interest in exploiting and utilizing the valuable properties of these minerals since from their first discovery. The name zeolite is of Greek origin simply meaning boiling stone considering the facts that water is fast lost from it when heated [1] and this is an important property of the zeolite opening door for many applications. These minerals occur in nature in sedimentary deposits and can also be artificially made in the laboratories [6], pore sizes being determined by intended purpose and application, in fact this is one of the advantages of the synthetic zeolites. They exist in 3D structures [8] with cavities that houses cations, organic and water molecules. The structure of the zeolite is not affected when elements and ions are removed from their cavities.

THE ZEOLITE STRUCTURE.

They are generally micro porous and the micro porosity plays an important role in the characteristics of the zeolites. The important and unique property of zeolites that distinguishes it from other structures is the formation of tetrahedron which can be connected to each other by bridging oxygen to form chains. A list of about 133 different framework structures has been identified [6]. The fundamental criterion for identification is the framework density which is the tetrahedral connected atoms per 1000Å. There are 21T atoms per 1000Å for porous tectosilicates. The structural composition can be changed by introducing metals such as Ge, B, Zn, and P. the basic structure of the zeolites can be separated into two broad classes. I) the basic tetrahedron which is the initial building block and ii) the composite consisting of many units joined together [6, 1]. The unit cell which is built up by

repeating itself in the format where T represents cations that is Al or Si etc and they are in turn connected to oxygen atoms at the corners. FIG2. In the basic building block each tetrahedron is connected to adjacent one by bridging oxygen eg. T-O-T. The angle between T-O-T does vary from 140 to 165 degrees for silica tetrahedra[6]. Angular variations give variety of zeolite framework types. Boron and zinc are the smallest and largest cations found attached to the zeolite structure with 1.44Å and 1.95Å bond sizes. Generally zeolites has a small range of pore sizes ranging from (1-20Å)[3], to be specific for FAU-type the pore size is 7.4Å, for alumophosphates the value is 12.1Å. Pore sizes greater than 20Å -500Å are mesoporous materials while greater than 50nm are considered as macroporous materials.[5].

NATURAL ZEOLITES

First discovered in 1756 by A. F. Cronstedt, it occurs by natural geological phenomena such as volcanic eruptions that has taken place in the earth crust and are found usually in alkaline lake sediments and soils.[5]. The basic composition is lower Si/Al ratio. Clinoptilolite with chemical composition $(Na, K)(Al_3)$ is one of the most important zeolites among the list of over 40 natural zeolites because of its fine grains. The clinoptilolite and another natural zeolite Mordenite (MOR) have great agricultural and sorbent applications. Some natural zeolites are inherently toxic causing lungs related illnesses [5] and should be handled with extra care. Another example of natural zeolite is Mutinaite whose artificial counterpart is the ZSM-5[4]. This mineral has a Si/Al ratio of 7.6 which seem to be the highest value for natural zeolites[4]. In addition the mineral is thermally stable with a high

rehydration capacity. Natural zeolites when exposed to environmental conditions for a very long time may lose a higher percentage of water content in their channels and left with residual amount. Channels could be destroyed by high rate of water removal from it. Other frameworks such as alumophosphate consist of tetrahedral units and are classified as zeolites[5] and this framework is uncharged as was the case with aluminosilicate frameworks for this reason the channel contains only water molecules. fig 3

ARTIFICIAL ZEOLITES.

The natural zeolite is inflexible in terms of their atomic structure and hence the properties cannot be altered this limitation calls for the need for synthetic counterparts that could be used for any desired application. For example one can make a zeolite with larger cavities than the natural one to suit certain application and it is worthy to note that some of the synthesized zeolites have not known natural counterparts [1]. The following methods are commonly used for zeolites synthesis.

1. Hydrothermal synthesis: the components are mixed in water to form aqueous solution and heated from room temperature to 300 degrees with PH maintained at > 7 . Some natural zeolites cannot be synthesized because their structure and stoichiometry is very difficult to predict [5, 6]. In the synthesis of aluminosilicates cabosil is used as the source of Si and Al while oxy hydroxide is the alumina source with organic cations and alkali hydroxide forming the template and base respectively. The template can

control the desired pore diameter and the shape of the zeolite to be made. The template can be removed by thermal decomposition.

