

Design of Zeolite Frameworks with Defined Pore Geometry through Constrained Assembly of Atoms

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A computational method for design of zeolite frameworks with specified pore geometry has been developed through constrained assembly of atoms around a specified pore structure. Forbidden zones, corresponding to a porous pattern, are first defined in a unit cell, and then, atoms are inserted on the basis of specified symmetry and distance constraints. Using the design of zeolite frameworks with a hexagonal space group $P6_3/mmc$ (No. 194) as an example, various structure topologies have been generated by our computer program, through enumeration of combinations of different pore sizes, different numbers of unique T atoms, and different site symmetries. These structures include a number of known zeolite frameworks, including GME, ERI, EAB, LOS, AFX, and AFG, as well as a number of novel zeolite frameworks that have comparable potential energies to known zeolites. Interesting frameworks with cross-linked channels can be obtained by assuming some particular space groups. A framework with 3-D interconnected 12-membered ring channels has been designed by assuming the tetragonal space group $P4_2/mmc$ (No. 131). This method provides a fast search of new and interesting zeolite frameworks with desired pore geometry and will be an aid for a synthetically oriented chemist.

Introduction

Zeolites constitute an important class of materials in the field of materials science. Their unique pore architectures have made them popular in a wide range of applications in catalysis, adsorption, separation, and host–guest assemblies. Our current understanding about their formational mechanism under hydrothermal conditions is very limited, making it a highly challenging task to rationalize the synthesis of these materials.

A prerequisite for rational synthesis is a capability for structure design with desired geometric and physicochemical properties. Computational modeling techniques have substantially aided in the prediction of crystal structures.^{1–9} Several approaches have been

developed and described. In 1988, Smith developed a mathematical theory of microporous materials and systematically assembled some of the building units into new microporous nets;¹⁰ Maddox combined first principles and molecular dynamics to generate crystal structures.¹¹ In 1989, Newsam and Deem developed a method using simulated annealing to determine the 4-connected framework crystal structures;¹² Akporiaye and Price used operator sequences and sheet coding to systematically enumerate the zeolite frameworks.¹³ In 1990, Catlow and Price performed electronic-structure calculations and “effective potentials” simulations to compute electronic and reactive properties of crystal structures.¹⁴ In 1999, Boisen, Jr., et al. generated a series of framework structures using a molecular-based potential energy function and simulated annealing strategies,¹⁵ Klinowski and Friedrichs et al. systematically enumerated a series of crystalline networks using a mathematical tiling method,¹⁶ and Xu and Zhou et al. systematically enumerated a series of 2-D layered

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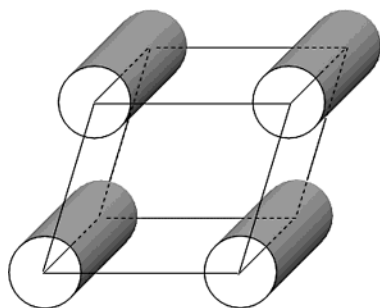


Figure 1. Forbidden zones defined as cylinders in one unit cell (the thickness of the pore wall is 0.05 Å).

aluminophosphates with $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$ stoichiometry using a divide-and-conquer algorithm and a genetic algorithm.¹⁷ In 2000, Draznieks and Férey et al. performed de novo prediction of inorganic structures developed through automated assembly of the secondary building units (SBUs) method.¹⁸ In general, all these methods can be regarded as a systematic assembly of particles, including atoms or ions, SBUs, meshes, or networks, under various constraints or penalty rules, to enumerate ideal framework structures that may have the lowest energy, or the minimum score of some cost function.

