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Design of Chiral Zeolite Frameworks with Specified Channels through Constrained Assembly of Atoms

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A computational method for the design of chiral zeolite frameworks has been developed through constrained assembly of atoms around a specified channel-like forbidden zone. The forbidden zone, corresponding to a channel pattern, is first defined in a unit cell under a chiral space group, and then, atoms are placed outside of the forbidden zone on the basis of specified symmetries and distance constraints. In employing such a method, a diverse range of hypothetical chiral zeolite frameworks has been generated through the enumeration of combinations of different channel sizes, different numbers of unique T atoms, and different unit cell parameters. The framework energies of these generated hypothetical structures are calculated by using a molecular mechanics method, as compared with those of the 161 known zeolite frameworks. The framework densities and the coordination sequences are also calculated for both the hypothetical structures and the known ones. These calculation results reveal that there exists not only the correlation between the framework energy and the framework density but also the correlation between the framework energy and the fourth shell of coordination sequences. On the basis of these correlations, feasible hypothetical zeolite frameworks could be predicted. This method provides a fast search of feasible chiral zeolite frameworks with desired channel geometries and will be an aid for a synthetically oriented chemist.

Introduction

Zeolites constructed from TO_4 tetrahedra forming unique pore architectures are an important class of materials in the field of materials science. They have been widely applied in the fields of catalysis, adsorption, separation, host−guest assemblies, and advanced functional materials. During the past decades, a variety of zeolites with novel framework structures has been prepared. However, there have been few reports on the synthesis of chiral zeolite frameworks. Chiral microporous materials are of particular interest because of their potential applications in heterogeneous catalysis and enantioselective separations.[1,2] However, the preparation of such materials has been proven to be very difficult. Up to now, to our knowledge, there are only a few chiral structures reported among all four-connected frameworks, including the chiral polymorph of zeolite β (BEA),[3] $NaZnPO_4 \cdot H_2O$ (CZP),[4] goosecreekite (GOO),[5] $KBGe_2O_6$ (FJ-9),[6] OSB-1 (OSO),[7] and UCSB-7.[8] The design and synthesis of chiral zeolite frameworks are a great challenge.

The design of zeolite frameworks with desired chiral geometries is a prerequisite for the rational synthesis of such materials. Although several approaches have been developed for the design of zeolite frameworks,[9−20] few methods were concerned with the design of chiral zeolite frameworks;[1,21] in particular, there was no report on the design of chiral zeolite frameworks with defined pore geometries. Recently, our group has developed a simple and efficient computational method for the generation and enumeration of zeolite frameworks with specified pore geometries through introducing forbidden zones in the simulation input.[18,19] The applica-

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(1) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756−768.
(2) Davis, M. E. *Nature* **2002**, 417 (*20*), 813−821.
(3) Higgins, J. B.; LaPierre, R. B.; Schlenker, J. L.; Rohrman, A. C.; Wood, J. D.; Kerr, G. T.; Rohrbaugh, W. J. *Zeolites* **1988**, *8*, 446−452.
(4) Rajic, N.; Logar, N. Z.; Kaucic, V. *Zeolites* **1995**, *15*, 672−678.
(5) Rouse, R. C.; Peacor, D. R. *Am. Mineral.* **1986**, *71*, 1494−1501.
(6) Lin, Z.; Zhang, J.; Yang, G. *Inorg. Chem.* **2003**, *42*, 1797−1799.
(7) Cheetham, A. K.; Fjellvåg, H.; Gier, T. E.; Kongshaug, K. O.; Lillerud, K. P.; Stucky, G. D. *Stud. Surf. Sci. Catal.* **2001**, *135*, 158.
(8) Gier, T. E.; Bu, X.; Feng, P.; Stucky, G. D. *Nature* **1998**, *395*, 154.
(9) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149. Jacobs, P. A., Ed.; *Zeolites: Facts, Figures, Future*; van Santen, Elsevier Science Publishers B. V.: Amsterdam, 1989; p 29.
(10) Maddox, J. *Nature* **1988**, *335*, 201. Cohen, M. L. *Nature* **1989**, *338*, 291. Hawthorne, F. C. *Nature* **1990**, *345*, 297. Catlow, C. R. A.; Price, G. D. *Nature* **1990**, *347*, 243.
(11) Deem, M. W.; Newsam, J. *Nature* **1989**, *342*, 260.
(12) Akporiaye, D. E.; Price, G. D. *Zeolites* **1989**, *9*, 23.
(13) Catlow, C. R. A.; Price, G. D. *Nature* **1990**, *347*, 243.
(14) Boisen, M. B.; Gibbs, G. V.; O'Keeffe, M.; Bartelmehs, K. L. *Microporous Mesoporous Mater.* **1999**, *29*, 219.
(15) Friedrichs, O. D.; Dress, A. W. M.; Huson, D. H.; Klinowski, J. *Nature* **1999**, *440*, 644.
(16) Zhou, B.; Yu, J.; Li, J.; Xu, Y.; Xu, W.; Qiu, S.; Xu R. *Chem. Mater.* **1999**, *11*, 1094. Zhou, B.; Li, J.; Yu, J.; Xu, Y.; Xu, W.; Qiu, S.; Xu, R. *Comput. Chem.* **1999**, *23*, 555−563.
(17) Draznieks, C. M.; Newsam, J. M.; Gorman, A. M.; Freeman, C. M.; Férey, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 2270.
(18) Li, Y.; Yu, J.; Liu, D.; Yan, W.; Xu, R.; Xu, Y. *Chem. Mater.* **2003**, *15*, 2780−2785.
(19) Li, Y.; Guo, M.; Yu, J.; Li, J.; Xu, R. *Stud. Surf. Sci. Catal.* **2004**, *154*, 308−316.
(20) Woodley, S. M.; Battle, P. D.; Gale, J. D.; Catlow, C. R. A. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1815−1822. Woodley, S. M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 1823−1829.
(21) Akporiaye, D. E. *J. Chem. Soc., Chem. Commun.* **1994**, 1711−1712.

