Hypothetical Zeolitic Frameworks: In Search of Potential Heterogeneous Catalysts

Dorota Majda,[†] Filipe A. Almeida Paz,[‡,§] Olaf Delgado Friedrichs,[||] Martin D. Foster,[⊥] Alexandra Simperler,[⊥] Robert G. Bell,*,[⊥,#] and Jacek Klinowski*,[‡]

Regional Laboratory of Physiochemical Analysis and Structural Research, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U.K., Department of Chemistry, CICECO, University of Aveiro, Campus Universitário de Santiago, Aveiro, 3810-193, Portugal, Wilhelm Schickard Institut für Informatik und ZBIT Zentrum für Bioinformatik, Universität Tübingen, Sand 14, D-72072 Tübingen, Germany, Davy-Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, U.K., and Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

Received: July 30, 2007; In Final Form: October 31, 2007

Hypothetical zeolitic structures were systematically enumerated using tiling theory and then characterized with a view to finding those that are chemically feasible. The energy of each framework, treated as a polymorph of silica, was first minimized using computational chemistry methods. Optimized structural parameters, framework energy relative to α-quartz, framework density, and internal volume accessible to sorption of small molecules were then calculated for each structure. Chemical feasibility was evaluated by means of a "feasibility factor" derived from the correlation between lattice energy and framework density. Finally, the structures most suitable for potential applications in heterogeneous catalysis and sorption (those with wide channels and/or cavities that are accessible to external molecules) were identified. Very few structures with one or two crystallographically distinct sites for silicon ("uninodal" and "binodal") were found to be promising in this respect. In contrast, there are 100 trinodal structures that are potentially suitable for practical applications. These are described and discussed.

Introduction

Aluminosilicate (zeolitic) and aluminophosphate (AlPO) molecular sieves are of considerable practical importance because of their large pore volumes, high thermal stability, and well-defined pore structure. These materials are used for gas storage, separation of molecules, ion exchange, and, crucially, for heterogeneous catalysis.[1] Open-structure aluminosilicates are employed in catalytic cracking, hydrocracking, alkylation, isomerization, and dehydroisomerisation in the petrochemical industry.[2] The catalytic conversion of methanol to gasoline[3] using zeolite ZSM-5 is now used on an industrial scale. Framework-substituted, open-structure AlPO catalysts are also important. For example, a SAPO-34 catalyst is active in the acid-catalyzed dehydration of methanol[4] to yield ethene and propene for the polymer industry. Transition-metal-substituted AlPOs are active in the selective conversion of cyclohexanone, NH_3, and air to ε-caprolactam and nylon-6,[5] and in the synthesis of many organic chemicals of value as pharmaceuticals.

There are now 176 recognized structure types of molecular sieves[6] with around 10 new types being added to the list each year. But this includes very few known structures with pores larger than those circumscribed by 14 tetrahedral atoms and very few with a framework density lower than 12 tetrahedral atoms per 1000 Å[3], limiting the size and number of molecules

that can enter the intracrystalline space.[7,8] New open structures are therefore urgently needed.

There are several reasons why the derivation of all possible structures for such solids is a matter of fundamental and practical interest. First, a set of chemically feasible hypothetical structures would facilitate design strategies and ultimately lead to their synthesis. Microporous materials are synthesized using structure-directing agents ("templates"), typically organic bases incorporated in the reactive mixture, which direct the shape of the resulting framework. A given microporous structure may thus be targeted by adroit choice of template. Second, theoretical X-ray, neutron, and electron diffraction patterns generated from hypothetical structures would be of great value in determining the atomic coordinates of newly prepared materials, simply entailing a comparison of the indexed experimental pattern with systematically enumerated crystallographic data. Third, a database of enumerated results provides a new technique for framework structure solution, as shown recently by Foster et al. for the zeolite structure known as ZSM-10.[9]

Using tiling theory arguments, we have previously systematically enumerated possible zeolitic structures involving one and two inequivalent tetrahedral sites for silicon ("uninodal" and "binodal"). Many of them correspond to naturally occurring and synthetic materials. We also assessed their "chemical feasibility" using quantum chemistry methods. Relatively few of these theoretical structures were found to be potentially suitable for practical applications. We now discuss the chemical feasibility of theoretical trinodal zeolites (those with three inequivalent sites for silicon). Because the number of structures involved is large, we will only focus on those with very open structures, which are of greatest interest for practical applications, par-

* Corresponding authors. E-mail: (J.K.) jk18@cam.ac.uk; (R.G.B.) rob@ri.ac.uk.
† Jagiellonian University.
‡ University of Cambridge.
§ University of Aveiro.
|| Universität Tübingen.
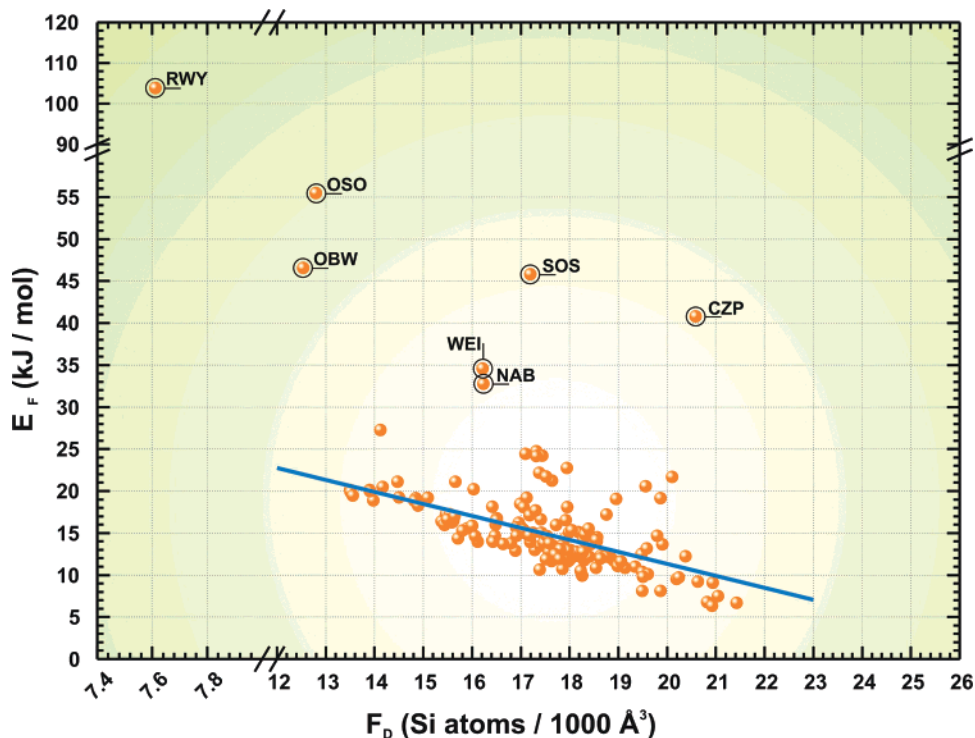⊥ The Royal Institution of Great Britain.
University College London.

Figure 1. Framework energy, E_F (kJ/mol), with respect to α-quartz versus framework density (Si atoms per 1000 Å³) for all 176 known zeolitic structure types.

ticularly heterogeneous catalysis and sorption. Previously enumerated structures are also examined from this aspect.