In this work, we have developed a simple and efficient computational method for generation and enumeration of zeolite frameworks with specified pore structures through introducing forbidden zones in the simulation input. The forbidden zone is similar to the pore term described by Newsam et al. in the framework crystal structure solution by simulated annealing.¹⁹ A forbidden zone is an area in a unit cell inside which no atoms can be placed during a generation process of a zeolite framework. A forbidden zone can be specifically designed to reflect a particular desired porous pattern in an open framework. Placement of atoms into a unit cell is carried out through placing unique atoms randomly outside of the forbidden zones and then through application of symmetry operations and distance constraints. As a consequence, this method prevents the generation of any nonporous frameworks, the so-called dense structures, and the calculation is inexpensive. The application of the idea of forbidden zones renders this method faster and much more straightforward compared to previous simulation methods. It can effectively generate the desired crystalline porous structures through defining the geometry of the forbidden zones. This method will be of considerable interest for a synthetically oriented chemist whose target is to synthesize materials with desired structures based on functional requirements.

Computational Methodology

As illustrated in Figure 1, the pore structure represented as four cylinders, called forbidden zones, is first defined in a unit cell, and then, atoms are placed outside of the forbidden

zones on the basis of specified symmetry and distance constraints. To ensure that the defined pore geometry is enforced, the first unique atom is confined to the pore wall. Two constraint conditions must be satisfied when placing the atoms: (i) no atom is allowed inside a forbidden zone, and (ii) the distance between any two atoms is no less than 3.0 Å, assuming a Si–Si distance. The center of the forbidden zone is typically placed in origin of the unit cell, or in some other particular positions.

This method allows a user to specify the pore size, the number and site symmetry of unique atoms, the unit cell, and the space group. The generation and enumeration procedure includes the following major steps:

- (1) A unit cell and the space group are first defined.
 - (2) The pore dimensions and the corresponding numbers of the unique atoms are selected in terms of zeolite framework density.
 - (3) Unique atoms are randomly placed outside of the forbidden zones in the unit cell followed by the automatic generation of their equivalent atoms based on symmetry operations. Placed atoms violating conditions i and ii will be removed from further consideration; otherwise, a data set containing unique T atom coordinates will be saved. For distance calculation, the crystal coordinates are converted to Cartesian coordinates.
 - (4) Multiple data sets will be generated and saved by repeating step 3 until certain criteria are met (e.g., a specified number of different data sets have been generated). We apply coordination sequences (CSs)²⁰ to distinguish different framework types, as well as to judge whether the generated configuration is a viable one. Only data sets with different framework topologies and viable configurations will be kept.
 - (5) For each data set, a structural model is built using *Cerius²* on an SGI silicon graphics O2+ workstation.²¹ Bridging atoms are added using Structure Solve_Bridging atom in the *Cerius²* package. Bridging oxygen atoms can be automatically added on the basis of the distances between the nearest atoms.²¹
 - (6) The idealized cell parameters are calculated using a DLS-refinement.²² The unit cell and atom positions of the models are allowed to change. The refinement is carried out assuming a SiO_2 composition and with the following prescribed interatomic distances given in the *Atlas of Zeolite Framework Types*:²³ $d_{\text{Si-O}} = 1.61$ Å, $d_{\text{O-O}} = 2.629$ Å, and $d_{\text{Si-Si}} = 3.07$ Å using the weights of 2.0, 0.61, and 0.23, respectively. The final determination of the symmetry of each generated structure is performed through a "Find-Symmetry" analysis.²¹
 - (7) The potential energy of each structural model is calculated using the Burchart 1.01 force field.²⁴
- Our program is written using Visual C programming language.²⁵

Results and Discussion

Here we first use the design of zeolite frameworks with hexagonal space group $P6_3/mmc$ (No. 194) as an example, to illustrate the efficacy of this method. For this example, we assume $a = 15$ Å and $c = 15$ Å for the