10.1021/cm050536p CCC: $30.25

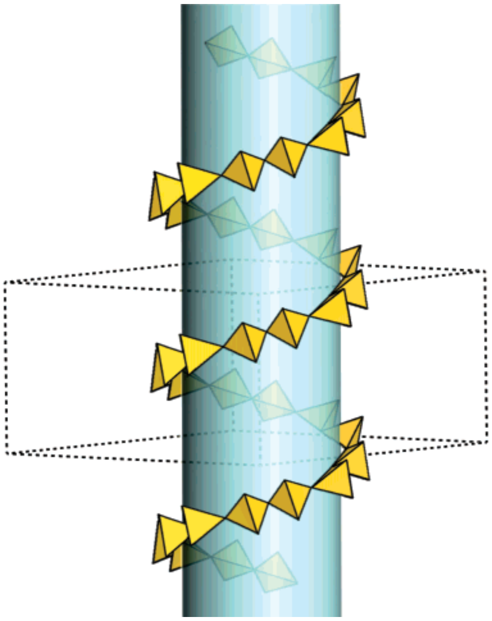

Figure 1. Generation of the chiral channel in the space group $P6_122$. The yellow polyhedra represent TO_4 tetrahedra, and the green cylinder represents the predefined forbidden zone. Assembly of TO_4 tetrahedra outside the forbidden zone by the 6_1 operation generates a chiral channel.

tion of the concept of forbidden zones or exclusion zones[20] in the unit cell under a specified space group renders this method faster and much more straightforward on generating zeolite frameworks with desired pore geometries as compared to previous simulation methods.[9−17] The forbidden zone is an area in a unit cell inside which no atoms can be placed during the generation process of a zeolite framework. Placement of atoms into a unit cell is carried out through placing unique atoms randomly outside of the forbidden zones and then through the application of symmetry operations and distance constraints. In this work, this methodology has been further applied to the generation of chiral zeolite frameworks through the assembly of atoms under chiral space groups. Energy calculations are performed for both the generated hypothetical frameworks and the 161 known zeolite frameworks.[22] According to the variations of the framework energies with the framework densities and coordination sequences (CSQs),[23] a range of feasible hypothetical frameworks could be predicted. This method will be of considerable interest for a synthetically oriented chemist whose target is to synthesize materials with desired pore structures based on functional requirements.

Computational Methodology

The details of this method for the generation of zeolite frameworks with defined pore geometries have been described before.[18,19] Herein, some key steps of this procedure will be mentioned. As illustrated in Figure 1, the channel structure represented as a vertical cylinder, called a forbidden zone, was first defined in a unit cell, and then T atoms were placed outside of the forbidden zone based on specified symmetries and distance constraints. Two constraint conditions must be satisfied when placing the T atoms: (i) no atom was allowed inside a forbidden zone, and (ii) the distance between any two T atoms was no less than 3.0 Å, assuming a Si−Si distance. After all the T atoms were introduced in the unit cell, bridging oxygen atoms were added automatically between neighboring T atom pairs using the Cerius^2 software package.[24] Chiral zeolite frameworks could be obtained under chiral space groups, in which only rotation and screw symmetries were considered. For example, assuming a hexagonal space group $P6_122$ (no. 178), and defining a forbidden zone (channel) along the 6_1 screw axis in the unit cell, as shown in Figure 1, the TO_4 tetrahedra would form a helical chain by the 6_1 operation and further convolve around the forbidden zone to form a chiral channel. The program code was written in Fortran90 in this work.

Structure models were built up using the Cerius^2 software package followed by geometry optimization using the Burchart 1.01 force field assuming SiO_2 compositions.[25] Repetitious framework types were identified by coordination sequences (CSQs)[23] and further removed. The energy of each refined framework was calculated, together with its framework density and mean coordination sequences. The framework density (FD) was defined as the number of T atoms per 1000 Å^3. For a framework with N unique T atoms, the weighted mean coordination sequence[26] of the kth shell was defined and calculated as follows:

$$\text{mean CSQ}_k = \left(\sum_{n=1}^{N} m_n \text{CSQ}_{kn}\right) / \left(\sum_{n=1}^{N} m_n\right)$$

where m_n stands for the number of equivalent sites (i.e., site multiplicity) for the nth unique T atom, and CSQ_{kn} is the coordination sequence of the kth shell for the nth unique T atom. To aid in the analysis of framework topologies with three-membered-rings (3MRs), another parameter (i.e., 3MR-density) was first defined as the quotient obtained by dividing the number of 3MRs in one unit cell by the number of T atoms in the unit cell. According to this definition, the 3MR density of a specified framework structure should vary in the range of 0 (no 3MR exists in the structure) to 2 (every vertex is shared by six 3MRs).

