Chemical Eval[illegible]pothetical Uninodal Zeolites

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Abstract: Optimized structural parame[illegible]rs, framework energies relative to α-quartz, and volumes accessible to sorption have been calculated for t[illegible]ystematically enumerated hypothetical uninodal zeolitic structures (structures in which all tetrahedral [illegible]re equivalent). The structures were treated as silica polymorphs, and their energies were minimiz[illegible] the GULP program with the Sanders−Catlow silica potential. Results are given for 164 struct[illegible]h include all 21 known uninodal zeolites, two known minerals (tridymite and cristobalite), and [illegible] zeolite topologies. Twenty-three hypothetical structures were identified as chemically feasi[illegible]structural information is provided, and several structures are discussed in detail. The resu[illegible]he design of new synthetic routes and in the identification of newly synthesized material[illegible]

Introduction

Given the wide amount of indu[illegible] as molecular sieves, ion excha[illegible] supports, as well as their intri[illegible] amount of work has been done[illegible] structures, of which 152 disti[illegible] identified.[1] The design of n[illegible] of considerable practical i[illegible] list of chemically feasibl[illegible] design strategies leading[illegible] neutron diffraction pa[illegible] structures will be of g[illegible] new zeolitic material[illegible]

Enumeration of h[illegible] related to the work[illegible] polyhedra. Smith a[illegible] and Bennett,[7] Ba[illegible] tors,[9,10] and Akpo[illegible] structures by link[illegible] work involves co[illegible] Treacy et al.[12] us[illegible] 6000 uninodal str[illegible] many duplicates, the authors considered 150 of these structures as the "most favorable" and refined them using simulated annealing.

We have used a completely new approach to the problem of systematic enumeration, based on advances in the mathematical

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tiling theory.[14] While almost all uninodal networks have been enumerated (but not chemically evaluated) previously, we believe that most of our binodal and trinodal networks are completely new. However, this statement is difficult to quantify because of the absence of an accessible collection of hypothetical structures and of a reliable method for the unique identification of different topologies. The recently developed topological identifier SYSTRE (symmetry structure recognition), which unambiguously distinguishes different nets,[15] will soon make it possible to cross-reference structures derived using the various enumeration methods.

Only a fraction of the mathematically enumerated structures are likely to be chemically feasible (many have "strained" frameworks requiring unrealistic bond lengths and bond angles), so that an effective selection process is needed to identify the most plausible frameworks. To assist the selection process, we have used a computational chemistry approach to calculate the structure, lattice energy, framework density, and other structural parameters of the hypothetical frameworks enumerated in this way. Each framework was assumed to have the empirical formula SiO_2 and was optimized using a lattice energy minimization program GULP,[16] to derive simulated lattice energies of the structures relative to α-quartz. This method of predicting the lattice energy was effective with ionic compounds[17] and silicates,[18,19] and the results of the calculations agree well with thermochemical measurements.[20]

Apart from identifying chemically feasible structures using the energetic criteria, we have identified structures of potential practical interest, that is, those containing channels and/or voids. The crucial parameters here are the amount of void volume and its accessibility (whether a molecule can enter the structure from the outside), which we have calculated for all of the hypothetical structures. The accessible volume for known zeolites is in the range of 0−28 $Å^3$ per Si atom, with α-quartz, as a compact material, having no accessible volume.

Enumeration of Structures. The essence of the tiling method of enumeration is as follows. A tiling is a periodic subdivision of space into connected regions, which we call tiles. If two tiles meet along a surface, the surface is called a face. If three or more faces meet along a curve, we call the curve an edge. If at least three edges meet at a point, we call that point a vertex. A network is formed by the vertices and edges. Periodic tilings of the Euclidean plane have been classified,[21,22] and all possible topological types of tilings for each two-dimensional symmetry group with 1, 2, 3, etc. kinds of inequivalent vertices have been enumerated.[22] We call these uninodal, binodal, trinodal, etc. tilings. Each periodic tiling is associated with a unique "Delaney symbol",[21,23] obtained by breaking the tiling down into simplices. Any $n + 1$ points in n-space which do not lie in an $(n - 1)$ dimensional space are the vertices of an n-dimensional simplex. A simplex in two dimensions is thus a triangle, and in three dimensions it is a tetrahedron. The Delaney symbol is obtained from the resulting adjacency graph by labeling the vertices and "coloring" the edges and can be written as a string of characters unique to the given tiling, forming an "inorganic gene". The classification of all periodic tilings then reduces to the enumeration of the Delaney symbols. This purely algebraic problem is solved using a computer program that considers all permissible permutations of the gene and then generates the corresponding tiling.

