Catalyst Design

DOI: 10.1002/anie.200700666

Systematic Enumeration of Microporous Solids: Towards Designer Catalysts

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Keywords:
heterogeneous catalysis · molecular sieves · systematic enumeration · zeolites

At first sight, it might seem that enumeration of all possible arrangements of atoms in open-structure solids amounts to no more than an arduous exercise in mathematical crystallography. Those who are oblivious to the nuances of modern solid-state chemistry may well label it an arid adventure in pure taxonomy. Nothing could be further from the truth.

First, a library (database) of well-characterized, chemically feasible, hypothetical structures facilitates design strategies that will ultimately lead to their syntheses. Second, theoretical X-ray, neutron, and electron diffraction patterns generated from such structures would be a great boon in determining the atomic coordinates of newly prepared open-structured materials: it would simply entail a straightforward comparison of the experimentally obtained pattern with the database. Third, the database can serve as a new technique for solving framework structures, as was done recently by Foster et al. for the zeolite structure known as ZSM-10 (idealized formula $K_{24}Al_{24}Si_{84}O_{216} \cdot x\,H_2O$). By examining all 18.4 million 4-coordinate graphs which are available on the web[1] with six unique tetrahedral (T) atoms in space group *P6/mmm* and knowing[2] that $a = b = 31.575$ and $c = 7.52$ Å (facts derived from diffraction measurements), these workers effectively solved the structure of ZSM-10 by identifying the topology (in the database) consistent with the observed unit-cell dimensions and space-group symmetry.[3]

Apart from their long-established role in separation science and technology and increasing relevance in gas storage, microporous aluminosilicate (zeolitic) and aluminophosphate (AlPO) molecular-sieve catalysts, of which there are now 176 recognized structure types[4] with around 10 new types being added to the compilation each year, are of paramount importance in present-day heterogeneous catalysis.[5] Not only are open-structure aluminosilicates centrally involved in the catalytic conversions of the petrochemical industry[6] (in cracking, hydrocracking, alkylation, isomerization, and dehydroisomerization), the ever-growing family of framework-substituted, open-structure AlPO catalysts are no less important.[7] Already a SAPO-34[8] (silicoaluminophosphate number 34) catalyst has been commercialized for the acid-catalyzed dehydration of methanol to yield ethene and propene for the polymer industry. Moreover, transition-metal, framework-substituted AlPOs exhibit a wide variety of catalytic action in selective oxidations[9] (such as the aerial oxidation of cyclohexane to adipic acid), the in situ production of hazardous reagents (such as hydroxylamine from NH_3 and air), the conversion of cyclohexanone, NH_3, and air to ε-caprolactam and nylon-6,[10] and the generation of many organic chemicals of value as pharmaceuticals (such as the vitamin niacin[11] from picolines).

The crucial point here, which applies both to open-structure AlPOs and zeolites, is that their inner walls may be easily provided with catalytically active sites that are readily accessible to reactants—these nanoporous catalysts also serve as a nanoreactor—and, furthermore, are amenable to in situ characterization. These functionalized open structures are prime examples of single-site heterogeneous catalysts[7,9–11] (where the active centers are spatially well-separated). Significantly, unlike the majority of other solid catalysts, they allow abundant scope for a strategy of design of new catalysts, as described in detail elsewhere.[9,11] Briefly, what becomes possible if one is equipped with deeper knowledge of how many and what kind of open-structure (microporous) solids may exist is scope to execute catalytic reactions that were hitherto difficult or impossible to achieve. Thus, one of us, with his co-worker Raja[11] and a commercial company, has succeeded in designing single-site catalytic variants of the AlPO-5 structure (pore diameter ca. 7.3 Å) that will permit the efficient synthesis of products such as vitamins, fragrances, flavors, and general pharmaceutical and agrochemical intermediates.[12] With the availability of other open structures with larger pore diameters, even greater scope for the catalytic synthesis of bulkier functionalized organic molecules will be possible by the judicious design of monofunctional or bifunctional (as illustrated in Ref. [10], which describes the "green" synthesis of nylon 6) heterogeneous catalysts.

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Finding new crystal architectures (including those where pore dimensions are up to 10 Å in diameter) is not at all easy, as the number of possible open-structure frameworks is infinite and, until relatively recently, there was no reliable procedure for their derivation. Enumeration procedures originated with the classic work of Wells on three-dimensional nets and polyhedra.[13] Others followed, notably Sherman and Bennett,[14] Alberti,[15] Sato,[16] Akporiaye and Price,[17] Smith,[18] and O'Keeffe et al.[19] All this work involved building structural models. More recent approaches by Treacy et al.,[20] Foster and Treacy,[1] and Newsam et al.[21] used computer search algorithms (which explored all combinations of connected atoms and crystallographic sites, seeking the 4-connected graphs), with Férey et al.[22] outlining de novo prediction of inorganic structures developed through automated assembly of secondary building units—known as the AASBU method.

