

Zeolites and zeolite-like materials

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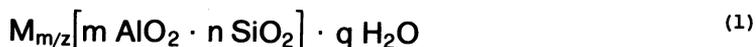
Abstract - Zeolite structural chemistry is no longer confined to porous aluminosilicates. The wide range of zeolite-type framework structures is outlined following a generalized formula for zeolitic materials. These include interrupted networks with terminal hydroxyl groups, anionic frameworks containing hydroxo bridges and other derivatives of tetrahedral framework structures, besides novel topologies. The diversity of structures is further enhanced by inherent and frequently observed faults.

Crystalline molecular polysiloxane and related compounds are of considerable interest in connection with the formation of polymeric networks of zeolites and zeolite-like materials. Configurations comprising a maximum of smallest possible rings are a prerequisite for creating very open networks. Observed structures containing combinations of 3- and 4-rings are of particular interest in this respect. Model considerations on this basis indicate that future syntheses of zeolitic materials of very low framework density should be feasible.

INTRODUCTION

Zeolites and zeolite-like materials comprise a broad range of porous crystalline solids. The structures of zeolite-type materials are based essentially on tetrahedral networks which encompass channels and cavities. Sorbate molecules of various sizes and shapes can be accommodated in these intracrystalline voids and undergo chemical reactions subject to stereochemical constraints.

According to orthodox views zeolites are based on open and fully crosslinked framework structures of corner-sharing SiO_4 and AlO_4 tetrahedra. This is reflected in the textbook formula



exchangeable anionic sorbate
cations framework phase

In recent years the definition of a zeolite has become a matter of debate (ref. 1, 2) reflected by titles like 'When is a zeolite not a zeolite?' (ref. 3). Extensive isomorphous substitution of framework atoms (ref. 4) and numerous structural analogues of aluminosilicate zeolites, as well as other recent developments in zeolite structural chemistry, make it seem logical not to impose artificial limits to this class of porous crystalline materials. This paper outlines the present scope of zeolite structural chemistry, selected developments of current interest and some prospects.

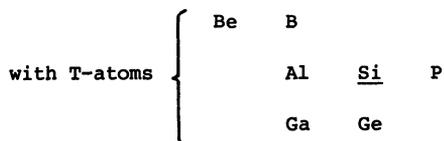
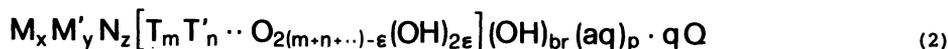
ZEOLITE-TYPE MATERIALS: STRUCTURAL CONSIDERATIONS

Considering new materials, recent advances in structural zeolite chemistry have been mainly in the areas of high silica zeolites, aluminophosphate-, SAPO- and other analogues of zeolite-like structures. Zeolite chemistry is evidently no longer limited to protokto-silicates though these still constitute the basis of the field.

Extended formula of zeolite-type materials

The textbook formula (1) does not take into account the profusion, which has become more and more apparent, of structural variants of zeolite-type frameworks. This is due to widespread isomorphous substitution (ref. 4), many homeo- or isotypes, interrupted frameworks, hydroxo

bridges, as well as aquo and other ligands of framework atoms. Taking this into account a more general formula for zeolite-type materials based on 4-connected networks is the following



where M & M' are exchangeable & non-exchangeable metal cations, N non-metallic cations (generally removable on heating), (aq) chemically bonded water (or other strongly held ligands of T-atoms), and Q sorbate molecules which need not be water. The essential part in square brackets denotes the 4-connected framework which is usually anionic.

Only main group elements are listed among the T-atoms, the most important of which is silicon. This should not exclude other possible T-atoms (ref. 4). An interesting example is zinc as illustrated by a zincosilicate $\text{Na}_2\text{ZnSi}_3\text{O}_8$ (synthesized at 450°C) which forms a paracelsian-type tetrahedral framework structure (ref. 5). More open zincosilicate structures with zeolitic properties may form at lower temperatures.

