Articles

The Zeolite Cage Structure

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Zeolites are typically aluminosilicates whose framework structures have pores of molecular dimensions. They are widely used as ion exchangers and sorbents and in hydrocarbon conversion catalysis and separations. Recent zeolite research has focused on widening the scope of synthetic procedures, on further exploiting zeolites in commercial processes, and on applying modern characterization techniques to unraveling the complexities of zeolite structural properties.

The term zeolite (*1–14*) was coined by Cronstedt in 1756 (*15*) as a name for an extraordinary aluminosilicate mineral that appeared to boil when heated. Since that time, some 41 naturally occurring zeolites have been identified (*12*). The breadth of zeolite structural chemistry has, however, been broadened enormously by the successes of laboratory syntheses that have yielded many structures and compositions that have no natural counterparts. The recent diversity of interest in zeolite chemistry has been fueled by the economic rewards of industrial applications of zeolites, by ongoing developments in synthetic procedures, and by the application of new techniques to zeolite characterization.

Zeolites are tectosilicates; that is, they have framework structures that are formally constructed from $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ tetrahedra that share vertices. The individual tetrahedra are always close to regular, but because the shared oxygen linkage can accommodate T–O–T angles [T, tetrahedral species (silicon or aluminum)] from 130° to 180°, they can be combined into a variety of framework structures (Fig. 1) (*16*). The 39 different framework topologies that have, to date, been observed for aluminosilicate zeolites have pores that vary in shape, size, and dimensionality (Fig. 2). The naked LTA and FAU frameworks, for example, have large cages, approximately 11.4 and 11.8 Å in diameter, respectively. These are interconnected through smaller constrictions or windows of diameters 4.1 and 7.4 Å. The naked CAN, LTL, MAZ, and MEL frameworks have one-dimensional channels of minimum diameters 6.2, 7.1, 7.4, and 5.1 Å, respectively. The MFI framework of ZSM-5 has two orthogonal interconnected channel systems with minimum diameters of 5.1 and 5.4 Å. The aperture sizes are limited by the number of tetrahedra in the ring that defines them. The above structures have pores with 8-ring (LTA), 10-ring (MFI and MEL), and 12-ring (CAN, FAU, LTL, MAZ, and MOR) windows (Table 1). The aperture dimensions control the accessibility of the zeolite's internal volume. Molecules that are too large will be completely excluded or "sieved" out. Molecules of suitable dimensions, however, can enter into the huge internal volume of the zeolite. The surface area of a typical FAU framework material measured by nitrogen adsorption, for example, is some 800 $m^2 g^{-1}$. The water sorption capacity of the same material may exceed 30 weight percent.

A particular zeolite is probably best defined by its framework topology because its chemical composition may vary greatly. A general formula for the aluminosilicate zeolites can be written as

$$\underset{\text{Nonframework cations}}{M_{x/m}} \cdot \underset{\text{Framework components}}{Al_xSi_{2-x}O_4} \cdot \underset{\text{Sorbed water}}{nH_2O}$$

The relative proportions of silicon and aluminum, first, are variable within $0 \leq x \leq 1$. The exact composition limits differ from structure to structure, and in the sodalite (SOD) framework the opposite end of the composition field ($1 \leq x \leq 2$) is also accessible. Second, partial or complete isomorphous substitution of silicon or aluminum (or both) is possible, giving rise to families of, for example, aluminophosphates (*17*), silicoaluminophosphates (*18*), gallosilicates (*3*), and ferrisilicates (*19, 20*). Third, the framework is anionic, and for charge compensation the structure contains mono- or divalent cations, *M*, equal in total charge to the number of framework aluminum atoms. These nonframework cations are, at least in hydrated materials, usually mobile and can generally be replaced by a range of mono-, di-, or trivalent cations through ion exchange in an appropriate solution or molten salt. Finally, as observed by Cronstedt, the water in the system can be dispelled by heating to leave an intact open framework structure that will sorb water, a variety of organic and inorganic molecules, or metal vapors.

Zeolite Synthesis

Natural zeolites occur in cavities in basaltic volcanic rock, in metamorphic rocks, and, on a much larger scale, in sedimentary tuff deposits (*3, 12*). In each case the zeolites result from modification of the native rock by mineralizing solutions. Although the composition of the zeolite formed depends somewhat on the elemental composition of the source rock, ratios of silicon to aluminum (Si:Al) are always in the range of 1 to 6. Such natural minerals generally contain a mixture of nonframework cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+} and may also contain trace amounts of other elements such as iron. Although the formation conditions for these natural deposits were probably quite mild, with typical temperatures in the range of 70° to 350°C, the deposits accumulated over geological time scales.

