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The Structure of Microcrystalline Zeolites: Symmetry with a Purpose

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The Structure of Microcrystalline Zeolites: Symmetry with a Purpose

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Zeolites are crystalline, hydrated aluminosilicates with open three-dimensional framework structures [1-3] built of $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedra linked by sharing of an oxygen atom, to form regular intracrystalline cavities and channels of molecular dimensions. Al-O-Al linkages in hydrothermally synthesized zeolite frameworks are forbidden by the Loewenstein rule [4] because they are thermodynamically less favourable than Al-O-Si or Si-O-Si linkages.

The first zeolite molecular sieve, stilbite, was discovered by Cronstedt in 1756 [5]. He named it 'zeolitos' which means boiling stone, because the mineral appeared to boil when heated. Since then about 45 natural zeolites have been identified. In 1862, St. Claire Deville attempted, unsuccessfully, to prepare a synthetic zeolite. It was only after 1945 that zeolites became recognized as important. In 1956, Linde A, the first commercial zeolite was synthesized by Breck [6].

Today at least 150 synthetic zeolites are known. Natural zeolites are formed as a result of chemical reaction of the volcanic ash and alkaline water a few thousand millennia ago. It is therefore not surprising that natural zeolites are found in abundant in volcanic areas. Almost an entire state of Nevada and most of the islands in Indonesia are covered with mordenite and clinoptilolite. Barrer's pioneering work in the 1940's demonstrated that a wide range of zeolites could be synthesized from aluminosilicate gels [1,2]. Zeolite crystals grow by condensation followed by polymerization of a supersaturated solution to form Si-O-Si or Si-O-Al bonds. Crystallization of zeolites follows the Ostwald rule of successive transformations This states that in competing species, the least stable phase crystallizes first until the most stable product results, and implies that successive nucleation of different zeolite species is possible before the zeolite which is thermodynamically most stable remains. The type of zeolite that crystallizes depends on the gel composition, the nature of reagents and the crystallization conditions.

The three main commercial applications of zeolites are directly linked to the different aspects of zeolite structural chemistry. Zeolite frameworks provide subtrates that support the mobilities of the nonframework cations that make them good ion exchangers. Due to the presence of never ending intricate pore and channel systems of controlled dimensions and accessabilities, zeolites become excellent sorbents and molecular sieves. Finally, the framework structure in zeolites provide highly active sites which make them remarkably active heterogeneous catalysts with shape selective capabilities.

Zeolites have been used in various parts of the world for centuries. Many of the pyramids in Mexico and buildings in Rome were built from zeolite blocks. Zeolites were used as talcum powder and other health products in Hungary. Animals are fed with zeolites in Japan for weight gain and health benefits. Zeolites have been widely used in industrial and environmental applications because they are environmentally friendly and generally recognised as safe. Research has been done to use zeolites for natural gas storage for vehicles and to cut air conditioning costs in homes and buildings by up to 90% using zeolite construction brick and tile. Currently zeolites are used in cat litter, shoe deodorizers, odour and moisture removers in animal stalls and refrigerators, soil enhancers and harmful gas removers in aquarium and pond filters.

Some of the earlier synthetic zeolites include zeolites X. Y, L, ZSM-5, omega and beta [7,8]. More recently, zeolites with low aluminium content have been produced: Silicalite, the pure silica analogue of ZSM-5, ferrierite, mordenite and zeolite beta [9,10]. Other molecular sieves such as the porous aluminophosphates (AlPOs) and their derivatives have been discovered [11,12]. The most recently synthesized molecular sieves are the VPI-5; the aluminophosphate based sieves with very large pores and MCM-41; the first siliceous mesoporous zeolite [13,14].

THE STRUCTURE OF ZEOLITES

The various types of zeolites are characterized by the distinct topology of their three-dimensional framework, the relative content of silicon and aluminium, the ordering of the silicon and aluminium atoms in the tetrahedral sites of the framework and the type and distribution of cations. The framework topology and morphology of zeolites contribute to the remarkable physical and chemical properties of these microcrystals.

The aluminosilicate zeolites are described by the formula:

$$M_{x/n}\ [(AlO_2)_x(SiO_2)_y) - ZH_2O$$

where $M_{x/n}$ is the non-framework exchangeable cation of valence n; [ ] is the aluminosilicate framework; zH_2O is the non-framework zeolitic water and $y > x$.

The Si/Al ratio (y/x) of the framework affects the structure and properties of the zeolite. For example, in zeolite A , Si/Al =1 and each silicon atom is linked, via oxygens, to four aluminium atoms and vice versa. As a consequence of the Loewenstein rule, Si and Al are completely ordered in zeolites with Si/Al = 1, but may be ordered or disordered in zeolites with higher ratios [15,16].

The silicon and aluminium may be isomorphously substituted by other tetra- and trivalent elements to form new families of porous solids. Gallosilicates [17,18] borosilicates [19] and ferrisilicates [20] are such materials.

In cases where framework silicons are substituted for elements with higher oxidation states to form less anionic or neutral frameworks, very little or no cations at all are needed. Non-framework cations, Mn^+, are required to balance the charge of the framework. Typically these are mono- or divalent cations such as Na^+, K^+, Ca^{2+} and Mg^{2+}, and their total charge is equal to the number of framework T' atoms. For example, when Al^{3+} is tetrahedrally substituted for Si^{4+}, the resulting framework has the composition $[(Al_xSi_{1-x})0_2]^{x-}$. Each electrostatic charge has to be balanced by a positive ion, such as sodium.