Results and Discussion

Design of chiral zeolite frameworks in the space group $P6_122$. Among the 161 zeotype frameworks collected in the IZA online database,[22] only four are chiral, including BEA ($P4_122$), CZP ($P6_122$), GOO ($C222_1$), and OSO ($P6_222$). Here, we choose the hexagonal space group $P6_122$ (no. 178) as an example for the simulation to illustrate the efficacy of this method on generating frameworks with chiral channels. During the simulation, the forbidden zones are defined as a cylinder running along the 6_1 screw axis (i.e., the [0 0 1] direction), and the cell parameters vary from 5 to 25 Å. The cylinder radii are defined at 3.0, 4.0, 5.0, and 6.0 Å, respectively. The numbers of unique T atoms range from 1 to 5. Under these conditions, a variety of hypothetical structures with chiral channels are successfully generated. The symmetry of each structure is rechecked after geometry optimization to confirm its chirality. Very few structures with

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(22) Baerlocher, Ch.; McCusker, L. B. *Database of Zeolite Structures*; http://www.iza-structures.org/databases/.

(23) Meier, W. M.; Moeck, H. J. *J. Solid State Chem.* **1979**, *27*, 349. O'Keeffe, M.; Hyde, S. T. *Zeolites* **1997**, *19*, 370.

(24) Cerius^2 4.6; Accelrys Software Inc.: 2001.

(25) de Vos Burchart, E. Studies on Zeolites; Molecular Mechanics, Framework Stability, and Crystal Growth. Ph.D. Thesis, Technische Universiteit Delft, 1992. de Vos Burchart, E.; van Bekkum, H.; van de Graaf, B.; Vogt, E. T. C. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2761.

(26) Akporiaye, D. E.; Price, G. D. *Zeolites* **1989**, *9*, 321.

Table 1. Framework Energies, Framework Densities, Fourth Shell Coordination Sequences (CSQ4), and 3MR Densities of the Hypothetical Structures

code	energy/*T* (kcal/ mol)	FD	CSQ4	3MR density
H178-1	−425.696	8.33	18	1
H178-2	−425.617	9.72	18	1
H178-5	−430.817	15.72	27	0.5
H178-7	−424.888	10.39	17	N/A
H178-22	−434.122	15.82	24.67	0.333
H178-41	−431.312	17.77	32.25	0.25
H178-54	−434.962	16.9	36	0.25
H178-67	−432.370	16.5	30	N/A
H180-1	−425.628	10.88	18	1

Table 2. Refined Space Groups, Unit Cell Parameters, and Numbers of Unique T Atoms of Hypothetical Structures

code	space group	cell parameters (Å)	no. of unique T atoms
H178-1	$P6_122$	$a = 15.1069$, $c = 14.5750$	2
H178-2	$P6_122$	$a = 16.5928$, $c = 10.3524$	2
H178-5	$P6_122$	$a = 13.1873$, $c = 10.1401$	2
H178-7	$P6_122$	$a = 14.4285$, $c = 25.6303$	4
H178-22	$P6_122$	$a = 13.0392$, $c = 15.4589$	3
H178-41	$P6_122$	$a = 15.5040$, $c = 12.9772$	4
H178-54	$P6_122$	$a = 17.3122$, $c = 10.9336$	4
H178-67	$P6_122$	$a = 12.9133$, $c = 5.0315$	1
H180-1	$P6_222$	$a = 10.4985$, $c = 11.5509$	1

acquired mirror planes, glide planes, or rotatory-inversion axes are removed.

Energy calculation has been proven to be a powerful tool to predict the feasibility of hypothetical structures.[27,28] The energies of the hypothetical structures are calculated after geometry optimization, as compared with those of the 161 known frameworks. The energy of each framework is divided by the number of T atoms assuming a SiO_2 composition. Among the 161 known structures, RWY has the highest framework energy, ca. −425.62 kcal/(mol T). Among all the generated hypothetical structures, only those ones will be kept whose energies are below −425.62 kcal/(mol T) or very close to it. Finally, 73 hypothetical structures generated under $P6_122$, including four transformed into $P6_222$ after refinement, are chosen for further discussion. Furthermore, the framework densities (FDs) and the coordination sequences of these frameworks are calculated. The energies and FDs of parts of these hypothetical frameworks are listed in Table 1, and their refined space groups and unit cells are listed in Table 2. Tables of the data for all 73 hypothetical structures, together with their atomic coordinates and coordination sequences, are available as Supporting Information.