Barrer's pioneering work in the 1940's and 1950's demonstrated that a wide range of zeolites could be synthesized quite readily in the laboratory from aluminosilicate gels (*3*). In a typical modern procedure, a solution of alumina in excess of a base such as sodium hydroxide is mixed intimately with a sol or solution of the silica component. The highly alkaline mixture forms a thick gel that crystallizes over a few hours when maintained at about 100°C. The product in this typical Na_2O-SiO_2-Al_2O_3-H_2O system depends on the gel composition, the nature of the reagents, and the crystallization conditions (*3, 21*). By suitable adjustments to the system parameters, LTA, FAU, SOD, ANA, MOR, and GIS framework materials can all be derived from this one system; this reflects the competing crystallization that occurs in the gel. Our knowledge of

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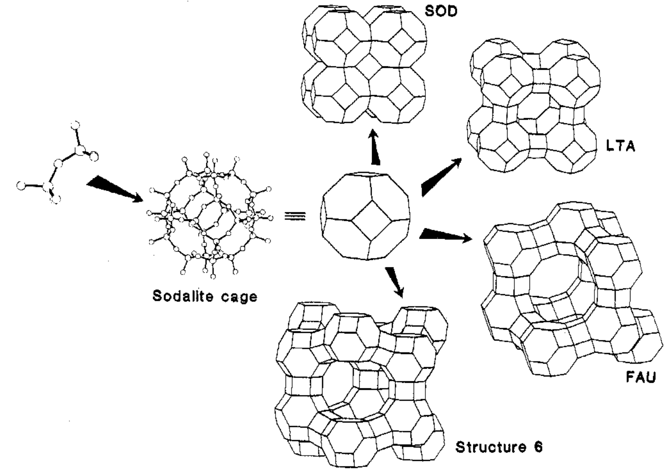

Fig. 1. The figurative construction of four different zeolite frameworks that contain sodalite cages. A pair of TO_4 tetrahedra sharing one vertex is linked into a single sodalite cage. In a less cluttered representation, the oxygen atoms are omitted and the cage is represented by straight lines connecting the tetrahedral sites. The sodalite cage unit is found in the SOD, LTA, and FAU frameworks. Structure 6, a hypothetical framework related to that of FAU, is also constructed from sodalite cages.

the molecular processes involved remains largely empirical (*3*). The products that have been observed as a function of each of the system variables define crystallization fields for the various possible products and, generally, the conditions that optimize the purity and yield of a desired material.

The nature of the countercation is a critical gel parameter. Replacing the sodium ions in the above system by any other cationic species gives rise to very different product distributions (*3*). Thus in the Li_2O-Al_2O_3-SiO_2-H_2O system, two new zeolites, ABW and LIH (*22*) are found, but no product frameworks are common to the sodium system. Similarly, in the K_2O-Al_2O_3-SiO_2-H_2O system (*3, 7*) no FAU or LTA products occur, but ANA, EDI, CHA, LTL, and PHI framework materials are observed. Similar differences are found for other mono- or divalent cations. The directing role of a given cation is not necessarily exclusive and can be modified by changes in the other gel parameters or by the addition of other species. The RHO framework, for example, is observed in systems containing both cesium and sodium ions (*8, 21*). The nature of any anions present in the gel can also alter the distribution of products.

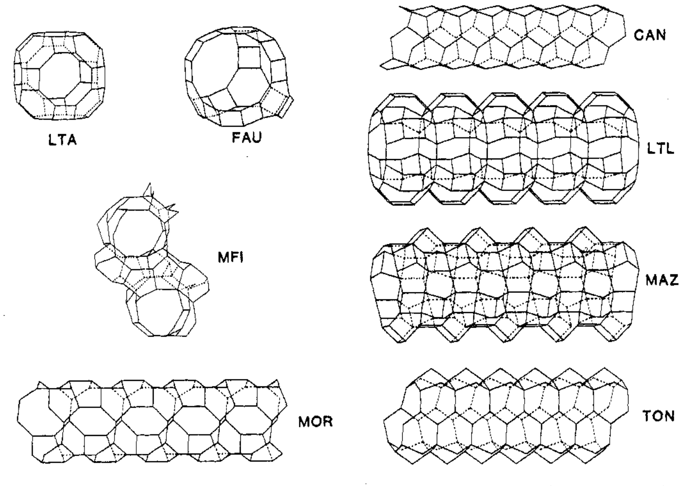

Fig. 2. Representations of selected members of the zeolite family, showing pores of various sizes, shapes, and dimensionalities. The outlines of the cages and channels are drawn as straight lines connecting adjacent tetrahedral sites (see Table 1).

The scope of these synthetic procedures was further enhanced when, in 1961, Barrer and Denny (*23*) and, apparently, Kerr and Kokotailo (*24*) demonstrated that organic bases such as tetramethylammonium (TMA) hydroxide could be used as whole or part replacements for the inorganic base component. The organic base modifies somewhat the chemistry of the gel but, more important, it apparently also provides a "template" around which the zeolite structure can form. This templating effect depends on the size, shape, and charge distribution of the organic cation. Thus the TMA^+ cation promotes the formation of sodalite cages (found in LTA, SOD, or FAU frameworks) and gmelinite cages (in the MAZ framework), although the nature of the final product is again influenced by other gel parameters. Barrer and Denny's pioneering work was soon extended to cover a wide range of tetraalkylammonium ions, neutral species such as amines, linear polyelectrolytes, alcohols, ketones, organic sulfur, and so forth (*3, 25*). These syntheses have yielded many new materials, including the commercially important ZSM-5 (MFI) zeolites that are synthesized in the presence of the tetrapropylammonium cation. Organic templating agents were also critical to the development of the aluminophosphate family of molecular sieves (*17*).

