

Zeolites - Earliest Solid State Acids

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Abstract

A description of zeolites is followed by applications in three important areas of catalysis, gas separation and ion exchange. Finally some examples of representative zeolite structures are cited.

Keywords: Adsorption, catalysis, cracking, gas separation, ion-exchange, MFI, molecular sieves, shape-selective catalysis, ZSM-5.

Introduction

Three-dimensional crystalline compounds formed with AlO_4 and SiO_4 tetrahedra are called zeolites (Mall-net 2007, Dwyer 1984), Figure 1. Normally they are made under conditions similar to hydrothermal conditions typically found in the earth's crust where some natural zeolites occur (Wikipedia 2007, Smith 1976). Sodium aluminate, sodium silicate, or sodium hydroxide solutions are used. Reactants and synthesis parameters such as temperature, time, and pH, determine the particular zeolite formed. The templating ion is especially critical. Usually an organic cation surrounded by an aluminosilicate lattice forms the templating ion. The main zeolite formula is $\text{M}_2/n\text{O}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_2\cdot y\text{H}_2\text{O}$, where M defines the "compensating" cation with valence n (Dwyer 1984). The structural component is $\text{M}_x/n[(\text{AlO}_2)_x(\text{SiO}_2)_y]\cdot z\text{H}_2\text{O}$, and a general structure of tetrahedral building units form ring structures and polyhedra. Zeolite catalysts are strongly desired because of their high density of active acid sites¹, their high thermal/ hydrothermal stability, and high size selectivity.

Their unique porous properties make zeolites useful in a variety of applications with a global market of several million tons per annum.

¹ Hence zeolites are solid state acids. In fact they are the earliest known solid state acids.

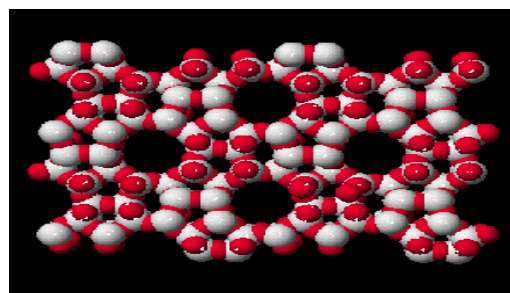


Fig. 1. Zeolite.

Major uses are in petrochemical cracking, ion-exchange (water softening and purification), and gas and solvent separations and removal. They are commonly known as molecular sieves. They are also useful in agriculture, animal husbandry and construction.

A list of interesting websites is shown in the International Natural Zeolite Association INZA page (INZA 2007).

Zeolites - Earliest Solid State Acids

Description (Wikipedia 2007, Mall-net 2007)

Classically a zeolite is defined as a crystalline porous aluminosilicate. But many materials with properties virtually identical to the classical zeolite have been discovered. They consist of oxide structures with elements other than silicon and aluminum. Hence current definitions include all types of porous oxide structures with well-defined pores caused by high crystallinity.

In classical zeolites the silicon or aluminum atoms are surrounded by four oxygen anions forming an approximate tetrahedron. The apex tetrahedral metals are called T-atoms. These tetrahedra stack in regular arrays and form channels. Stacking possibilities are virtually limitless giving hundreds of unique structures.

The zeolitic channels (or pores) are microscopically small (molecular size dimensions) and are therefore called "molecular sieves". The size and shape of the channels influence the adsorption properties of these materials making them useful in separation processes. Molecules can be separated via shape and size effects related to their possible orientation in the pore, or by differences in adsorption strength.

Silicon is typically in a 4+ oxidation state and the silicon-oxygen tetrahedra are electrically neutral. But aluminum in zeolites exists in the 3+ oxidation state, making anionic zeolite frameworks. To maintain electrical neutrality cations populate the pores. These "compensating" cations participate in ion-exchange processes, and give some important properties to zeolites. "Soft" cations such as sodium make zeolites excellent water softeners because they can replace the "hard" magnesium and calcium cations in water. If protons are the compensating cations, the zeolite becomes a strong solid acid. Such solid acids are the basis of zeolite catalysis, including the fluidized-bed cat-cracking refinery process. Other metal cations can also populate the pores giving unique catalytic materials. Thus zeolites are also used in "shape-selective catalysis".

The nature of acid sites in zeolites and the factors that influence enhanced catalytic activity have been of much interest. Whether all of acid sites are homogeneous or heterogeneous in acid strength requires quantifying the acidity. In this context, density functional theory (DFT) becomes crucial. For example, investigation of the reactivity of the acid sites in the zeolite chabazite (SSZ-13) revealed that the proton affinities of the four acidic oxygens at the aluminum T-site are all roughly the same. The deprotonation energy is not connected to the O-H bond length or the

vibrational stretch frequency. The strength of the acid sites in chabazite is not influenced significantly by chemical or structural variations in the framework near the acid site.