H178-1 is generated in the space group $P6_122$, assuming a forbidden zone with a cylinder radius of 5.0 Å at the origin of a unit cell. Figure 2a shows its chiral channel, and parts of the T atoms are omitted for clarity. The basic building block of H178-1 is a T2 supertetrahedron (Figure 2b), which has been proposed to be in the family of sulfides by O'Keeffe and Yaghi et al.,[29] and the first reported example in the family of zeolites is RWY.[30] Five such supertetrahedra form a super-5MR (five-membered ring, Figure 2c), and the linkages of super-5MRs further form a chiral channel through sharing edges. Figure 2d,e shows its framework viewed along the [001] and [010] direction, respectively. Interestingly, the supertetrahedra building blocks could also be found in H178-2, H178-7, and H180-1 (Figure 3). H178-2 contains chiral channels constructed by supertetrahedra similar to those in H178-1 (Figure 2a). The difference between H178-1 and H178-2 lies in that, in H178-1, only a right-handed chiral channel runs through (0,0,0), while in H178-2, in addition to the right-handed chiral channel originated at (0,0,0), another left-handed chiral channel originated at (1/3,1/3,0) also exists (Figure 3a). In H178-7, four supertetrahedra form a super-4MR (four-membered ring), and the super-4MRs connect with each other through sharing edges to form a super edge-sharing chain (ESC). This super edge-sharing chain convolves around the 6_1 screw axis forming a chiral

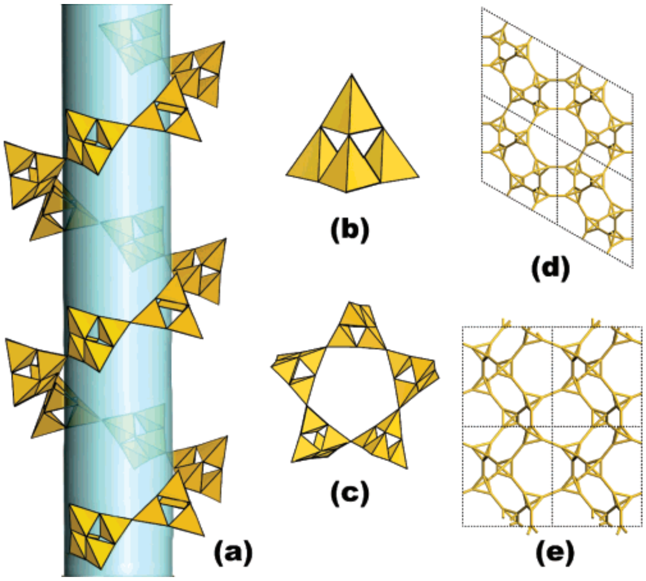

Figure 2. (a) Chiral channel of the hypothetical framework H178-1 (cylinder diameter of 9.5 Å), (b) supertetrahedron T2 building block, (c) super-5MR constructed by T2 building blocks, and the framework viewed along (d) the [001] direction and (e) the [010] direction.

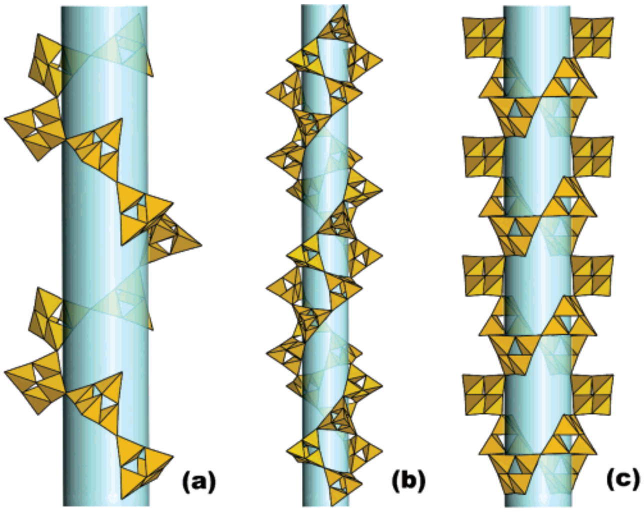

Figure 3. (a) Left-handed chiral channel in the hypothetical framework H178-2 (cylinder diameter of 8.4 Å), (b) chiral channel formed by super ESC in the hypothetical framework H178-7 (cylinder diameter of 5.2 Å), and (c) the chiral channel formed by double helical chains in the hypothetical framework H180-1 (cylinder diameter of 6.9 Å).

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(27) Simperler, A.; Foster, M. D.; Bell, R. G.; Klinowski, J. *J. Phys. Chem. B* **2004**, *108*, 869−879.

(28) Foster, M. D.; Simperler, A.; Bell, R. G.; Friedrichs, O. D.; Almeida Paz, F. A.; Klinowski, J. *Nat. Mater.* **2004**, *3*, 234−238.

(29) Li, H.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145−1147.

(30) Zheng, N.; Bu, X.; Wang, B.; Feng, P. *Science* **2002**, *298*, 2366−2369.

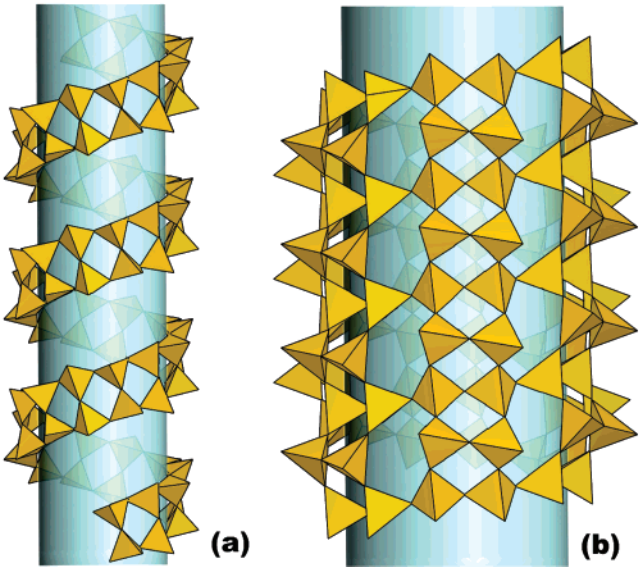

Figure 4. (a) Chiral channel formed by helical edge sharing chain in the hypothetical framework H178-5 (cylinder diameter of 9.4 Å) and (b) the chiral channel formed by parallel ESCs in the hypothetical framework H178-67 (cylinder diameter of 9.9 Å).