Valuable as all these approaches have proven to be, they suffer from the drawback of being non-systematic: one can never be quite certain that, through their use, all the structural possibilities have been considered. The seminal work of Delgado Friedrichs et al.,[23] which takes care of this fact, is based on advances in combinatorial tiling theory by A. W. M. Dress et al.[24,25] Just as a two-dimensional floor can be covered with tiles of various shapes, three-dimensional space can be filled with polyhedral tiles. Such a tiling is a periodic subdivision of three-dimensional space into connected regions, termed *tiles*. When two tiles meet along a surface, the surface is called a *face*. If three of more faces meet along a curve, we call the curve an *edge*. If at least three edges meet at a point, that point is termed a *vertex* (Figure 1). A network is thus formed by the vertices and edges.

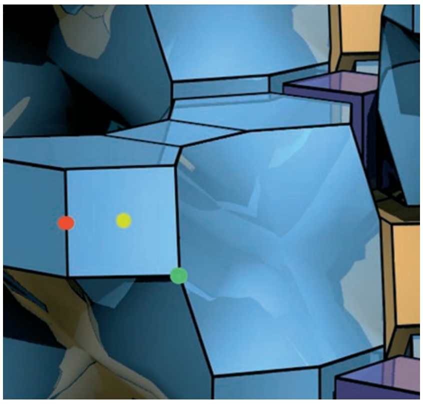

Figure 1. Edges (marked in red), faces (yellow), and vertices (green) in a tiling (adapted from Ref. [23]).

The configuration of edges, faces, and tiles around a given vertex can be described by what is known as the "vertex figure", obtained by placing the center of a small notional sphere at the vertex and considering the tiling of that sphere formed by the intersections with the different tiles touching that vertex. A particular periodic tiling is then associated with a unique Delaney symbol.[25] This is arrived at by breaking the tiling down into tetrahedra ("simplices" in three-dimensional space) and mapping their connectivity. The Delaney symbol can alternatively be written as a string of characters, an "inorganic gene". The classification of all periodic tilings of a given kind then reduces to the enumeration of the corresponding Delaney symbols using computational algorithms, which is equivalent to "mutating" the inorganic gene, thereby yielding all possible structures.

In principle, the approach pioneered by Delgado Friedrichs et al.[23] will enumerate any structure, although in practice one is interested only in those unit cells of reasonable dimension: in the context of microporous solids, those that have unit cell dimensions of about $30\times30\times30$ Å^3 should take care of all experimentally accessible new structures. Known zeolitic structures usually involve no more than 12 distinct types of vertices (or T sites—see above). These structures are called n-nodal, where n is an integer between 1 and 12. For example, faujasite (a well-known zeolite, with idealized formula $Na_{58}[Al_{58}Si_{134}O_{384}]\cdot240\,H_2O$) is a 1-nodal (uninodal) structure, but ZSM-5, another zeolite catalyst (idealized formula $Na_n[Al_nSi_{96-n}O_{192}]\cdot16\,H_2O$, $n<27$) is 12-nodal.

Even if one limits oneself to "simple" tilings, the number of structures involved would run into billions. So far, all possible Euclidean uni-, bi-, and trinodal tilings, based on "simple" vertex figures (i.e. tilings with vertex figures which are tetrahedra) and all "simple" and "quasi-simple" uninodal tilings with vertex figures containing up to six extra edges (in "quasi-simple" tilings, the vertex figures are derived from tetrahedra but contain double edges) have been described using this approach.[23,26] It transpires that there are exactly 9 and 117 topological types of 4-connected uninodal and binodal nets, respectively, which are based on simple tilings. In addition, there are at least 157 additional uninodal nets derived from quasi-simple tilings.

When the critical paper by Delgado Friedrichs et al.[23] was published in 1999, the International Zeolite Association database contained 121 recognized structure types. The 55 new structures that have emerged in the intervening time could all, in principle, be obtained using the methods outlined in that report and discussed above. Among the structures synthesized and characterized since 1999, the following (Figure 2) were specifically described: RWY[27] (structure 1_1 in Ref. [28]); NPO[29] (structure 1_88); BCT[30] (1_211) and UFI[31] (3_835). Structure NPO is a particularly interesting oxonitridophosphate with a zeolite-like framework composed of 3-rings.

The work of the Cambridge–Tübingen–London (CTL) team[26] goes further than simply enumerating structures: it assesses quantitatively the chemical feasibility of the hypothetical open structures. It is reasonable to expect that only a fraction of the mathematically generated networks (or graphs) are chemically feasible—there could be very many "strained" frameworks requiring unrealistic bond lengths and bond angles (quantum mechanical laws cannot be vitiated!)—and that an effective filtering process is needed to identify the most plausible frameworks. To do this, due recognition of known bond lengths and angles, as encountered in open-structure microporous solids, must be incorporated into the overall process. In other words, mathematical points must be replaced by atoms and straight lines must be replaced by chemical bonds, and the energy of the resulting framework, allowing for slight adjustments of angles and distances, has to be calculated for a predefined chemical composition; the lower the energy, the more