The directing role of the organic cations in these systems is manifested by their occlusion in the final zeolite product, where they can be observed crystallographically or by ^{13}C nuclear magnetic resonance (NMR) (Fig. 3). The organic cations are bulky. Thus, for example, only a single TMA^+ cation can be housed in a sodalite cage. To satisfy charge neutrality, therefore, the anionic charge on the framework is limited, giving rise to higher Si:Al ratios. Thus, although in the Na_2O-Al_2O_3-SiO_2-H_2O system LTA framework materials occur only with Si:Al values close to 1.0, more silica-rich materials ($1.4 \leq \text{Si:Al} \leq 3.0$) are produced on addition of suitable proportions of TMAOH (*23, 24*).

In some senses it is a restriction that the gel components and composition direct the structure of the final product. All zeolites are, however, amenable to postsynthesis modification. The nonframework cations incorporated during the synthesis can be replaced through ion exchange. Organic templates that are generally too large to escape intact from their trapped positions can be burned out, and the sorbed water is likewise expelled on calcination. The framework composition itself can also be altered.

Although most zeolites dissolve rapidly in acid solutions, experiments on clinoptilolite (HEU) by Barrer and Makki (*26*) demonstrated that acid treatments can leach aluminum from the framework. Shortly after those experiments, steam treatment of ammonium-exchanged zeolite Y was also found to yield dealuminated materials, which were termed "ultrastable" in view of their much improved resistance to degradation under acid and hydrothermal conditions (*1, 10, 11, 27*). Other workers have demonstrated controlled dealumination by means of a variety of reagents such as $SiCl_4$ (*28*), $(NH_4)_2SiF_6$ (*9*), and ethylenediaminetetracetic acid (*3, 4*). This dealumination must initially leave framework defects, but under the proper conditions extensive healing can occur, yielding siliceous zeolites that have structural integrities comparable with those of their parent precursors. Studies of the dealumination process by infrared spectroscopy (*10*), powder diffraction (*5, 11, 29*), and solid-state NMR (*30, 31*) all confirm the removal of aluminum from framework positions and the generally good crystallinities of the silicon-rich materials produced by the process. The complement to dealumination is aluminum insertion, and, although this process has been less well studied, there is evidence that aluminum can be inserted into zeolite frameworks by treatment with aluminum halides (*32*). Silicon removal has also been demonstrated.

Until 1982, the scope for the incorporation of framework cations other than silicon and aluminum into zeolite materials was believed to be rather limited. Such constraints have, however, been largely dispelled by the recent announcements of new families of aluminophosphate (*17*) and silicoaluminophosphate (*18*) molecular sieves and of significant framework substitution by various transition-metal ions (*19, 20*). These materials all derive from slight modifications to the gel synthesis procedures first explored by Barrer in the 1940's and 1950's. If these recent developments are indicative of future trends, it would appear that within these techniques there remains considerable scope for the preparation of new microporous materials.

Zeolite Exploitation

The three main commercial applications of zeolites in some senses exploit different aspects of zeolite structural chemistry. As ion exchangers, zeolite frameworks provide substrates that support the mobilities of the nonframework cations. As sorbents and molecular sieves, the zeolites offer hydrophilic or, in siliceous materials, organophilic micropores of controlled dimensions and accessibilities. Finally, in catalysis, zeolite materials provide highly active sites and the possibility of reaction outcomes being governed by shape-selective constraints.

The major use of zeolite ion exchangers (*33*) is in low-phosphate detergents, in which zeolite A (LTA) is used in partial replacement for sodium tripolyphosphate builders and water softeners (*9*). Zeolites are also used in agriculture, particularly in Japan, and in certain waste-water treatments (*9, 33*). In addition, the ion-exchange capacity of the zeolite provides a medium for introducing transition-metal cations into the structure for subsequent catalytic applications.

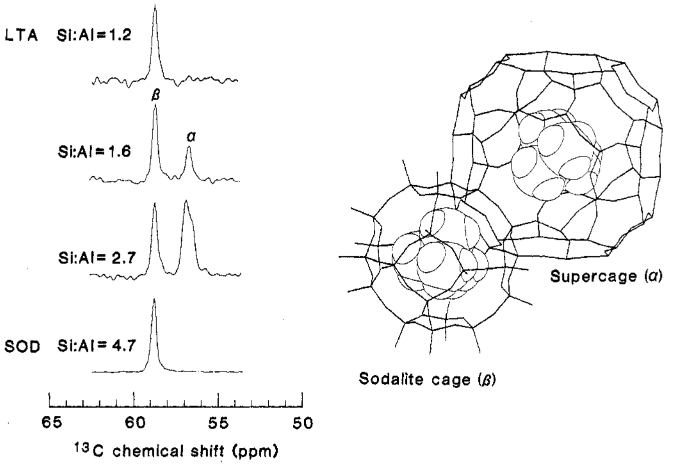

Fig. 3. The ^{13}C chemical shifts of tetramethylammonium (TMA) template ions, which are dependent on the sizes of the zeolite cages in which they reside. The ^{13}C NMR data for TMA sodalite (SOD) and TMA-containing ZK-4 zeolites (LTA) indicate preferential siting of the TMA template ions within the sodalite cages (β) (*69*).

Zeolites, by definition, reversibly sorb and desorb water. In particular, the zeolites with lower Si:Al ratios have strongly polar, anionic frameworks and large complements of nonframework cations so that they interact strongly with polar molecules. They are widely used as dessicants. The siliceous zeolites, on the other hand, have frameworks that are close to neutral and are therefore organo-

Table 1. Selected aluminosilicate zeolite frameworks. The nomenclature of the pore structure is that of Meier and Olson (*54*). The bold integers indicate the number of tetrahedral atoms (Si or Al) that define the aperture. The subsequent numbers indicate the size of the aperture (in angstroms). For structures with more than one channel system, ↔ and ∣ indicate respectively whether or not the channels are interconnected. The number of asterisks indicates the dimensionality of the system.