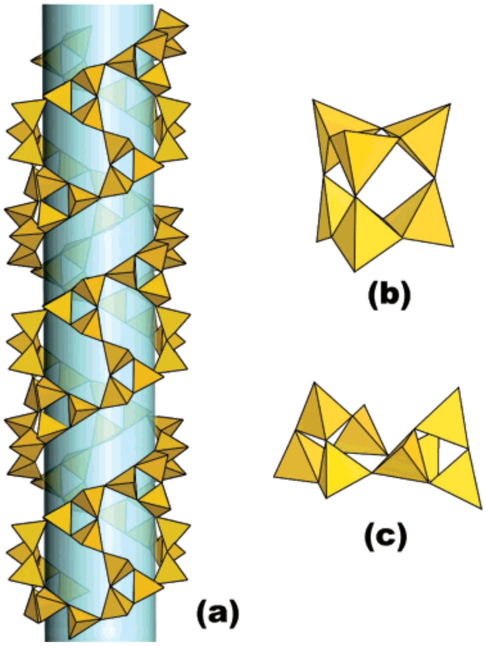

Figure 5. (a) Chiral channel formed by the $3^2 8^1$ net found in both framework H178-22 and framework H178-41 (cylinder diameter of 9.5 and 9.2 Å, respectively), (b) the D3R building block in H178-22, and (c) the $3^4 6^2$ building block in H178-41.

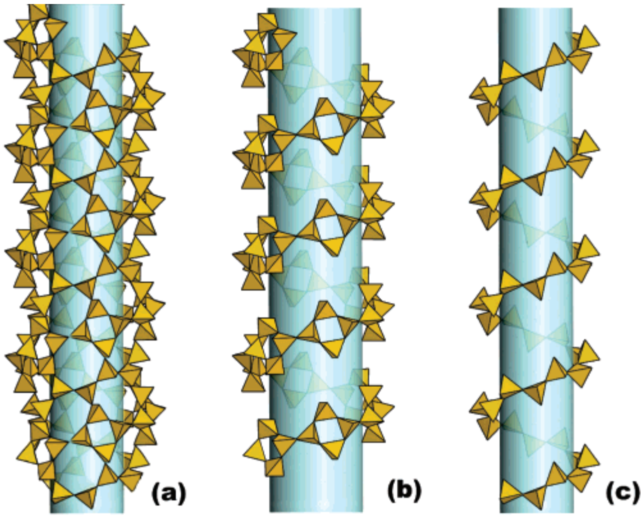

Figure 6. (a) Chiral channel formed by the $4^1 7^2$ net in the hypothetical framework H178-54 (cylinder diameter of 4.8 Å), together with (b) its outer part (cylinder diameter of 6.9 Å), and (c) its inner part (cylinder diameter of 4.8 Å).

channel (Figure 3b). H180-1 is first generated in space group $P6_122$ but transforms into space group $P6_222$ after refinement. The supertetrahedra in this framework form a corner-sharing right-handed helical chain, and two such right-handed helical chains construct a channel enclosed by a double-helix (Figure 3c). It should also be noted that the related structures constructed by replacement of the supertetrahedra T2 with single tetrahedra T1 could also be generated using our method. For example, H178-27 could be viewed as replacing all the supertetrahedra with single tetrahedra in H178-1. Interestingly, such correlativity could also be found between H180-1 and quartz.

H178-5 and H178-67 are another two frameworks generated in the space group $P6_122$. There are two independent T atoms in H178-5 and one in H178-67. The two independent T atoms and their equivalent ones in H178-5 construct a 4MR edge-sharing chain (ESC), which convolves into a right-handed helix (Figure 4a). This helical chain is similar to the helical-ribbon found in UCSB-7.[8] Helical chains running along the *c* axis in H178-5 are connected with each other through bridging oxygen atoms. In H178-67, equivalent T atoms also construct a 4MR edge-sharing chain, and six edge-sharing chains parallel to the *c* axis are connected with each other through bridging oxygen atoms to form a large chiral channel (with aperture dimensions of 9.9 Å × 9.9 Å, Figure 4b). Parallel channels link to each other through sharing the edge-sharing chains and further form the whole framework.

H178-22 and H178-41 are both generated in a unit cell with $a = c = 15$ Å. There are three independent T atoms in H178-22 and four in H178-41. In H178-22, the three independent T atoms form a 3MR. This 3MR and its crystallographic equivalents form a belt with a $3^2 8^1$ net. The $3^2 8^1$ net convolves along the *c*-axis to form a right-handed chiral channel (Figure 5a). The channels are connected with each other through double 3MRs (D3Rs, Figure 5b), which are formed by the linkages between 3MRs on the $3^2 8^1$ net and those on the adjacent channels. As with the channels in H178-22, the channels in H178-41 are also constructed by the helical $3^2 8^1$ nets (Figure 5a), but the linkages between the parallel channels in these two frameworks are different. In H178-41, four independent T atoms and their four equivalents construct a $3^4 6^2$ building block (Figure 5c), through which the channels are connected with each other and further form the H178-41 framework.