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Table 1. Generation Conditions and Results Assuming a $P6_3/mmc$ Space Group (No. 194) with Unit Cell $a = b = c = 15 \text{ \AA}$ ^a

defined pore radius(Å)	unique T atoms	refined unit cell a, c (Å)	formula	structure type	energy (kJ/mol/T)
6.0	l	13.7, 9.8	Si ₂₄ O ₄₈	GME	-1824.6
6.0	lj	12.5, 15.7	Si ₃₆ O ₇₂	H1	-1819.8
6.0	ll	16.8, 14.2	Si ₄₈ O ₉₆	H2	-1815.2
6.0	ll	16.8, 14.2	Si ₄₈ O ₉₆	H2	-1815.2
6.0	ljj	19.6, 5.3 ^b	Si ₂₄ O ₄₈	H3	-1818.6
6.0	ljj	16.9, 14.4	Si ₄₈ O ₉₆	H2	-1815.6
6.0	ljj	17.4, 5.3 ^b	Si ₂₄ O ₄₈	H4	-1814.5
6.0	jlj	17.6, 5.3 ^b	Si ₂₄ O ₄₈	H5	-1821.0
6.0	ljj	19.6, 5.3 ^b	Si ₂₄ O ₄₈	H3	-1818.6
6.0	ljj	17.6, 5.3 ^b	Si ₂₄ O ₄₈	H5	-1821.0
6.0	ljj	17.4, 5.3 ^b	Si ₂₄ O ₄₈	H4	-1814.5
5.0	jlj	17.6, 5.3 ^b	Si ₂₄ O ₄₈	H5	-1821.0
4.0	ij	12.6, 10.3	Si ₂₄ O ₄₈	LOS	-1817.4
4.0	il	13.2, 15.0	Si ₃₆ O ₇₂	EAB	-1823.6
4.0	lj	13.1, 15.2	Si ₃₆ O ₇₂	ERI	-1824.5
4.0	jl	12.6, 15.6	Si ₃₆ O ₇₂	H1	-1820.1
4.0	jlj	17.6, 5.3 ^b	Si ₂₄ O ₄₈	H5	-1821.0
3.0	ij	12.6, 10.3	Si ₂₄ O ₄₈	LOS	-1817.4
3.0	jl	12.6, 15.6	Si ₃₆ O ₇₂	H6	-1820.1
3.0	il	13.2, 15.0	Si ₃₆ O ₇₂	EAB	-1823.6
3.0	lj	13.1, 15.2	Si ₃₆ O ₇₂	ERI	-1824.5
3.0	ll	13.7, 19.8	Si ₄₈ O ₉₆	AFX	-1824.5
3.0	ll	12.9, 20.0	Si ₄₈ O ₉₆	H7	-1823.4
3.0	jlj	12.5, 20.8	Si ₄₈ O ₉₆	AFG	-1819.3
3.0	jlj	16.8, 10.5	Si ₄₈ O ₉₆	H8	-1823.3
3.0	ilj	12.5, 20.8	Si ₄₈ O ₉₆	AFG	-1819.3

^a Bold indicates the unique atoms confined to the pore wall.^b Space group changes to $P6/mmm$ (No.191) after refinement.

unit cell. We then generate various structure topologies, using combinations of different pore sizes, different numbers of unique T atoms, and different site symmetries. Table 1 lists the generation conditions and results. The pore 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 3. The atoms are placed in the general site symmetry *l* and/or special site symmetry *k, j*, and *i* (Wyckoff letter).²⁶ Each general position corresponds to 24 equivalent atoms, whereas each special position corresponds to 12 equivalent atoms. A number of known zeolite frameworks, including GME, ERI, EAB, LOS, AFX, and AFG,²³ are successfully produced by our program. Their refined unit cells are identical to the idealized cell parameters given in the *Atlas of Zeolite Framework Types*.²³ More interestingly, a number of hypothetical structural models have been generated, which have comparable potential energies ranging from -1814.5 to -1824.6 kJ/mol/T to known zeolites. Their atomic coordinates and coordination sequences are listed in Tables 2 and 3, respectively.