Code	Examples	Maximum space group	*Q*†	*N*‡	Typical Si:Al ratio	Pore structure
ABW§,‖	Li-A(BW)	Imam	1	8	1	**8** 3.6 × 4.0*
ANA	Analcime, Leucite, Pollucite, Viseite, Wairakite, Na-B	Ia3d	1	48	2	6-ring maximum apertures
CAN	Cancrinite	$P6_3/mmc$	1	12	1	**12** 6.2*
CHA	Chabazite, Herschelite, Linde D, Linde R	$R\bar{3}m$	1	36	2	**8** 3.6 × 3.7***
EDI	Edingtonite	$P\bar{4}2_1m$	2	10	1.5	**8** 3.5 × 3.9** ↔ **8** variable*
ERI	Erionite, Linde T¶	$P6_3/mmc$	2	36	3	**8** 3.6 × 5.2***
FAU	Faujasite, Linde X, Linde Y	$Fd\bar{3}m$	1	192	2.3	**12** 7.4***
GIS	Gismondine, Garronite, Gobbinsite, B, P	$I4_1/amd$	1	16	1	(**8** 3.1 × 4.4** ↔ **8** 2.8 × 4.9*)
HEU	Heulandite, Clinoptilolite	C2/m	5	36	3.5	**8** 4.0 × 5.5* ↔ (**10** 4.4 × 7.2* + **8** 4.1 × 4.7*)
KFI§	Ba-P, Ba-Q, ZK-5	Im3m	1	96	2.2	**8** 3.9*** ∣ **8** 3.9***
LTA§	Linde A, alpha, ZK-4, ZK-21, ZK-22, N-A	Pm3m	1	24	1	**8** 4.1***
LTL§	Linde L, (K, Ba)-G	P6/mmm	2	36	2.6	**12** 7.1*
MAZ	Mazzite, Omega, ZSM-4	$P6_3/mmc$	2	36	2.6	**12** 7.4*
MEL§	ZSM-11	$I\bar{4}m2$	7	96	30	**10** 5.1 × 5.5***
MFI§	ZSM-5, silicalite	Pnma	12	96	30	(**10** 5.4 × 5.6 ↔ **10** 5.1 × 5.5)***
MOR	Mordenite, Ptilotite, Zeolon	Cmcm	4	48	5	**12** 6.7 × 7.0* ↔ **8** 2.9 × 5.7*
OFF	Offretite, Linde T¶,O	$P\bar{6}m2$	2	18	3.5	**12** 6.4* ↔ **8** 3.6 × 5.2**
PHI	Phillipsite, Harmotome, ZK-19	Cmcm	2	16	4	**8** 4.2 × 4.4* ↔ **8** 2.8 × 4.8 ↔ **8** 3.3*
RHO§	Rho	Im3m	1	48	3	**8** 3.9 × 5.1*** ∣ **8** 3.9 × 5.1***
SOD‖	Sodalite, Nosean Tugtupite, Ultramarine	$I\bar{4}3m$	1	12	1	6-ring maximum apertures
TON§	Theta-1, Nu-10, KZ-2, ISI-1, ZSM-22	Cmcm	4	24	30	**10** 4.7 × 6.1*

†Number of topologically inequivalent tetrahedral atoms per unit cell. ‡Number of tetrahedral atoms per unit cell. §This framework has not been found to occur naturally. ‖Nonzeolite materials with this framework are also known. ¶Linde T has a structure comprised of intergrowths of OFF and ERI frameworks.

philic. The access of molecules larger than water to the interior of a particular zeolite is controlled by the dimensions of the pore windows, which can thus discriminate between molecules on the basis of their size and shape.

The characteristics of a particular zeolite as a molecular sieve (*2*) are determined primarily by its framework topology (Table 1), but they are also modified by the nature of the counterions or other sorbed species and by variations in external conditions. Zeolite 4A, the sodium form of zeolite A (LTA), will admit molecules with minimum cross sections of up to about 4.0 Å (whence the term 4A). Partial calcium ion exchange, however, removes sodium ions from partially blocking sites in the pore windows, admitting species of up to 5 Å in minimum cross section. This difference is small but extremely important in molecular terms. The zeolite (termed 5A) will now sorb *n*-paraffins while completely excluding the branched iso-paraffins. Alternative methods for achieving this separation would be complicated and costly. Exchange of the sodium ions by the larger potassium ions reduces the free aperture dimensions such that the zeolite (3A) will admit water and ammonia but not hydrocarbons or alcohols. Zeolite 3A is the material of choice for intensive drying of unsaturated hydrocarbon gas streams and polar liquids such as methanol and ethanol, in which water contents as low as 0.04 parts per million (ppm) can be achieved.