The configuration of edges, faces, and tiles around a given vertex can be described by a 2D Delaney symbol via the so-called vertex figure, obtained by placing the center of a small notational sphere at the vertex and considering the tiling of that sphere formed by the intersections with the different tiles touching that vertex. To enumerate all possible tilings on the basis of a given vertex figure, we must consider all possible "3D extensions" of its 2D symbol, while making sure that the resulting 3D symbols give rise to Euclidean tilings.[24] The computer program used for this task is available from the authors upon request (delgado@informatik.uni-tuebingen.de).

The tilings were derived as follows: first, all feasible vertex figures (in the case of uninodal nets, tetrahedra with possible double edges) were enumerated and encoded by Delaney symbols (for uninodal nets, tetrahedra with possible double edges were also included).[14] These were then extended to three dimensions in all possible ways.[25] The extension process itself is a simple matter of combinatorial enumeration, in which three steps are crucial. The first, and the most important, is to select, from a large collection of candidate symbols, those which actually encode tilings of ordinary space, using methods from combinatorial group theory and topology.[24] Second, multiple occurrences of the same structure must be eliminated from the list. In our case, this may include multiple tilings giving rise to topologically identical networks. Using recent advances in network identification,[15] we were able to establish that, except for the well-known examples of structure types LTA-RHO and ATN-ABW, all pairs of structures from our list with identical coordination sequences (see below) did indeed give rise to topologically identical networks. Finally, initial cell parameters and node positions were generated to serve as initial crystallographic parameters for subsequent refinement. A simple way of doing this is by barycentric division, that is, positioning every node in the unweighted center of gravity of its neighbors, followed by basic refinement which equalizes edge lengths while maximizing volumes.

Chemical Evaluation. The systematically enumerated nets[14] were first converted into atomistic models. This was done by inserting a Si atom at each vertex point in the network and by placing a bridging oxygen between each pair of adjacent Si atoms. Each net was scaled such that the vertices were separated by about 3.1 Å, a typical Si−Si distance. The resulting structure was then preoptimized using the DLS (distance least squares) method,[26] which performs geometric refinement of the structure

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by fitting bond lengths and angles to the prescribed values and reduces the amount of computer time needed for the subsequent minimization of lattice energy. Its use was found to have no influence on the final result: using lattice energy minimization from the outset gives the same structure, but at greater computational expense.

The GULP framework energy minimization subroutines used the Sanders−Catlow silica potential[19] (see Supporting Information) with the modified oxygen shell charge described by Schröder.[27] The potential set used by Kramer et al.,[28] which does not incorporate a shell model and uses partial, rather than formal, ionic charges, was used for comparison. In all cases, the DLS optimization was carried out assuming the highest possible space group symmetry for the topology under consideration, while for the lattice energy minimization the full primitive unit cell was generated and minimized under constant pressure conditions. After minimization, the symmetry of the fully optimized structure was again determined. The interatomic potential methods are fast, reliable, and effectively reproduce known structures[29] and experimental lattice enthalpy trends.[20,30] In addition, we have calculated the structural properties of the initial and optimized frameworks, such as density, volume, framework density (F_D, in units of the number of Si atoms per 1000 Å^3), coordination sequences (CS), and internal volume.

The concept of "coordination sequence" identification of structures[31] is as follows. In a four-connected network, each vertex is connected to $N_1 = 4$ neighboring vertices. These are then linked to N_2 vertices in the next shell, in turn connected to N_3 vertices etc., including each vertex only once. Although the coordination sequence for each kind of vertex is not unique to a given structure, it is a useful numerical guide, because structures with different coordination sequences are necessarily different. Brunner[32] correlated the CS with framework density and found that density decreases with the decreasing size of the smallest ring in the framework. In simple terms, the coordination sequence reflects the "growth" and "branching" of the tetrahedra tree. When no branches turn back on themselves and form rings, the sequence is the series with $N_n = 4 \quad 3^{n-1}$.[33]

The Cerius[2] software suite[34] was used for visualizing and manipulating the structures and for calculating free volumes, space group symmetry, and other parameters. In addition to calculating the energetics of the hypothetical structures, it is important to compare the calculated values with the values for all known zeolite frameworks. Thus, all procedures for calculating properties were also performed on the siliceous forms of the known zeolite topologies. Quartz was used as a reference for all calculations, and we quote lattice energies with respect to that of α-quartz, the most stable form of the mineral at ambient temperature.

