PROGRESS IN
INORGANIC CHEMISTRY

Edited by

STEPHEN J. LIPPARD

VOLUME 35

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

VOLUME 35

Progress in
Inorganic Chemistry

Volume 35

Contents

New Light on the Structure of Aluminosilicate Catalysts

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I. INTRODUCTION

Aluminosilicates, which constitute one of the largest classes of minerals, have, from the earliest times, been used as catalysts or catalyst supports for a number of commercially important reactions. Acid-treated clays, for example, were used from the 1920s to the mid-1940s for the cracking of oils (1) and for the reforming (i.e., the isomerization) of short-chain hydrocarbons such as pentanes to octanes (2). Since the early 1960s synthetic aluminosilicates in the form of zeolites (3–5) have been the dominant catalysts in the petrochemical industry. Zeolites Y and the so-called pentasils, of which ZSM-5 and ZSM-11 are the most renowned (4, 6, 7) members, are nowadays extensively used worldwide. Ultrastabilized (8) zeolite Y, the structure of which is essentially that of the rare zeolite mineral faujasite (9), is the cornerstone of present-day petroleum cracking and hydrocracking processes; annual consumption is close to 2,000,000 tons. ZSM-5 is the catalyst of choice in the conversion of methanol to gasoline and benzene and ethene to ethylbenzene. It is also used in so-called dewaxing and selectoforming processes (4). Acid-washed mordenite is used as a catalyst support (for the platnium group metals) for reforming; and the aluminosilicate mineral erionite, like the pentasils ZSM-5 and ZSM-11, also finds use as a commercial shape-selective catalyst.

During the last decade there has been a resurgence of interest in the utilization of clays, and more recently, pillared clays, as versatile catalysts for the conversion of organic species into more useful products. In Table I some of the reactions that have recently come into prominence are enumerated (10–14).

Elucidating the structure of zeolites and clays is not, in general, an easy task. Very few of the zeolites (especially the highly siliceous ones that currently figure emminently as novel catalysts)—and hardly any of the clays—are available as single crystals, so that the classical X-ray techniques cannot be used. Even in the rare situations when good quality crystals are available, distinguishing structural Al from Si is difficult because of the similarity in scattering strength of these two elements. However, enough background X-ray work, along with inspired powder-diffraction studies (15, 16), has been done to compile an atlas of zeolite structures, embracing both natural and synthetic ones (17). A compilation of the positions of extra-framework (exchangeable) cations in a wide range of zeolites is also available (18).

The open structures of zeolites can be envisaged as having been assembled from building blocks such as those shown in Figs. 1 and 2. Zeolite structures can then be readily classified according to the secondary building units (shown in Fig. 1) that are present (see Table II).

The name "zeolite" (from the Greek ζεω "to boil" and λιθο "stone") was coined by Cronstedt in 1756 to describe the behavior of the newly discovered mineral stilbite. When heated, stilbite loses water rapidly and thus seems to boil. Zeolites are a class of framework silicates (other classes include feldspars and feldspathoids) that are built from corner-sharing SiO_4^{4-} and AlO_4^{5-} tetrahedra and contain regular systems of intracrystalline cavities and channels of molecular dimensions. The net negative charge of