Although there are many other examples of true molecular sieving, a wider range of separations relies on the different diffusion rates or adsorption affinities of different molecules within the zeolites (*34*). The equilibrium composition of the sorbate within a zeolite in contact with a binary gas or liquid mixture depends on the relative affinities of the zeolite for the two components. These will in general not be equal and may differ widely. Nitrogen, for example, has a molecular quadrupole moment and is much more strongly sorbed into zeolites with lower Si:Al ratios than oxygen. The Lindox and Unox processes exploit this difference in separating oxygen from air by means of pressure-swing adsorption (*14, 34*). The pressure-swing, a reduction in the external pressure, is used to regenerate the zeolite and, if desired, to recover the preferentially sorbed component after it has been selectively sorbed in the first half of the separation cycle. In cases where the components to be separated from the mixture do not have markedly differing sorption affinities, pressure- or thermal-swing approaches (*14, 34*) become impractical.

Zeolites continue to be useful, however, in chromatographic separations essentially similar to those achieved by an analytical gas chromatograph. The Parex process of Universal Oil Products (*34, 35*), for example, uses FAU framework zeolites to separate *p*-xylene from a mixture of the other xylene isomers and ethylbenzene, all C_8 aromatics. Whereas a conventional gas chromatograph operates discontinuously on small amounts of material, the column in the Parex process is engineered to simulate movement of the sorbent in counterflow to the flow of the hydrocarbon mixture and diethylbenzene desorbent. This is achieved by gradually switching the position of mixture and desorbent inlets, and of extract and raffinate outlets, down the zeolite column. Thus, although the zeolite bed is fixed, the unit provides continuous operation.

The third and most vital area of zeolite application is in heterogeneous catalysis (*10, 14, 28, 36*). In the early 1960's, stabilized FAU framework zeolites were found to have several properties much superior to those of traditional amorphous silica-alumina materials in catalytic cracking (*37*). 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. The need for an efficient catalyst for this process is driven by the diminishing crude oil supply and the requirement for high proportions of lighter liquid fragments from available crudes. As-synthesized FAU framework zeolites have only limited stability to steam and are therefore inappropriate for the testing conditions of the catalytic cracker and regenerator. Introduction of small amounts of rare earth ions such as La^{3+} or Ce^{3+} by ion exchange, however, yields materials with good stabilities in steam atmospheres. Such materials have activities up to 10^4 times greater than conventional materials (*38*). Indeed, the advantages of the new zeolite materials were such that within 5 years of their development they were being used in more than 90 percent of the catalytic cracking units in the United States.

The rare earth cation is not an essential ingredient. On replacing the sodium ions in the as-synthesized zeolite by ammonium ions, with subsequent suitable heat treatments (generally in the presence of steam), it is possible to prepare ultrastable zeolite Y materials (*1, 10, 27*). These dealuminated materials, although somewhat more expensive to prepare, have activities and stabilities that are similar to the rare earth–exchanged materials.

Much of the chemistry that occurs in catalyzed cracking involves carbocations (*36*) and therefore derives from the acidity of sites within the zeolite. Brønsted acidity is provided mainly by bridging hydroxyl groups whose acid site strengths depend on their local environments. The stronger acidity is associated with isolated aluminum sites in an otherwise silica-rich environment, such as that provided in materials with high Si:Al ratios. Recent measurements by Haag and co-workers (*39*) on ZSM-5 (MFI) materials indicate that this is a very interesting composition regime. For compositions in the range of $10^1 < \text{Si:Al} < 10^5$, log-log plots of the rates of *n*-hexane and 1-hexene cracking and of 1-hexene double-bond isomerization against aluminum content were linear. These data were taken as clear evidence for the catalytic role of a protonated tetrahedral aluminum site in the silica framework. The turnover values at 454°C for 1-hexene double-bond isomerization were 4×10^7 min^{-1} per active aluminum site or greater, which is comparable with values found in enzyme catalysis. The Brønsted acidity of such sites, however, is similar for zeolites and for the traditional amorphous silica-alumina catalysts (*28*). The vastly superior activity of the zeolite must then derive from other factors, such as the particular natures of the acid site environments, concentration effects, or, perhaps, the stabilizing effect that an anionic or near-neutral zeolite framework may have on an enclosed carbocation. This area is one that is currently under intense experimental and theoretical study.

The ZSM-5 (MFI) zeolites have high activities for other conversions, such as xylene isomerization and the production of gasoline from methanol. Aspects of both these processes illustrate the second important feature of zeolite catalysts—their shape selectivity (*10, 28, 40–42*). Approximately 99.5 percent of the accessible zeolite surface is in the interior of the structure. The pore structure of the zeolite therefore controls the approach of reactant molecules to the active site and the departure of products from it. In the MFI framework, "molecular traffic control" has also been postulated, which involves separate diffusion of reactant and product molecules along the distinct, but connected, pore systems (Fig. 2). Further, the steric environment of the site imposes constraints on the geometry of the transition state in a given reaction and may, for example, serve to stabilize one particular configuration of a carbocation species.

Each of these controls, either separately or in combination, can impose shape selectivity on the outcome of the process. There have been many examples of each of these selectivities since the first report of shape selectivity in zeolites in 1960 (*40*). The field has been reviewed recently (*41*). A simple example of reactant selectivity is provided by the dehydration of alcohols over calcium-exchanged zeolite A (LTA). As discussed above, only the normal alcohols can enter this framework, and they undergo reasonably rapid conversion to olefinic products. However, the secondary alcohols—which yield more stable carbonium ions and which, in a non–shape-selective system, therefore convert much more rapidly—are excluded from the zeolite and are thus relatively inert.