H178-54 is constructed by four independent T atoms. Its channel in the framework is shown in Figure 6a. This channel could be regarded as a tube convolved by the $4^1 7^2$ net. However, viewed from the helical axis, one can find that the channel could also be regarded as the conjunction of two concentric parts: one is a chiral channel formed by 4MRs, which stands for the outer circle (Figure 6b); the other is a chiral channel formed by single tetrahedral chain, which

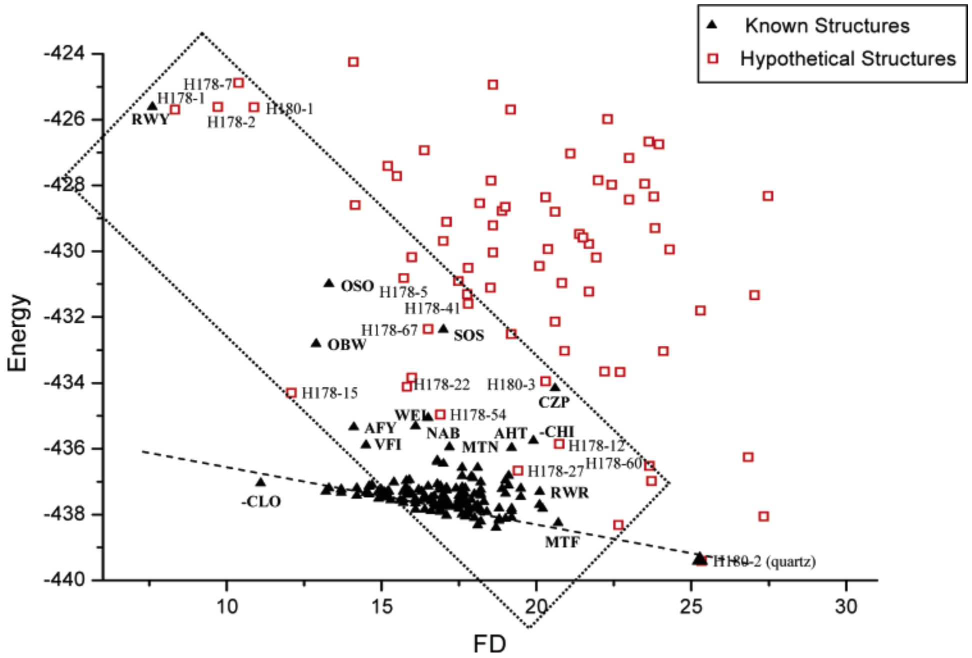

Figure 7. Framework energy vs framework density. Black triangles denote the data for the 161 known frameworks, and red squares denote the data for hypothetical structures obtained under space group $P6_122$.

stands for the inner circle (Figure 6c). Both of these two chains are right-handed.

Correlation between the Framework Energy and the Framework Density. Figure 7 shows the plot of the framework energy versus the framework density. The black triangles represent the data for the 161 known structures, while the red squares represent the data for hypothetical structures. For most of the known frameworks, a linear correlation between the framework energy and the framework density could be easily found, as illustrated by the dashed line in Figure 7. The larger the framework density is, the lower the framework energy would be. This trend obtained from our calculations using a Burchart force field is consistent with the previously reported results calculated using core−shell models.[27,28,31,32] However, it should also be noted that the energies of some of the known structures, such as RWY, OSO, OBW, SOS, OBW, CZP, WEI, -CHI, AFY, etc., are a little higher than those of the normal silicate frameworks. This is because all the framework energies are calculated assuming a pure SiO_2 composition. In fact, however, the type materials of these frameworks are with non-SiO_2 compositions. The bond distances and bond angles in their peculiar building units differ largely from the standard Si−O bond geometries. For example, T_3O_3 3MRs could be found in many non-SiO_2 zeolite structures, such as beryllium silicates (LOV, NAB, OBW, and OSO) and zinc silicates (RSN, VNI, and VSV),[22] etc. To our knowledge, there is no zeotype structure consisting of 3MRs with a pure SiO_2 composition found thus far. One possible reason is that the T−O−T angle in 3MR (ca. 120−130°) is smaller than the Si−O−Si angle in a normal SiO_2 zeolite framework (ca. 140−150°). This geometric deviation will no doubt increase the framework energy since the molecular mechanics calculates the deviation from the standard geometry as the energy. Figure 8 shows the plot of framework energy versus the number of 3MRs per T atom (3MR density) in the framework. For both of the known structures and hypothetical ones, an interesting linear correlation could be found. It is easy to deduce that more 3MRs will result in more geometric deviations of the framework and the higher framework energy. Such a non-SiO_2 geometry is one of the most important reasons that increases the framework energy assuming a SiO_2 composition. That is to say, a framework with a non-SiO_2 geometry is hard to be synthesized using Si and O as framework elements. Introduction of other elements, such as B, Be, Zn, Ge, and S, etc., might lower the energy of the framework with a non-SiO_2 geometry and make the framework possible to be synthesized. As illustrated by the dotted rectangle in Figure 7, for those known non-SiO_2 structures, the correlation between the framework energy and the framework density still exists, but in a slightly discrete way. It should be noted that there are also some hypothetical structures in this area, such as H178-1, H178-2, H178-5, H178-12, H178-15, H178-27, and H178-54, etc., which obey the linear correlation between the framework energy and the framework density for zeotype structures.