Applications

A wide variety of industrial applications of zeolites, mainly catalysis and separations, exist. Development of the methanol to gasoline (MTG) process by Mobil in the 1970's (increased gasoline yield from each barrel of crude oil by 50 percent and improved octane number) (ExxonMobil 2007) and development of methanol to olefins (MTO) process by UOP/Hydro in 1996 (UOP/Hydro 2007) spurred petrochemical zeolite applications. Heterogeneous catalysts have an edge over liquid-phase processes. Waste minimization, wide range of possible process operating conditions, and ease of product separation are some advantages.

However, solid-acid catalysts cannot replace all industrial homogeneous catalysts. Difficulties in reactant and product diffusion to and from the zeolite surface in the absence of a solvent are a major obstacle.

There are three main zeolites industrial applications: catalysis, gas separation and ion exchange (Lentech 2007). A more detailed description is available elsewhere (Wikipedia 2007).

Catalysis (Lentech 2007): This is the most important application. Several important organic reactions are catalyzed by zeolites. The most important are cracking, isomerisation and hydrocarbon synthesis. A diverse range of catalytic reactions including acid-base and metal induced reactions can be promoted by zeolites. The reactions occur within the zeolite pores and allow greater product control.

Hydrogen-exchanged zeolites, whose framework-bound protons yield very high acidity, form an important class of catalysts. Many organic reactions, including crude oil cracking, isomerisation and fuel synthesis use this type of zeolite catalyst. Zeolites can also catalyze oxidation or reduction, often after metals have been introduced into the framework. For example titanium ZSM-5 is

used in the production of caprolactam, and copper zeolites are used in NO_x decomposition.

The unique microporous nature of zeolites causes the shape and size of a particular pore system to exert a steric influence on the reaction. This allows access control of reactants and products. Thus zeolites are *shape-selective catalysts*. Currently attention has focused on minute details of the properties of zeolite catalysts with a view to making very specific syntheses of high-value chemicals like pharmaceuticals and cosmetics.

Gas Separation (Lentech 2007): Molecular adsorption is also based on the shape-selective properties of zeolites. The preferential adsorption ability has induced a wide range of molecular sieve applications. Sometimes it is just controlling access into the zeolite by the size and shape of pores. In others different molecule types enter the zeolite; differences in diffusion rates execute separation, as in the purification of *para*-xylene by silicalite.

Due to high affinity for water, cation-containing zeolites are extensively used as desiccants. Molecules may be differentiated on the basis of their electrostatic interactions with the metal ions and this forms a basis for gas separation application. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Thus separation of molecules based on differences of size, shape and polarity is achieved by zeolites, see Fig. 2.

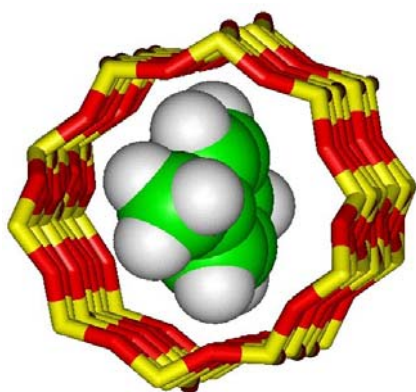


Fig. 2. A Molecule in a channel.

Ion Exchange (Lentech 2007): Extra-framework metal ions are loosely-bound (as in zeolite NaA, Fig. 3). When in aqueous solution

they are readily exchanged for other metals. For example in water softening alkali metals such as sodium or potassium exchange out of the zeolite, and are replaced by the "hard" calcium and magnesium ions from water. Thus many commercial washing powders contain zeolite. Commercial waste water containing heavy metals and radioisotopes in nuclear effluents may also be treated by zeolites.

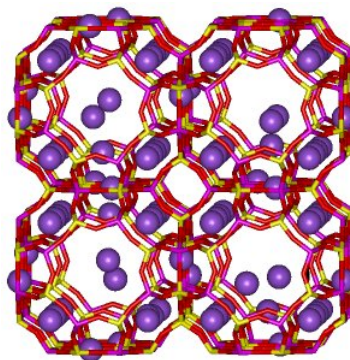


Fig. 3. Loose extra-framework metal ions.

Representative Structures (INZA 2007)

Some examples of various zeolite structures are shown below:

Theta-1

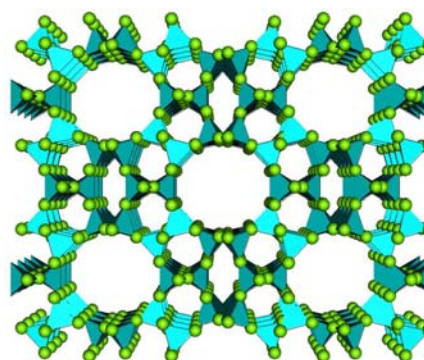


Fig. 4. Zeolite Theta-1 TON.