Selected examples of recently investigated zeolite-type materials

Parthéite $\text{Ca}[\text{Al}_4\text{Si}_4\text{O}_{15}(\text{OH})_2] \cdot 4 \text{H}_2\text{O}$, a mineral zeolite, has been shown to have an interrupted framework containing terminal hydroxyl groups attached to tetrahedral Al atoms (ref. 6). It is one of several known examples of aluminosilicate zeolites which demonstrate that the conventional formula (1) is too restrictive.

A particularly large variety of T-atoms has been observed in sodalite-type frameworks. One of the latest examples is a hydrated gallosilicate sodalite (ref. 7) in which the T-positions are occupied alternately by Ga and Si atoms (ref. 8).

One of the most remarkable structures is that of the beryllilosilicate zeolite lovdarite, $\text{Na}_{12}\text{K}_4[\text{Be}_8\text{Si}_{28}\text{O}_{72}] \cdot 18 \text{H}_2\text{O}$, which has been synthesized recently by Ueda et al (ref. 9). The framework structure of the mineral, reported by Merlini (ref. 10), has been confirmed using X-ray powder data of the synthetic zeolite (ref. 9). As shown in Fig. 1 it is made up of a combination of secondary building units (rather than one kind), 4-rings and novel spiro-5 units comprising 3-rings. So far, this is the only known tektosilicate containing 3-rings, the significance of which will be further discussed since it opens up new horizons.

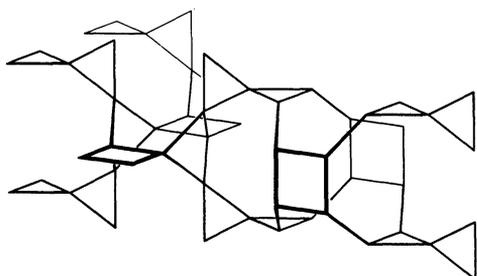


Fig. 1 Framework structure of lovdarite

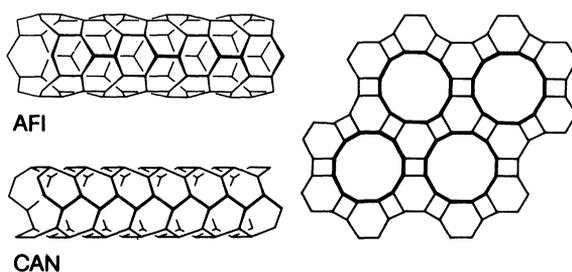


Fig. 2 Tubular units in $\text{AlPO}_4\text{-5}$ (AFI) and cancrinite (CAN)

The remarkable features of $\text{AlPO}_4\text{-5}$ (AFI), the structure of which has been well established by Bennett et al (ref. 11), are the perfectly cylindrical channels. The AFI-type framework structure can in fact be thought to be composed of these tubular units (ref. 12) as indicated in Fig. 2. Cancrinite (CAN), which has the same skeletal projection as AFI, can likewise be built from tubular units (ref. 13). However, it should be noted that the tubular 6^3 nets of AFI and CAN are not identical as shown in Fig. 2.

Other noteworthy structures of zeolite-like aluminophosphates which have been studied in detail in recent years include further examples of analcime-type frameworks (ANA). Artioli, Pluth and Smith (ref. 14) investigated the ordering of Al, P and Si atoms in what they termed an 'aluminosilicophosphate zeolite' having an ANA-type framework. They demonstrated that P

substitutes for Si in the synthetic material of composition $\text{Na}_{13}[\text{Al}_{24}\text{Si}_{13}\text{P}_{11}\text{O}_{96}] \cdot 16 \text{H}_2\text{O}$. Complete substitution by P has been observed in $\text{AlPO}_4\text{-P1}$ (ref. 15), a synthetic pollucite analogue containing Cs, where Al and P have been noted to alternate as expected. The noteworthy feature of the $\text{AlPO}_4\text{-P1}$ structure is that the framework is anionic as a result of thermally stable Al-OH-Al bridges in the 4-rings. The Al-atoms are actually 5-coordinated as a result and based on the structure the formula is properly represented by $\text{Cs}_{12}[\text{Al}_{24}\text{P}_{24}\text{O}_{96}](\text{OH})_{12}$. Such hydroxo bridges have also been found in the structure of $\text{AlPO}_4\text{-21}$ (ref. 16, 17). In this instance the primary tetrahedral framework configuration is probably that of $\text{AlPO}_4\text{-25}$ (ref. 18).