TABLE I
A Selection of Organic Reactions Catalyzed by Clays

Cracking and hydrocracking of hydrocarbons
Dehydration of alkanols, with the formation of ethers, alkenes, and naphthenes
Isomerizations, alkylations, and cyclizations
Conversion of primary amines to secondary ones
Dimerizations, oligomerizations, and polymerizations
Oxidations and reductions
Hydration, alkylation, and acylation of alkenes to form alkanols, ethers, and esters
Hydrogen exchange and hydrodesulfurizations
Decarboxylations and lactonizations
Polycondensations (e.g., peptides from amino acids)
Porphyrin formation from benzaldehyde and pyrrole
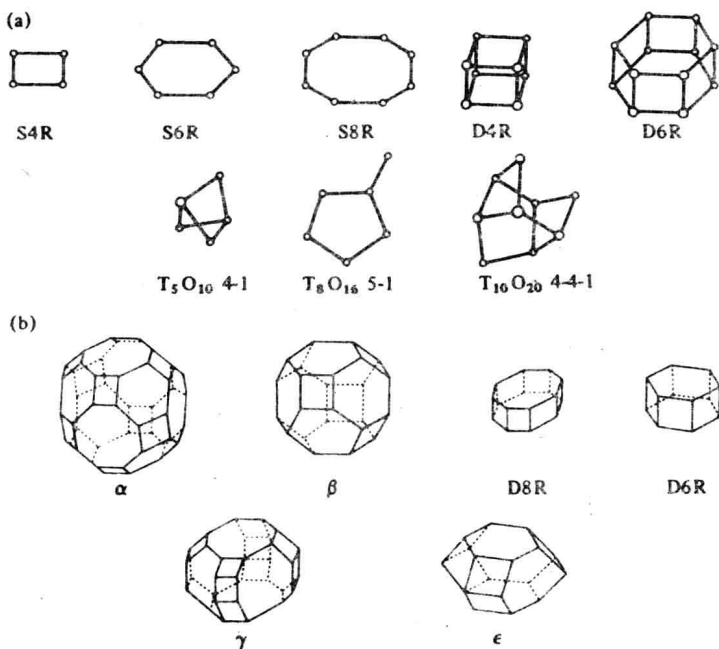
Figure 1. A selection of the secondary building units [double-four (D4), double-six (D6) rings; double-eight (D8), sodalite (β), cancrinite (ϵ), gmelinite (γ) cages] from which the structures of zeolites are derived. The α-cage is synonymous with the supercage in zeolites A and ZK-4.

the framework equal to the number of the constituent aluminum atoms is balanced by exchangeable cations, M^{n+}, typically sodium, located in the channels that normally also contain water. The general oxide formula of a zeolite is

$$M_{x/n}AlO_2)_x(SiO_2)_y \cdot mH_2O$$

It is invariable found that $y \geq x$. The simplest interpretation of this inequality, given that each silicate and aluminate tetrahedron is linked via oxygen bridges to four other tetrahedra, is that aluminate tetrahedra cannot be neighbors in a zeolite framework, that is, that Al—O—Al linkages are forbidden. This requirement, known as the Loewenstein rule (19), will be discussed later.

It has been traditional until very recently to regard all zeolites as having been derived from aluminosilicates, but the definition must now be ex-
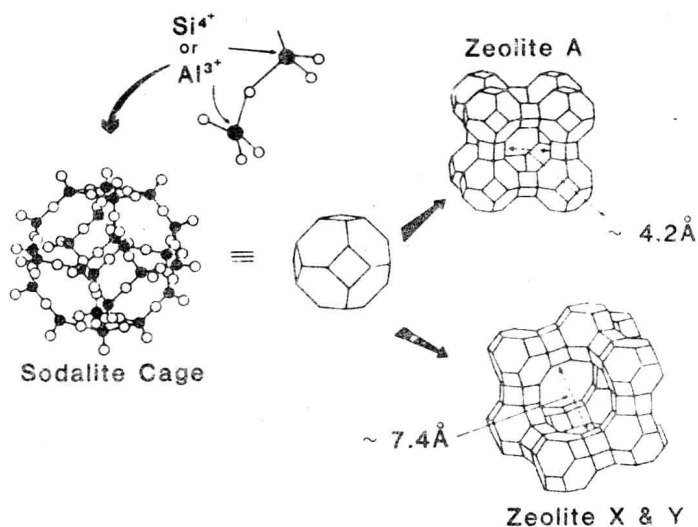
Figure 2. Illustration of how zeolites X and Y and zeolites A and ZK-4 may be pictured as having been assembled from primary (TO₄) (where T is Si⁴⁺ or Al³⁺) and secondary building units (cubes, D6, etc.).

TABLE II
Classification of Some Well-Known Zeolites According to Secondary Building Units

Classification	Zeolite	Number of tetrahedral atoms in main channel or cage	Aperture of channel or cage (Å)
D4R	Types A and ZK-4	8	4.2
D6R	Chabazite	8	3.7×4.2
	Gmelinite	12	7.0
	Faujasite	12	7.4
	Types X and Y	12	7.4
	Type ZK5	8	3.9
	Type L	12	7.1
S6R	Erionite	8	3.6×5.2
	Offretite	12	6.9
	Levyne	8	3.2×5.1
	Mazzite	12	7.4
	Omega	12	7.4
	Losod	6	2.2
5-1	Mordenite	12	6.7×7.0
	Dachiordite	10	3.7×6.7
	Ferrierite	10	4.3×5.5
	ZSM-5	10	5.4×5.6
	Silicalite	10	5.2×5.8

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tended to encompass many other tetrahedrally (T) bonded atoms, besides Si and Al. Evidently there are numerous open-framework structures, of stoichiometry TO_2, all made up of corner-sharing tetrahedra, which can, in practice, be formed. As well as preparing many pure, crystalline silica variants of aluminosilicate zeolites (e.g., faujasitic silica—see Fig. 12) it is established that materials such as $AlPO_4$, $GaPO_4$, and $FePO_4$, as well as those containing three or more different elements as tenants of tetrahedral sites, can be prepared (20–22). In such open structures it is possible for many of the heteroatoms (notably Fe, Cr, Ti, V, and Zn) of the zeolite to have six- or five- as well as the customary four-coordinated sites.