Theta-1, shown in Fig. 4, and Mobil's ZSM-22 has the same basic structure. It is a 10-ring pore structure that consists of 10 oxygen atoms surrounding the circumference of the straight pores that run in one dimension. The pore has a free aperture of about five Angstroms. Smaller pores (6-ring and less) also constitute the structure.

Boggsite International Zeolite Association Framework Designation: BOG

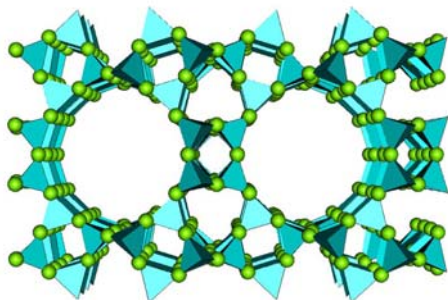


Fig. 5. Boggsite.

Boggsite, shown in Fig. 5, is an important mineral because it contains 10- and 12-ring pores that intersect perpendicularly.

SSZ-33. It is a synthetic zeolite with both 12- and 10-ring pores (Fig. 6).

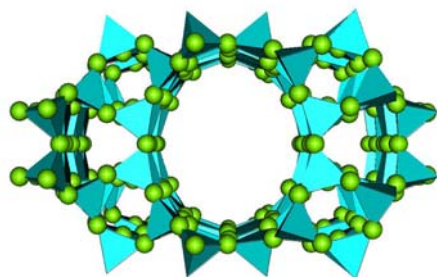


Fig. 6. Zeolite SSZ-33.

Faujasite (Zeolite Y) (Smith 1976).

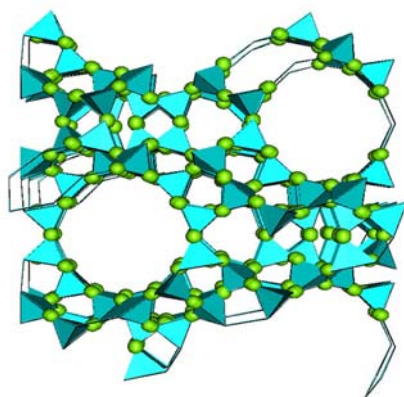


Fig. 7. Faujasite (Zeolite Y).

Structure and Characterization: Zeolite Y has a 3 - dimensional FAU (faujasite) pore structure as shown in Fig. 7. Similar to LTA, pores run perpendicular to each other in the x,

y, and z planes. Secondary building units 4, 6, and 6-6 create a large pore diameter of 7.4Å, defined by a 12 member oxygen ring. This leads to a 12Å diameter larger cavity. Ten truncated octahedra (sodalite cages) surround the cavity.

Synthesis: A gel is made by mixing alumina (sodium aluminate) and silica (sodium silicate) in an aqueous alkaline (NaOH) solution. To crystallize the zeolite, the gel is heated to 70-300°C. The zeolite that is present in Na⁺ form is converted to the acid form. But to prevent disintegration from acid attack, it is first converted to the NH₄⁺ form, before conversion to acidic form. Impregnation or ion exchange deposition is used if a hydrogenation metal such as platinum is required.

Application: Cracking catalyst is the most important function of zeolite Y (Corma 1992). The acidic form is an important item in petroleum refinery catalytic cracking units. It helps increase gasoline yield and diesel fuel yield from crude oil feedstock. This is achieved by cracking heavy paraffins into gasoline grade naphthas. The higher Si/Al ratio in zeolite Y makes it both more active and more stable at high temperatures. Thus zeolite Y has superseded zeolite X. In hydro-cracking units it serves as a platinum/palladium support that increase aromatic content of reformulated refinery products.

Mobil ZSM-57 Shown in Fig. 8.

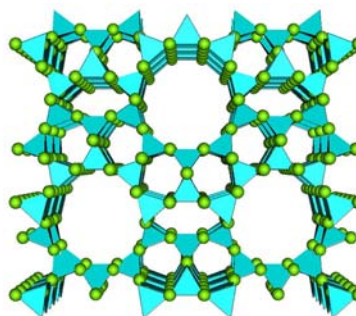


Fig. 8. Zeolite ZSM-57 MFS.

The structure of Mobil ZSM-57 consists of intersecting 8 and 10 ring pores. The 10 ring pores are slightly larger than in ZSM-5.