Figure 2 illustrates the generation process for a hypothetical framework, denoted as H1. The pore radius is set at 6.0 Å. Two unique atoms are placed, one at the general position *l* and the other at the special position *j*. The first unique atom is constrained to the pore wall, and the position on the wall is randomly selected. Then its 23 equivalent atoms are generated using the symmetry operation (Figure 2a). The distance between any two atoms is calculated. If the 24 atoms satisfy conditions i and ii, i.e., all atoms outside of the forbidden zones and T-T distances no less than 3.0 Å, the atomic coordinate of the first unique atom is saved. The second

Table 2. Atomic Coordinates of Hypothetical Zeolite Structures

structure	atom	<i>x</i>	<i>y</i>	<i>z</i>
H1	T1	0.3349	0.9227	0.0851
	T2	0.9233	0.5898	0.2500
H2	T1	0.1452	0.4783	0.5193
	T2	0.5814	0.6074	0.1466
H3	T1	0.6687	0.4941	0.0000
	T2	0.9080	0.3723	0.5000
H4	T1	0.2681	0.3730	0.0000
	T2	0.3628	0.8939	0.5000
H5	T1	0.1580	0.6692	0.0000
	T2	0.7282	0.6289	0.5000
H6	T1	0.9984	0.7466	0.2500
	T2	0.3352	0.9178	0.9150
H7	T1	0.2370	0.2373	0.3271
	T2	0.6652	0.0937	0.0606
H8	T1	0.1853	-0.0022	0.2500
	T2	0.2954	0.0000	0.0000
	T3	0.5146	0.6657	0.8976

Table 3. Coordination Sequences of Hypothetical Zeolite Structures

structure	atom	coordination sequence									
H1	T1	4	10	20	34	54	78	104	134	168	210
	T2	4	10	20	34	54	78	104	134	168	210
H2	T1	4	9	16	25	38	55	73	95	126	161
	T2	4	8	15	27	38	49	71	100	123	147
H3	T1	4	10	18	27	39	55	74	93	116	150
	T2	4	9	17	28	40	52	68	93	122	148
H4	T1	4	10	19	31	49	72	97	127	164	202
	T2	4	9	17	30	49	70	90	116	152	193
H5	T1	4	10	20	33	50	73	102	134	165	196
	T2	4	10	21	35	51	72	97	127	162	202
H6	T1	4	10	20	34	52	74	100	130	166	208
	T2	4	10	20	34	53	76	103	135	170	209
H7	T1	4	9	17	30	49	72	96	121	150	187
	T2	4	10	20	33	49	69	94	125	160	197
H8	T1	4	12	25	42	63	88	120	160	204	252
	T2	4	12	23	40	63	90	122	158	200	252
	T3	4	10	20	37	61	91	124	160	201	246

unique atom is placed in the special position *j* followed by the generation of its 11 equivalent atoms (Figure 2b). The distance between any two atoms of the 36 atoms is calculated. If the atoms satisfy conditions i and ii, the position of the second unique atom is kept; otherwise, the atoms, generated by the second unique atom, will be replaced until all the atoms satisfy the conditions. For each set of unique T atom coordinates, a structural model is built using *Cerius*.²¹ Bridging atoms are added (Figure 2c). The optimized structure has a unit cell $a = 12.5 \text{ \AA}$ and $c = 15.7 \text{ \AA}$ with an empirical formula Si₃₆O₇₂. The potential energy of H1 is -1819.8 kJ/mol per T atom, which is comparable to those of known zeolites. As shown in Figure 2d, the structure of H1 consists of one-dimensional 12-membered ring (MR) channels along the [001] direction. It contains columns of *can* cages along the *c* axis; six of such columns enclose a 12-MR channel. Its simulated X-ray powder diffraction pattern is also shown in Figure 2d.

From Table 1, it can be seen that by changing the pore size and the number of T atoms, as well as the site symmetry, different zeolite frameworks can be systematically enumerated and generated.

