REVIEW

Characteristics of Zeolites

Going Yim

*Department of Inorganic Materials Engineering,
Pai Chai University, Taejon 302-735, Korea*

Zeolite의 特性

任 宏

培材大學校 理工大學 無機材料工學科

  Zeolites were discovered as a natural mineral more than two hundred years ago. In the beginning, the mineral was used as ion-exchange material and adsorbent. After the end of World War Ⅱ, however, a variety of zeolites have become available in large amounts because of the establishment of low temperature synthesis and the discobery of natural zeolite deposits of sedimentary origin. Various uses of xeolite were developed utilizing the unique crystal strucrure and function of these minerals. In connection with this development, remarkable progress has also been made in basic studies on the related geology and mineralogy, crystallization from sols and gels, structure, ion exchange, adsorption and cataiysis.

  As a result, zeolites, which had been known only as mineral specimens displayed in museums, established a firm position among the high-technology masterials with excellent functional capabilities.

  Zeolite는 氣孔을 통한 吸着과 分離作用의 특징을 지닌 吸着劑·分離劑로서는 물론, 氣體나 液體의 乾燥劑 및 觸媒로 그리고 化學工學的 工程技術에있어서 混合物의 分離精製工程에 널리 이용되고 있고, 다른 silica gel, 活性炭, 活性 alumina 및 酸性白土등에 비하여 독특한 特性을 가지고 있으며, aluminosilicate 鑛物의 일종인 天然 zeolite가 鑛物學的 特性과 化學的 表面活性으로 인하여 多方面에 있어서 공업的 利用度가 날로 증가하고 있다.

  鑛物學上 zeolite는 Na, Ca등 陽이온을 함유하는 硅酸鹽物質로서 酸素環의 孔徑이 3~11Å 정도인 立體網狀構造로 되어있어 脫着이 자유스러운 水分을 함유하고 있으며 鑛物中에서 陽이온 交換能(C.E.C가 대략 100~300)이 대단히 높기 때문에 氣體에 대한 選擇的 吸着力이 큰 鑛物로 알려져 있다. 더욱이 天然 zeolite는 土壤改良劑나 家畜飼料用, 混合肥料 및 農藥등에도 사용되고 있으며 공업用으로 製紙原料로서 白色度가 높고 硬度가 낮다는 特性뿐만 아니라 斷熱·保溫材 및 建材등 공업材料로서의 活用性, 그리고 吸着劑, 吸濕劑, 乾燥劑, 이온交換體, 增量劑 및 molecular sieve 로서의 이용은 괄목할 만 하다. 특히 높은 陽이온 交換能을 이용한 重金屬 廢水處理劑나 放射性 廢水의 處理劑, 廢水의 軟化劑로서의 利用度가 높아지고 있어 앞으로 zeolite의 工業化에 따른 새로운 製造方法과 活用可能性을 모색해야 한다.

As every student of mineralogy or geology knows, zeolites are ubiquitous constituents in the vugs and cavities of basalts and other traprock formations. Beautiful assemblages of well-formed crystals up to several inches in size are prized by mineral collectors and adorn the mineral museums of every country. Several dozen individual species have been identified among which are mordenite, chabazite, erionite, and faujasite whose adsorption properties rival those of several synthetic molecular sieves. In addition to their occurrence in basic eruptive rocks and related late-stage hydrothermal environments, zeolites are recognized today to be among the most abundant and widespread authigenic silicates in sedimentary rocks.

The high purities and flat-lying nature of the sedimentary deposits have aroused considerable commercial interest both here and abroad, and applications based on their unique physical and chemical properties have been developed for them in many areas of industrial and agricultural technology.

Zeolites have been known for more than two hundred years, but it was not until the middle of this century that the scientific community became generally aware of their attractive properties or of their geological significance in the genesis of tuffaceus sediments. During the last thirty years, interest in zeolites has increased at a remarkable rate, and it is currently difficult to pick up an issue of any of the leading geological or chemical journals without finding at least one article devoted to these materials. Most of the recent effort has centered around synthetic molecular sieves, an area that has grown into multi-million dollar businesses in several countries, or natural zeolites as they occur in sedimentary rocks of volcanic origin. Amygdaloidal zeolites are still the principal source of high purity specimens for x-ray structure determinations or for sophisticated experimentation, but most of the geological and industrial activity has concentrated on "sedimentary" zeolites.