The "available volume", defined as the difference between the volume of the unit cell and the effective volume of all of the atoms, depends on the van der Waals radii used for each atom. "Occupiable volume" is the volume which can be occupied by a probe molecule with a given radius as it probes the surface of the structure. The "accessible volume" is determined by tracing out the volume by the center of the probe molecule as it follows the structure contours, but with the extra requirement that the probe must enter the unit cell from the outside via sufficiently wide pores or channels. The calculations of the accessible volume were performed using the Free Volume module of the Cerius[2] package. This applies the Connolly method,[35] consisting of "rolling" a probe molecule with a given radius over the van der Waals surface of the framework atoms. We have used a probe molecule with a radius of 1.4 Å (such as water) and 1.32 and 0.9 Å for the radii of O and Si atoms, respectively. The void volume, enclosed within the Connolly surface, was calculated first. The accessible volume was then calculated by requiring the probe molecule to enter the unit cell from the outside.

Results and Discussion

A total of 294 uninodal frameworks were originally enumerated.[14] This set included quasi-simple tilings with tetrahedral vertex figures with up to six double edges (as explained in ref 14), and also the nine uninodal frameworks derived from simple tilings. After the removal of duplicates, together with tilings which could not be refined to within a sufficiently narrow range of Si−Si distances, 166 uninodal structures were available for evaluation. We were able to carry out an energy minimization calculation on the structures of all but two of them. Among the 164 minimized structures were all 21 known uninodal zeolites (structure types ABW, ACO, AFI, ANA, ATN, ATO, BCT, CAN, CHA, DFT, FAU, GIS, GME, KFI, LTA, MER, MON, NPO, RHO, RWY, and SOD),[1] two known minerals (tridymite and cristobalite), and 78 unknown zeolite structures. The remaining structures comprised duplicate topologies, which, in most cases, arise from different tilings (but with the same framework topology) and minimize to identical structures. In several cases, however, qualitatively different structures were obtained with the same topology, because different unit cell definitions can result in minimized structures with different symmetries. For example, several low and high symmetry forms of both cristobalite and trydimite were generated. While most of the structures have previously been found by other enumeration methods, our enumeration is systematic, and ranking by simulated lattice energies gives a different "order of preference" as compared to those of Boisen et al.[10] (who used a calculated force field) and Treacy et al.[12] (who relied on an empirical cost function based on geometries of known silicate zeolites), thus arriving at a different set of chemically feasible structures.

The reason our enumeration did not find quartz is that this compact structure requires a quasi-simple tiling with a tetrahedral vertex figure with more than the six double edges that we have considered. In the most natural tiling for quartz,[36] a relatively intricate structure, as many as four different tiles meet.

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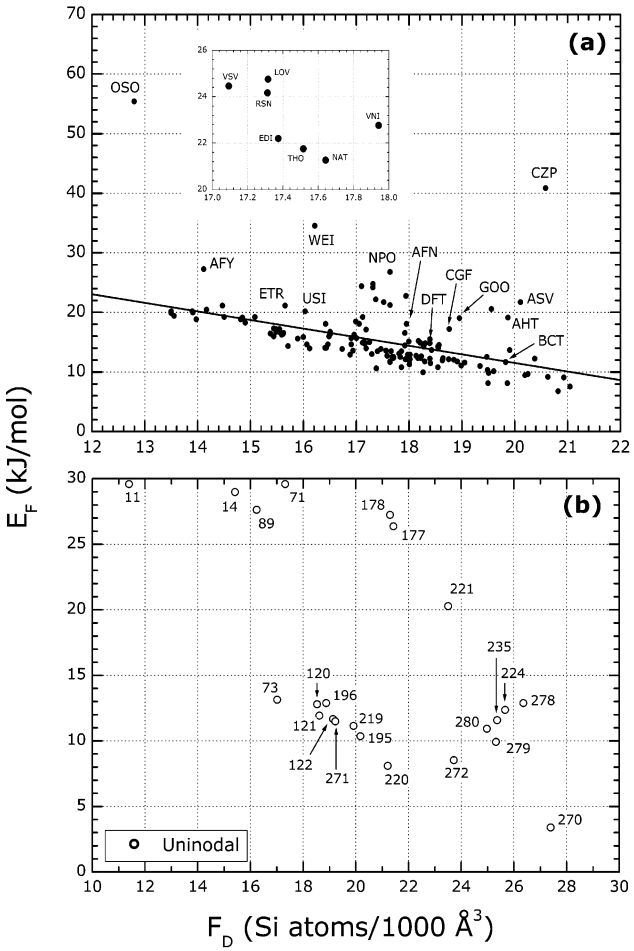