Correlation between Framework Energy and CSQ4. Regarding the relation with the framework density, the framework energy has a similar correlation with the coordination sequences, especially for the fourth shell (CSQ4).[26,33] Figure 9 shows the variation of the framework energy with the fourth shell of the coordination sequences. For most of the known structures, more linear correlations could be found, as illustrated by the dashed line in Figure 9. As its variation with the framework density, the framework energy varies

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(31) Henson, N. J.; Cheetham, A. K.; Gale, J. D. *Chem. Mater.* **1994**, *6*, 1647−1650.

(32) Henson, N. J.; Cheetham, A. K.; Gale, J. D. *Chem. Mater.* **1996**, *8*, 664−670.

(33) Price, G. D.; Wood, I. G.; Akporiaye, D. E. *Modeling of structure and reactivity in zeolites*; Catlow, C. R. A., Ed.; Academic Press: London, 1992; pp 19−42.

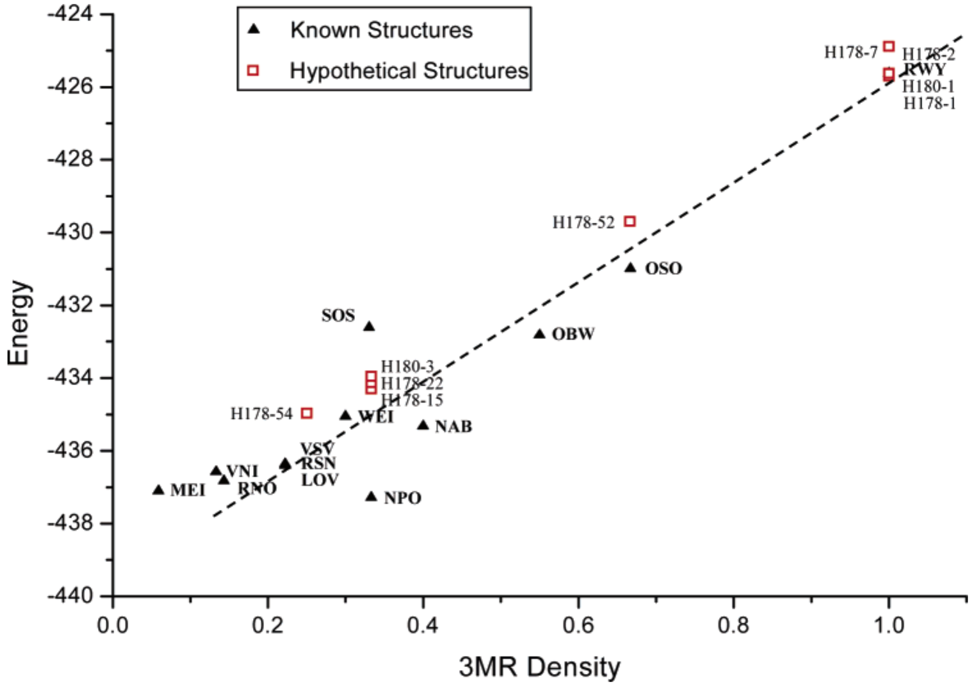

Figure 8. Framework energy vs the density of 3MRs in the framework. Black triangles denote the data for the 161 known frameworks, and red squares denote the data for hypothetical structures obtained under space group $P6_122$.

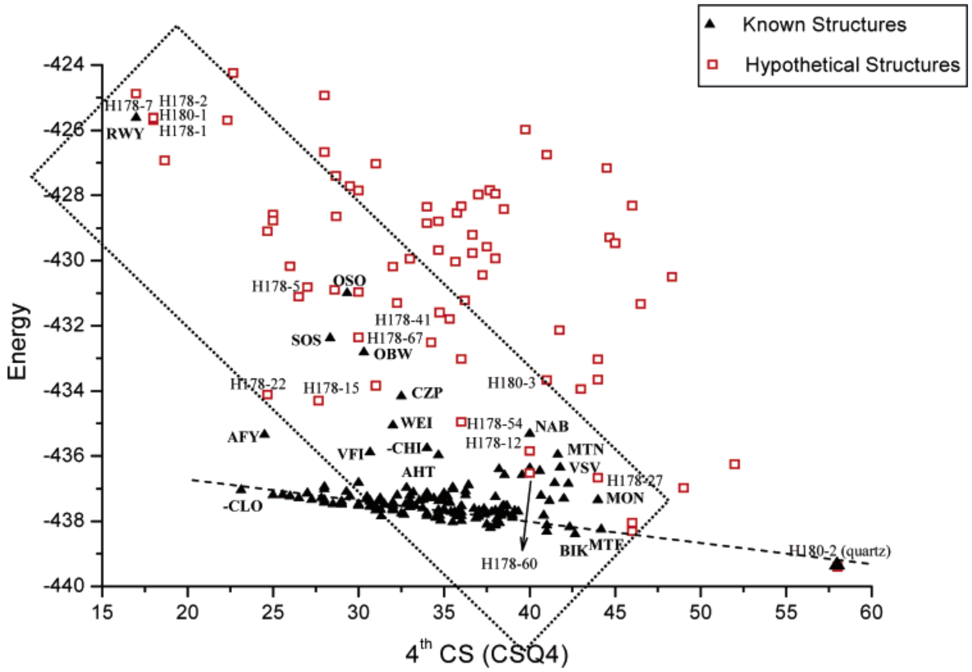

Figure 9. Framework energy vs the mean fourth shell of the coordination sequence (CSQ4). Black triangles denote the data for the 161 known frameworks, and red squares denote the data for hypothetical structures obtained under space group $P6_122$.