The charge-balancing cations can undergo ion exchange when the zeolite is treated with salt solutions. The other non-framework component is the zeolitic water, which fills the channels and cavities and may be removed by heating. In some zeolites, heating or dehydration irreversibly alter the framework structure and cation positions. On the other hand, removal of zeolitic water may leave the framework of some zeolites intact to sorb other water, organic and inorganic molecules. Such zeolites are used as molecular sieves.

The topology of zeolite framework types is described in terms of finite component units called "secondary building units" (SBU) as shown in **Figure 1**. In these SBUs the Si or Al is present at each corner as represented by the circles. The oxygen atoms which are located near the mid-points of the lines are not shown.

There are a wide variety of possible zeolite structures due to the large number of ways in which the SBU can be linked to form various polyhedra which when combined create networks of regular channels and cavities [3,21]. One such polyhedron is the truncated octahedron, which is also known as the "sodalite cage" or the "beta cage", as illustrated in **Figure 2**. Some other polyhedra found in zeolite structures are shown in **Figure 3**. Each sodalite cage consists of 24 linked tetrahedra. The cages are further linked to form different zeolites. Three of the most common ways are shown in **Figure 4a, b, and c**.

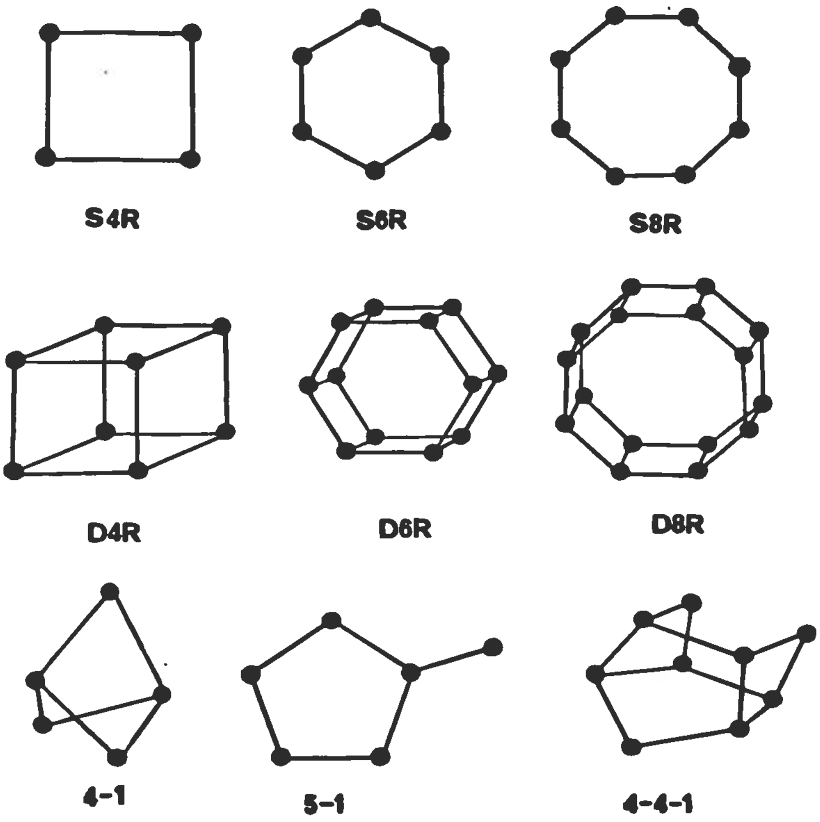


Figure 1: Secondary building units. The oxygen atoms in between silicons and aluminiums are omitted for simplicity