Figure 1. Framework energy, E_F (kJ/mol), with respect to α-quartz, versus framework density (Si atoms per 1000 Å^3) for (a) all known zeolitic structure types; (b) hypothetical uninodal zeolitic structures with framework energies below 35 kJ mol^{-1}.

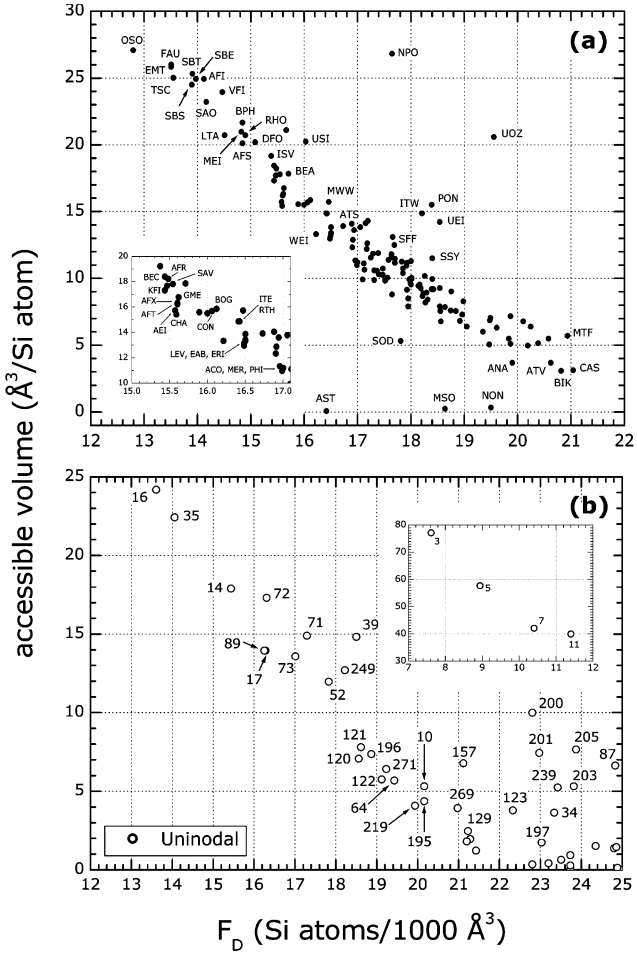

Figure 2. Accessible volume (Å^3 per Si atom) versus framework density for (a) all known zeolitic structure types; (b) hypothetical uninodal zeolitic structures with accessible volumes below 80 Å^3 per Si atom.

We note, however, that enumeration of all known uninodal zeolitic structures never requires such complicated vertex figures.

Relative Energy and Framework Density. Figure 1a gives the plot of framework energy relative to α-quartz, E_F, versus the framework density, F_D, for all known zeolites. Instead of considering only zeolites that exist in the purely siliceous form, we have treated all of the known topologies as though they were realized as silica polymorphs. The four structures that substantially deviate from the rest are all non-silicate structure types, WEI (calcium beryllophosphate), CZP (sodium zincophosphate), OSO (potassium berylosilicate), and RWY (gallium germanium sulfide). OSO, RWY, and WEI are frameworks containing three-membered rings, and the higher energy of these structures in the siliceous form indicates a strained framework.

Using regressional analysis, we fitted a straight line through all of the data points of relative framework energy versus the framework density for all known zeolites. Figure 1a contains 147 data points (146 for zeolites and one for α-quartz), excluding structures −CHI, −CLO, −PAR, −RON, and −WEN, which have interrupted frameworks and cannot be treated as SiO_2. The straight line shows the fit for all data except those for CZP, RWY, WEI, and OSO. The fit ($E_F = -1.441 F_D + 40.323$, with $R^2 = 0.3351$) is similar to those reported by Henson et al.[20,37] and Aporiaye and Price,[11,30] and to those derived from calorimetric measurements.[38] We note that the purely siliceous counterparts of structures BCT (magnesiosilicate) and DFT (cobaltophosphate) have energies similar to those of other known structures of similar framework density.