Using a different pore size of 4.0 or 3.0 Å but the same number and site symmetry of unique atoms (1*l*, 1*j*) as that for H1, the ERI structure²³ with 8-MR openings is produced. When using the same pore size of 6.0 Å but

(26) *International Tables for Crystallography*, Hahn, T., Eds.; The International Union of Crystallography by D. Reidel Publishing Company: Dordrecht, The Netherlands., 1983, p 591.

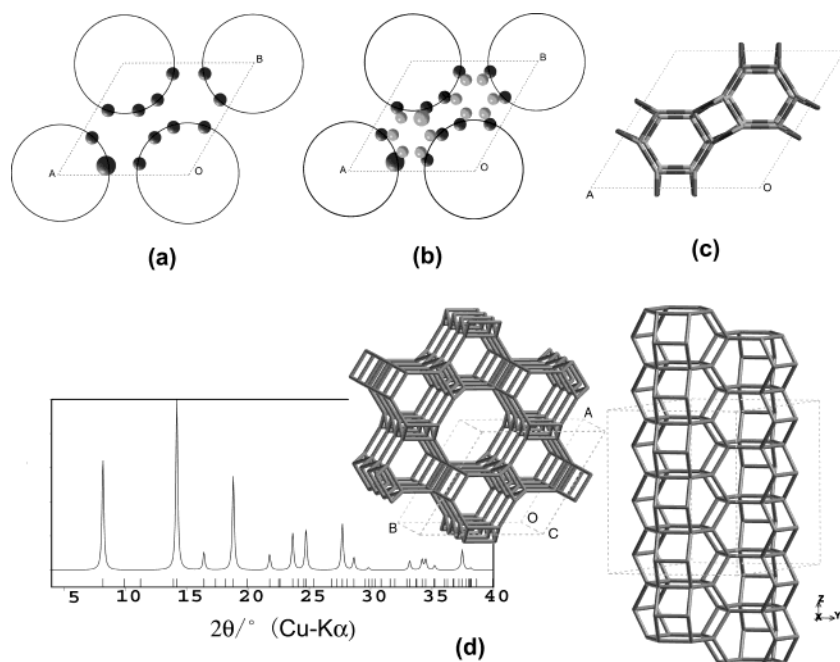


Figure 2. Generation process for hypothetical framework H1: (a) the first unique atom represented by a larger ball is confined to the pore wall followed by the generation of 23 equivalent atoms using symmetry operation i ; (b) the second unique atom represented as a larger ball is randomly placed outside of the forbidden zones followed by the generation of 11 equivalent atoms by symmetry operation j ; (c) bridging atoms are added; (d) framework structure containing 12-MR channels. The simulated XRD pattern is shown.

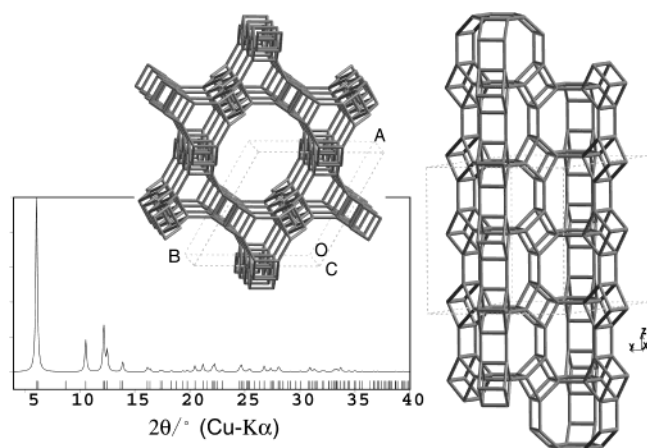


Figure 3. Hypothetical framework structure of H2 and its simulated XRD pattern.

different site symmetry for unique atoms ($1i, 1i$), a hypothetical framework with 18-MR channels, denoted as H2 ($\text{Si}_{48}\text{O}_{96}$), is generated. The optimized cell parameters are $a = 16.8 \text{ \AA}$, and $c = 14.3 \text{ \AA}$. Figure 3 shows its framework structure. The 18-MR channel circumscribed by 18 T atoms has free aperture dimensions of $9.4 \times 9.4 \text{ \AA}^2$ (O...O distance). It contains columns of *gme* cages, each of which is connected through double 4-MRs (D4Rs).

