Complex Zeolites

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Flipping Marvelous: New Zeolites by New Methods

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Zeolites are among the most valuable of inorganic materials, finding extensive use in a wide variety of applications, such as catalysis (particularly in the petrochemicals industry), in separations (notably N_2 and O_2 from air), as ion exchangers (e.g. as water softeners in detergents and elsewhere), and as adsorbents (desiccants). They are produced at the rate of millions of tons a year.[1]

The underlying structural feature of zeolites is a framework of tetrahedral cations, most commonly silicon, aluminum, and phosphorus, linked by two-coordinated oxygen atoms. The topology of the structure is characterized by a four-coordinated net in which the tetrahedral atoms (T) are vertices and -O- links serve as edges. For the last 50 years or so there have been extensive efforts devoted to the synthesis of new materials, and the number of recognized[2] distinct framework topologies has risen from 27 in 1970 to 179 today; about 30 of these are found as minerals. Only about 10 framework types are those of widely used industrial materials.

On the other hand, it is believed that the number of distinct frameworks suitable for stable zeolites is extremely large,[3] and an intriguing question is why, after all this effort, so few structure types are known. Part of the answer is that zeolite synthesis is generally very demanding, requiring specific organic bases as structure-directing agents and a narrow range of composition of reagents and of temperature.

Another reason is that zeolites are metastable with respect to the simpler forms of the component oxides (for example, the stable form of silica is quartz), so synthesis requires low temperatures, and products are generally poorly crystallized. Thus the structures, often of daunting complexity, have to be solved from powder X-ray diffraction (PXRD) patterns of indifferent quality, and owing particularly to the large number of overlapping reflections, many structures remain unsolved. However, there have been a number of significant recent developments that can confidently be expected to have great impact on both PXRD and zeolite science.

The first development was the combination of electron microscopy (EM) with PXRD.[4] In this work phases determined from EM were combined with the PXRD data to solve the structure of a zeolite (TNU-9, zeolite framework code TUN) of unprecedented complexity—the framework has 24 topologically and crystallographically distinct vertices. For this and related work, Baerlocher, McCusker, and Terasaki won the 2007 Breck Award of the International Zeolite Association.

At about the same time, a new approach to direct methods of structure determination was described by Oszlányi and Sütő.[5] This is the so-called "charge flipping" method. Recall that an X-ray diffraction pattern is the Fourier transform of the crystal electron density, but only the amplitudes, not the phases of the Fourier coefficients (structure factors) are known. Charge flipping makes use of the fact that the electron density in a crystal is always positive and relatively large only in a small fraction of the volume around the atomic nuclei (these are the properties of electron density that make all "direct methods" feasible). The algorithm starts by combining random phases with the known amplitudes. The corresponding Fourier transform produces a density function with positive and negative values. Basically (there are some minor variations in various implementations), the large negative values are changed to positive ("flipped") and then a new set of phases is calculated for that density function.[*] The process is iterated and is found to rapidly converge on the correct structure for a variety of single crystal datasets. Despite the overlapping of peaks it was shown that the flipping algorithm could also successfully be applied to powder data.[6] A nice feature of the flipping method is that it does not require any a priori knowledge of symmetry, and indeed it has been applied to nonperiodic structures by several groups.[7] It is also very attractive in that, in contrast to other direct methods, the underlying principle is easily explained to first-year chemistry students. This feature is important because X-ray crystallography is a major tool of synthetic chemists, very few of whom really understand how it works.

There was one more crucial step that made possible the determination of the crystal structures of complex materials from PXRD: the introduction of histogram matching.[8] This technique, which originated in image processing, was first applied to protein crystallography.[9] It relies on the fact that histograms of the frequency distribution of electron densities in similar materials will be similar. So in solving a zeolite structure, the calculated electron densities are modified so that a histogram of their magnitudes matches a corresponding

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[*] The words "flip" and "flipping" have many meanings in English. In colloquial British English "flipping" is used as an intensifier (much like "very" or "greatly"). Thus in this dialect if one were to say that Oszlányi and Sütő are flipping geniuses it would carry a delightful double meaning. Hence also the title of this Highlight.

histogram calculated for a zeolite of known structure. In particular, the peaks corresponding to overlapping reflections are periodically reapportioned to individual components in a way that allows histogram matching.