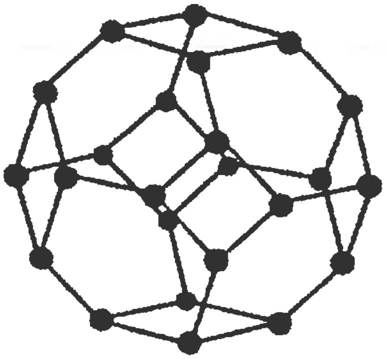


Figure 2: The truncated octahedron – a primary building block in zeolites

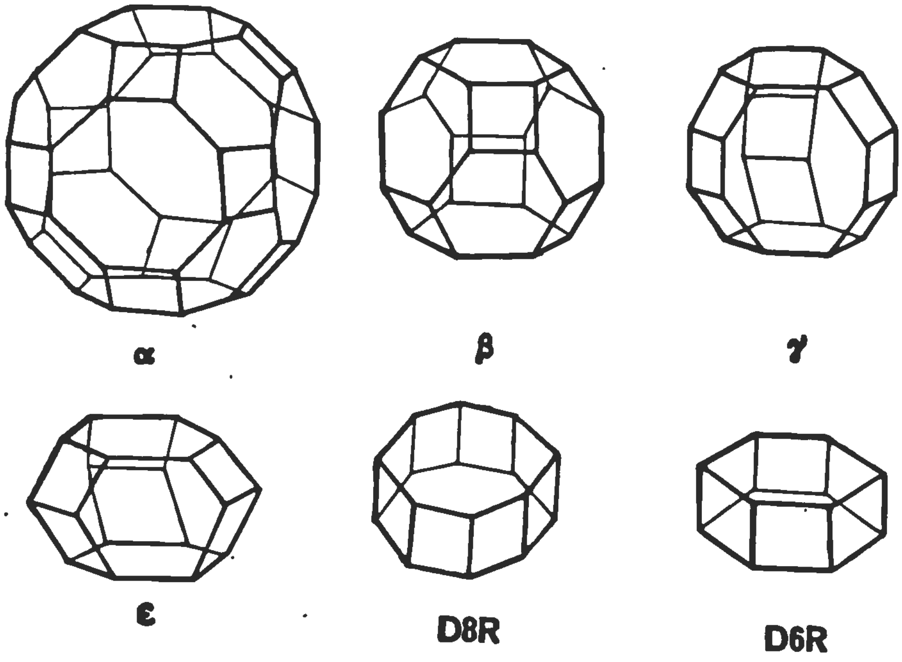


Figure 3: Some polyhedra found in zeolitic structures.

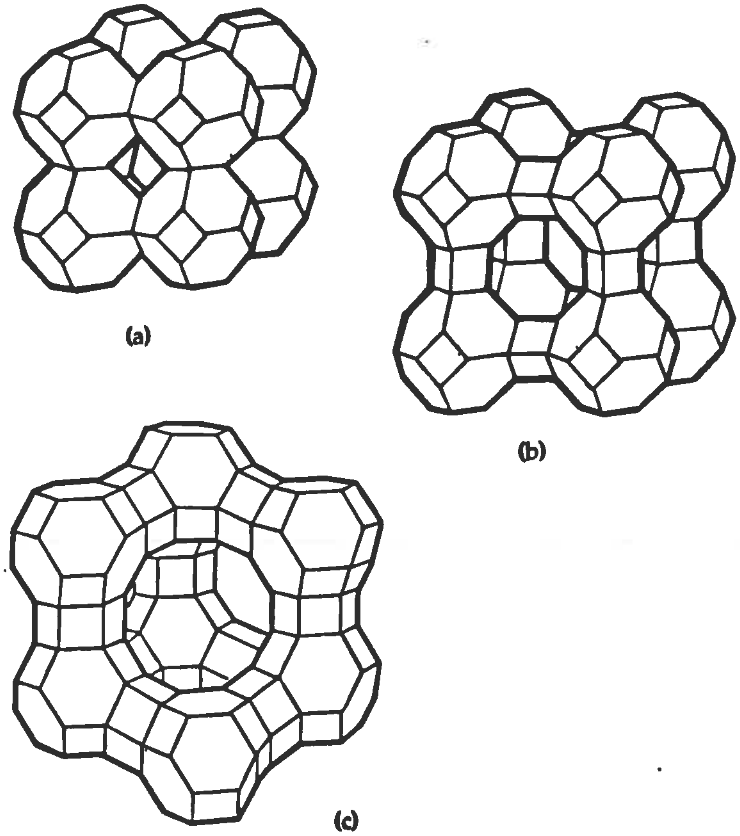
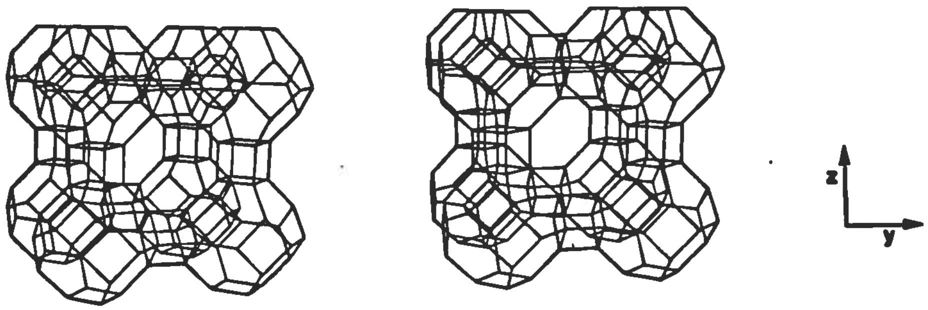


Figure 4: Zeolitic structures of (a) sodalite (b) zeolite A and (c) zeolite X and Y

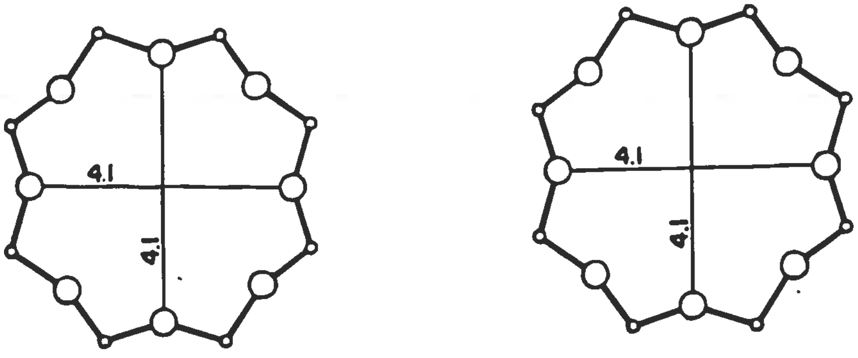
Some of the most important zeolites with their framework topologies are demonstrated in the following:-

(i) Zeolite A

When sodalite cages are linked through double four-membered rings, zeolite A is formed. The aluminosilicate framework of zeolite A consists of an array of truncated octahedra linked via double 4-rings as shown in **Figure 5a**. It has a chemical formula of $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$ - $27H_20$ and is cubic in symmetry (**Figure 5b**) with a unit cell constant a_o = 12.32Å. The framework contains cavities of 11.4 Å in diameter and the Si/Al composition of 1. The distribution of Si and Al in zeolite A with Si/Al = 1 is strictly ordered and obeys the Loewenstein's rule which states that no Al-O-Al bonds are allowed.