Relative framework energies of the hypothetical zeolitic frameworks range from 3.38 to as much as 609 kJ mol^{-1}, and it is clear that the structures with high framework energies will be highly strained and not chemically viable. Figure 1b shows the plot of the framework energy versus the framework density for the hypothetical uninodal structures with energies below 30 kJ mol^{-1}, the range considered as the most "desirable", and with framework densities typical of the known zeolites. There are 23 hypothetical uninodal structures in this range: 11, 14, 71, 73, 89, 120, 121, 122, 177, 178, 195, 196, 219, 220, 221, 224, 235, 270, 271, 272, 278, 279, and 280.

The deviation of the relative lattice energy from the best fit in Figure 1a can be easily quantified. If the equation of the regression line is written as $y + ax + c = 0$ (where $y = E_F$ and

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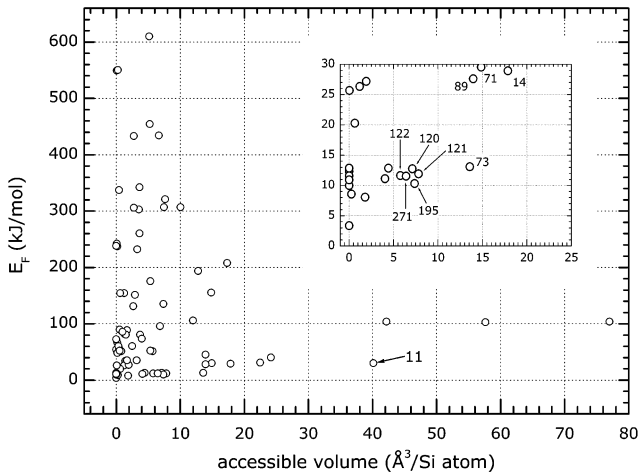

Figure 3. Framework energy with respect to α-quartz versus accessible volume (Å^3 per Si atom) for all hypothetical uninodal zeolitic structures. The inset identifies the chemically feasible structures.

$x = F_D$), then the distance of a point with coordinates (x_1, y_1) from that line is # = j($ax_1 + y_1 + c$)/aj, where υ is a dimensionless deviation parameter.

To identify chemically feasible structures, Akporiaye and Price[11,30] plotted F_D versus the number of Si atoms in the fourth coordination shell (N_4). The framework density increases with decreasing N_4, because structures with low framework density must contain large cavities and/or channels outlined by large rings, which can only occur for low degrees of branching of the framework. These plots provide information similar to that given here, but are significantly easier to perform, as the calculation of N_4 does not involve high-computing-cost lattice minimization.

Accessible Free Volume. The accessible free volume determined by a probe molecule gives an indication of the space available within each structure for applications in molecular sieving and catalysis. Figure 2a gives the plot of accessible volume (Å^3 per Si atom) versus framework density for all known zeolitic structure types. There are structures, such as AST, MSO, and NON, with zero accessible volume for the given size of the probe molecule. Known zeotype OSO has the highest accessible volume, closely followed by FAU, EMT, and SBT. All of them contain large cavities.

Figure 2b gives the plot of accessible volume versus framework density for the hypothetical uninodal zeolites with accessible volumes below 80 Å^3 per Si atom. Low framework density structures are of particular interest, as they have very high accessible free volumes. Of the structures with framework densities below 18 Si atoms/1000 Å^3, structures 11, 14, 71, 73, and 79 are energetically stable (Figure 1b). We note that structure 11 is one of the nine enumerated using simple tilings and six of the others in that group are known zeolites. Most of the hypothetical uninodal structures have dense frameworks, which are largely inaccessible. However, as many known zeolite topologies have low accessible volumes (Figure 2a), a structure cannot be ruled out as a feasible topology on the basis of the low accessible free volume, even though it may not be of interest to sorption, ion exchange, or catalysis. A plot of framework density for known zeolites and for dense silicate frameworks against the size of the smallest ring in the structure[39] shows