Methods

Structural Enumeration. Enumeration of possible structures originated in the classic work by A. F. Wells on three-dimensional nets and polyhedra.[10,11] Sherman and Bennett,[12] Alberti,[13] Sato,[14,15] Akporiaye and Price,[16] Smith,[17] and O'Keeffe and co-workers[18,19] found many possible new structures by building structural models. A more recent approach employed computer search algorithms, exploring all combinations of connected atoms and crystallographic sites, seeking the four-connected graphs,[20−22,22−24] or considering a constrained assembly of atoms around a specified pore structure.[25] The database listing hypothetical structures, enumerated by exploring all combinations of connected atoms and crystallographic sites, currently contains a total of 933 672 structures.[23]

We use a new method of systematic enumeration[26] based on advances in combinatorial tiling theory.[27] Just as a floor can be covered with tiles of various shapes, three-dimensional space can be filled with polyhedral tiles, and the number of ways in which this can be done can be calculated. The principle of the method is briefly as follows.[26] A tiling is a periodic subdivision of three-dimensional 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 thus formed by the vertices and edges. The configuration of edges, faces, and tiles around a given vertex can be described through what is known as a vertex figure, obtained by placing the center of a small notional sphere at a vertex and considering the tiling of the sphere formed by the intersections with the different tiles touching the vertex. A particular tiling can be encoded in the form of a unique "Delaney symbol"[28,29] and encoded as an "inorganic gene".[26] This is then systematically permuted using computational algorithms, giving all possible structures.

The number of possible tilings of three-dimensional space is infinite. However, two factors make the number of tilings of interest finite. First, known zeolitic structures involve up to 12 inequivalent vertices (i.e., inequivalent silicon atoms), which we call *n*-nodal, where *n* is an integer between 1 and 12.[26] For example, faujasite is a 1-nodal (uninodal) structure and ZSM-5 is 12-nodal. Second, the largest unit cell of any known molecular sieve is that of cloverite with unit cell volume 138 284.66 Å³ and $a = b = c = 51.712$ Å.[6] We are therefore interested only in structures within certain limits. Even so, the number of possible structures is enormous. We have so far enumerated all possible Euclidean uni-, bi- and trinodal tilings based on "simple" vertex figures (tilings with vertex figures that are tetrahedra) and all "simple" and "quasi-simple" uninodal tilings with vertex figures containing up to six extra edges.[30−33] In quasi-simple tilings, the vertex figures are derived from tetrahedra but contain double edges.[34]

When our original paper[26] was published, the database administered by the International Zeolite Association contained 121 recognized structure types: currently there are 176. While the 55 new structures can, in principle, all be obtained using our method, we specifically described structure types RWY[35] (our structure 1_1);[36] NPO[37] (our structure 1_88);[36] BCT[38] (not registered by the IZA until June 14, 2001) (our structure 1_211)[36] and UFI[39] (our structure 3_835).

Enumeration of chemically realizable frameworks containing large amounts of internal space (i.e., frameworks containing channels and/or accessible voids) is of particular interest for industrial applications, because such materials can act as "microreactors" containing chemically implanted catalytically active groups or encapsulated transition-metal complexes.[40] The crucial structural parameters here are the amount of void volume and its accessibility to external molecules.

Energy Minimization. Because only a fraction of the mathematically generated networks can be expected to be "chemically feasible" (there could be many "strained" frameworks requiring unrealistic bond lengths and bond angles), an
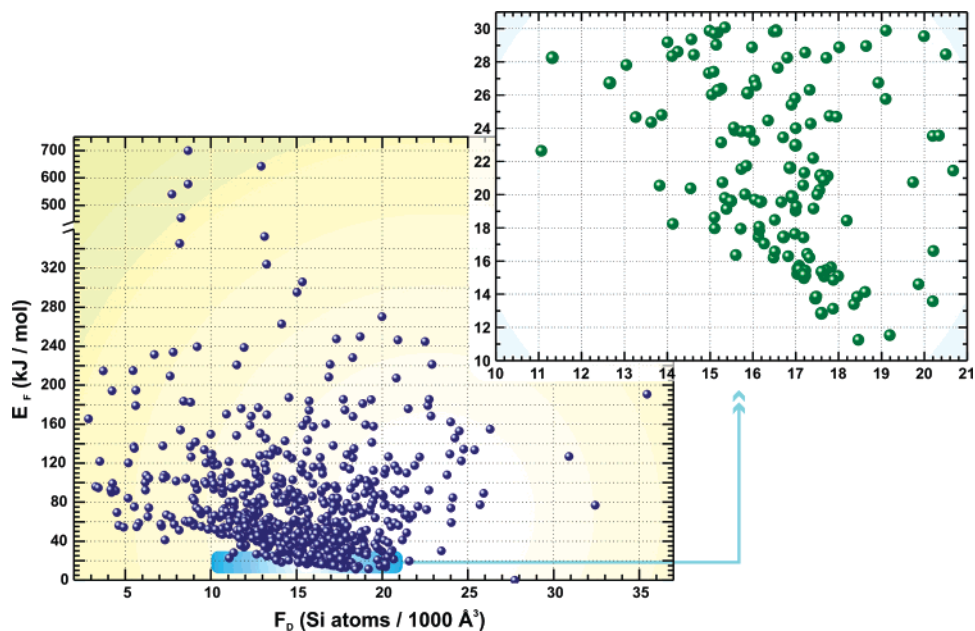
Figure 2. Framework energy, E_F (kJ/mol), with respect to α-quartz versus framework density (Si atoms per 1000 Å^3) for the hypothetical trinodal zeolitic structures. The region corresponding to framework energies and densities found in known zeolites is magnified in the inset.

effective selection process is required to identify the most plausible frameworks. To do this, we must inject the basics of chemistry into the problem, replacing the mathematical points by atoms and the straight lines by chemical bonds, and calculate the energy of the resulting frameworks through slight adjustments of angles and distances.

Many of the known zeolite structure types cannot be constructed from simple tilings. Calculations based on simple tilings can therefore give only a subset of all possible trinodal structures. Even so, this subset is very large; we originally reported that there are exactly 926 trinodal structures based on simple tilings,[31] mistakenly dismissing a further 424 structures. However, only a handful of the trinodal structures had previously been enumerated, while nearly all the uninodal structures derived from the tilings were previously known, either as crystal structures or as hypothetical nets. It is therefore still useful to describe trinodal structures derived from simple tilings, especially because many have turned out to be most interesting.

To identify the chemically realizable structures, we followed procedures identical to those used in our previous work.[30−33,36] The method is briefly as follows. The systematically enumerated nets[26] were first converted into atomistic models. This was done by inserting a Si atom at each vertex point and placing a bridging oxygen between each pair of adjacent Si atoms. Each net was scaled such that the vertices were separated by ca. 3.1 Å, a typical Si · · · Si distance. The resulting structure was then pre-optimized using the DLS (distance least squares) method,[41] which performs geometric refinement of the structure by fitting bond lengths and angles to the prescribed values. We next used the GULP framework energy minimization subroutines with the Sanders−Leslie−Catlow silica potential[42] and the modified oxygen shell charge described by Schröder.[43] We also 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), and accessible volume, V_{acc}, for each pore system. The latter was determined by tracing out the volume using the center of a 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. V_{acc} gives an indication of the space

available within each structure for applications in molecular sieving and catalysis. A "feasibility factor", ϑ, derived from the correlation between lattice energy and density, calculated for known zeolite structure types, served as a further measure of thermodynamic feasibility. We discuss the structures in terms of the calculated stability, chemical feasibility, and framework openness. Taken together, these parameters provide a good guide as to which of these structures could be most readily synthesized and may have promising applications.

