Zeolites: The “Magic Stones”

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Zeolites are hydrated aluminosilicates having a microporous crystalline structure. There are 48 different types of zeolites known to occur naturally as minerals and more than 150 zeolite types have been artificially synthesized. The first zeolite, stilbite; a natural mineral was discovered in 1756 by a Swedish mineralogist and a chemist Friedrich Axel Cronstedt. He observed a rapid loss of water vapor upon gentle heating of this mineral, thus, Cronstedt coined the name ‘zeolite’ derived from the Greek words ζέω; zeo (to boil) and λίθος;'lithos' (stone), meaning 'boiling stones'.[1]

Even though zeolites have been discovered more than 200 years ago, their attractive versatile physical and chemical properties were identified by the researchers and scientists only in the middle of this century. Since then extensive work has been conducted by the scientific community on the structure, synthesis, properties and applications of zeolites and today they are used worldwide in a wide range of applications including industrial, technical, medicinal, agricultural and commercial, etc. This article discusses the chemical structure, properties, general synthesis of zeolites and some of their applications important in day-today-life.

The Chemical Structure

The aluminosilicate framework of zeolites is composed of MO_4 tetrahedra, where M stands for Si or Al. In this arrangement, Si and Al atoms are tetrahedrally coordinated to four oxygen atoms. Oxygen atoms located at corners of each tetrahedron are shared with adjacent tetrahedra resulting in a macromolecular three-dimensional "honeycomb-like" structure containing micro pores in the 0.3-20 Å diameter range (Figure 1). These pores are connected by internal channels. The framework of zeolite may consists of Si-O-Si linkages and Si-O-Al linkages but Al-O-Al linkages are forbidden by the Loewenstein rule[2] (no framework Al–O–Al linkages are present as they are thermodynamically less stable).[3] As Si is tetravalent and Al is trivalent, AlO_4 tetrahedra are negatively charged, therefore, this negative charge is compensated by having positively charged non-frame work counterions that belong to alkaline and alkaline earth metals such as Na^+, K^+, Ca^{2+} and Mg^{2+}. As these mobile cations are situated in pores and loosely bound with the aluminosilicate structure, they are easily exchangeable with other cations in a contact solution. Since the aluminosilicate framework is hydrophilic, it can adsorb water from the atmosphere and thus, the pores of the zeolites at low temperatures are also occupied by H_2O molecules. Therefore, zeolites can be defined as hydrated alumino-silicates with an "open" structure that can accommodate a wide variety of mobile cations, such as elements mainly from the IA and IIA groups of the periodic table.

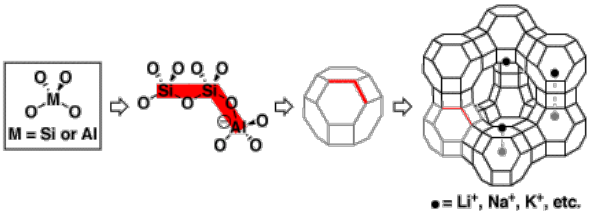

Figure 1: Schematic diagram of formation of macromolecular three-dimensional "honeycomb-like" structure of zeolite.

The general chemical formula of hydrated natural zeolite is expressed as follows;[3]

$$Mx/n, [(AlO2)x (SiO2)y]. zH2O$$

where M is non-framework exchangeable cation with valence n.

The Si/Al ratio of the framework is an important factor which affects properties of the zeolites. For example, high-silica zeolites (high Si:Al ratio) are hydrophobic whereas low-silica zeolites (low Si:Al ratio) are hydrophilic.

Occurrence of Zeolites

Many natural zeolites were formed as a result of volcanic activity millions of years ago and it is believed that natural zeolites were formed when volcanic ash layers reacted with alkaline water in ancient lakes and alkaline ground water. Therefore, large deposits of natural zeolites are found near active volcanoes or extinct volcanic areas especially in cavities of volcanic lava flows.[4] Hence, naturally occurring zeolites are often contaminated with other minerals. Approximately over 40 naturally occurring zeolites have been identified and among them analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite are considered as the most commonly mined zeolite minerals.[5]

Europe, Australia, and Asia are the leading natural zeolite suppliers in the world and currently, about 4 million tons of natural zeolites are produced annually.[4]

Even though zeolites occur naturally, they are also made commercially with different functional groups for specific uses on a large scale. Some important synthetic zeolites with wide variety of applications include A, X, Y, and ZSM-5 type zeolites.