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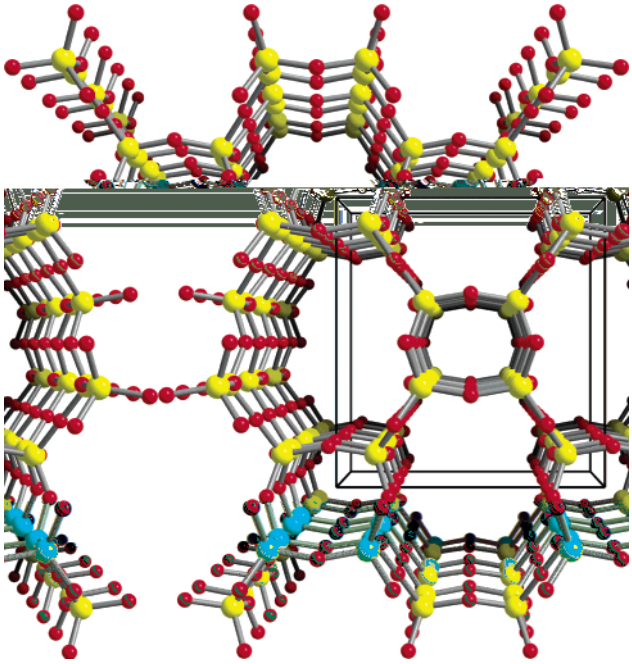

Figure 4. Structure 120 contains a one-dimensional channel system of eight-membered rings (4.8 4.4 Å) along (001), built up from chains of edge-sharing four-membered rings (E_F = 12.79; F_D = 18.54 Si atoms/1000 Å^3; accessible volume = 7.11 Å^3 per Si atom).

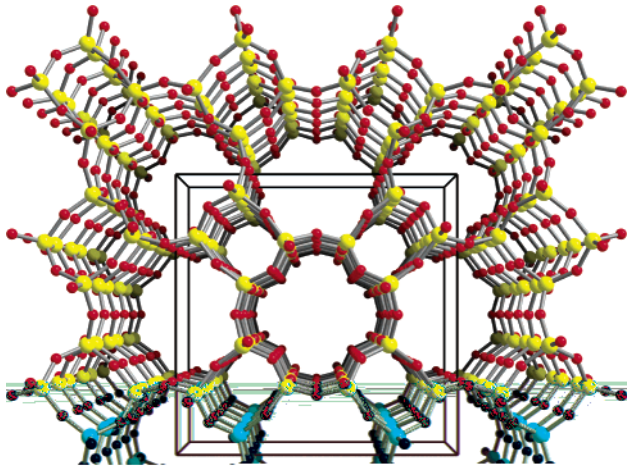

Figure 5. Structure 121 contains two kinds of one-dimensional channels (3.9 3.9 and 3.1 3.1 Å) of eight-membered rings along (001), built up by chains of edge-sharing four-membered rings (E_F = 11.91; F_D = 18.63 Si atoms/1000 Å^3; accessible volume = 7.80 Å^3 per Si atom).

that very open frameworks with low F_D have the largest number of four- and three-membered rings and that there is a clear gap in F_D between compact minerals, such as quartz and tridymite, and the zeolite frameworks. The lower boundary of F_D for known zeolites is from about 11 tetrahedral atoms per 1000 Å^3 in materials with four-membered rings to about 17 tetrahedral atoms in materials with 5+ rings, where the plus sign signifies that some tetrahedral atoms are associated only with the larger rings.