The lattice energy and crystallographic data were extracted from the GULP minimizations, whereas coordination sequences, bond distances, and angles were calculated with zeoTsites (version 1.2).[44] The connectivity was additionally checked with the software tool KRIBER (version 1.1).[45] The lattice energy is relative to that of α-quartz, calculated using the same potential model and is thus analogous to the heat of transition reported for several high-silica zeolites.[46−48] The Cerius^2 software suite[49] was used for visualizing and manipulating the structures and for calculating accessible volumes, space group symmetry, and other parameters. The structural illustrations for publication were generated through several software packages in combination, including Crystal Impact Diamond,[50,51] Mercury,[52] Chimera,[53,54] and POV-Ray.[55] The computation of zeolitic surfaces was performed using the routines implemented in the software package MSMS[56] embedded in Chimera,[53,54] selecting probe radius 1.4 Å and vertex density 2. The MCAVITY program[57] was used to calculate the limiting sphere radius (and approximate volume) of the internal cavities. Calculations of V_{acc} were done with the Free Volume module of the Cerius^2 package, which applies the Connolly method,[58] consisting of "rolling" a probe molecule with a given radius over the van der Waals surface of the framework atoms. Here we also 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 the O and Si atoms. The void volume, enclosed within the Connolly surface, was calculated first, then the accessible volume, by requiring the probe molecule to enter the unit cell from the outside.

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 relevant

Potential Heterogeneous Catalysts

J. Phys. Chem. C, Vol. 112, No. 4, 2008 **1043**

TABLE 1: Hypothetical Trinodal Frameworks with Feasibility Factor $\vartheta \leq 5$

framework	E_F (kJ/mol)	F_D (Si atoms/1000 Å³)	V_{acc} (Å³/Si atom)	ϑ	framework	E_F (kJ/mol)	F_D (Si atoms/1000 Å³)	V_{acc} (Å³/Si atom)	ϑ
3_789	15.57	17.08	12.04	0.01	3_1077	13.13	17.87	3.64	0.91
3_793	15.50	17.08	11.36	0.05	3_698	18.25	14.13	23.74	1.08
3_981	15.43	17.22	10.63	0.05	3_660	22.64	11.06	43.02	1.09
3_786	15.54	17.04	9.98	0.06	3_1149	19.61	15.48	17.22	1.22
3_788	15.73	17.08	11.54	0.11	3_759	19.81	15.34	17.83	1.22
3_787	15.40	17.08	11.54	0.12	3_1139	17.64	16.98	14.37	1.34
3_969	16.58	16.51	13.40	0.13	3_1141	12.85	17.61	11.60	1.36
3_967	16.20	16.48	13.48	0.15	3_778	17.42	17.18	12.30	1.39
3_991	15.25	17.15	11.17	0.15	3_1073	18.48	16.51	12.95	1.46
3_914	13.85	18.43	8.25	0.16	3_918	11.25	18.46	7.92	1.63
3_1075	15.13	17.22	10.45	0.16	3_922	13.58	20.20	5.45	1.73
3_818	18.64	15.10	20.05	0.16	3_770	20.74	15.29	18.70	1.81
3_993	15.17	17.19	11.09	0.17	3_760	20.02	15.82	16.18	1.84
3_792	15.27	17.08	11.39	0.21	3_754	19.70	16.04	15.46	1.84
3_958	20.56	13.82	25.13	0.21	3_806	19.54	16.16	15.43	1.85
3_776	17.06	16.26	15.10	0.22	3_756	19.58	16.19	15.95	1.91
3_866	13.41	18.36	7.81	0.23	3_846	14.61	19.86	5.37	2.11
3_790	15.08	17.66	10.73	0.24	3_681	19.03	16.99	12.74	2.32
3_780	16.30	16.82	13.21	0.25	3_757	19.56	16.66	15.35	2.36
3_710	19.16	14.84	21.13	0.26	3_700	24.67	13.27	27.96	2.52
3_785	15.22	17.03	12.06	0.29	3_894	19.30	17.01	13.17	2.53
3_819	17.95	15.72	2.89	0.29	3_699	24.36	13.63	26.95	2.67
3_730	17.98	15.10	18.88	0.30	3_1278	19.82	16.91	12.73	2.79
3_791	14.86	17.88	9.77	0.30	3_506	21.55	15.73	17.04	2.82
3_1085	14.97	17.19	11.23	0.30	3_772	19.17	17.41	12.29	2.84
3_766	17.46	16.13	14.45	0.36	3_821	19.93	16.89	12.46	2.85
3_1134	15.37	17.60	10.67	0.39	3_777	21.73	15.84	16.64	3.06
3_835	17.33	15.43	18.33	0.42	3_971	28.26	11.32	41.07	3.08
3_913	14.14	18.62	7.35	0.54	3_737	18.44	18.19	9.90	3.11
3_848	15.47	17.71	10.74	0.56	3_558	24.80	13.87	24.00	3.22
3_925	15.09	17.99	5.86	0.58	3_1003	26.73	12.66	31.27	3.35
3_783	15.11	17.99	9.99	0.59	3_765	23.15	15.26	18.28	3.46
3_768	17.84	16.15	14.44	0.65	3_836	20.02	17.50	12.86	3.52
3_926	12.18	18.75	7.65	0.69	3_682	20.56	17.17	12.98	3.57
3_837	16.22	17.32	11.90	0.69	3_774	20.27	17.55	11.28	3.74
3_1293	11.54	19.19	7.11	0.70	3_1331	16.61	20.21	3.83	3.86
3_782	15.62	17.82	10.70	0.78	3_933	21.63	16.86	13.19	4.00
3_781	16.44	17.26	11.78	0.79	3_724	21.33	17.20	12.01	4.13
3_758	19.15	15.38	18.47	0.79	3_755	23.87	15.57	18.26	4.27
3_904	13.86	17.48	10.05	0.79	3_1076	20.91	17.66	9.72	4.30
3_903	13.86	17.47	10.32	0.80	3_507	23.27	16.03	16.05	4.31
3_769	18.08	16.14	14.59	0.81	3_1071	24.05	15.55	16.51	4.38
3_900	13.85	17.47	10.44	0.81	3_827	23.81	15.72	16.05	4.38
3_715	20.38	14.54	22.05	0.81	3_1140	21.16	17.59	13.95	4.41
3_898	13.82	17.47	10.07	0.83	3_428	27.82	13.05	29.41	4.50
3_902	13.81	17.47	10.32	0.84	3_1135	23.77	15.91	17.28	4.54
3_897	13.76	17.45	10.63	0.88	3_825	21.13	17.75	10.80	4.54
3_899	13.73	17.46	10.62	0.89	3_950	26.98	13.75	99.92	4.61
3_896	13.73	17.45	10.35	0.91	3_511	22.20	17.40	11.82	4.94

properties were also calculated for the purely siliceous forms of all known zeolite topologies. Lattice energies were calculated relative to α-quartz, the most stable form of the mineral at ambient temperature.