2. High pressure hydrothermal: analogous to the natural phenomenon zeolites can be synthesized in the laboratories under the influence of high temperature, pressure and the presence of water. The magnitude of these parameters range from 12hrs to 72 days for time taken during synthesis, 100bar to 4kbar is the applied pressure range and from 25 degrees to about 700 degrees is the temperature [5]. Laumontite is an example of zeolite synthesized by this process. The Si/Al order in zeolite framework as well as crystal behavior can be influenced by synthesis temperature. The disadvantages associated with this method are the use of high pressure and the longer process time.

The synthesis of zeolite is one very important way of dealing with the issue of how to dispose sludges generated from paper industries, drainages and coal processing[2]. The good work of Dr Teruo Henmi helped saved the environment by converting ashes from these sludges to zeolites which has a lot of uses covering areas in agriculture, public health and cosmetics etc[2]. so artificial zeolite is now seen as an avenue to recycle wastes ashes which use to be an environmental problem.

DIFFERENCE BETWEEN NATURAL AND ARTIFICIAL ZEOLITES.

1. The ratio of silica to alumina is small in synthetic zeolites compared to the natural one. We have 1: 1 and 5: 1 in clinoptilolite.[9]

2. To synthesize we need chemicals and considerable consumption of energy but the natural ones occur by geological processes.[9]

3. Natural type like the clinoptilolite is stable in low acid environment while the synthetic one breaks under this condition. The stability of the clino type is because of the high silica content. And this clino type is preferred for agricultural application like land amendment and forms part of livestock feeds.[9]

APPLICATIONS OF ZEOLITES

Zeolites both natural and synthetic one has found great deal of application areas be it activities involving chemical reactions or biochemicals[2].

Synthesis of these minerals creates a wider opportunity to extend the field of application of the zeolites, some most common applications include separation and purification of mixtures whether in liquid or gaseous forms using popular methods like sieving, or filtering and sorption[5] the molecular sieving ability can be possible because of the uniformity of pore sizes of the zeolites which make easy to separate molecular compositions with different sizes for example sizes less than 1A[6]. zeolites have been used as molecular sieve since 1925 to date[1] when it was released that gas could be separated due to variation in molecular sizes. Chabazite with a small pore size of 0.5nm is commonly used for gas separation. Other applications include ion exchange and for storage purposes. The simplest application of zeolite that touches every home is in water softening in kitchens and laundries used for washing, the history of this application dates back to

1913[1]. Synthetic zeolite such as Linde (Na-LTA) and the GIS type Na-gismondine are commonly used for this purpose. LTA is also used for water purification in treatment plants. Some other zeolites used for this purpose are synthetic type like ABW, and GIS and Phillipsite (PHI) both its natural and artificial forms are also used [5]. These has windows that are medium sized and can be effectively used to treat water containing radioactive elements as contaminants common example being cesium or strontium and waste water from mining sites. Conservation and drying of food items especially the perishable one is very important and this can be simply done by the sorption property of zeolites. There is no doubt every living place needs fresh air for good health zeolites are used to remove odours e. g ammonia which smell bad in industrial environments[5, 2]. Naturally occurring zeolites like clinoptilolite (HEU) are good sources of fertilizers when applied on agricultural soils they simply enrich the soil by elements like potassium and these minerals also improve the water retention capabilities of the soils. Animals and birds feed containing zeolites provides good and nitrification and improves their yields [5, 6]. The petrochemical companies are not left out as zeolites Mordenite type (MOR) and ZSM-5 are used in the production of gasoline and dewaxing of fuels.[2].

CONCLUSIONS:

Zeolites are one of the most important minerals that have direct bearing in the lives of mankind. Both natural and synthetic ones play a number of important roles in many areas such as agriculture, horticulture, and industries to mention a few[8]. The ability to synthesize these minerals to

desired pore sizes and shape is one way of dealing with the problems of inflexibilities of the natural types to suit many applications. Zeolites contribute enormously to the economy as an estimated \$130 billion circulates in the market, major share coming from oil companies buying zeolite products.

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