framework viewed along [100]



B ring viewed along [100]

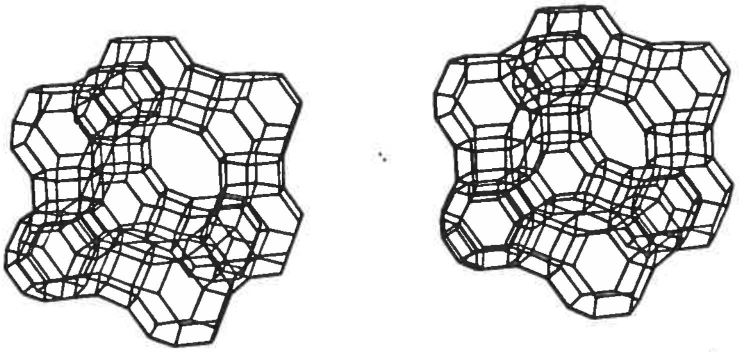
Figure 5a: Framework structure of zeolite A

Figure 5b: Scanning electron micrograph of zeolite A

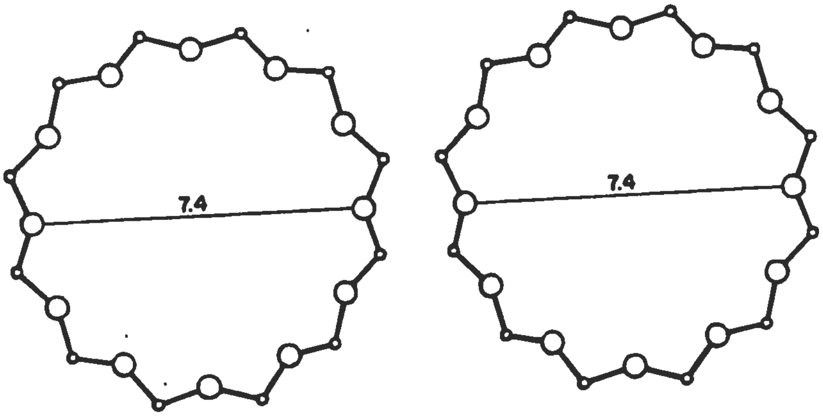
(ii) Zeolite X and Y

Zeolites X and Y are the variable Si/Al ratio synthetic counterparts of the mineral faujasite. The framework consists of truncated octahedra joined via double 6-rings in a tetrahedral arrangement as in **Figure 6**. This results in the formation of larger cages consisting of 26 tetrahedral units known as “supercages” or alpha cages with free diameters of 12.7 Å. Each three-dimensional zeolitic framework structure contains channels uniquely arranged to form various regular one, two or three-dimensional networks.

The crystal structures are face-centred cubic and a unit cell of hydrated zeolite X and Y consists of 12 rings with free apertures up to 7 Å in diameter and 6-rings of 2.2 Å in diameter. The Si/Al ratio of zeolites X and Y varies from 1.1 to 3.4 The materials with $1.0 < \mathrm{Si/Al} < 1.5$ are conventionally known as zeolite X, while those with Si/Al ratio > 1.5 as zeolite Y. The distribution of Si and Al in the framework gives rise to five possible building blocks: Si(4Al), Si(3Al), Si(2Al), Si(1Al), Si(OAl) which result in more than one ordering schemes of the Si and Al atoms in the framework.



Framework viewed along [111]



12-ring viewed along [111]

Figure 6: Framework structure of zeolite X and Y

(iii) Zeolite ZSM-5

The microstructure of ZSM-5 is based on pentagonal units of the type shown in **Figure 7** where the intersections of lines define the positions of the T atoms (T = Si or Al). Zeolites such as ZSM-5 is of a high silica nature of such structure is designated as pentasil type unit. **Figure 8** show how the microstructure of ZSM-5 is built up to create pore apertures incorporating 10T atoms with 10 intervening oxygen atoms. The structure of the three dimensional channel system as defined by the pore is shown in **Figure 9**. The pore aperture of the linear channels is slightly elliptical with principal axial dimensions of 5.6 and 5.4 Å. The 96 silicate tetrahedra per unit cell form a 4-connected framework with a system of intersecting channels composed of near-circular zig-zag channels viewed along [100], crosslinked by elliptical, straight channels along [010]. The symmetry of ZSM-5 is orthorhombic at room temperature. However the crystals undergoes a phase change to monoclinic when heated at a temperature of above 600 °C or when the aluminium content in the framework is reduced.