Synthesis of Zeolites

In general, zeolites are synthesized via a hydrothermal method which can be defined as crystallizing substances from aqueous solutions at high-temperature and high pressures. In this method, zeolites are formed by a process of slow crystallization of an aluminosilicate gel in the presence of alkali hydroxide (eg. NaOH) and organic templates. Templating agents are large cations such as quaternary ammonium salts which play an important role in zeolite synthesis as they control the size and shape of the pores of zeolites by growing the zeolites around the template molecular mold producing the porous network.

Properties and Applications

Zeolites are widely used worldwide in variety of applications in different fields and these applications are mainly related to the highly porous structure and ion exchange potential of zeolites. Some of the important applications of zeolites are discussed in the following section.

(a) Water purification

Zeolites are used as water purification agents for the remediation of heavy metals, radioactive isotopes as well as water hardness in both drinking and wastewater. In all these cases purification of water is based on the high cation-exchange behavior/ability of zeolites. Loosely bound mobile cations situated in micro-pores of zeolites are replaced by metal ions from waste and drinking water. For instance, many commercial washing powders contain substantial amounts of zeolites that enhance washing efficiency. Natrolite, $Na_2[Al_2Si_3O_{10}]\ 2H_2O$, is one of the natural ion exchangers that can be found in many washing powders as a water softening agent. In the softening process, non-framework cations, Na+ in zeolite are replaced by Ca^{2+} and Mg^{2+} ions from hard water. A schematic diagram of water softening process of Natrolite is shown in Figure 2.

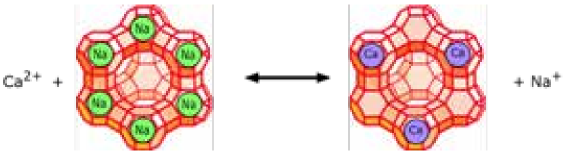

Figure 2: Removal of water hardness using zeolite by cation exchange process: Na^+ ions in zeolite are replaced by Ca^{2+} ions from water.

Similarly, zeolites are used for cleaning up of commercial wastewater containing heavy metals and nuclear effluents containing radioactive isotopes. For example, Zeolites with good selectivity for radioactive 137Cs and 90Sr are now commercially available to treat radioactive waste streams. According to Kalló,6 metal ions such as Cu^{2+}, Ag^+, Zn^{2+}, Cr^{3+}, Mo^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+} and highly toxic metal ions such as Cd^{2+}, Hg^{2+}, and Pb^{2+}, can be selectively removed from industrial effluents by using natural zeolites including clinoptilotite, mordenite, philtipsite, chabasite.[4]

(b) Catalysis

Zeolites are used as catalysts in a wide variety of chemical reactions including catalytic cracking in petrochemical industry, isomerization and alkylation reactions for the production of chemicals, dyes, detergents, perfumes and advanced materials.[4] All these catalytic reactions take place within the cavities/pores of acidic zeolites. Often zeolites function as Brønsted acids in catalytic reactions and the structure of the Brønsted acid form of zeolite is shown in Figure 3. As zeolites are good cation exchangers, H^+ ions are readily exchanged for mobile cations (such as Na^+) by washing with acid to form Brønsted acid type zeolite. Other desirable properties that enable zeolites to function as catalysts include large surface areas due to their highly porous structure, unique pore size, crystallinity, thermal stability, and possibility of producing zeolites with desirable pore sizes.