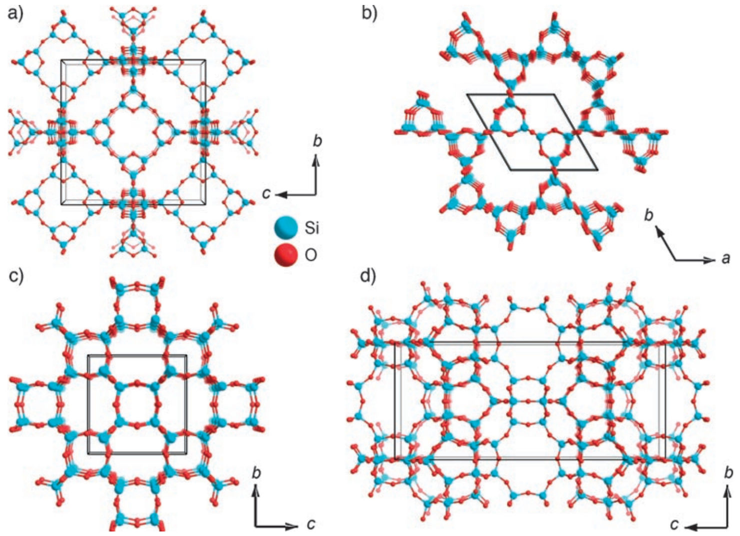

Figure 2. Zeolitic structure types a) RWY (structure 1_1; $a=b=c=18.47$ Å); b) NPO (structure 1_88; $a=b=9.068$ Å, $c=5.19$ Å); c) BCT (structure 1_211; $a=10.23$ Å, $b=8.83$ Å, $c=5.18$ Å); and d) UFI (structure 3_835; $a=b=12.16$ Å, $c=28.04$ Å).

stable the structure and the more likely it is to exist.

Care is needed in discussing hypothetical structures and thermodynamic stability, as was recently eloquently discussed by Jansen and Schön,[32] who rightly emphasized that the only necessary condition for a hypothetical structure being accessible synthetically is that it is associated with a local minimum on a vast energy landscape,[33] that is, it must be kinetically stable.

CTL scientists treated the open structures as polymorphs of SiO_2, that is, silicon atoms occupied each vertex of the enumerated networks, and a bridging oxygen was placed between each pair of neighboring Si atoms, which, in turn, were predefined to be separated by a typical Si–Si distance (derived from known silicate structures).[26] Using what is known as Gale's GULP procedure[34]—a computer program for the symmetry-adapted simulation of solids—and interatomic potentials applicable for SiO_2 (derived by Sanders et al.[35]), it is a straightforward matter to calculate the framework energy relative to α-quartz, the most stable polymorph of silica. Also readily computable is the framework density (the number of tetrahedral atoms per 1000 Å^3) for each structure. These were then compared with the corresponding values for known zeolite frameworks, also treated as silica polymorphs. In addition, they calculated other useful structural properties of the optimized frameworks such as density, volume, framework density (in units of the number of Si atoms per 1000 Å^3), coordination sequences (i.e. numbers of 4-connected neighbors in the successive coordination spheres), and internal volume. Also computed, as stated at the outset of this Essay, are the X-ray powder diffractograms of each structure, which, to cite a particular example, made it very straightforward to identify the structure NPO of Correll et al.[29] with structure 1_88 enumerated by the CTL team.

Enumeration of chemically realizable open-structure frameworks (Figure 3) containing large accessible internal areas (which can be made to function as catalysts) will continue to be of prime importance, not only because of the striking catalytic successes already achieved through them but because germanium oxides, like SiO_2, have been demonstrated by Zou et al.[36] to be capable of being produced as mesoporous structures with crystalline pore walls. As well as the widely known and already harnessed (as catalysts) aluminosilicates and aluminophosphates, one may foresee germanate-based single-site solid catalysts which will further extend the remarkable range of selective conversions implicated in present-day heterogeneous catalysis. This will present further new strategies for catalytic design.

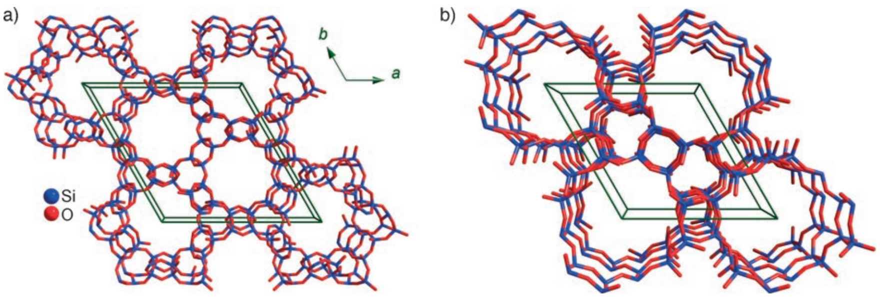

Figure 3. Two of the very open chemically realizable (but not yet synthesized) hypothetical zeolitic structures enumerated by the CTL team. a) Structure 1_71 ($a=b=21.981$, $c=4.974$ Å, framework density 17298 Si atoms per 1000 Å^3); b) structure 1_73 ($a=b=13.550$, $c=8.878$ Å, framework density 17000 Si atoms per 1000 Å^3).

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