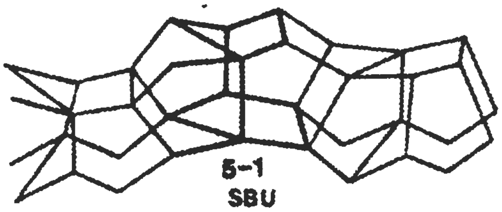


Figure 7: Pentagonal units of ZSM-5

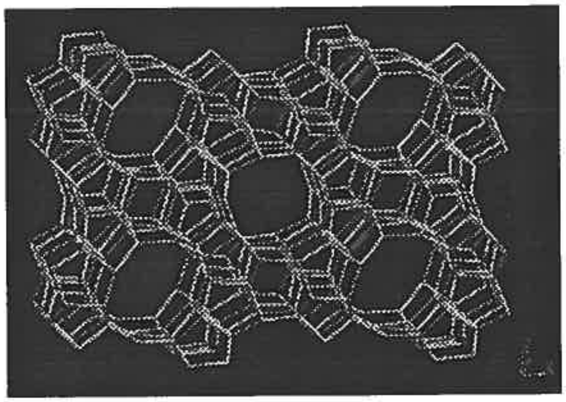


Figure 8: Framework topology of ZSM-5

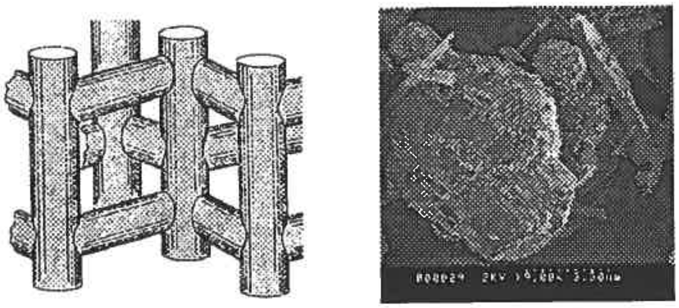


Figure 9: Three-dimensional channel system and SEM micrograph of ZSM-5

(iv) Zeolite Beta

Zeolite beta is an old zeolite discovered by Mobil. However, the structure of zeolite beta was only recently determined because the structure is very complex and interest was not high until the mineral became important for some dewaxing operations. Zeolite beta consists of an intergrowth of two distinct structures termed Polymorphs A and B. The polymorphs grow as two-dimensional sheets and the sheets randomly alternate between the two. Both polymorphs have a three dimensional network of 12-ring pores. The intergrowth of the polymorphs does not significantly affect the pores in two of the dimensions, but in the direction of the faulting, the pore becomes tortuous, but not blocked. The nonplanar framework topology showing the hypothetical polymorphs are depicted in **Figure 10**. It is the only large pore zeolite to have chiral intersections [22].

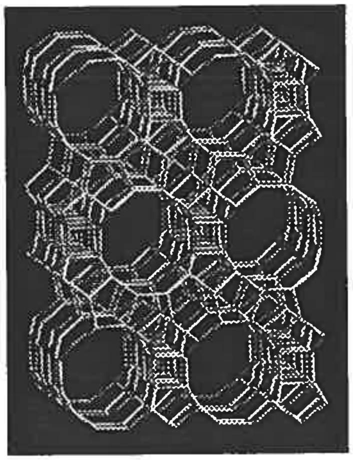


Figure 10: Framework topology of zeolite beta

(v) MCM-41

MCM-41 has channel like pores of uniform size which are arranged in a regular hexagonal pattern with pore diameters ranging from 16 to 100 Å. The schematic structure model of this hexagonal phase is shown in **Figure 11**. The MCM-41 structures were found to be constructed mainly from amorphous inorganic silica walls around surfactant molecules. In most studies, the wall thickness was found to be in the range of 9 to 12 Å [23]. The calcined material have specific surface areas of about 700 m^2 per gram. A so-called liquid crystal templating mechanism in which surfactant liquid crystal structures serve as organic templates has been proposed to explain the formation of such large pore sizes in the mesoporous materials. It assumes that the cylindrical micelles are formed from the surfactants, around which the aluminosilicates form. Burning off of the organic material then leaves back the cylindrical pores.

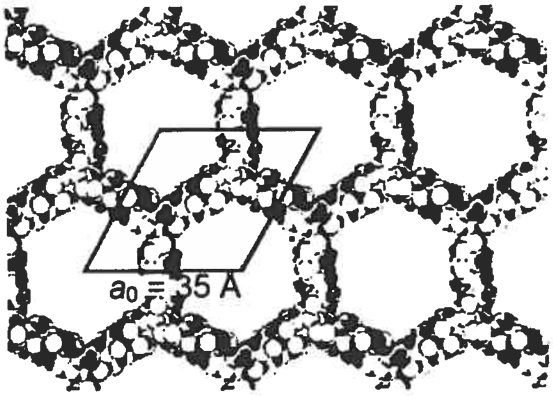


Figure 11: Schematic representation of the structure of a MCM-41 phase with an interpore distance of ≈ 35 Å, amorphous wall structure and hexagonal pores.

(vi) Aluminophosphate Molecular Sieves

In 1982 a major discovery of a new class of aluminophosphate molecular sieves was reported by Wilson *et al.* [24]. By 1986 some elements were reported to be incorporated into the aluminophosphate frameworks, which include Li, Be, B, Mg, Mn, Fe, Co, Zn, Ge and As [25]. These new generations of molecular sieve materials which are designated as $AlP0_4$-based molecular sieves, comprise more than two dozen structures and two hundred compositions.

Framework topology of the $AlPO_4$–5 and its tubular unit are depicted in **Figure 12**. It is an aluminophosphate molecular sieve consisting of alternating Al and P tetrahedra and in one-dimensional structure with a 12-membered ring along the c-axis with a pore size of 7–8 Å. Medium pore structures which are outlined by 10–membered rings or elliptical 12-rings with pore diameter of 6–6.5 Å, include $AlPO_4$-11, $AlPO_4$-31 and $AlPO_4$–41. Small pore size materials such as $AlPO_4$-17 (ERI), on the other hand consist of 8-membered ring pores with 3.5–4.5 Å in diameter.