The Feasibility Factor. The relationship between framework density and calculated lattice energy[30−33,36] was confirmed experimentally[59] for known zeolites. Figure 1 gives the plot of framework energy relative to α-quartz, E_F, versus the framework density, F_D, for all known zeolites treated as silica polymorphs. We excluded the −CHI, −CLO, −LIT, −PAR, −RON, and −WEN structure types with interrupted aluminosilicate frameworks, and eight non-silicate structure types that substantially deviate from the rest: WEI (beryllophosphate), SOS (borogermanate), CZP (zincophosphate), NAB, OBW and OSO (berylosilicates), AFI (aluminophosphate), and RWY (gallium germanium sulfide). The line of best fit, obtained by the least-squares method, has the formula $y = -1.429(\pm 0.141)x + 39.914(\pm 2.465)$, where x is F_D and y is E_F, and $R = -0.626$. The feasibility factor, ϑ, is then simply the distance of a data

point (x_1, y_1) from the line of best fit, given by the vertical offset $\vartheta = (|1.429x_1 + y_1 + 39.914|/1.429)$.

This factor is a convenient way of discriminating between candidate structures and can be compared with the values obtained from known zeolites. We minimized all the known zeolite topologies as silica polymorphs, regardless of the actual composition in which they occur, and we believe that ϑ is a better measure of the feasibility of a structure than E_F alone. Virtually all of the topologies that are known in the form of silicates, aluminosilicates, or aluminophosphates, including those with low levels of heteroatom substitution, have $\vartheta \leq 5$. This reflects the similarity of preferred geometry between aluminosilicates and AlPOs. We consider structures with $\vartheta \leq 5$ as feasible "conventional" zeolites, that is, those for which natural zeolites, high-silica, and the AlPO forms are known. Many other compositions, such as metal-organic frameworks, are possible. This means that although a structure may be deemed highly unfeasible as a zeolite, it may exist in other chemical forms. To assess the feasibility of a particular topology in a different
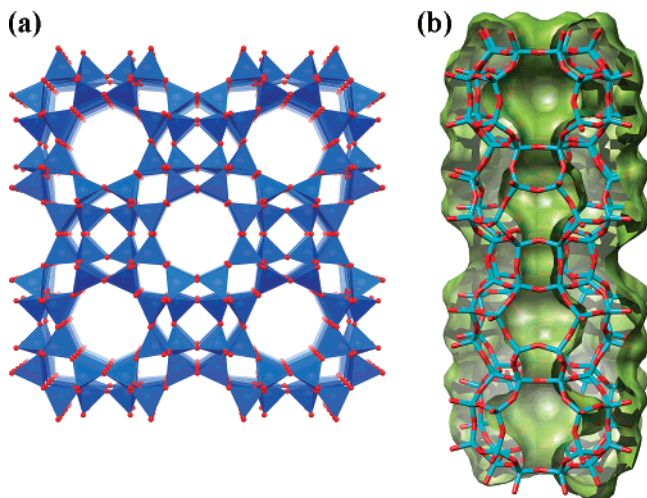
(a)   **(b)**

Figure 3. (a) Trinodal framework 3_789 containing a 3D system of intersecting channels formed by face-sharing $[4^{12}8^7]$ cages with eight-membered ring apertures ($E_F = 15.57$ kJ/mol, $F_D = 17.08$ Si atoms/1000 Å^3, $V_{acc} = 12.04$ Å^3/Si atom, and $\vartheta = 0.01$). (b) Detailed view of the channels running along the [001] direction showing the internal solvent-accessible surface area.

(a)   **(b)**

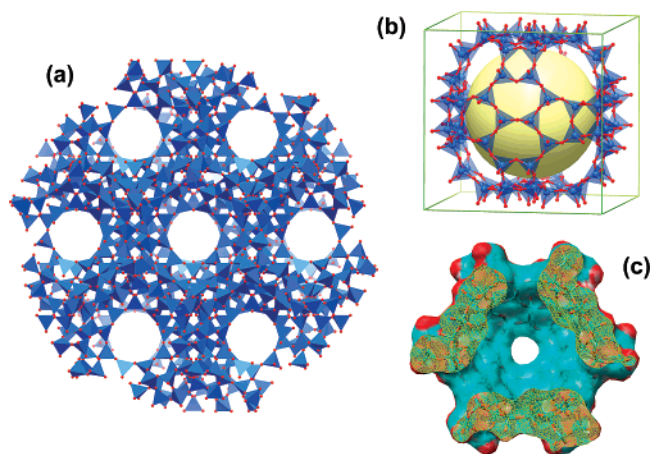   **(c)**

Figure 4. (a) Trinodal framework 3_699 containing a 3D system of intersecting channels outlined by nine-membered ring apertures. The figure shows the channels running along the [111] direction ($E_F = 24.36$ kJ/mol, $F_D = 13.63$ Si atoms/1000 Å^3, $V_{acc} = 26.95$ Å^3/Si atom, and $\vartheta = 2.67$). (b,c) Apertures constitute windows to large $[4^85^86^89^8]$ cages that can accommodate a sphere with radius of ca. 7.4 Å (estimated volume ca. 1688 Å^3).

composition, it is necessary to carry out separate series of computations, taking the actual composition into account, which is outside the scope of the present report.

Results and Discussion

When the feasibility factor criterion described above is applied to the uni- and binodal data sets that we previously reported,[30,31] the number of "highly chemically feasible" frameworks is just 14 for each set. Most of these structures are either dense or have channels outlined by small eight-membered rings, rendering them of little interest as catalysts. Nevertheless, two uninodal structures (1_11 and 1_73) and one binodal (2_103) contain channels outlined by twelve-membered rings. These materials have large accessible volumes and can thus be considered as potential catalysts and sorbents. By contrast, the number of trinodal structures with these properties is surprisingly large. Describing all these in turn would be a tedious exercise in chemical taxonomy. We shall therefore focus on those with wide channels, large cavities, or interesting topological features. A complete list of all crystallographic CIF files is provided as Supporting Information or can be obtained on application to the authors.

Of the total of 1350 hypothetical trinodal structures, 613 could not be optimized, either because in some cases refinement was not possible or because of failure during minimization, usually resulting in loss of the original network topology. The most interesting of the remaining 737 structures are described below.

Figure 1 gives the plot of framework energy relative to α-quartz, E_F, versus the framework density, F_D, for all known zeolites. We see that the values of E_F in silicate zeolites with unbroken frameworks are below 30 kJ mol^{-1} and F_D ranges from 13.4 to 21.4 Si atoms/1000 Å^3. The accessible volume (results not shown) lies in the range of 0−28 Å^3 per Si atom.

Relative framework energies of the hypothetical trinodal frameworks range from 11.25 kJ mol^{-1} (structure 3_918) to as much as 700.01 kJ mol^{-1} (structure 3_126) (Figure 2). The range of F_D is also very wide: from 2.85 (structure 3_36) to 35.451 (structure 3_873). Most will not be chemically realizable. The inset in Figure 2 plots E_F versus the F_D for the hypothetical trinodal structures with energies below 30 kJ mol^{-1} and densities in the range 11 to 21 Si atoms/1000 Å^3.