Rarely in our technological society does the discovery of a new class of inorganic materials result in such a wide scientific interest and kaleidoscopic development of applications as has happened with the zeolite molecular sieves.

Zeolites is originally natural mineral. For a long time, many adsorbents such as silica gel, active carbon, activated alumina, acidic clay, activated clay and others were used widely. In the adsorbents, especially, in recent years, zeolite was very much noticed, because its characteristic nature.

The properties and uses of zeolites are being explored in many scientific disciplines : modern inorganic chemistry, physical chemistry, surface chemistry, colloid chemistry, catalysis, biochemistry, environmental science, mineralogy, geology, and in all types of chemical engineering process technology. The wide variety of applications includes separation and recovery of normal paraffin hydrocarbons, catalysts of hydrocarbon reactions, drying of refrigerants, separation of air components, carrying catalysts in the curing of plastics and rubber, recovering radioactive ions from radioactive waste solutions, removing carbon dioxide and sulfur compounds from natural gas, cryopumping, sampling air at high altitudes, solubilizing enzymes, separating hydrogen isotopes, and removal of atmospheric pollutants such as sulfur dioxide.

Until about thirty years ago, zeolite was only natural mineral, and so its utilization was limited, although its specific character are partly known.

At 1955, synthetic zeolite are commercialized as named " Molecular Sieves". From that time, industrial uses and research works to zeolite developed spiritedly.

Cracking catalysts containing crystalline zeolite molecular sieves were first used in 1962[1,2].

The first experimental observations of the adsorption of gases on zeolites and their behavior as molecular sieves were conducted on the zeolite minerals. The first definitive experiments on the separation of mixtures using the dehydrated zeolite mineral chabazite as a molecular sieve were performed by Barrer in 1945[3]. He classified zeolites into three groups based upon their ability to adsorb or exclude molecular species of different sizes. The classification defined the approximate intrachannel dimensions.

Commercial adsorbents which exhibit ultraporosity and which are generally used for the separation of gas and vapor mixtures include the activated car-

bons, activated clays, inorganic gels such as silica gel and activated alumina, and the crystalline aluminosilicate zeolites.

At present, the most important molecular sieve effects are shown by the dehydrated crystalline zeolites. These materials all have a high internal surface area available for adsorption due to the channels or pores which uniformly penetrate the entire volume of the solid. The external surface of the adsorbent particles contributes only a small amount of the total available surface area.

Structurally zeolites are "framework" aluminosilicates which are based on an infinitely extending three-dimensional network of AlO_4 and SiO_4 tetrahedra linked to each other by sharing all of the oxygens(Figure 1).
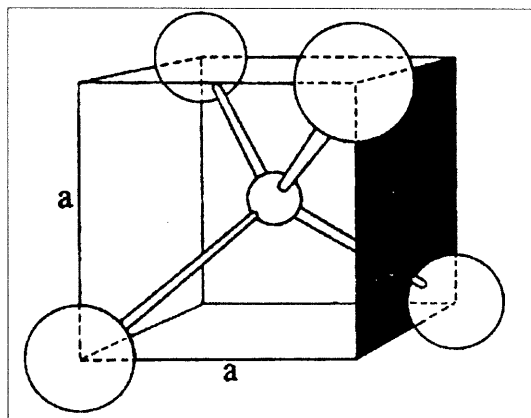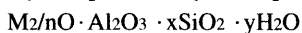

Figure 1. The tetrahedron of oxygen coordinated with silicon. In the isolated complex ion the overall charge is 4⁻. Occupancy of the tetrahedral site by Al^{3+} would produce an overall charge of 5⁻. O-O= a 2=2.62Å ; Si-O=a$\sqrt{(3/2)}$=1.61Å ; O-Si-O angle=109° 28'.