In $\text{AlPO}_4\text{-H3}$ there are equal numbers of tetrahedrally and octahedrally coordinated Al-atoms (ref. 19). The latter are bonded to 4 framework oxygen atoms and 2 water ligands. On heating $\text{AlPO}_4\text{-H3}$ to 110° the ligand water is removed and the resultant framework structure has been observed to be perfectly tetrahedral (ref. 15).

The ability of hydroxide ions to form bridges between metal ions is well known in inorganic chemistry. This and the likelihood of other charged or uncharged ligands of T-atoms gives rise to derivative zeolite-type framework structures.

General considerations

The textbook formula (1) implies 100% crosslinking of the tetrahedra in a zeolite framework. This assumption and other implications of the corresponding zeolite definition are very widespread and may even be responsible for some biased data in the literature. The terms zeolite and molecular sieve are frequently used interchangeably though they are by no means synonymous (ref. 2, 20). Not all zeolites and zeolite-type materials are molecular sieves. Many tetrahedral network structures (like that of natrolite e.g.) contract on dehydration. Characteristically molecular sieves have relatively rigid framework structures with well-defined pore-openings which do not change appreciably on dehydration.

Well over 50 topologically distinct structure types of zeolitic materials have been established so far. X-ray powder diffraction data are still the basis for determining structure types. However, the available 'Collection of Simulated XRD Powder Patterns' by R. von Ballmoos (ref. 21) should not convey the impression that the identification of a particular sample with respect to structure type is invariably mere routine. There is indeed no such thing as the XRD powder diffraction pattern of a particular zeolite structure type. Apart from intensity changes due to differences in composition, diffraction patterns are fairly sensitive to changes in framework conformation and associated differences in symmetry. In practice the assignment of a structure type is frequently based on the simulation and careful inspection of the diffraction patterns of a number of closely related framework topologies. The procedure is illustrated by a number of structure types of high silica zeolites which have been published recently (ref. 22, 23, 24, 25, 26).

Faults are quite abundant in zeolite crystals and, together with microtwinning and intergrowth, can pose major problems in resolving details of structure. Fig. 3 serves as an illustration of a potential fault plane (FP) encountered in lovdarite. Likely FP have been listed for the known structure types (ref. 27). Faults need not be conservative (ref. 28) and this brings about a large number of structural variants which can be described in terms of σ -expansions and σ -contractions.

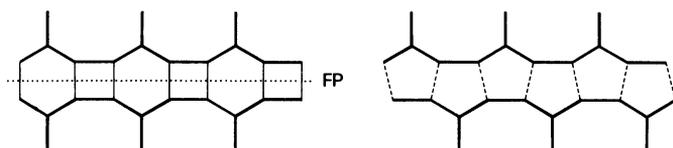


Fig. 3 Simple example of a fault plane (FP)

MOLECULAR CRYSTALS AND POLYMERIC STRUCTURES

The characterization of silicate and comparable oligomeric species in solution is of considerable interest for zeolite synthesis and crystal chemistry (ref. 29). The striking resemblance of molecular species which have been recognized to exist in solution to some of the secondary building units (SBU) of the crystalline polymeric networks has been noted (ref. 30). Despite recent progress in applying ^{29}Si NMR techniques etc. it should be realized that crystallographic methods are still the most reliable in structural studies of molecular species, provided suitable crystals containing these can be grown. This is a matter of choosing adequate conditions, suitable solvents and appropriate counterions in the case of charged oligomers.