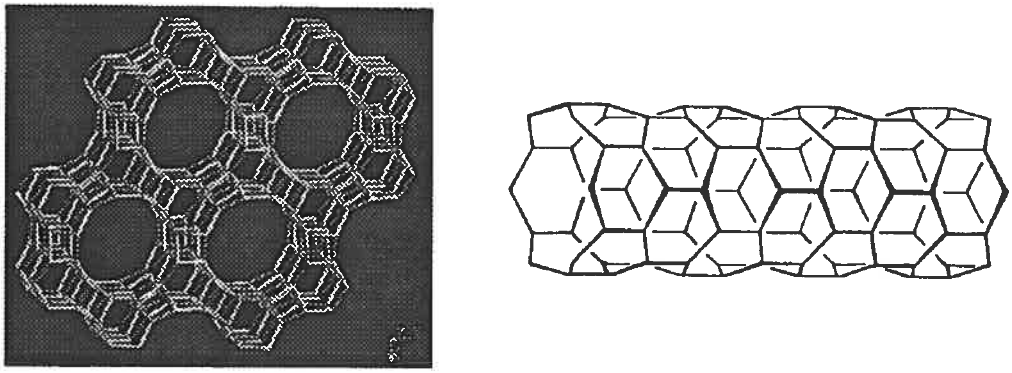


Figure 12: Framework topology of the $AlPO_4$–5 and its tubular unit

A new family of aluminophosphate materials is VPI–5; a material with very large pores, reported by Davis *et al.* [13]. The VPI-5 structure is outlined by a unidimensional channel of an 18-membered ring with a free pore diameter of 12.5 Å (**Figure 13**). The topology of VPI-5 can be generated by inserting a four-membered ring adjacent to each four-membered ring in $AlPO_4$. The total volume of VPI-5 is very large and the framework is stable without any phase transition even after being heated above 800 °C. The symmetry of VPI-5 is hexagonal with unit cell dimensions of a = 18.99 Å , c = 8.11 Å.

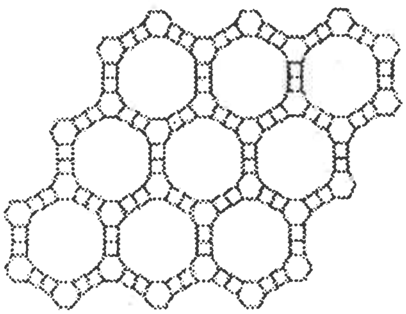


Figure 13: Framework structure of VPI-5

The next familiy of molecular sieves is the silicoaluminophosphates (SAPO). The name of the silicon analogue family of the 12-ring AlPO$_4$-5 is SAPO$_4$-5. In the metal aluminophosphate (MeAPO) family, the framework composition contains metal, aluminium and phosphorus. The metal (Me) species include the divalent forms of Co, Fe, Mg, Mn and Zn, and trivalent Fe. The MeAPSO family further extends the structural and compositional diversity found in the SAPO and MeAPO molecular sieves. These quaternary frameworks contain Me, Al, P, and Si species. Additional elements such as Li, Be, B, Ga, Ge, As and Ti have been incorporated into the AlP04and SAPO framework to form ElAPO and ElAPSO families respectively.

CHEMICAL PROPERTIES

Zeolites possess remarkable physical and chemical properties [1-3]. The most important chemical properties are selective sorption, ion exchange and catalytic activity. The sorption and diffusion properties of zeolites are due to the presence of different size channels and cavities which is related to the free space or void volume. Zeolites are able to absorb up to 30% of their dry weight in gases such as nitrogen and ammonia, over 70% in water and up to 90% of certain hydrocarbons. Zeolite Y has been used as a drying agent for a long time.

The pore sizes which vary from 2.3 Å in sodalite to over 100 Å in MCM-41, for example, explain why a zeolite can sorb only certain organic molecules which cannot be sorbed by another. Dehydrated chabazite with pore openings of less than 5Å wide can sorb water, methanol, ethanol and formic acid, but not ether or benzene. Faujasites on the other hand, can sorb not only ether or benzene but also molecules as large as $(C_2F_5)3N$.

Microporous materials can offer extremely large specific surface areas. A spoonful of zeolite Y of about 1 gram in weight for example, has a surface area of 800 m^2, which is as large as the size of a football field! Pores are classified on the basis of their diameters, *d;* the smallest are micropores ($d < 20$ Å), intermediate are mesopores (20 Å $< d \leq$ 500 Å) and larger are macropores ($d > 500$ Å). There are eight pore apertures in the A-type zeolite and twelve in X– and Y–type zeolites. These pore apertures are uniform throughout th entire structure of a particular zeolite. As a result, regular channels run through the pore apertures, linking between the larger void volume known as supercages. In the A type zeolite, the free (i.e. unobstructed) pore aperture has a diameter of 4.2 Å whilst the supercage has a diameter 11 Å. In X- and Y-type zeolites, the free pore apertures have diameters of 7.4 Å whilst the supercage diameter is 13 Å.