Using a pore size of 6.0 \AA , and the number of unique atoms of 3 (i, j, j), three structural models H2 ($\text{Si}_{48}\text{O}_{96}$), H3 ($\text{Si}_{24}\text{O}_{48}$), and H4 ($\text{Si}_{24}\text{O}_{48}$) are generated. The refined frameworks of H3 and H4 have space group $P6/mmm$ (No. 191). Figure 4 shows the structure of H3 with 18-MR channels. Its structure consists of columns of *can* cages, which are connected together through D6Rs forming the 18-MR channels. The framework structure of H4 is shown in Figure 5. It contains columns of D6Rs;

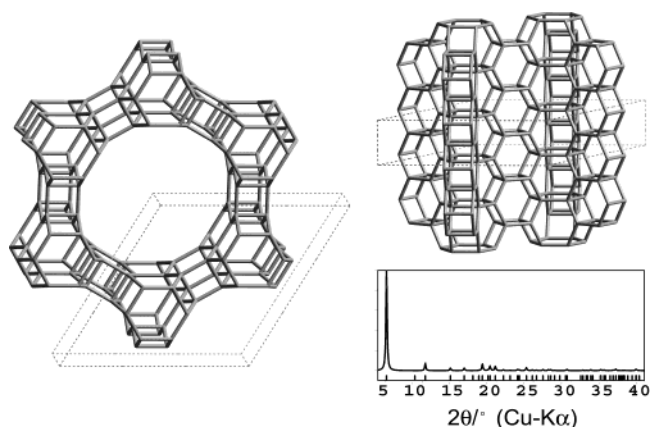


Figure 4. Hypothetical framework structure of H3 and its simulated XRD pattern.

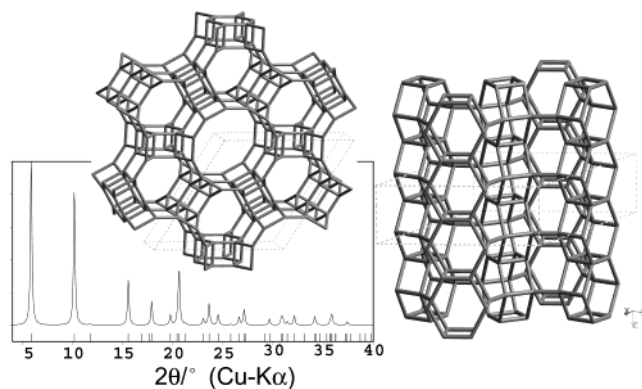


Figure 5. Hypothetical framework structure of H4 and its simulated XRD pattern.

six such columns connected together form two kinds of parallel 12-MR channels. The large and regular 12-MR channel is surrounded by six pear-like 12-MR channels.

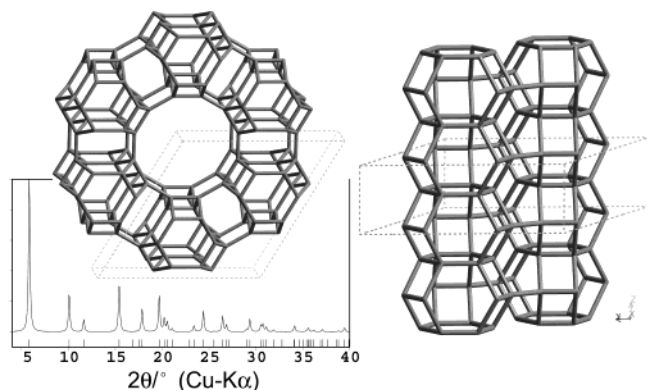


Figure 6. Hypothetical framework structure of H5 and its simulated XRD pattern.