Zeolites may be represented by the empirical formula

$$M_2/nO \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

In this oxide formula, x is generally equal to or greater than 2 since AlO_4 tetrahedra are joined only to SiO_4 tetrahedra, n is the cation valence. The framework contains channels and interconneted voids which are occupied by the cation and water molecules. The cations are quite mobile and may usually be exchanged, to varying degrees, by other cations. Intracrystalline "zeolitic" water in many ze-

olites is removed continuously and reversibly. In many other zeolites, mineral and synthetic, cation exchange or dehydration may produce structural changes in the framework.

Zeolites are crystalline aluminosilicates which are widely distributed in nature but are also readily synthesized in the laboratory.

The structural formula for a zeolite is best expressed for the crystallographic unit cell as:

$$Mx/n[(AlO_2)x(SiO_2)y] \cdot mH_2O$$
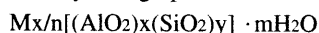
where M is the cation of valency n, the ratio y/x usually has values of 1-5 depending upon the structure (occlusion of AlO_2^- species within the zeolite structure may lower the ratio below one) and m is the number of water molecules. The sum (x + y) is the total number of tetrahedra in the unit cell. The portion with [ ] represents the framework composition.

In many zeolites, the zeolitic water can be readily removed without lattice collapse, leaving a porous crystal with void volumes which can be a large as 50 per cent of the crystal volume. This void volume consists of a network (frequently three-dimensional and interconnected) of channels of molecular dimensions. Zeolites have found wide use, therefore, as molecular sieves and as acid catalysts. When the M cations are replaced by H^+ ions, very active cracking, hydrocracking and isomerization catalysts are produced which are extensively used by the petroleum industry.

Various terms have been used to describe the penetration by, and containment of, molecules in dehydrated, crystalline zeolites. These include sorption, adsortion, occlusion, persorption, imbibition, and intercalation. The author shall use adsorption because it best describes the interaction between a molecule and a surface, whether it is the external surface of a solid or the internal convoluted surface of a dehydrated, microporous zeolite crystal.

The three types of zeolitic frameworks were considered to exist : (1) three-dimensional framework structures with uniform bonding, (2) lamellar-type structures with aluminosilicate sheets weakly bonded to one another, and (3) fiber-like structures with weakly crosslinked aluminosilicate chain units. This classification, introduced by Bragg, has been used

until recent years [4,5]. It should be reiterated that all zeolites are framework aluminosilicates and all of the zeolite structures are three-dimensional.

In some zeolites, the bond density in certain crystallographic directions is not uniform. Some of these have been referred to as lamellar and / or fibrous. The terms are used to indicate the crystal habit or cleavage, i.e., the lamellar zeolites possess fibrous habits. No zeolite is, in a true sense, a layer structure or a one-dimensional structure.

The framework structure of the cubic zeolite mineral faujasite [6] and detailed structure of the cubic synthetic zeolite A [7] were reported in 1956. A list of zeolites according to the early classification is shown in Table 1.

Several of these zeolites were not properly classified ; in some instances no direct relationship between habit and detailed structure existed. For example, the mineral erionite is fibrous in habit but has a robust, three-dimensional structure. Recent structural analyses of many zeolites have led to systems for the identification and classification of zeolites which are based upon structural and physicochemical characteristics rather external appearance.

Similar problems have existed with other large mineral groups such as the clay minerals ; the structures of clay minerals were not resolved in detail until the last two decades. An understanding of the feldspar minerals, which is so important to an understanding of the formation and geological history of