Mobil ZSM-5

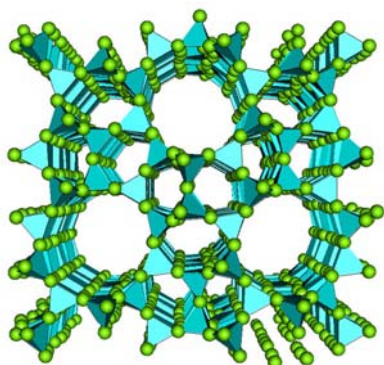


Fig. 9. Zeolite ZSM-5 MFI.

ZSM-5, Tetrapropylammonium (TPA) is shown in Fig. 9. M stands for Mobil where this zeolite was discovered. It is a shape-selective catalyst with remarkable catalytic properties and high thermal stability. ZSM-5 has one set of pores zig-zag or sinusoidal. ZSM-5 has a very strong ability to promote hydrocarbon reactions. See picture in Fig. 10.

ZSM-5 - A Size and Shape Selective Catalyst for Xylene Isomerization (Song et al 2004): Oil refinery fluid cat-cracking (FCC) units use ZSM-5 zeolite catalyst to increase the octane number of gasoline, increase the total LPG and also the olefin content of fractions - secondary "cracking" of gas oil.

ZSM-5 Properties/Formation of p-Xylene: ZSM-5 zeolite has orthorhombic symmetry, as determined by model building, and single crystal or powder x-ray methods (Wikipedia 2007, Mall-Net 2007). Aluminum/silicon ratio is one important feature. For syntheses $\text{pH} < 10$, incorporated Al increases. The Si/Al ratio is between 5 and 20 (Song *et al.* 2004), due to structure stabilization by electrical interactions. Similarly for increased Si/Al ratio, cation density and electrostatic field strengths decrease, resulting in increased affinity of the zeolite surface for non-polar adsorbates. Silica-rich zeolites "prefer" hydrocarbons over water.

Thus the zeolite's catalyst ability is determined by several parameters, such as presence of active sites (acidic, basic, cationic, etc.), spatial arrangement and size of the channels and pores, and the presence of

extraneous compounds. Most active sites are located in intra-crystalline pores or cavities of molecular dimensions. This makes the compound shape-selective. In ZSM-5 the channel links are by intersections, and interior access to the molecule occurs by 8, 10, or 12 peripheral oxygen atoms (ExxonMobil 2007).

These properties make ZSM-5 an effective "molecular sieve" with characteristic absorption properties. For example consider the production of p-xylene from o-xylene. Friedel and Crafts catalysts produce isomerization, accompanied by a transalkylation, giving toluene and trimethylbenzene. A high isomerization to disproportion ratio is observed. This is because ZSM-5 pore size matches the xylene molecular diameter. The only reaction path is through a unimolecular 1,2 methyl-shift mechanism. Thus ZSM-5 is a crucial catalyst for p- to o-xylene conversion.

Characterization of Zeolite ZSM-5: The acid sites are characterized by using ^{31}P solid-state NMR of the probe molecule trimethylphosphine oxide adsorbed onto zeolites, ZSM-5 in this case. The ^{31}P nucleus is very sensitive and has a large chemical shift range and is therefore suitable to resolve different acid sites based on 'proton donating ability'.

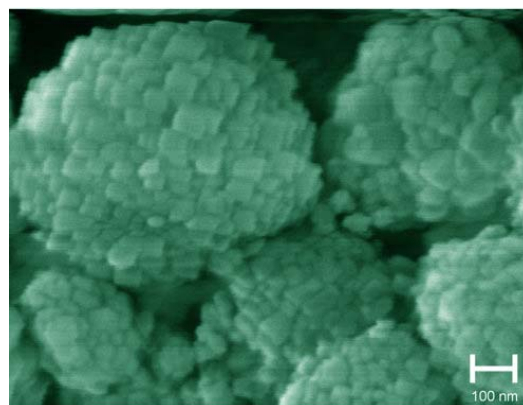


Fig. 10. ZSM-5 nm view.

Conclusion

In conclusion impact of zeolites on the environment is mentioned. Zeolites or solid state acids keep the environment cleaner and

safer in many ways. Several zeolites applications were initiated by environmental concerns, including reduction of toxic waste and energy consumption.

Zeolites replaced harmful phosphate builders in powder detergents.² Catalysts save energy and thereby reduce pollution. Moreover, processes require fewer steps, minimizing unnecessary waste and by-products.

As solid acids, zeolites can remove atmospheric pollutants, such as engine exhaust gases and ozone-depleting CFCs. Zeolites can clean water by separating out harmful organics and removing heavy metal ions, including radioactive ones produced by nuclear fission.

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² Banned in many parts of the world because of water pollution risks.