The molecular structure of methylated spiropentasiloxane was solved by X-ray crystal structure analysis as long ago as 1948 (ref. 31) and thus the novel constituent of the lovdarite framework could have been anticipated. Siloxane molecules corresponding to other SBU have also been investigated by X-rays, e.g. the bicyclopentasiloxane corresponding to the 4-1 SBU (ref. 32). Of particular interest for zeolite chemistry are oligomeric silicate and aluminosilicate anions in aqueous solutions containing alkylammonium ions (ref. 33, 34). Molecular crystals containing double 3- and double 4-ring species have been studied in considerable detail by Smolin et al (ref. 35, 36, 37). The most striking molecular structure from the point of view of zeolite chemistry has been reported by Bissert and Liebau (ref. 38). Hydrogen bonds connect the double 4-ring silicate oligomers in the structure, shown in Fig. 4, which strongly resembles Linde type A. The large cage is occupied by tetrabutylammonium ions and water. Such structures may help to resolve the role of so-called 'templating' agents in zeolite synthesis.

FRAMEWORK DENSITIES AND LOOP CONFIGURATIONS

Gramlich and Meier (ref. 13) have shown that the constituent units of zeolite structure types can be related to the framework density (FD) values, i.e. the number of T-atoms per nm^3 . Structures of lowest FD are characterized by double rings. The minimum observed values of FD are those of faujasite (FAU), 12.7, and synthetic zeolite A (LTA), 12.9. It should be noted that the FD is not a measure of channel dimensions but of the void volume which is just over 50% of the crystal volume in case of FAU- and LTA-type materials. This brings up the question of possible tetrahedral networks of lower density and of the likely limit.

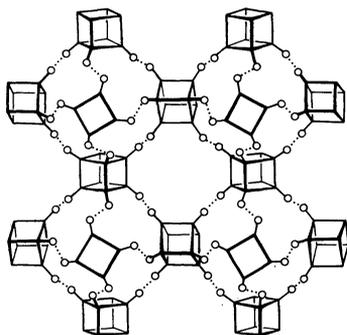


Fig. 4

Molecular structure with double 4-rings resembling zeolite type A

Table 1. Loop configurations of T-atoms and framework densities^a

Number of 4-rings attached to each T-atom	Loop configuration together with known representative of lowest framework density ^b
4	unobserved
3	Faujasite 12.7 Linde Type A 12.9
2-3	Offretite 15.5
2	Mazzite 16.1 Sodalite 17.2
1-2	Brewsterite 17.5 Yugawaralite 18.3
1	$\text{AlPO}_4\text{-5}$ 17.5
0-1	Mordenite 17.2
0	Ferrierite 17.7

^a number of T-atoms per nm^3

^b bold face figures

A very useful concept in this context is that of the loop configuration of the T-atoms in a framework. In terms of the work by Sato (ref. 39, 40) the loop configuration is defined by the '2nd coordination networks', i.e. by the number and topological constellation of the smallest rings the T-atoms are part of. Since there is only one known network with 3-rings (lovdarite) we need only consider 4-ring configurations here. Structurally related network types can be shown to have the same loop configurations (ref. 41, 42). For instance, offretite, erionite and Linde type L have the same (average) loop configuration and their FD values range from 15.5 (OFF) to 16.4 (LTL). Table 1 lists the lowest observed framework density for each loop configuration. (A more detailed account on loop configurations is to be published elsewhere (ref. 42)). It is evident from Table 1 that the lowest FD value results in the case of a maximum number of small rings attached to each T-atom of the framework. In order to postulate structures of $FD < 12$ one has to consider networks with loop configurations involving more than three 4-rings and/or 3-rings. This is in line with earlier predictions by Brunner (ref. 43) which were based on coordination sequences.

VERY OPEN NETWORKS

One indispensable tool in structure research - which is not mentioned often enough - is model building (including computer-aided modelling). Model considerations and the study of hypothetical frameworks point the way for future synthesis work. A particularly intriguing point is that of the feasibility of very open networks with $FD < 12$ and/or channel openings exceeding those of the known 12-rings.