From the entire data set of hypothetical trinodal structures, only 148 meet the criterion $E_F \leq 30$ kJ/mol. When the feasibility factor is taken into account, this data subset is further reduced to 100 "very chemically feasible" structures (Table 1).

As previously found for the uni- and binodal structures, in the vast majority of chemically feasible trinodals the largest apertures are formed by eight-membered rings. This structural feature is commonly observed among known zeolitic structures with the channels easily accommodating charge-balancing alkaline counter-ions (such as Na$^+$ or K$^+$) and water molecules. The internal surfaces of these structures would therefore be largely inaccessible to substrate molecules useful for heterogeneous catalysis. Moreover, many of the structures have elongated channels with even smaller effective cross-sections or only run along one or two crystallographic directions. Nevertheless, several structures, such as 3_789 (Figure 3), 3_958, and 3_1134 (not shown) contain a three-dimensional (3D) system of intersecting channels outlined by rectangular eight-membered rings. While not expected to appear in aluminosilicates in view of Loewenstein's rule, which forbids aluminum atoms occupying neighboring tetrahedral sites,[60] structures with 3D systems of intersecting channels outlined by nine-membered rings were also found in this subset. These include structures 3_700 (not shown) and 3_699 (Figure 4) in which the nine-ring apertures lead to large internal cavities. Wider channels (e.g., 12-membered) appearing together with the small 8-membered channels give more open structures such as 3_1003 (Figure 5) in which the accessible volume is as much as three times larger than, for example, that in framework 3_789 (Figure 3).

Structures with mixed 8- and 12-membered rings are much more abundant and include 3_818, 3_710, 3_1149, 3_770, 3_772, 3_836, 3_755, and 3_1135. As shown for structure 3_710 (Figure 6), such frameworks contain large accessible channels in only one crystallographic direction, which significantly limits the accessible volume (usually below 20 Å^3/Si atom, Table 1). By increasing the dimensionality of the intersecting channel system to three dimensions, even structures with narrower 10-membered channels are more accessible (e.g., structure 3_558, Figure 7) and therefore better candidates as catalysts.

Just as in known zeolites, chemically feasible hypothetical trinodal frameworks with channels outlined by 12- or more membered rings are much more rare. The most promising for
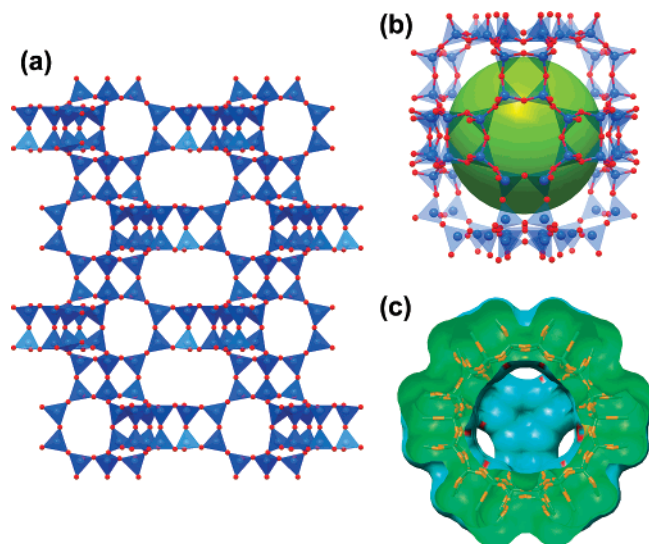
Figure 5. (a) Trinodal framework 3_1003 containing a 3D system of intersecting channels outlined by 8-membered rings and containing 12-membered ring apertures (E_F = 26.73 kJ/mol, F_D = 12.66 Si atoms/1000 Å^3, V_{acc} = 31.27 Å^3/Si atom, and ϑ = 3.35). (b,c) Apertures constitute windows to large $[4^{27}6^28^312^6]$ cages that can accommodate a sphere with radius of ca. 7.0 Å (estimated volume ca. 1493 Å^3).
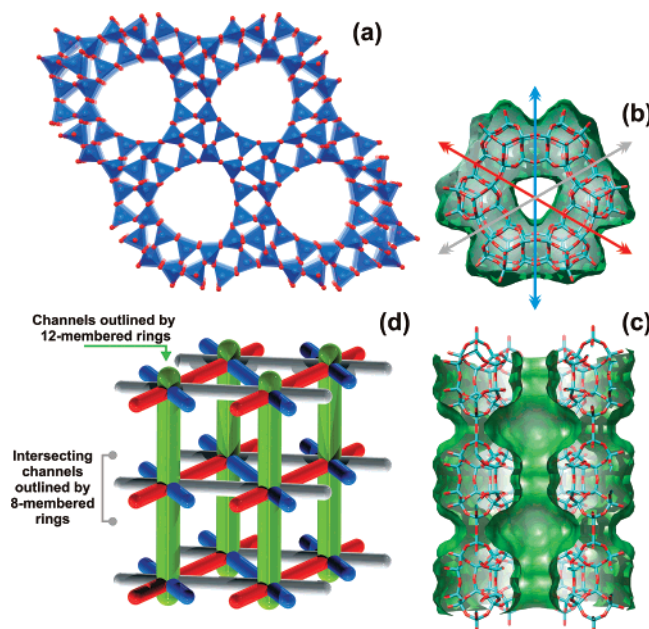

Figure 7. (a) Trinodal framework 3_558 containing a 3D system of intersecting channels outlined by 10-membered ring apertures (E_F = 24.80 kJ/mol, F_D = 13.87 Si atoms/1000 Å^3, V_{acc} = 24.00 Å^3/Si atom, and ϑ = 3.22). (b) Pictogram representing their intersections. (c,d) Apertures also constitute windows to large $[4^{10}6^810^4]$ cages able to accommodate a sphere with radius of ca. 6.4 Å (estimated volume ca. 1088 Å^3).

Figure 6. (a−c) Trinodal framework 3_710 containing a 3D system of intersecting channels outlined by 12- and 8-membered rings (E_F = 19.16 kJ/mol, F_D = 14.84 Si atoms/1000 Å^3, V_{acc} = 21.13 Å^3/Si atom, and ϑ = 0.26). (d) Pictogram representing the intersection of the various channels in the structure.