Table 1. Early Classification of Zeolite Minerals

Name	Composition Ideal Formula[8]	Interstitial Volumeme Available to H_2O (cc/g Dehydrate Zeolite)
A. Three-dimensional frmework structures		
Analcime	$NaAlSi_2O_6 \cdot H_2O$	0.089
Chabazite	$(Ca,Na_2)Al_2Si_4O_{12} \cdot 6H_2O$	0.29
Gmelinite	$(Ca,Na_2)Al_2Si_4O_{12} \cdot 6H_2O$	0.27
Harmotome	$(Ba,K_2)Al_2Si_5O_{14} \cdot 5H_2O$	0.18
Levynite	$CaAl_2Si_3O_{10} \cdot 5H_2O$	0.23
Mordenite	$(Ca,Na_2,K_2)Al_2Si_{10}O_{24} \cdot 6.7H_2O$	0.15
B. Lamellar structure-weakly bonded aluminosilicate sheets		
Epistilbite	$CaAl_2Si_6O_{16} \cdot 5H_2O$	0.19
Heulandite	$CaAl_2Si_6O_{16} \cdot 5H_2O$	0.21
Stilbite	$(Ca,Na_2)Al_2Si_6O_{16} \cdot 6H_2O$	0.22
C. Fibrous structure-weakly crosslinked chains		
Edingtonite	$BaAl_2Si_3O_{10} \cdot 3H_2O$	0.15
Mesolite	$Na_2Ca_2Al_6Si_9O_{30} \cdot 8H_2O$	0.15
Natrolite	$Na_2Al_2Si_3O_{10} \cdot 2H_2O$	0.11
Scolecite	$CaAl_2Si_3O_{10} \cdot 3H_2O$	0.16
Thomsonite	$(Ca,Na_2)Al_2Si_2O_8 \cdot 2.5H_2O$	0.16
D. Unclassified		
Brewsterite	$(Sr,Ca,Ba)Al_2Si_6O_{16} \cdot 5H_2O$	0.17
Faujasite	$(Ca,Na_2)Al_2Si_5O_{14} \cdot 10H_2O$	0.33
Gismondine	$CaAl_2Si_2O_8 \cdot 4H_2O$	0.28
Laumonntite	$CaAl_2Si_4O_{12} \cdot 4H_2O$	0.17
Phillipsite	$(Ca,K_2)Al_2Si_4O_{12} \cdot 4.5H_2O$	0.20

rocks and an understanding of the chemistry of the earth's crust, is fairly recent. Many unsolved problems still exist in classifying these mineral groups. These minerals continue to receive attention as more sophisticated experimental techniques are developed. Some of the methods employed in the characterization and identification of zeolite minerals and synthetic zeolites are the same as those used extensively in these other problems. For many years minerals were characterized and identified on the basis of chemical composition, optical properties, certain physicochemical properties, and morphology. Modern methods include x-ray diffraction, which is based on the crystal structure, for identifying fine-grained materials.

The most extensive application of zeolite minerals in commercial products seems to have been made in Japan. The two zeolite minerals occurring in usable deposits in Japan are mordenite and clinoptilolite.

Zeolite minerals are used in several countries in the following applications : (i) in papermaking ; (ii) in air separation adsorption processes ; (iii) in fertilizers ; (iv) as desiccants ; (v) as soil conditioners-this application is based upon the ability of the zeolite to ion exchange with soil nutrients ; (vi) in agricultural applications-these include the use as deodorants in the raising of the domestic animals ; (vii) in the treatment of radioactive wastes ; (viii) as carriers for toxic materials ; (ix) as adsorbents for toxic gases ; (x) as ignorganic materials-building materials ; and (xi) as treatment of environmental pollution.

On the other hand about thirty years ago, some high-grade zeolite beds were recognized by the mining profession at Yeongil area in our country, and thereafter, they have been intermittently mined for agricultural uses. In the late 1970s, geologists of the Korea Institute of Energy and Resources (KIER) initiated an exploration project of zeolites and bentonite in the Yeongil-Gampo areas, and found several zeolite deposits from the Tertiary sedimentary formation[9].

In the Yeongil area, zeolites are found in nearly all the tuffaceous rocks of the Janggi Group. The subordinating basaltic lavas and rock fragments of

this group and the perlitic parts of the Nuldaeri volcanics are also partly transformed to zeolites. Zeolite species found in the area include clinoptilolite, mordenite, heulandite. ferrierite, erionite, analcime, chabazite, mesolite, and natrolite. They usually occur as cryptocrystalline aggregates in association with silica minerals, quartz, K-feldspar, gypsum, calcite, and gibbsite, etc[10].