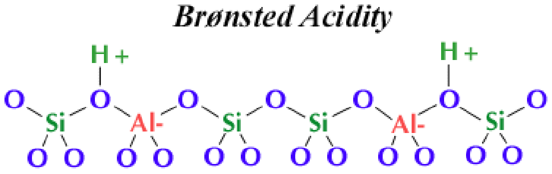

Figure 3: Brønsted acid form of zeolite.

Catalytic cracking

The process of catalytic cracking involves breakdown of heavier high-molecular weight more complex hydrocarbons of petroleum crude oils into simpler and lighter alkanes and olefins. In this process acidic zeolites are used as catalysts under lower temperatures. Nowadays, gasoline with a higher octane rating is produced by the process of catalytic cracking which was originally done by thermal cracking. An example of catalytic cracking of a long chain hydrocarbon is depicted in Figure 4.

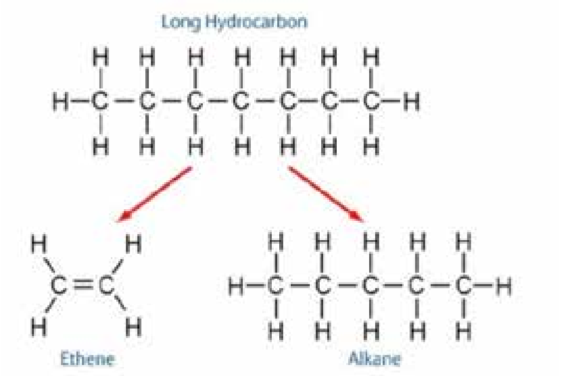

Figure 4: Catalytic cracking of a long chain hydrocarbon.

Shape selective catalysis

Zeolites which act as shape selective catalysts provide specific reaction pathways leading to desired products due to its selectivity towards a particular reactant, product or transition state according to their pore size and shape. Here, the catalytic reaction selectively proceeds if the size and shape of the reactants, transition states or products fit the pore size of the catalyst. Shape selective catalysis can be categorized into three types as (i) reactant, (ii) product, and (iii) transition-state shape selectivity. Reactant selectivity occurs, when only some of the reactant molecules of a reactant mixture are small enough to enter the zeolite pores. As depicted in Figure 5, a straight chain hydrocarbon passes through the catalytic pore whereas a too bulky branched hydrocarbon is excluded from the reaction.[4]

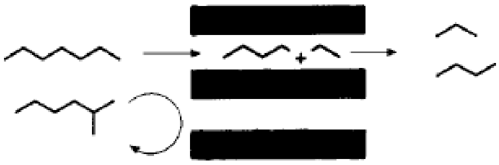

Figure 5: A schematic diagram of reactant selectivity through pores of a zeolite catalyst.

The product selectivity results when bulky products formed within the pores are restricted from diffusing out as products. Alkylation of toluene with methanol in the presence of a synthetic zeolite zms-5 to selectively produce p-xylene is an example for product selectivity. In this reaction, all three isomers; ortho, meta and para xylenes are formed within the pores but ortho and meta xylenes are too bulky to diffuse out like para xylene (Figure 6). These restricted products may be converted to less bulky para-xylene through equilibration or they may ultimately deactivate the catalyst by blocking the pores.

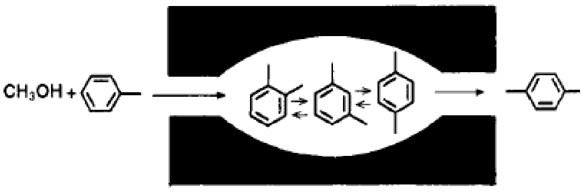

Figure 6: A schematic diagram of an example of product selectivity through a pore of zeolite catalyst.

The third type of shape selectivity, the restricted transition-state selectivity arises, when certain reactions are prevented due to the limitation of formation of corresponding transition state which requires more space than available in the zeolite pores. Reactions with smaller transition states proceed unhindered.[7] Disproportionation of meta-xylene to toluene and trimethylbenzene over acidic mordenite is an example for restricted transition-state selectivity of acidic zeolite. As depicted in Figure 7, acid catalyzed alkylation of meta-xylene over mordenite, yields 1,2,4-trimethylbenzene but not the 1,3,5 – trimethylbenzene which requires a formation of a bulky transition state.