When only powdered samples of synthetic or naturally occurring zeolites are available, how are we to

1. Determine the atomic structure and hence identify the secondary building units?
2. Assess the distribution of the Si and Al among the tetrahedral sites?
3. Characterize the nature of intergrowths and defects within a given structure or between two or more related ones?
4. Pinpoint the positions of sorbed species and/or the exchangeable cations?
5. Identify and characterize the catalytic sites in the zeolite?

Fortunately, thanks to the relatively recent arrival of many important new structural techniques these questions can be answered, in some cases with a degree of precision that rivals, if not exceeds, that achievable with conventional, single-crystal X-ray methods.

With clays and their pillared variants (see Figs. 3 and 4 and Table III) much progress in structural elucidation has been accomplished using the techniques that have also found value for polycrystalline zeolites, especially spectroscopic ones utilizing multinuclear, solid-state NMR (see below). Greater insight has also been achieved as a result of the methods now available for the laboratory syntheses of ultrapure specimens of clay, which are free from the obscuring influences of paramagnetic and other impurities. Because, in general, sheet silicates lack well-developed three-dimensional order, the newer techniques of neutron-powder profile and X-ray powder profile analysis using the Rietveld procedures (see Section II.A) is inapplicable. X-ray-diffraction and neutron-diffraction studies are nevertheless valuable for structural elucidation of clays and their intercalates, especially when supplemented by FTIR and NMR spectroscopic analysis.

Of importance, in view of the recent febrile growth of computer science in the whole domain of silicate and aluminosilicate structural chemistry,
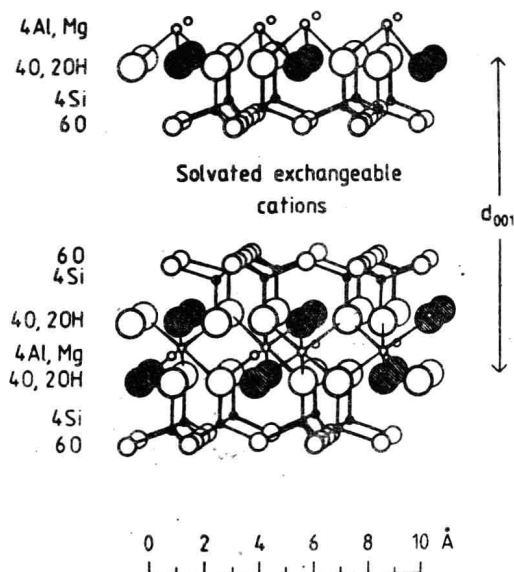
Figure 3. Schematic illustration of the structure of montmorillonite.

are computer modeling techniques. Zeolites, in particular, have been eminently amenable to this approach (see Sections II.A and III.A), but so also have the pyroxenoid silicates (general formula $MSiO_3$) consisting of corner-linked SiO_4^{4-} tetrahedra. Such solids, such as wallastonite ($CaSiO_3$), because they exhibit high-temperature stability, possess attractive properties as catalyst supports. In this regard, the aluminosilicate cordierite
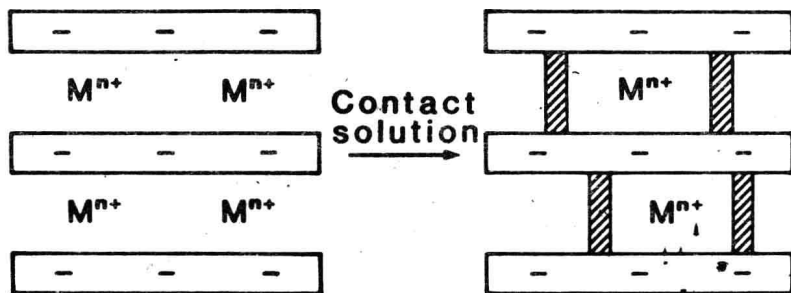
Figure 4. Illustration of how a clay mineral (typically montmorillonite or beidellite) is converted into its pillared form.