Figure 8. (a) Trinodal framework 3_715 containing a 3D system of intersecting channels outlined by 12-membered ring apertures (E_F = 20.38 kJ/mol, F_D = 14.54 Si atoms/1000 Å^3, V_{acc} = 22.05 Å^3/Si atom, and ϑ = 0.81). (b) Pictogram representing their intersections. (c,d) Sections of the van der Waals surface (in green) of a portion of the framework showing the intersecting channels (holes surrounding the green surface).

applications in catalysis include frameworks 3_715 (Figure 8) and 3_660 (not shown), which contain a complex 3D system of intersecting channels. This feature significantly increases the openness and accessibility to small molecules (accessible volumes of 22.05 and 43.02 Å^3/Si atom, respectively). As shown in Figure 8c,d, the internal surface area (green contour) is very large, and the presence of a significant number of apertures is bound to facilitate the diffusion of substrate molecules. More common are hypothetical structures with 12-membered channels running along just one crystallographic direction. Striking examples include frameworks 3_1139 (Figure 9) and (not shown) 3_756, 3_681, 3_757, 3_765, and 3_1140. As summarized in Table 1, despite the presence of large channels, the
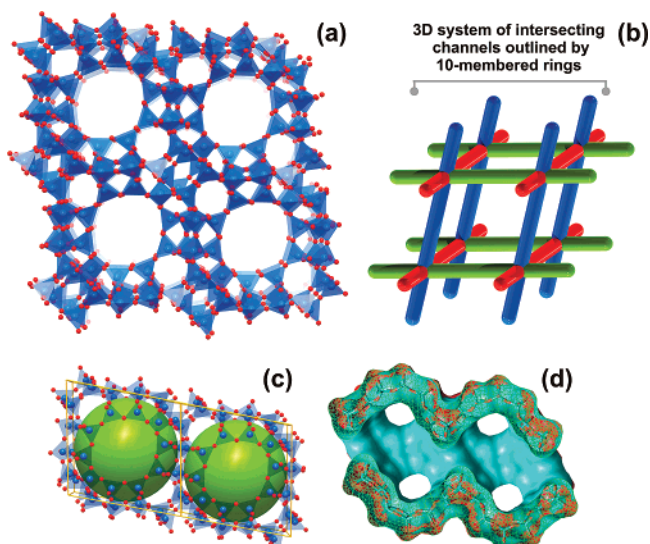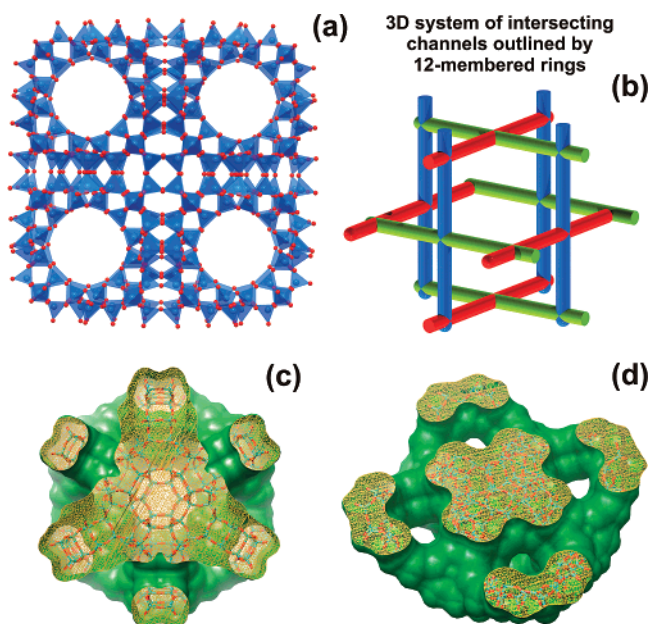
absence of channel crossings significantly reduces the accessibility for small molecules with the accessible volumes comparable to those for structures with mixed 8- and 12-membered rings (see above).

The list of feasible structures contains the remarkable framework 3_971 (Figure 10) with a rather low ϑ (3.08) and "acceptable" E_F (28.26 kJ/mol), which, while superficially similar to framework 3_715, contains channels outlined by 16-membered rings. The larger window size of structure 3_971 is accompanied by a doubling of the accessible volume to 41.07
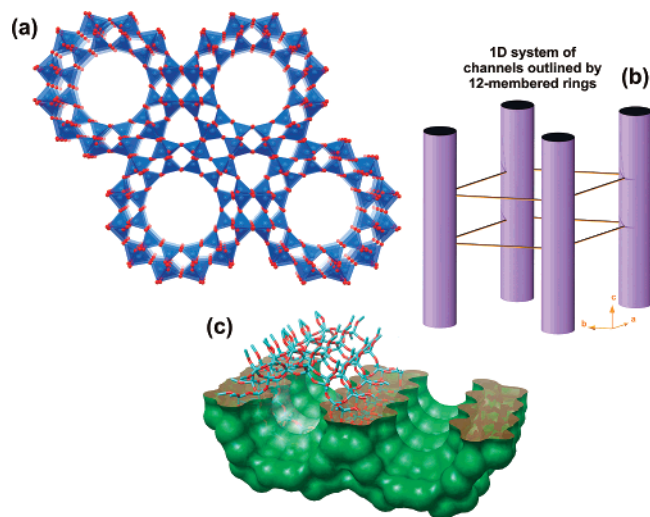
Figure 9. (a,b) Trinodal framework 3_1139 that contains only channels outlined by 12-membered ring apertures running along the [001] direction ($E_F = 17.64$ kJ/mol, $F_D = 16.98$ Si atoms/1000 Å^3, $V_{acc} = 14.37$ Å^3/Si atom, and $\vartheta = 1.34$). (b) Pictogram representing their intersections. (c) Section of the van der Waals surface (in green) showing the internal and accessible surface area of the channels.
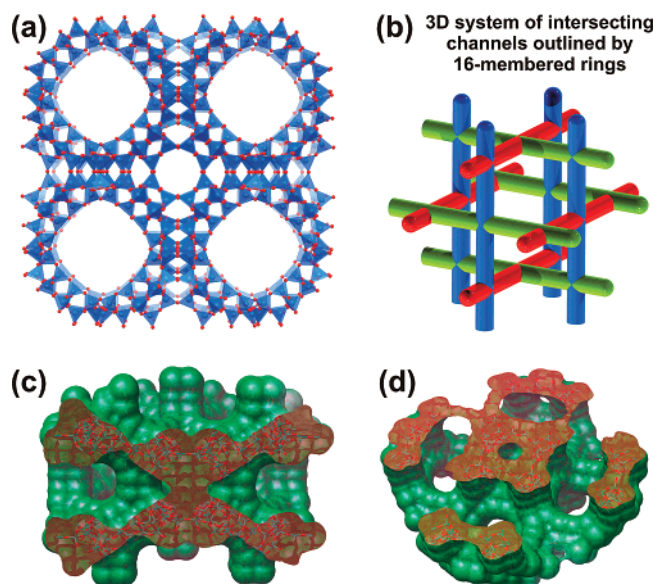

Figure 10. (a) Trinodal framework 3_971 containing a 3D system of intersecting channels outlined by 16-membered ring apertures ($E_F = 28.26$ kJ/mol, $F_D = 11.32$ Si atoms/1000 Å^3, $V_{acc} = 41.07$ Å^3/Si atom, and $\vartheta = 3.08$). (b) Pictogram representing their intersections. (c,d) Sections of the van der Waals surface (in green) of a portion of the framework showing the intersecting channels (holes surrounding the green surface).

Å^3/Si atom and a noticeable increase of the internal surface area compared with structure 3_715 (Figure 10c,d).