The most striking feature of the occurrence of zeolites and associated minerals is that the abundance and nature of mineral species are controlled by the composition and lithology of their original host rock. Zeolites usually occur in the original finer-grained tuffaceous rocks, showing congruent relation to their host rock. Vitric tuff is the main host rock of the zeolites. High-silica zeolites, viz., clinoptilolite, mordenite, and ferrierite occur chiefly in the tuffaceous rocks, whereas low-silica zeolites, viz., heulandite, chabazite, erionite, analcime, natrolite, and mesolite are included in the basaltic tuffs.

Most of the zeolites in altered tuffs are extremly fine grained and defy reliable microscopic characterization. Particle sizes range from less than $0.1 \mu m$ to a few μm ; however, as shown by scanning electron microscopy, crystal shapes are well developed and generally mimic those of megascopic crystals found in basalt amygdules(Figures 2 and 3)[11].

Figure 2. Scanning electron micrograph of clinoptilolite from a lacustrine tuff near Castle Creek, Idaho. Note characteristic monoclinic symmetry of blades and laths, some of which are similar to the coffin shape of megascopic heulandite from basalt amygdules.
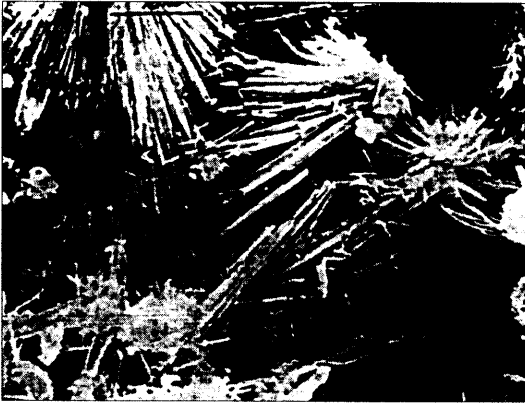
Figure 3. Scanning electron micrograph of mor-
denite needles from a lacustrine tuff
near Lovelock, Nevada. Needles are
about 5 to 20 μm in length and 0.5
to 1 μm wide.

The main material mined is the clinoptilolite and
mordenite which exist in a white or green tuff ap-
proximately 100 m in width and more than 400 m in
extension line in the area of Guryongpo located in
the southeastern coast (Figure 4). This is one of the
larger deposits and estimated to contain about 206,
159 M/T in amount of prospective mining and about
604,728 M/T in amount of deposits from the only
Guryongpo claim No.111[10].

Figure 4. View of horizontal zeolite bed outcrop
in the area of Guryongpo, Yeongil-
gun, Kyungsangbuk-do, Korea (au-
thor in photograph).

In conclusion a discussion of the characteristics
on the zeolite minerals, their classification, occur-
rence, formation, and properties is very important to
our understanding of the sysnthesis and properties of
zeolites.

References

1. Eastwood. S. C., Drew, R. D., and Hartzell,
F. D., Oil Gas J., 60, 152 (1962).
2. Elliott, K. M. and Eastwood, S. C., Oil Gas
J., 60, 142 (1962).
3. Barrer, R. M., J. Soc. Chem. Ind., 64, 130
(1945).
4. Bragg, W. L., Atomic Structure of
Minerals, Cornell University Press, Ithaca,
1937, P.251.
5. Barrer, R. M., Ann. Rep. Prog. Chem., 41,
31 (1944).
6. Bergerhoff, G., Koyama, H., and Nowacki,
W., Experientia, 12, 418 (1956).
7. Reed, T. B. and Breck, D. W., J. Amer.
Chem. Soc., 78, 5972 (1956).
8. Dana, E. S., System of Mineralogy, 6th
Ed., John Wiley & Sons, New York, 1942.
9. Kim, J. H. and Moon, H. S., Report on
Geosciences and Mineral Resources, 4, 53
(1978).
10. Sang, K. N. and Shin, H. J., and Lee. S.
R., Geological Investigation of Non-
Mettalic Mineral Deposits, 82-Mineral
Resources-2-12, KIER, 1983.
11. Mumpton, F. A. and Ormsby, W. C., Clay
and Clay Minerals, 24, 1 (1976).