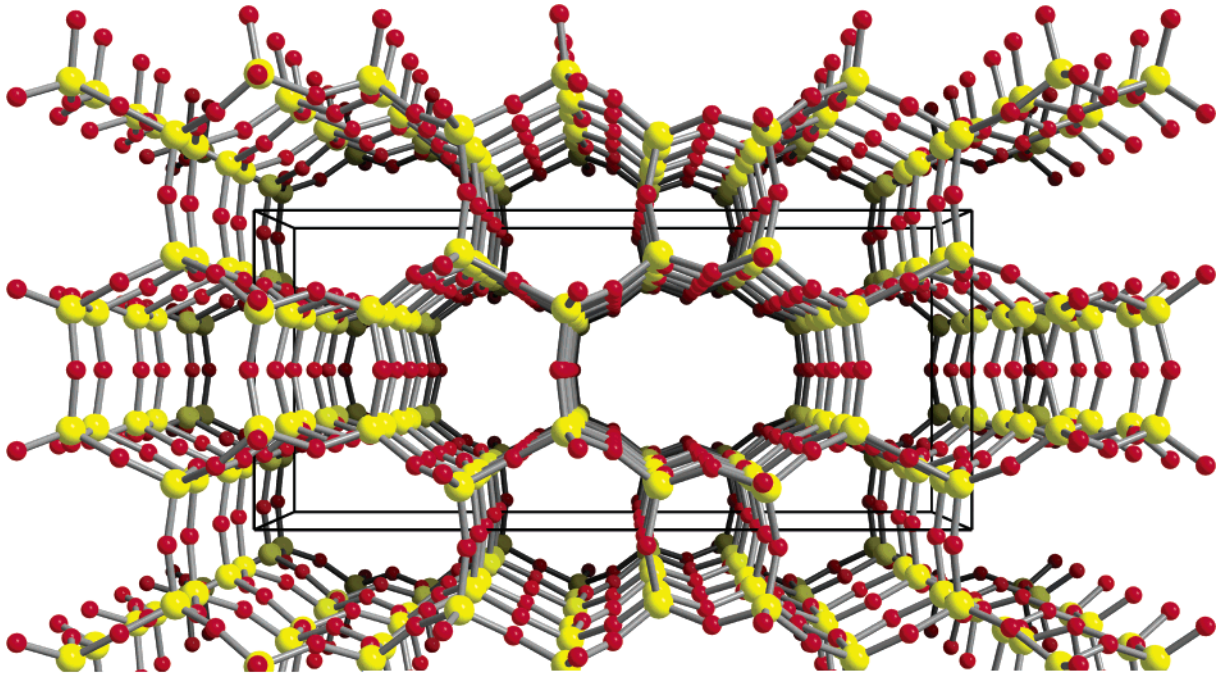

Figure 6. Structure 122 contains a one-dimensional ring channel system, with channels outlined by eight-membered rings (2.4 5.3 Å) (E_F = 11.64; F_D = 19.13 Si atoms/1000 Å^3; accessible volume = 5.79 Å^3 per Si atom).

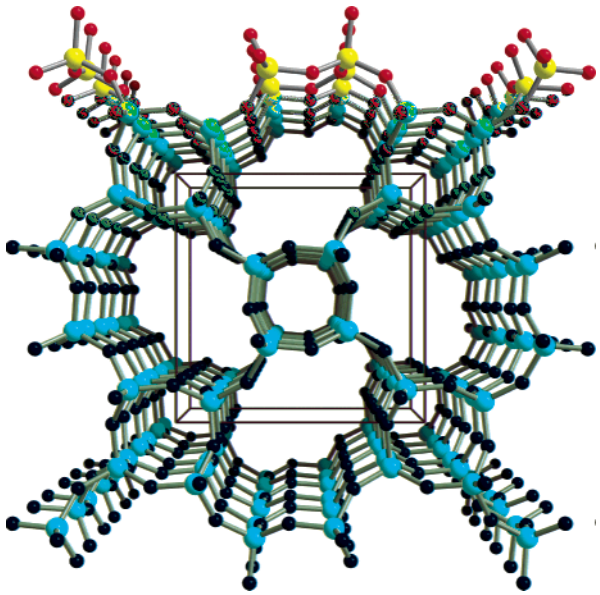

Figure 7. Structure 195 has a one-dimensional channel system along (001) of elongated eight-membered rings (2.7 5.8 Å) in a "propeller" arrangement around four-membered rings (E_F = 10.35; F_D = 20.16 Si atoms/1000 Å^3; accessible volume = 4.39 Å^3 per Si atom).

Figure 3 plots the framework energy with respect to α-quartz for all hypothetical uninodal zeolitic structures versus the accessible volume, thus combining information contained in Figures 1b and 2b. Structures of the greatest practical interest are those with low energies and large volumes (see inset). Figures 4−8 show the structures of five selected hypothetical uninodal zeolites, while full details of all of the structures together with the crystallographic CIF files (from which powder X-ray diffraction patterns can be easily calculated) are given in Supporting Information.

Although some of the known frameworks exist only as aluminum phosphates or other compounds which do not have silicate counterparts, evaluation of the topologies with the $AlPO_4$ composition shows that their stability is similar to that of the SiO_2 compositions[40] and that the correlation between energy and density for purely siliceous systems is also valid for the AlPOs.[37] This is not unexpected, given the similarity of the atomic radii of silicon and aluminum,[41] but new calculations would have to be made for materials with other chemical compositions. One way forward might be to perform simulations using "virtual" atoms, that is, atoms with properties not based on a specific element but with variable radius, bond length, and bond angles.