Of the structures listed in Table 1, nearly one-fifth are "dense" structures with windows outlined by six-membered rings or smaller, too narrow to allow the diffusion of small organic molecules: 3_914, 3_819, 3_913, 3_925, 3_768, 3_926, 3_1293, 3_904, 3_903, 3_900, 3_898, 3_902, 3_897, 3_899, 3_896, 3_1077, 3_894, 3_1331, and 3_724 (in order of increasing ϑ). However, most of these structures contain internal cavities of various diameters and occupiable volumes. Figure 11 shows three of these structures with internal cavities with sizes ranging from rather small volumes to the astonishingly large, like that in structure 3_819 of ca. 953 Å^3, which clearly contrasts with its small accessible volume of only 2.89 Å^3/Si atom, imposed
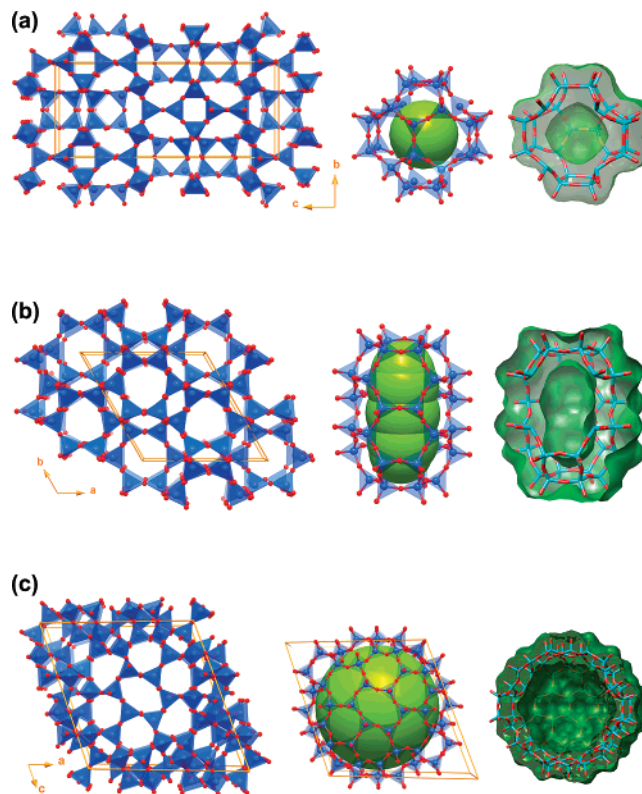

Figure 11. Dense trinodal frameworks (i.e., with apertures composed of six- or fewer membered rings) depicting the internal empty cavities that can accommodate spheres of different radii: (a) 3_914 with [4^{6}5^{4}6^8] cages ($E_F = 13.85$ kJ/mol, $F_D = 18.43$ Si atoms/1000 Å^3, $V_{acc} = 8.25$ Å^3/Si atom, and $\vartheta = 0.16$; sphere radius of ca. 3.4 Å for a total volume of ca. 170 Å^3); (b) 3_899 with [4^{6}6^{14}] cages ($E_F = 13.73$ kJ/mol, $F_D = 17.46$ Si atoms/1000 Å^3, $V_{acc} = 10.61$ Å^3/Si atom, and $\vartheta = 0.89$; sphere radius of ca. 3.9 Å for a total volume of ca. 253 Å^3); (c) 3_819 with [4^{6}6^{40}] cages ($E_F = 17.95$ kJ/mol, $F_D = 15.72$ Si atoms/1000 Å^3, $V_{acc} = 2.89$ Å^3/Si atom, and $\vartheta = 0.29$; sphere radius of ca. 6.1 Å for a total volume of ca. 953 Å^3).

by the highly distorted six-membered rings tiling the surface of the [4^{6}6^{40}] cage (Figure 1c). This feature of structure 3_819 is not unique, and structure 3_724 also contains a large internal inaccessible void that can accommodate a sphere with radius of ca. 6.4 Å (volume ca. 1095 Å^3). However, an important feature distinguishes structures 3_819 and 3_724: in the latter, the surface of the cage is tiled by four-, six- and eight-membered rings, increasing the corresponding accessible volume (12.01 Å^3/Si atom) by a factor of 6.

It is often implied that the rarity of known zeolites with pores circumscribed by more than 14 tetrahedral atoms and/or with framework density lower than 12 tetrahedral atoms per 1000 Å^3 arises from topological or geometric constraints inherent to tetrahedral frameworks. Although more open inorganic materials have been prepared,[7,61,62] they are generally insufficiently stable for catalytic applications or lack a regular pore structure. By examining the recently enumerated hypothetical frameworks[20,21,26,33,63] using computational chemistry methods, one of us has demonstrated[64] that there is no constraint on framework density and pore size in siliceous zeolites. There are thus potentially many very low density or very wide pore materials with thermodynamic stability comparable to already synthesized materials. The use of very large templating molecules, not previously considered because of the perceived topological restrictions on channel and cavity size, will doubtless lead to many interesting new structures.

Potential Heterogeneous Catalysts

J. Phys. Chem. C, Vol. 112, No. 4, 2008 **1047**

Conclusions

While there are only 14 uninodal and 14 binodal hypothetical zeolite structures that are chemically feasible and contain wide channels and/or large internal cavities, as many as 148 trinodal structures with these properties were systematically enumerated. Of these, we consider two, one, and 100 uni-, bi-, and trinodal structures, respectively, as very promising for applications in heterogeneous catalysis and sorption.

Supporting Information Available: A complete list of all crystallographic CIF files is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) van Santen, R. A.; Neurock, M. *Molecular Heterogeneous Catalysis: A Conceptual and Computational Approach*; Wiley-VCH: Weinheim, 2006.

(2) Corma, A.; Diaz-Cabanas, M. J.; Jorda, J. L.; Martinez, C.; Moliner, M. *Nature* **2006**, *443*, 842.

(3) Meisel, S. L.; McCullough, J. P.; Lechthaler, C. H.; Weisz, P. B. *Chemtech* **1976**, *6*, 86.

(4) Anderson, M. W.; Sulikowski, B.; Barrie, P. J.; Klinowski, J. *J. Phys. Chem.* **1990**, *94*, 2730.

(5) Thomas, J. M.; Raja, R. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 13732.

(6) Baerlocher, C.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*, 5th ed.; Elsevier: London, 2001 (updates on http://www.iza-structure.org/).

(7) Davis, M. E. *Nature* **2002**, *417*, 813.

(8) Corma, A. *J. Catal.* **2003**, *216*, 298.

(9) Foster, M. D.; Treacy, M. M. J.; Higgins, J. B.; Rivin, I.; Balkovsky, E.; Randall, K. H., *J. Appl. Crystallogr.* **2005**, *38*, 1028.

(10) Wells, A. F. *Further Studies of Three-Dimensional Nets, American Crystallographic Association Monograph No. 8*; Polycrystal Book Service: Pittsburgh, PA, 1979; Vol. 9.

(11) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, 1984.

(12) Sherman, J. D.; Bennett, J. M. In *Molecular Sieves*; Meier, W. M., Uytterhoeven, J. B., Eds.; American Chemical Society: Washington, DC, 1973; Vol. 121, pp 52−65.

(13) Alberti, A. *Am. Mineral.* **1979**, *64*, 1188.

(14) Sato, M., In *Proceedings of the 6th International Zeolite Conference*, Reno, NV, July 10−15, 1983; Olson, D. H., Bisio, A., Eds.; Butterworths: Guildford, U. K., 1984.

(15) Sato, M. *J. Phys. Chem.* **1987**, *91*, 4675.

(16) Akporiaye, D. E.; Price, G. D. *Zeolites* **1989**, *9*, 23.