TABLE III

Idealized Formulas for Some Selected Clays

Clay	Formula
Pyrophillite[a]	$(Al_4)^{oct}(Si_8)^{tet}O_{20}(OH)_4$
Montmorillonite[a]	$M_{x/n}^{n+}aH_2O(Al_{4-x}Mg_x)^{oct}Si_8)^{tet}O_{20}(OH)_4$
Beidellite[a]	$M_{x/n}^{n+}aH_2O(Al_4)^{oct}(Si_{8-x}Al_x)^{ter}O_{20}(OH)_4$
Talc[b]	$(Mg_6)^{oct}(Si_8)^{tet}O_{20}(OH)_4$
Hectorite[b]	$M_{x/n}^{n+}aH_2O(Mg_{6-x}Li_x)^{oct}Si_8)^{tet}O_{20}(OH)_4$
Saponite	$M_{x/n}^{n+}aH_2O(Mg_6)^{oct}Si_{8-x}Al_x)^{tet}O_{20}(OH)_4$

[a]In these clays, two-thirds of the available octahedral sites are occupied. These are termed dioctahedral.

[b]In these clays, all (three-thirds) of the octahedral sites are occupied, and they are termed trioctahedral.

(23), idealized formula of the synthetic form $Mg_2Si_5Al_4O_{18}$, consisting of both rings and chains of linked tetrahedra, is especially important. It is the support material favored for most automobile exhaust catalysts, the active components being finely dispersed rhodium and platinum. Computer-modeling promises to disentangle the fundamental factors governing the nature of the Si, Al ordering in this material, the ordering itself having been established by ^{29}Si solid-state NMR (23).

To answer the questions posed previously we invoke the combined use of powerful techniques, some of which have not been widely deployed hitherto by inorganic chemists. We begin (Section II) by outlining the essential features of these techniques before proceeding, in Section III, to consider some specific examples. Finally, we briefly assess future prospects in this area of inorganic solid-state chemistry.

II. FOUR DISTINCT APPROACHES TO THE STRUCTURE OF ALUMINOSILICATES

When single-crystal X-ray crystallographic methods are inapplicable, one or more alternative techniques are employed. Provided the material under study is monophasic and well-ordered, powdered samples can be solved structurally by means of neutron scattering, which yields quantitative information comparable in quality to that obtained from X-ray crystallography. Solid-state NMR spectroscopy is another powerful technique, but it is at its best when used to determine the local environment of certain

atoms and local ordering preferences. Seldom does it provide quantitative data pertaining to bond length and bond angles. The third approach is high-resolution electron microscopy (HREM) and its allied procedures of electron diffraction and electron-induced X-ray emission, both of which greatly assist in the identification and characterization of crystallographic phases. The fourth approach is computational, involving, as outlined previously, simulation and calculation of likely structures. Many comprehensive reviews deal with the principles of these four approaches; only techniques for which the relevant details are less readily available will be discussed at some length here with the background principles.

A. Neutron Diffraction and Developments in X-Ray Diffraction

If aluminosilicate specimens are not of adequate dimension to be suitable for X-ray single-crystal diffractometry, they are hardly likely to be suitable for neutron diffraction single-crystal methods. But because of the pioneering work of Rietveld (24), who capitalized on the fact that the peaks of elastically scattered neutrons can be represented by Gaussians or other well-defined functions, some progress can still be made. This means that, provided a model structure is available, the neutron-powder profile can be refined, to yield structural parameters. The procedure (25) is to arrive at a final refinement R_{pr} for the profile of the neutron powder diffraction pattern, in which all the peaks are of Gaussian shape:

$$R_{pr} = \sum \left| y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc}) \right| \sum |y_i(\text{obs})| \qquad (1)$$

where $y_i(\text{obs})$ and $y_i(\text{calc})$ are the observed and calculated intensities, respectively, at the ith position on the profile, and c is the scale factor.

With the dramatic improvements in neutron fluxes [available at IPNS, Chicago, IL, Grenoble, and the SNS (spallation source) at the Rutherford-Appleton Laboratory], many dramatic new developments can be expected from this technique. Not only is it the case that neutron diffraction experiments can be made over a wide range of temperatures and atmospheres (coupled with the sensitivity they provide towards light atoms such as hydrogen), but very precise time-of-flight measurements can be carried out. A recent study (26) (on a nonzeolitic material) shows the great potential of this approach, in that an *ab initio* structure determination has been demonstrated, thereby indicating that such determinations should ultimately become routinely possible for zeolites and other powdered solids.