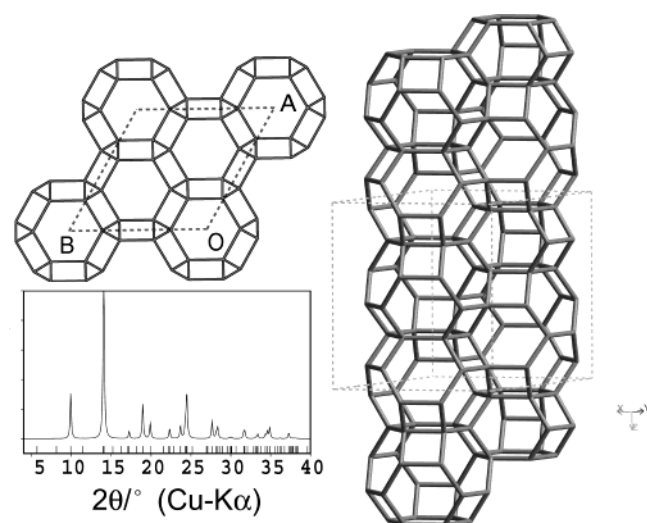


Figure 7. Hypothetical framework structure of H6 and its simulated XRD pattern.

Using a pore size of 6.0, 5.0, or 4.0 Å, and the number of unique atoms of 3 (j, l, j), a structural model denoted as H5 ($\text{Si}_{24}\text{O}_{48}$) is produced. It has cell parameters $a = 17.5$ Å and $c = 5.3$ Å with space group $P6/mmm$ (No. 191). Figure 6 shows its framework structure. It contains columns of face-sharing *can* cages. Six of such columns connected together form parallel 12- and 8-MR channels along the [001] direction.

H6 ($\text{Si}_{36}\text{O}_{72}$) and H7 ($\text{Si}_{48}\text{O}_{96}$) are generated using the pore size of 3.0 Å and the site symmetry for unique atoms ($1j, 1l$) and ($1l, 1l$), respectively. H6 has refined cell parameters of $a = 12.6$ Å and $c = 15.6$ Å with space group $P6_3/mmc$ (No. 194). Figure 7 shows its framework structure. Its framework consists of three types of cages, i.e., *sod*, *los*, and *can* cages. The refined framework of H7 has cell parameters $a = 12.9$ Å and $c = 20.0$ Å with space group $P6_3/mmc$ (No. 194). Its structure contains three types of cages, i.e., *sod*, *gme*, and *eab* cages.

Using a pore size of 3.0 Å and the number of unique atoms of 3 (j, l, j), H8 ($\text{Si}_{48}\text{O}_{96}$) and a known zeolite framework AFG are generated. H8 has refined cell parameters of $a = 16.8$ Å and $c = 10.5$ Å with space group $P6_3/mmc$ (No. 194). Its framework contains the *ber* cage¹⁰ and a new type of $4^35^66^26^26^6$ cage.

We have shown here a few examples designed under the $P6_3/mmc$ space group with the same unit cell. This method certainly allows designing zeolite frameworks under any crystal system, including the cubic, hexago-

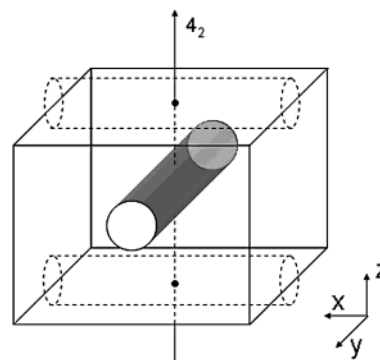


Figure 8. Forbidden zone corresponding to the channel in the unit cell and its cross-linked channels generated by the 4_2 operation