Catalytic dewaxing and selectoforming are commercially important processes that also exploit zeolite shape selectivities for *n*-paraffins (*42*). The *n*-paraffins have lower melting points, which contributes to thickening of fuel oil and lower octane numbers in gasoline. Although zeolite 5A (LTA) selectively sorbs the *n*-paraffins, ZSM-5 (MFI) has a slightly larger pore size (Table 1) and can also accommodate long-chain paraffins with single methyl groups. Under process conditions the sorbed phase is selectively cracked to lighter components such as propane (itself a valuable side product), increasing the value of the remaining fuel oil or gasoline. The diffusivity of *p*-xylene in ZSM-5 (MFI) is some 10^3 times faster than that of the *o*- or *m*-isomers. In xylene isomerization the *p*-xylene product then escapes from the zeolite much more rapidly than the other isomers, enabling the overall product distribution to be biased strongly toward *p*-xylene production. The restricted environments of the reaction sites in ZSM-5 (MFI) also limit the formation of the undesirable *o*- and *m*-isomers in toluene alkylation or disproportionation and prevent coking inside the zeolite channels (*41, 42*).

In addition to their attractions in acid catalysis, zeolites also provide possible supports for metal atoms such as platinum, palladium, ruthenium, iron, and nickel (*10, 43*). These metals, when dispersed within zeolites, can compare in activity with those dispersed on conventional supports. At the same time, they offer shape selectivity consequent on the use of reaction sites within the zeolite structures. Platinum, ruthenium, and nickel are active in hydrogenation and dehydrogenation. Iron is active catalytically in Fisher-Tropsch ($CO + H_2$) chemistry. Further progress can be anticipated, particularly in exploiting the catalytic potential of the newer zeolites and of developing techniques for maintaining the activities of zeolite-supported metal dispersions over extended periods under process conditions.

Zeolite Structural Characterization

Although zeolites are crystalline, they have complex structures and large unit cells. Further, the diffraction techniques that are the workhorse of crystal structure analysis provide only an averaged view of the structure, in which local orderings or local deviations from the mean are represented merely as disorder. Our present understanding of zeolite structure thus derives from a combination of techniques.

Local structural features can be sampled spectroscopically. The frequencies of certain zeolite framework vibrations in the mid-infrared region depend on the framework composition and on the manner in which the individual TO_4 tetrahedra are interlinked. The appearance of features in the infrared spectra can therefore correlate with the occurrence of particular types of structural units (*10*). Extended x-ray absorption fine structure (*13*), Mössbauer spectroscopy, and electron spin resonance spectroscopy together with the related electron spin echo spectrometry (*13*) can monitor the nature and environments of target nonframework cations.

In contrast, all primary zeolite constituents are amenable to study by solid-state NMR. By using magic-angle spinning (the magic angle is that at which sample rotation will average to zero the chemical shift and dipole interaction anisotropies) combined where necessary with cross polarization, dipolar decoupling, or multiple pulse sequences, high-resolution NMR spectra can be readily obtained from zeolitic materials (*30, 31, 44, 45*). Although most work to date has been done on the ^{29}Si and ^{27}Al nuclei, measurements on other probe nuclei including ^{17}O, ^{7}Li, ^{205}Tl, ^{13}C, and ^{129}Xe have also been described (*9, 31, 43, 45*). For zeolites that have a single crystallographic silicon site, the ^{29}Si NMR spectrum consists of up to five peaks, each corresponding to a different number of first-neighbor aluminums [Si-O-(Al_n, Si_{4-n}); $n = 0$ to 4]. The intensity of each peak is a direct measure of the number of corresponding units in the sample. The Si:Al ratio of the framework is then readily deduced from the relative intensities of the five Si-*n*Al peaks, assuming only Loewenstein's rule of Al-O-Al linkage avoidance (*46*).

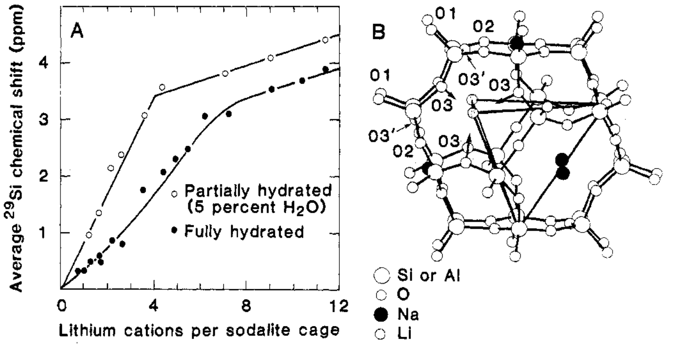

Fig. 4. (A) The variation in the magnitude of the ^{29}Si chemical shift with the extent of lithium substitution into sodium zeolite A, which shows a discontinuity close to the composition $Na_{2/3}Li_{1/3}$, and the discontinuity can be understood in terms of an ordering of equal numbers of sodium and lithium ions at the six-ring window sites (B) (*49*).