Barrer and Villiger (ref. 44) were the first to come up with a possible network with unidimensional 18-ring channels. A comparable hypothetical network has been proposed by Smith and Dytrich (ref. 12). This network, labelled 81(1) by these authors, also has 18-ring channels (analogous to those in AFI shown in Fig. 2), $FD \sim 14.0$ and is stereochemically feasible in contrast to the more open networks proposed in the same study. These and other investigations seem to indicate that very open zeolite-type networks are likely to encompass unidimensional channel systems only.

As has been pointed out in the preceding section, tetrahedral nets of very low density must contain constituent units incorporating a maximum of 3- and/or 4-rings. Prime examples of such constituents are the 8-valent spiro-5 and the 6-valent double 3-rings. In Fig. 5 these configurations are shown together with equi-valent units. Very open networks can be derived by supplanting such configurations in known frameworks of low FD by equi-valent units with a higher proportion of smallest rings. An example is presented in Fig. 6. In this particular case the double 4-ring in Linde type A, (a2) in Fig. 5, is substituted by (a3). The network has been tested by DLS and appears quite feasible on these grounds. It is cubic (maximum symmetry $P43m$), $a = 11.3 \text{ \AA}$ for $T = \text{Si}$, $FD = 10.4$ and the apertures of the 3-dimensional channel system are formed by 12-rings.

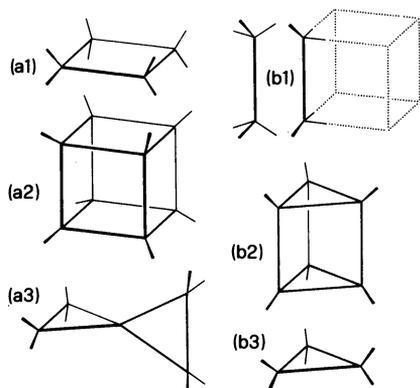


Fig. 5 Selection of 8- and 6-valent building units

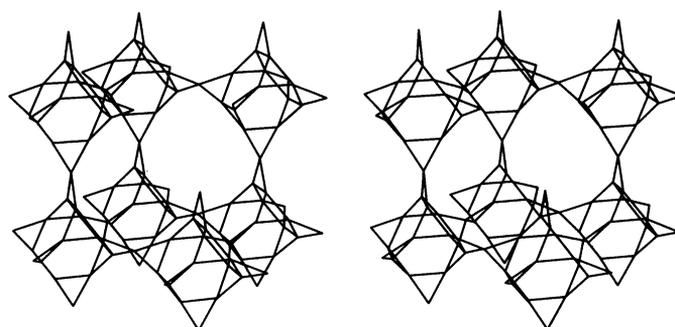


Fig. 6 Stereopair of hypothetical low-density framework built from spiro-pentasiloxane units

Further examples of very open networks with three-dimensional channel systems can be derived using this approach. They are too numerous to be covered here except by way of selected examples. Thus, replacement of (b1) of Fig. 5 in the Linde type A framework by (b2) leads to a cubic network with ideal symmetry $Pm3m$, $a = 19.4 \text{ \AA}$, $FD = 9.9$ and channels with 12-ring apertures. If the same procedure is applied to the RHO type framework, a cubic network with maximum symmetry $Pm3m$, $a = 24.9 \text{ \AA}$, $FD = 9.3$ and 16-ring channel openings is obtained. The substitution of pairs of eclipsed tetrahedra in open zeolite frameworks by double 3-rings is thus of particular interest in deriving hypothetical networks of very low density. Extensive studies in this field are presently in progress (Brunner, Meier et al, to be published).

CONCLUSIONS AND PROSPECTS

The structural chemistry of zeolite-type materials has become a sizable field which should not be defined too narrowly, however. Even framework types containing 5- or 6-coordinated Al etc can, on closer examination, be described as derivatives of a tetrahedral network. Zeolite-type structures should include all such materials, i.e. porous crystalline solids which are based on three-dimensional tetrahedral frameworks or derivatives thereof.

Potential possibilities in zeolite structural chemistry are far from being exhausted considering e.g. that the use of non-aqueous media in zeolite synthesis has barely been explored (ref. 45). Major challenges include reaction path studies in synthesis and the exploration of very open networks.

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