Using the tiling method, it is possible to enumerate every possible periodic three-dimensional network, subject only to the availability of computer resources. It can be readily extended not only to six-coordinated and mixed six-/four-coordinated structures, but to any arbitrarily prescribed coordination. For six-coordinated structures, the starting point would be a list of six-faced generalized polyhedra instead of the tetrahedra used for four-coordinated structures,[14] and the number of resulting structures would be much larger. The advantage of the tiling method of enumeration as compared to other approaches is that it is systematic and that certain aspects of the enumerated topologies, such as ring size and cage topology, can be prescribed in advance.

The synthesis of microporous materials is facilitated by the use of structure-directing agents (templates), which are typically organic bases. Template molecules are incorporated in the synthesis mixture, with the resulting framework of the product reflecting the shape of the template. A given microporous

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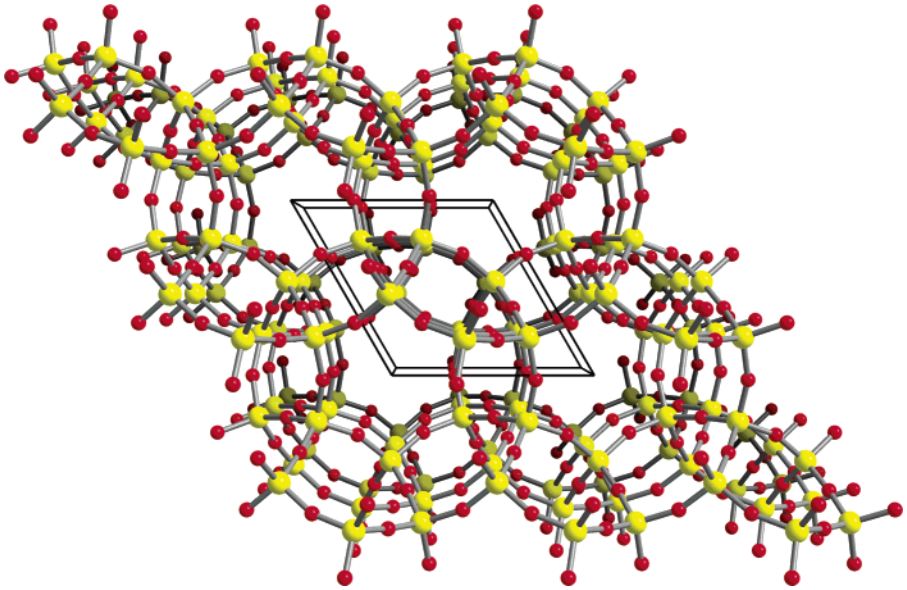

Figure 8. The compact framework of structure 271 consists of five- and six-membered rings ($E_F = 11.54$; $F_D = 19.24$ Si atoms/1000 Å^3; accessible volume = 6.43 Å^3 per Si atom).

structure may thus be targeted by adroit choice of the template using ZEBEDDE,[42] a computational method of de novo design of template molecules which are "grown" within the desired inorganic framework. ZEBEDDE suggests the optimum shape of a template molecule suitable for the synthesis of this framework and has generated templates used for the synthesis of known microporous materials. ZEBEDDE will soon be used to assist in the synthesis of the zeolitic structures that we have identified as chemically plausible.

Finally, we note that a zeolite-like material with a framework composed of phosphorus, nitrogen, and oxygen, and the structure corresponding to our net 88, has recently been reported.[43] Complete structural information on all of the enumerated structures is currently being placed on a website.[44]

Summary

We have considered 164 systematically enumerated uninodal hypothetical four-connected as silica polymorphs and evaluated them with respect to calculated lattice energies and other structural properties. Among the minimized structures were 21 known zeolites, two known minerals (tridymite and cristobalite), and 78 unknown zeolite topologies. We have calculated optimized lattice energies relative to α-quartz, framework densities, coordination sequences, and volumes accessible to a probe molecule 1.4 Å in diameter, and we established correlations between these quantities. We identified 23 hypothetical structures as chemically feasible.

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Supporting Information Available: Potentials used in the calculations, structural information for all optimized structures, crystallographic CIF files for all optimized structures, and structural information on the structures shown in Figures 4−8. This material is available free of charge via the Internet at http://pubs.acs.org.

JA037334J

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