As a direct consequence of the extension of the channel system throughout zeolite crystals, up to half of the total volume defined by the external surfaces is in fact void and available for penetration by gas phase molecules. By comparison, the internal surface areas of zeolites exceed the external surface area greatly, even for very small zeolite crystals. However, it is important to realize that this internal surface area will only be accessible to fluid phase molecules which are small enough to pass through the geometrical restrictions of the pore apertures. Here then there is what is termed *molecular sieve* action, when there is selective adsorption on the internal surfaces governed by the size and shape of, the molecule concerned. For example, it is evident from comparison of **Figures 14** that benzene will be unable to penetrate through the pore aperture of an A-type zeolite and is thus excluded from adsorption on the internal surfaces. In fact, the largest molecules which are able to pass through the unobstructed A-type aperture are linear alkanes, whilst branched chain alkanes are excluded. Even at this early stage, it should be apparent that molecular sieve or size selective action by zeolites should be a very significant aspect of heterogeneous catalysis. Obviously it is the crystalline nature of zeolites; which is vital in this respect. Amorphous porous materials, such as silica-alumina, will not usually have regular pore structures. Thus whilst silica-aluminas do offer high specific surface areas, they will not show size selective action.

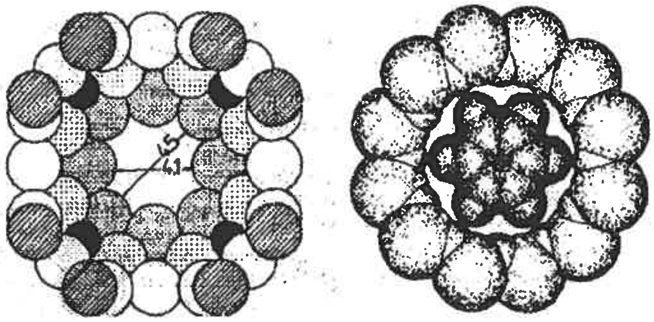


Figure 14: Space-filling models of pore apertures in zeolite A (left): On the right, similar model of the benzene molecule appears, aligned in the same plane as the pore aperture of zeolite Y

Due to its stable and flexible framework of variable sizes, the zeolite lattice may also be used as a host for encapsulated complexes or metallic clusters allowing the control of nuclearity of these active species and the steric contraints imposed on the reactants. MCM-41 and VPI-5, for example, have been used to host polymer, metal complexes and enzymetic species to form molecular wires and zeozymes.

Aluminosilicates are not only useful as molecular sieves, but also exhibit surface selectivity. Like most solid surfaces, zeolite surfaces show high preference for water and other polar molecules. This is due to the presence of polar groups such as cations and hydroxyls in the intracrystalline void space and of electric field gradients brought about by the presence of aluminium in the tetrahedral framework. As the zeolite becomes more siliceous, its affinity for water decreases and for organic molecules increases. An example of an organophilic hydrophobic material is silicalite, the pure-silica form of zeolite ZSM-5. Silicalite has no aluminium and no cations in its structure, and a certain amount (ca. 6%) of water molecules adsorbed on its surface are associated with the surface hydroxyl groups. However, silicalite is electrically neutral, and so there is no strong interaction with the water molecules which are excluded from the crystal.

The sorptive properties of zeolites are modified by the charge-balancing cations. These are coordinated to the framework oxygen atoms. In fully hydrated zeolites the cations are mobile and can be exchanged by other cations, not necessarily monovalent. This is possible through ion exchange with an appropriate solution or molten salt. Exchange of cations with other cations of different size or different electric charge affect the size of the pores and hence the sorptive properties. Changes in the pore size which result will vary the selectivity patterns exhibited by the zeolite. For example, the sodium form of zeolite A will admit molecules with a maximum size of about 4Å. Ion exchanging the sodium ions, which partially block the "windows" in the structure, with calcium requires half as many ions. Zeolite Ca-A permits species up to 5Å to be adsorbed. Conversely, exchanging the sodium ions by the larger potassium ions reduces the free aperture dimensions and will only admit smaller molecules. The cations which neutralize the electrical charge of the framework can be ion exchanged not only in solution but also by simple physical contact between crystallites.

In general, cationic selectivities in zeolites, do not follow easily identifiable rules. The exchange behaviour depends on the nature and size of cation species, temperature, pressure, the concentration of solutions and zeolitic structure. Zeolites with low Si/Al ratios have higher exchange capacity compared to those with high silicon content. The cations present in a given zeolite strongly influence its physical properties. Thus, the framework dimensions increase with increasing ionic radius of the cations. For example, when Na^+ is exchanged for Li^+ in zeolite A, the lattice parameter of the cubic unit cell decreases from 24.99 to 24.88Å. The Li^+ cation, being smaller in size, takes up less space than the Na^+ cation. This is why ion exchange can modify molecular sieving properties of zeolites. This is useful in isolating certain cations in solutions, collecting harmful products of radioactive reactions and softening water.

The third and most important application of zeolites is as heterogeneous catalysts [25-28]. Zeolite catalysts are different from most other heterogeneous catalysts in that the catalytically active sites are distributed uniformly throughout their bulk. The voids and channels are accessible to certain reactant molecules. In order to be useful as catalysts, the zeolites must have channels which are at least 4Å wide. Much of the chemistry that takes place in catalysis derives from the acidity of sites within the zeolites.