The ^{29}Si chemical shifts are also sensitive to the geometry of the local environment of the ^{29}Si nucleus. There is a general correlation between the mean of the bond angles about the four oxygens that coordinate the silicon and the magnitude of the chemical shift (*45, 47*). Although the details of this correlation are still under study, it has already been used in assigning the spectra of more complex zeolites such as synthetic mazzite (*48*). The position of the resonance is also influenced by nonframework species. Although diamagnetic nonframework cations do not have a large direct effect, when coordinated by framework oxygen atoms they modify both the electron density distribution on the oxygen and its bonding geometry. The ^{29}Si resonance is sensitive to both effects. This sensitivity has been exploited to study the structural effects of lithium substitution into sodium zeolite A (LTA) (Fig. 4). The NMR data, in combination with powder x-ray diffraction results, suggested a novel sodium-lithium cation ordering scheme in the mixed material $Na_{2/3}Li_{1/3}$ zeolite A (LTA) (*49*). Neutral sorbed species can likewise modify the framework geometry. A preliminary study of MFI materials used the sensitivity of the ^{29}Si spectrum to changes in framework geometry in demonstrating the occurrence of framework adjustment during hydrocarbon adsorption (*50*).

The ^{29}Si spectra of zeolites that contain more than one independent silicon site can be quite complex. The hexagonal MAZ and OFF frameworks have two independent silicon sites, and their ^{29}Si NMR spectra can therefore contain up to ten features representing the superposition of the five Si-*n*Al peaks from each site. In offretite (OFF), the geometries of the two silicon environments are such that the Si-*n*Al peaks of one site almost coincide with the Si-($n - 1$)Al peaks from the second, giving rise to what superficially appears to be a single-site spectrum. In synthetic MAZ materials, however, the components from the first site are displaced from the second by some 8 ppm, considerably more than the difference (~6 ppm) that separates the *n* and $n - 1$ peaks.

Interpretation of such multiple-site spectra is difficult, and, in the MAZ case, data from other experiments were used to assist the spectral assignment (*48, 51*). Chemical dealumination provides, in some cases, a means of simplifying the spectrum (*30, 31, 51*). The fully dealuminated material has only Si-0Al components and indicates the minimum number of crystallographic silicon sites. The chemical shifts of the Si-0Al components can potentially also be combined with a knowledge of the framework topology and the quantitative effects of first- and second-neighbor aluminum atoms to make it possible to calculate each of the Si-*n*Al peak positions at other compositions (*52*).

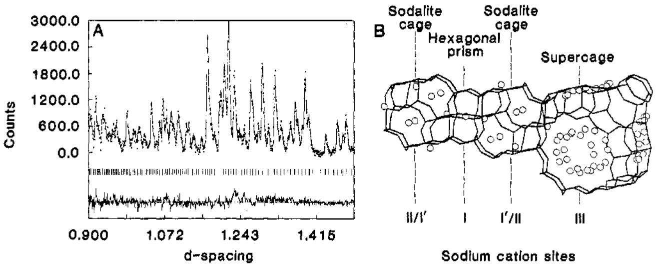

Fig. 5. (A) Portions of the observed (topmost pattern), calculated (continuous line), and difference (lower) powder neutron diffraction profiles for a dehydrated gallosilicate zeolite XY (FAU) (*70*). The diffraction data, which were analyzed by full profile analysis, were collected at the Intense Pulsed Neutron Source at Argonne National Laboratory. In FAU framework zeolites the mean framework T–O bond lengths and T–O–T angles vary consistently with aluminum or gallium content, but the cation configuration varies discontinuously because each of the cation sites (B) has a maximum population limit.

Electron microscopy forms a bridge between these local-structure probes, which sample length scales in the range of 1 to 10 Å, and x-ray and neutron diffraction techniques, which provide the average of the unit-cell repeats over scales greater than 5000 Å. Analytical electron microscopy is widely used in determining sample purity and homogeneity and for elemental analysis. The small spot size of the electron beam has also been used to sample variations in the aluminum content over larger synthetic crystals of MFI materials (*9*). Electron diffraction patterns are difficult to interpret quantitatively, but, for unknown structures, they can indicate possible unit cells and symmetries. Zeolites are very sensitive to the electron beam, however, and it is only recently that the full potential of the electron microscope has been realized in providing direct lattice images of regions of various zeolite structures (*53*). When conditions permit, zeolites are good subjects. They have large unit cells and thus give lattice fringes even under moderate resolution. Their pore structures provide good scattering contrasts so that, for example, the channels in MAZ and LTL materials are readily seen. Because of the similarity between the various frameworks and the competing crystallization that is present during synthesis, zeolites also provide examples of defects of various types, structural intergrowths, and coincidence boundaries (*53*).

In elucidating zeolite structures, several indirect physical techniques provide useful data. Sorption and molecular sieving experiments indicate the size and volume of the micropores. Density measurements can yield the number of tetrahedral units. Ion-exchange experiments indicate which cations are accessible and can, in addition, provide scattering contrast for diffraction measurements. The framework composition itself can also provide clues to the framework structure. All the zeolites with high Si:Al ratios that are made by direct crystallization, for example, have five-ring units in their structures (*54*). Finally, the zeolite's stability and its sensitivity to dealumination and to framework cation substitution are all influenced by aspects of its structure.

These indirect methods are all important because single-crystal x-ray diffraction, the conventional method of determining crystal structures, is of only limited use. Synthetic zeolites generally occur only as small crystallites less than some 5 μm in size. Many known zeolite structures have thus been derived by protracted analyses of powder x-ray diffraction patterns combined with indirect structural data and some inspired guesswork. Even the TON framework first described in 1984 was determined in this way (*55*). Recent developments in diffraction experimentation and analysis techniques, however, promise to contribute significantly to this difficult area of zeolite structural characterization (*56*).