(17) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149.

(18) O'Keeffe, M.; Hyde, S. T. *Z. Kristallogr.* **1996**, *211*, 73.

(19) Boisen, M. B.; Gibbs, G. V.; O'Keeffe, M.; Bartelmehs, K. L. *Microporous Mesoporous Mater.* **1999**, *29*, 219.

(20) Treacy, M. M. J.; Randall, K. H.; Rao, S.; Perry, J. A.; Chadi, D. J. *Z. Kristallogr.* **1997**, *212*, 768.

(21) Treacy, M. M. J.; Rivin, I.; Balkovsky, E.; Randall, K. H.; Foster, M. D. *Microporous Mesoporous Mater.* **2004**, *74*, 121.

(22) Treacy, M. M. J.; Foster, M. D.; Randall, K. H. *Microporous Mesoporous Mater.* **2006**, *87*, 255.

(23) Foster, M. D.; Treacy, M. M. J. *Hypothetical Zeolites: Enumeration Research*; 2004. (updates on http://www.hypotheticalzeolites.net/).

(24) Newsam, J. M.; Freeman, C. M.; Leusen, F. J. J. *Curr. Opin. Solid State Mater. Sci.* **1999**, *4*, 515.

(25) Li, Y.; Yu, J. H.; Liu, D. H.; Yan, W. F.; Xu, R. R.; Xu, Y. *Chem. Mat.* **2003**, *15*, 2780.

(26) Delgado Friedrichs, O.; Dress, A. W. M.; Huson, D. H.; Klinowski, J.; Mackay, A. L. *Nature* **1999**, *400*, 644.

(27) Dress, A. W. M.; Huson, D. H.; Molnár, E. *Acta Cryst.* **1993**, *A49*, 806.

(28) Dress, A. W. M. Regular polytopes and equivariant tessellations from a combinatorial point of view. *Springer Lecture Notes In Mathematics* **1985**, *1172*, 56.

(29) Dress, A. W. M. *Adv. Math.* **1987**, *63*, 196.

(30) Foster, M. D.; Delgado Friedrichs, O.; Bell, R. G.; Paz, F. A. A.; Klinowski, J. *J. Am. Chem. Soc.* **2004**, *126*, 9769.

(31) Simperler, A.; Foster, M. D.; Delgado Friedrichs, O.; Bell, R. G.; Paz, F. A. A.; Klinowski, J. *Acta Cryst.* **2005**, *B61*, 263.

(32) Foster, M. D.; Delgado Friedrichs, O.; Bell, R. G.; Paz, F. A. A.; Klinowski, J., *Angew. Chem., Int. Ed.* **2003**, *42*, 3896.

(33) Foster, M. D.; Simperler, A.; Bell, R. G.; Delgado Friedrichs, O.; Paz, F. A. A.; Klinowski, J. *Nat. Mater.* **2004**, *3*, 234.

(34) Delgado Friedrichs, O. *Discrete Comput. Geom.* **2001**, *26*, 549.

(35) Zheng, N. F.; Bu, X. G.; Wang, B.; Feng, P. Y. *Science* **2002**, *298*, 2366.

(36) Simperler, A.; Foster, M. D.; Bell, R. G.; Klinowski, J. *J. Phys. Chem.* **2004**, *B108*, 869.

(37) Correll, S.; Oeckler, O.; Stock, N.; Schnick, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 3549.

(38) Dollase, W. A.; Ross, C. R. *Am. Mineral* **1993**, *78*, 627.

(39) Blackwell, C. S.; Broach, R. W.; Gatter, M. G.; Holmgren, J. S.; Jan, D. Y.; Lewis, G. J.; Mezza, B. J.; Mezza, T. M.; Miller, M. A.; Moscoso, J. G.; Patton, R. L.; Rohde, L. M.; Schoonover, M. W.; Sinkler, W.; Wilson, B. A.; Wilson, S. T. *Angew. Chem., Int. Ed.* **2003**, *42*, 1737.

(40) Thomas, J. M.; Raja, R.; Sankar, G.; Bell, R. G. *Nature* **1999**, *398*, 227.

(41) Meier, W. M.; Villiger, H. *Z. Kristallogr.* **1969**, *128*, 352.

(42) Sanders, M. J.; Leslie, M.; Catlow, C. R. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1271.

(43) Schröder, K. P.; Sauer, J.; Leslie, M.; Catlow, C. R. A.; Thomas, J. M. *Chem. Phys. Lett.* **1992**, *188*, 320.

(44) Sastre, G.; Gale, J. D. *Microporous Mesoporous Mater.* **2001**, *43*, 27.

(45) Bialek, R. KRIBER, version 1.1.; Institut für Kristallographie und Petrographie; ETH: Zürich, Switzerland, 1995.

(46) Piccione, P. M.; Woodfield, B. F.; Boerio-Goates, J.; Navrotsky, A.; Davis, M. E. *J. Phys. Chem.* **2001**, *B105*, 6025.

(47) Moloy, E. C.; Davila, L. P.; Shackelford, J. F.; Navrotsky, A. *Microporous Mesoporous Mater.* **2002**, *54*, 1.

(48) Piccione, P. M.; Yang, S. Y.; Navrotsky, A.; Davis, M. E. *J. Phys. Chem.* **2002**, *B106*, 3629.

(49) Cerius², version. 4.0; Molecular Simulations Inc.: San Diego, CA, 1999.

(50) Brandenburg, K. *DIAMOND*, Version 3.1d; Crystal Impact GbR: Bonn, Germany, 2006.

(51) Pennington, W. T. *DIAMOND* - Visual crystal structure information system. *J. Appl. Crystallogr.* **1999**, *32*, 1028.

(52) Macrae, C. F.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Shields, G. P.; Taylor, R.; Towler, M.; van De Streek, J. *J. Appl. Crystallogr.* **2006**, *39*, 453.

(53) UCSF Chimera package. The Resource for Biocomputing, Visualization and Informatics at the University of California, San Francisco.

(54) Pettersen, E. F.; Goddard, T. D.; Huang, C. C.; Couch, G. S.; Greenblatt, D. M.; Meng, E. C.; Ferrin, T. E. *J. Comput. Chem.* **2004**, *25*, 1605.

(55) Cason, C. J. *POV-RAY for Windows*, Version 3.5; 2002.

(56) Sanner, M. F.; Olson, A. J.; Spehner, J. C. *Biopolymers* **1996**, *38*, 305.

(57) Barbour, M. L. *MCAVITY:* Program for calculating the molecular volume of closed capsules; University of Missouri-Columbia: Columbia, MO, 2003.

(58) Connolly, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1118.

(59) Henson, N. J.; Cheetham, A. K.; Gale, J. D. *Chem. Mater.* **1994**, *6*, 1647.

(60) Loewenstein, W. *Am. Mineral.* **1954**, *39*, 92.

(61) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed.* **1999**, *38*, 3268.

(62) Eddaoudi, M.; Moler, D. B.; Li, H. L.; Chen, B. L.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319.

(63) Earl, D. J.; Deem, M. W. *Ind. Eng. Chem. Res.* **2006**, *45*, 5449.

(64) Zwijnenburg, M. A.; Bell, R. G. submitted for publication, 2007.