in a more discrete way with CSQ4 for those non-SiO_2 structures, which is illustrated by the dotted rectangle in Figure 9. As shown in Figure 7, there are also some hypothetical frameworks in this area, such as H178-1, H180-1, H178-5, H178-12, H178-15, H178-22, H178-27, H178-54, and H178-60, etc., which obey the correlation between framework energy and CSQ4 for zeotype structures. The hypothetical frameworks within the rectangle areas in both Figures 7 and 9 could be selected as the feasible candidates for the purpose of synthesis.

Rational Synthesis of Chiral Zeolite Structures. We have shown the design of zeolite frameworks with chiral pore geometries under chiral space group $P6_122$. Applications on the other chiral space groups, such as $P6_222$ and $P4_122$, etc. are also proven to be successful. The main focus of our current and future research is the synthesis of desired zeolite frameworks with predetermined pore geometries based on functional requirements. Chiral zeolite frameworks can be designed on purpose using our method. Then, the key issue is how to rationalize the syntheses of desired target structures. According to our calculation results, most four-connected frameworks with chiral channels are not energetically favorable for SiO_2 compositions because of the special geometric torsions in such structures. However, introducing other T atom elements, such as beryllium, boron, germanium, and arsenic, etc., instead of silicon, and other bridging atom elements, such as sulfur, instead of oxygen, might stabilize such frameworks more effectively; this is because they could offer more reasonable bond distances and bond angles than SiO_2 compositions. Two successful examples for such an approach are the preparations of FJ-9 (borogermanate)[6] and UCSB-7 (zinc and beryllium arsenates and gallium germanate).[8] In addition to choosing favorable framework elements, choosing appropriate structure-directing agents (SDAs) is another feasible approach for the synthesis of desired target structures. It is believed that the host−guest interactions between the inorganic frameworks and the SDAs play an important role in the formation of frameworks with cavities and channels. This special host−guest interaction could be further understood with the aid of modern computer modeling and simulations.[34−38] Some templating molecules that might potentially direct the formation of frameworks with specified pore geometries can be reasonably predicted by computer simulations. Notice that chiral zeolite frameworks generally exist as a 50:50 enantiomeric mixture in the bulk product. To synthesize an enantiopure zeolite framework, it is believed that the use of enantiomerically pure chiral SDAs is perhaps necessary.[2,39]

Conclusions

The approach we describe here provides an efficient way for designing zeolite frameworks with chiral channel structures based on requirements. Atoms can be placed outside of the forbidden cylinders that correspond to the channel structures by symmetry and distance constraints. Through combinations of different channel sizes, different numbers of unique T atoms, and different unit cell parameters, various chiral framework topologies can be generated under a given chiral space group by our methodology. In principle, any structure that is topologically reasonable can possibly exist. Upon investigation of the framework energies, the framework densities, and the coordination sequences, the most feasible hypothetical structures could be predicted as candidates for the designed synthesis. Rational selection of the non-Si framework elements and the chiral SDAs will greatly aid the synthesis of the target chiral structures. We are currently building up a database of hypothetical zeolite framework structures with various topological and geometric features. This will not only provide important information on the range of crystalline porous structures but also help to rationalize the synthesis for a synthetically oriented chemist. It is believed that, with the development of new synthetic techniques, the diverse hypothetical crystalline porous structures with specified chiral pore geometries might ultimately be accessed synthetically.

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Supporting Information Available: Tables of framework energies, framework densities, cell parameters, atomic coordinates, and coordination sequences. This material is available free of charge via the Internet at http://pubs.acs.org.

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(34) Haase, F.; Sauer, J. *J. Am. Chem. Soc.* **1995**, *117*, 3780.

(35) Lewis, D. W.; Willock, D. J.; Catlow, C. R. A.; Thomas, J. M.; Hutchings, G. J. *Nature* **1996**, *382*, 604. Lewis, D. W.; Sankar, G.; Wyles, J. K.; Thomas, J. M.; Catlow, C. R. A.; Willock, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2675.

(36) Lewis, D. W.; Freeman, C. M.; Catlow, C. R. A. *J. Phys. Chem*. **1995**, *99*, 11194.

(37) Wagner, P.; Nakagawa, Y.; Lee, G. S.; Davis, M. E.; Elomari, S.; Medrud, R. C.; Zones, S. I. *J. Am. Chem. Soc*. **2000**, *122*, 263.

(38) Yu, J.; Li, J.; Wang, K.; Xu, R.; Sugiyama, K.; Terasaki, O. *Chem. Mater.* **2000**, *12*, 3783−3787.

(39) Wang, Y.; Yu, J.; Li, Y.; Shi, Z.; Xu, R. *Chem.−Eur. J.* **2003**, *9*, 5048−5055.