Because improvements in neutron fluxes have also been matched by comparable improvements in X-ray fluxes (from synchrotron sources) and because, in principle, there are many similarities between recording neutron-powder and X-ray-powder made in structure determination by X-ray diffraction. To be sure, conventional-powder X-ray diffraction is used analytically in distinguishing different zeolites. There is also a tradition (27) of quantitatively utilizing the peak intensities of powder X-ray pattern in the solution and refinement of zeolite structures by invoking additional, indirect items of evidence and plausible model structure. But the approach based on X-ray peak integration is now being superseded by full profile (X-ray) refinement (28, 29). 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 constraints that can be imposed on the (desired) structure, it is possible to refine quite complex zeolitic structures. ZSM-23, which is described in Section III.D falls into this category.

It is to be noted that, spurred by the success of neutron profile methods, corresponding X-ray powder methods have been dramatically resuscitated. It is now possible with ordinary laboratory X-ray sources to track the delicate structural changes that active zeolitic catalysts undergo during the course of high-temperature pretreatment or during actual use as an active catalyst (30).

Synchrotron radiation is potentially of very great value for the structural elucidation of zeolitic catalysts, as the recent work of Newsam (31, 32) elegantly reveals. Such radiation is very intense, polarized, sharply focused, and continuous over a wide range of wavelengths. In view of the "white" nature of the radiation experiments based on variations in scattering contract become possible with anomalous scattering. Moreover, because of their high intensity, synchrotron radiation sources make so-called energy-dispersive determinations of powder diffraction patterns a feasible proposition, particularly for time-resolved studied or experiments with samples under a controlled atmosphere. High intensity, as well as intrinsic resolution, confers extra advantages on this mode of recording X-ray powder diffractograms.

Furthermore, the brightness of the synchrotron source also enables conventional single-crystal diffraction measurements of very small crystals. Newsam (31) and his co-workers were able to determine the details of the framework structure of a minute specimen (1 μm^3 in size) of a cancrinite crystal in this way. There is another important practical feature, associated with the use of synchrotron sources, that is likely to assume increasing importance in future years, namely, the great ease (in principle)—com-

pared with rotating anode sources—with which position-sensitive detectors (PSDs) can be employed to dramatically reduce data collection times. It is known that some zeolites, under the influence of X radiation, undergo induced structural changes that perturb the equilibrium or dynamic positions of exchangeable ions. Use of PSD's should greatly assist in ameliorating this problem.

Finally, it has become (33–35) almost routine to determine the precise location of organic species and others (including water) accommodated within the intracrystallite cavities of a zeolite, as we shall illustrate in Section III.

B. Solid-State NMR

NMR spectra cannot normally be measured in solids the same way that they are routinely obtained from liquids and solutions. The reason for this is the existence of net anisotropic interactions which, in the liquid state, are averaged by the rapid thermal motion of molecules. This is generally not the case in the solid state; although certain solids have sufficient molecular motion for NMR spectra to be obtainable without resorting to special techniques—a situation which is met when intercalated species in clays or sorbed species in zeolites execute a fair degree of thermal motion (36)—in the overwhelming majority of solids, and for every zeolite, there is little internal motion of the framework atoms. Conventional NMR for solids consequently yields broad signals up to 100 kHz wide, which conceals information of interest to the chemist. High-resolution spectra—where magnetically nonequivalent nuclei of the same spin species are resolved as individual peaks—of solids can be obtained only when the anisotropic interactions giving rise to line broadening are substantially reduced. The predominant interactions are dipolar, chemical shift anisotropy, and quadrupolar. When a solid sample is rapidly spun about an axis set at the "magic angle" with respect to the magnetic field, most of the broadening influences disappear and extremely sharp lines may be produced (37–39). The so-called magic angle ($54°44'$) technique yields the sharpest lines possible when the magnetically active nuclei in the sample are of spin $\frac{1}{2}$. Samples with quadrupolar nuclei yield lines that have residual width at the magic angle, but this width is inversely proportional to the strength of the applied magnetic field. Solid-state NMR also suffers from two other intrinsic disadvantages: low abundance and/or sensitivity of the observed nucleus, and long spin–lattice relaxation times. Both these disadvantages can be overcome using a double-resonance technique known as cross-polarization (40). Full details of the principles of high-resolution solid-state NMR as it applies to solids of catalytic interest have been given elsewhere (39, 41–45). Al-