The catalytically active centres are the acidic hydroxyl groups associated with the tetrahedral aluminium atoms. The framework aluminiums can be modified by hydrothermal dealumination [29] and alumination by secondary isomorphous substitution [30]. There are two kinds of acidic sites in zeolitic frameworks. Brönsted acid sites are the protons attached to framework oxygens bonded to silicon atoms which are present in the vicinity of aluminium atoms. The acid strengths of these sites depend on their environment. The protons can be introduced into the structure by ion exchange, thermal decomposition of the ammonium-exchanged forms, hydrolysis of water of hydration of cations or reduction of cations to a lower valency state. Upon further heating, Lewis acid sites are produced. Lewis acid sites are believed to be more acidic than Brönsted sites, although relatively little is known about their nature.

In the early 1960's, stabilised framework zeolites were found to be more superior than the amorphous silica-alumina in catalytic cracking. Cracking is the molecular weight reduction process by which the heavier components of crude oil are converted to lighter, more volatile materials such as those used in gasoline. Gasoline (petrol) is a complex mixture of a large number of individual hydrocarbons containing 5 to 11 carbon atoms generally. A conventional organic chemist would regard that it is practically impossible to produce gasoline from synthesis gas or from a simple alcohol. Within less than 20 years the initial laboratory synthesis of gasoline from alcohol in a single stage process by the outstanding ZSM-5 catalyst has led to a commercial production process for gasoline which is able to satisfy about one-third of New Zealand's transportation fuel needs [31]. The ability to control the flow of molecules by ZSM-5 zeolites involves separate diffusion of reactant and product molecules along the connected pore systems. In addition, the steric environment of the site restricts the geometry of the transition state in a reaction.

Zeolite ZSM-5 also have high activities for xylene isomerization which further illustrate the shape selectivity of zeolite catalysts. Since most of the accessible zeolite surface is in the interior of the structure, it is therefore the pore structure that determines the admittance of reactant molecules and the exit of the products. For instance, alkylation of toluene using ethylene over ZSM-5 modified with silicon (SiZSM-5) has yielded a selectivity of over 90% for the generation of p-ethyltoluene, relative to the combined production of o-, m- and p-ethyltoluenes (**Figure 15**).

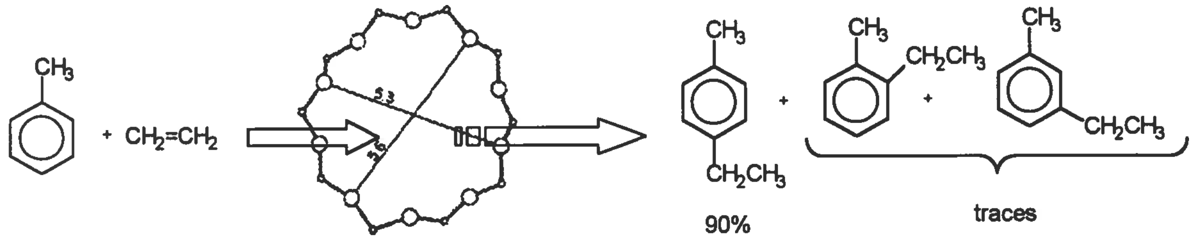


Figure 15: Shape selectivity of ZSM-5.

The spectacular selectivities for p-xylene formation in the lower half of the figure resulted from the modification of the species sites by the presence of phosphorus or magnesium oxides in the vicinity of the pore apertures. This restricts the dimension of the pores slightly in comparison with HZSM-5 itself. The attenuated pore aperture can still be penetrated with relative ease by benzene, toluene and p-xylene, but is almost impenetrable to m- and o-xylenes. Continuous adjustment of the equilibria within the supercages to respond to the selective loss of p-xylene results in 97% production of this isomer into the vapour phase when the alkylation reaction is catalysed by the phosphorus-modified zeolite (PZSM-5).

Small alkenes are vital feedstocks for many processes in the chemical industry. A route for the generation of these from methanol is likely to become of importance in the future when supplies of crude oil are less available. High-silica zeolites such as ZSM-5 have the ability to catalyse the conversion of methanol to small alkenes (olefins); however with HZSM-5 these alkenes are intermediates on the pathway to other products. But a high-silica zeolite with a smaller pore aperture than ZSM-5 might be expected to inhibit the conversion of methanol beyond the synthesis of short linear chains of carbon. An A-type zeolite has this structural characteristic, but the low silicon-to-aluminium ratio does not induce the catalytic activity required.

Fortunately there exist other zeolites with similar pore aperture dimensions to A-type zeolite but with higher silicon-to-aluminium ratios. Natural examples are the minerals erionite and clinoptilolite which have silicon-to-aluminium ratios of 3: 1 and 6: 1 respectively. Synthetic materials designated as Zeolite T and ZSM-34 have corresponding ratios of 3.5:1 and 4-10:1 respectively. The pore aperture dimensions of these various zeolites lie in the range 3.6–5.2 Å, small enough to preclude the emergence of aromatic hydrocarbon molecules from within crystallites. The action is governed substantially by the strongly acidic centres within high silica zeolites and the geometrical restrictions imposed by the pore apertures. Zeolite beta, on the other hand, being the only large pore zeolite to have chiral pore intersections could then be used for the separation of chiral molecules. MCM-41 and VPI-5 having large pores are potential catalysts in petroleum refining for cracking macromolecules.

CONCLUSION

Several features of the structural chemistry of zeolites are related to their importance as sorbents, molecular sieves and catalysts. Zeolites are potentially very active catalysts due to the topology of the framework, shape and size of the pores which can be modified to accommodate sorbates and impose shape selective contraints on the products of the reaction. It is apparent that more applications of these remarkable zeolite systems will be realised as our knowledge of the chemistry and structure of the framework continues to grow.

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