Conventional single-crystal x-ray structure analysis requires crystals larger than about 50 μm on an edge or 10^5 μm^3 in volume. There are limited supplies of larger crystals of the naturally occurring zeolites, but suitable synthetic crystals of only LTA, FAU, and MFI materials are available, and these only at certain limited compositions. Such crystals have already been widely studied, generally in hydrated and dehydrated states, often in various cation-exchanged forms, and, on occasion, containing various sorbed species (*57*).

Conventional powder x-ray diffraction is used analytically in distinguishing different zeolites. As discussed above, there is also a tradition of quantitatively using the powder x-ray diffraction pattern in the solution and refinement of zeolite structures. This is, however, a complex process because the direct methods and Patterson techniques for structure solution that work so well with single-crystal data are not directly applicable in the powder case. Accidental peak coincidence and overlapping of adjacent reflections, particularly at smaller *d*-spacings, imply that an accurate measurement of each unique structure-factor cannot be made. This difficulty is particularly acute in the case of zeolites that have large unit cells and hence many closely spaced reflections and, frequently, sample-related contributions to peak broadening. The traditional approach of peak integration is now being superceded by full profile refinement (*9, 58*). This least-squares curve fitting procedure can be used either in deconvolution of the diffraction pattern or in optimizing directly the parameters that describe an approximate structural model. By supplementing the observed diffraction data with reasonable structural constraints, it is possible to refine even very complex zeolite structures, such as that of ZSM-5 (MFI) (*58*). Structure solution, the derivation of reasonable trial values for the atomic coordinates, must, however, often be achieved largely through trial and error.

Synchrotron radiation potentially provides significant advantages in the structure analyses of zeolite materials (*9, 56*). It is very intense, sharply focused, highly polarized, and continuous over a wide range of wavelengths. The white nature of the radiation makes scattering contrast variation experiments possible with anomalous scattering. Combined with the beam intensity, it also makes energy-dispersive powder diffraction attractive, particularly for time-resolved studies or experiments under controlled atmospheres. The source intensity and its intrinsic resolution can also be used to provide a great improvement (about a factor of 4) in the resolution of a powder diffraction experiment that will dramatically increase the amount of information that can be extracted from the powder diffraction profile. The brightness of the synchrotron source also enables conventional single-crystal diffraction measurements to be made on very small particles. Although microcrystal diffraction as a technique is still under development, initial data from a CAN framework zeolite indicate that complete sets of diffraction data will be accessible from individual particles down to some 1 μm^3 in size (*59*). This is an exciting prospect for zeolite chemistry.

The next generation of neutron sources promises flux gains up to 10^2 greater than those currently available, but this will still be insufficient to permit single-crystal data acquisition from most synthetic zeolites. The attractive features of neutron scattering are, however, being exploited in powder diffraction measurements combined with full profile analysis (*60*). An interesting early result was the observation of a subtle rhombohedral distortion of the LTA framework (*61*) that apparently derives from ordering of the nonframework cations (*13*). The ease with which powder neutron diffraction experiments can be made over a wide range of temperatures and atmospheres, coupled with the sensitivity they provide to scattering by light atoms such as hydrogen, makes the technique very attractive. Several groups are now active at both conventional reactor sources and, with time-of-flight techniques, at pulsed spallation neutron facilities (*62*). The first structure refinements of relatively simple, cubic zeolites [FAU, LTA, KFI, RHO, and so forth (*13, 62*); Fig. 5] are now being extended to systems with lower symmetry (*63*) and to zeolites containing sorbed species (*64, 65*).

The characterization techniques described above have benefited enormously from computer developments in both data acquisition and subsequent analysis. Computer modeling, in its own right, also plays an important role. The distance least-squares program was developed with zeolite problems in mind (*66*). This program performs a least-squares optimization of atomic coordinates subject to comparison not against a measured diffraction pattern but rather against a defined set of expected atomic separations and angles. This makes it possible to predict crystal structures on the basis of accumulated chemical and structural information. Monte Carlo methods have been applied to modeling aluminum distributions in zeolites, giving good agreement with those measured by ^{29}Si NMR (*67*). These calculations are now being extended to accommodate general zeolite framework topologies. A third area of ongoing development is interactive molecular graphics, which provides a modern approach to generating and manipulating structure images (*68*). This technique also makes it possible to model cation configurations and new frameworks, which can be very helpful during structure determination (*63*). Once reasonable atomic coordinates are known, interactive molecular graphics routines enable sorbates to be introduced and various interaction energies to be computed as a function of their position, orientation, and conformation within the zeolite. This type of modeling is directly analogous to that already used for several years in probing drug receptor site fitting. The scope of these modeling methods is being rapidly expanded as we accumulate more detailed structural data, more information about framework flexibilities and charge distributions, and more empirical data on sorption and catalytic processes.

Conclusion

Several features of the structural chemistry of zeolites support comparison with enzyme systems. Zeolites can provide extremely active catalytic sites within frameworks that can adjust somewhat to accommodate sorbates and that impose shape-selective constraints on reaction outcomes. The scope of further utilizations of these remarkable inorganic systems can only continue to grow as our understanding of zeolite synthesis, chemistry, and structure develops.

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71. I thank many colleagues for their guidance, knowledge, and input, most notably R. Hulme, A. J. Jacobson, D. E. W. Vaughan, R. A. Beyerlein, M. T. Melchior, and M. E. Tunison.