These methods have led to several further spectacular results. IM-5 (zeolite framework code IMF), another zeolite that had long resisted structure solution, was solved from PXRD data with help from electron microscopy.[10] This zeolite structure again had 24 topologically distinct tetrahedral atoms. Yet another structure solved by the same methods and again with 24 tetrahedral atom sites (but remarkably in this instance with one of them vacant) was zeolite SSZ-74.[11]

The three zeolites mentioned so far (TNU-9, IM-5, and SSZ-74) have different and very interesting catalytic properties, but they were all synthesized with very similar bases acting as structure-directing agents and have structures with features encountered in other zeolites (except for the vacancies in SSZ-74).

The last zeolite structure that I call attention to is that of a material (ITQ-37) prepared using a novel organic structure-directing agent, and it was again solved by a combination of electron microscopy and the flipping method applied to PXRD data;[12] it seems safe to state that it could not have been solved by any other known method. This material, which is a cubic germanosilicate with 10 topologically distinct tetrahedral sites, has a framework structure quite unlike that of other known zeolites. Notably, it has the lowest framework density (tetrahedral atoms per unit volume) and the largest pore apertures (30-rings) of any known zeolite. To further discuss the structure, it is useful to first to briefly discuss the net underlying its topology.

The net in question, known by the symbol srs, is the only three-coordinated net with three-fold symmetry at the vertices (and thus the only one with all edges equivalent). Although ubiquitous in materials, it often remains unrecognized.[13] It is intrinsically chiral, and left- and right-handed forms can be nicely intergrown (Figure 1 a). Now imagine these nets first as narrow tubes that are subsequently uniformly inflated until they meet. They will meet at a periodic surface which is in fact the famous gyroid or G surface.[13] This surface is well-known to zeolite chemists as the basis for the geometry of mesoporous silicates of the MCM-48 type.[1] In these materials, a layer of amorphous silica follows the G surface leaving a bicontinuous channel system with the topology of the two intergrown srs nets; as both the left- and the right-handed nets occur, the structure is not chiral. Recently an ordered mesoporous germanate (SU-M) based on this structure was reported.[14] This was not a zeolite in the accepted sense of the term, which is restricted to structures with tetrahedral framework atoms (SU-M has also six-coordinate germanium centers). This material had unprecedented pore size and ring size for a crystalline oxide.

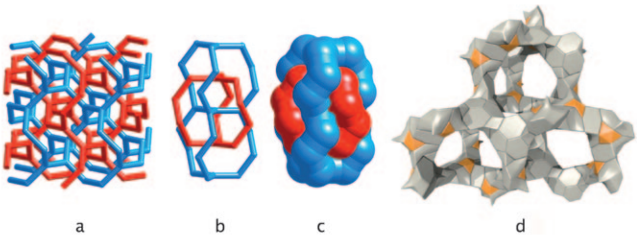

Figure 1. a) Two interpenetrating srs nets of opposite handedness. b) A fragment of (a) showing in red the skeleton of a basic unit (a tile). c) The nets of (b) inflated. d) Part of the ITQ-37 structure shown as a tiling of a surface topologically the same as the G surface (image courtesy of C. Bonneau).

The structure of ITQ-37 is a fascinating variation on this theme. Imagine again the two srs nets, but now let them be inflated so that one expands at a faster rate than the other. Again, they will meet at a periodic surface with the topology of the G surface, but now there will be "fat" channels and "thin" channels, and the structure will be intrinsically chiral. The structure of ITQ-37 is based on this principle: the framework atoms occupy the thin channels (Figure 1 d), and the pore system follows the fat channels. There are other zeolites with frameworks based on tilings of periodic surfaces (see reference [3] for examples). The two previously known to be based on the G surface, analcime (zeolite code ANA) and UCSB-7 (BSV), have just one kind of tetrahedral atom. In contrast, in ITQ-37 eight of the ten tetrahedral atoms are involved in the surface tiling (the original paper should be consulted for details), and the 10-rings of the srs net become 30-rings in the zeolite structure.

Thus, the new methods of analysis of PXRD patterns, especially when combined with electron microscopy, have led to spectacular advances in our knowledge of zeolite frameworks. Three of the new structures mentioned herein have much greater complexity (greater numbers of topologically distinct framework vertices) than previously known. The fourth has the lowest framework density and largest ring sizes of any zeolite and a framework structure that displays novel features. More creative use of structure-directing agents and better methods of structure determination will certainly reveal many more surprises down the road. Nevertheless, the question of why so few of the many predicted zeolite topologies have yet been found remains puzzling.

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