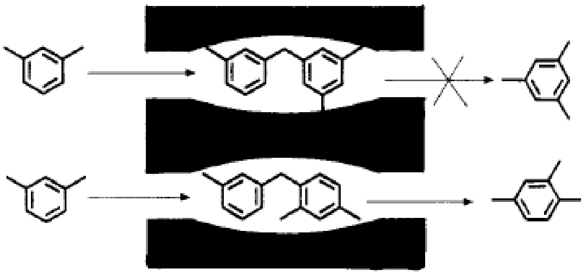

Figure 7: A schematic diagram of an example of restricted transition-state selectivity through the pores of a zeolite catalyst.

(c) Selective adsorption and separation

Selective adsorption and separation of molecules by zeolites is based on the size and shapes of the pores and the polarity (hydrophilicity/hydrophobicity) of zeolites. The size and the shape of pores determine which molecules can enter, or remain outside the crystal structure. As zeolites can selectively adsorb molecules of a specific size they are also known as 'molecular sieves'. This property of zeolites is industrially used to selectively separate gases such as CO_2, NH_3, SO_2, etc. from gas mixtures. For instance, the synthetic zeolite type 3A having a pore diameter of 3 A0, is used to selectively separate molecules with an effective diameter <3 A0, such as H_2O and NH_3 by adsorbing them into the pores of zeolites. Furthermore, dehydrated zeolites are extensively used as desiccants or drying agents to remove water from organic solvents in laboratories due to their high affinity for water. Most importantly, the zeolite used as desiccants can be regenerated as water molecules can be reversibly driven off by heating.

(d) Medicinal uses

Natural zeolites have also shown diverse biological activities which lead to their use in a wide range of medicinal applications. It was discovered that some zeolites have potential anticancer, antioxidant, antiapoptotic and anti-inflammatory activities.[3] Furthermore, zeolites are used in tissue engineering, implant coating and wound healing. They are also considered as promising drug and gene delivery carriers as well as promising materials for making biosensors.[3]

(e) Agriculture

Zeolites have also been used in agriculture especially in soil management as both carriers of nutrients and a medium to free nutrients. For example, the natural zeolite, clinoptilolite functions as a fertilizer of slow-released potassium.3 The possibility of using zeolites as insecticides, fungicides, and herbicides, and as a trap for heavy metals in soils have also been investigated.[8]

The objective of this article was to discuss the chemical structure, synthesis, properties and applications of zeolites. Even though this article covers some of the applications in brief, zeolites have great potential for a wide range of applications in many fields. Hence, due to its outstanding characteristics this wonderful gift of nature has also been referred to as "magic stones".

References

1. Cronstedt, A. F., Natural zeolite and minerals, Kongl Vetenskaps Academiens Handlingar Stockholm, 17, **1756**, 120.
2. Loewenstein, W., The distribution of aluminium in the tetrahedral of silicates and aluminates, American Mineralogist, **1954**, 39, 92.
3. Bacakova, L., Vandrovcova, M., Kopova, I., Jirka, I., Applications of zeolites in biotechnology and medicine – a review, Biomaterials Science, **2018**, 6, 974.
4. Moshoeshoe1, M., Nadiye-Tabbiruka, M. S., Obuseng, V., A Review of the chemistry, structure, properties and applications of zeolites, American Journal of Materials Science, **2017**, 7(5), 196.
5. https://en.wikipedia.org/wiki/Zeolite.
6. Kalló, D., Applications of natural zeolites in water and wastewater treatment, Reviews in Mineralogy and Geochemistry, **2001**, 45, 519.
7. Beyer, H. K., Nagy, J. B., Karge, H. G., Catalysis by microporous materials, 1995, 4th edition, Elsevier.
8. Kulasekaran, R., Reddy, D. D., Zeolites and their potential uses in agriculture, Advances in Agronomy, **2011**, 113, 219.