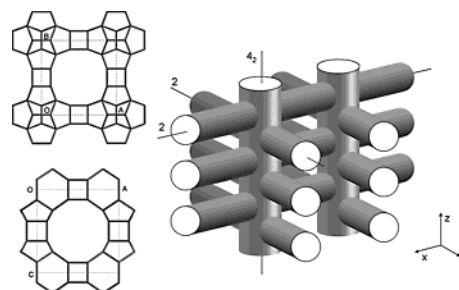


Figure 9. Hypothetical framework structure of H9 viewed along the [001] and [010] direction and a schematic showing its channel system with three interconnected 12-membered ring channels along all three crystallographic axes

nal, rhombohedral, tetragonal, orthorhombic, monoclinic, and triclinic systems with unit cells of various dimensions. More interesting frameworks such as cross-linked channels can be obtained when defining a forbidden zone (channel) whose direction is perpendicular to the principal axis under a specified space group. For example, assuming a tetragonal space group $P4_2/mmc$ (No. 131), as shown in Figure 8, and defining a forbidden zone (channel) perpendicular to the 4_2 screw axis in the unit cell, a channel perpendicular to this defined channel will be naturally produced by the 4_2 operation. Defining the cell parameters of $a = b = c = 15$ Å, using a pore size of 5.0 or 6.0 Å and the number of unique atoms of 3 (n, r, o),²⁶ H9 ($\text{Si}_{32}\text{O}_{64}$) with refined cell parameters of $a = 12.8$ Å and $c = 13.0$ Å is obtained. Its atomic coordinates and coordination sequences are listed in Tables 2 and 3, respectively. Figure 9 shows its framework structure viewed along the [001] and [010] directions, respectively. It consists of intersecting 12-membered ring channels along all three crystallographic axes. The topology of H9 is analogous to that of germanium dioxide $(\text{Me}_3\text{N})_6[\text{Ge}_{32}\text{O}_{64}] \cdot (\text{H}_2\text{O})_{4.5}$ crystallized in the tetragonal space group $I4_1/amd$ (No. 141) with lattice parameters of $a = 22.990(3)$ Å and $c = 27.271(3)$ Å.²⁷ Interestingly, H9 was actually described as a hypothetical polymorph C of zeolite β by Newsam et al.,²⁸ and further crystallographic details have been provided on a recent synthetic material.²⁹

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In general, there is no restriction to the space group and the geometry of the forbidden zones. It is noted that our refinement is carried out assuming a hypothetical SiO_2 composition. However, some hypothetical frameworks might be suitable for other compositions such as germanium oxide and various metal phosphates on considering the reasonable bond distances and bond angles. Using our method, a large number of hypothetical frameworks with desired porous structures can be effectively generated. What is of vital importance for a synthetically oriented chemist, however, is how to approach such diverse structures. Recently computer modeling and simulation approaches have greatly enhanced researchers' ability to target materials with specific structures upon understanding the interaction of the host frameworks and the guest molecules.^{30–34} Some templating molecules that might potentially direct the formation of the open-frameworks can be reasonably predicted by computer simulations on investigation of the interactions between the host frameworks and the guest templating molecules. This will provide important clues for the synthesis of materials with desired structures.

Conclusions

The approach we describe here provides an efficient way for designing zeolite frameworks with specified pore

structures. Atoms can be placed outside the forbidden cylinders that correspond to the pore structures by symmetry and distance constraints. Through combinations of different pore sizes, different numbers of unique T atoms, and different site symmetries, various structure topologies including known, and new hypothetical structures can be generated under a given space group by our methodology. This method can be naturally applied to generate interesting zeolite frameworks by defining any desired porous pattern based on function requirements. We are currently setting up a database of hypothetical 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. Despite the large number of structures that has been synthesized, the number of hypothetical topologies is infinite. It is believed that, with the development of new synthesis strategies, the diverse hypothetical crystalline porous structures might ultimately be accessed synthetically.

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