Prediction of Open-Framework Aluminophosphate Structures Using the Automated Assembly of Secondary Building Units Method with Lowenstein's Constraints

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In this paper, we describe an approach to generate hypothetical open-framework aluminophosphate structures with specified Al/P stoichiometry using the automated assembly of secondary building units method. For each specified Al/P stoichiometry, all the possible combinations of Al and P atoms with different coordination states could be calculated according to the Lowenstein's rule. The Al and P atoms of different coordination states, together with the clusters constructed by them, could be selected as the building units for the structure generation. To satisfy the Lowenstein's rule, additional constraints are introduced into the simulation. The force field which controls the assembly of the building units is parametrized to favor the formation of Al−O−P linkages while avoiding the formation of Al−O−Al or P−O−P linkages. This method will not only aid the prediction of hypothetical aluminophosphate frameworks but also serve as a tool to set up the initial structural models for the solution of unknown aluminophosphate structures.

Introduction

Aluminophosphate molecular sieves, known as the AlPO$_4$-*n* family,[1] are an important class of microporous materials which have been widely used in the fields of catalysis, separation, and host−guest assemblies. Their frameworks are typically built up from the strict alternation of AlO_4 and PO_4 tetrahedra through corner-sharing of their vertex oxygen atoms. In these structures, no Al−O−Al or P−O−P connection is allowed because of Lowenstein's rule.[2] Thus, for such zeolite-type aluminophosphate structures, the Al/P ratio is exclusively unity[3] and their frameworks are electronically neutral. In contrast to these neutral framework aluminophosphates, recently a large number of anionic aluminophosphate frameworks have been prepared with an Al/P ratio of less than unity, including three-dimensional (3D) open-framework, two-dimensional (2D) layer, one-dimensional (1D) chain, and zero-dimensional cluster structures.[4] The anionic frameworks of these aluminophosphates are made up of AlO_m ($m = 4, 5, 6$) polyhedra and $P(O_b)_n(O_t)_{4-n}$ (b, bridging; t, terminal; $n = 1, 2, 3, 4$) tetrahedra to form a variety of stoichiometries, including AlP_4O_{16},$^{9-}$ $AlP_2O_8^{3-}$, $Al_2P_3O_{12}^{3-}$, $Al_3P_4O_{16}^{3-}$, $Al_3P_5O_{20}$,$^{6-}$ $Al_4P_5O_{20}^{3-}$, $Al_5P_6O_{24}^{3-}$, $Al_{11}P_{12}O_{48}^{3-}$, $Al_{12}P_{13}O_{52}^{3-}$, $Al_{13}P_{18}O_{72}$,$^{15-}$ and so forth. Their frameworks exhibit fascinating structural architectures; for example, JDF-20 has the largest channel ring size of 20 among the open-framework aluminophosphates,[5] and AlPO−CJB1 is the first aluminophosphate molecular sieve with Brönsted acidity.[6]

Up to now, over 200 open-framework aluminophosphate structures have been reported. Recently, our group has built up an aluminophosphate database including all these structures.[7] However, the number of theoretically feasible structures is enormous. Prediction of hypothetical aluminophosphate structures is very important for the understanding of their rich structural chemistry, as well as for the solution of unknown structures. Although some approaches have been described for the prediction of zeolite frameworks,[8−16] which could be used for the design of zeolite-type aluminophosphate structures with the Al/P ratio of unity, few methods have been developed for the prediction of aluminophosphate structures with an Al/P ratio of nonunity.[17] The diverse

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coordination states of Al and P atoms will increase the degrees of freedom, thus, making the simulation more complicated. Recently, Férey et al. reported an automated assembly of secondary building units (AASBU) method for the prediction of inorganic structures.[18−21] When this method is used, secondary building units are assembled in one, two, or three dimensions to form a whole framework under a special "force field". Using secondary building units instead of primary building units will greatly reduce the degrees of freedom. Moreover, the desired structures could be designed on purpose.

In this paper, we will describe an approach to predict hypothetical aluminophosphate structures with the Al/P ratio of nonunity based on the AASBU method. Compared with the existing AASBU method reported by Férey et al., additional constraints based on Lowenstein's rule are introduced in our approach. As a result of Lowenstein's rule, no Al−O−Al or P−O−P linkages are allowed. Before the simulation, all the combinations of various kinds of building units are calculated according to a specified Al/P stoichiometry. Only those combinations which obey Lowenstein's rule are introduced in the simulation. During the simulation, the assembly of the building units is controlled by a "force field", which favors the formation of Al−O−P linkages while avoids the formations of Al−O−Al and P−O−P linkages. This method will not only serve as an effective tool for the prediction of hypothetical aluminophosphate structures but also be an effective approach for setting up the initial structural models for the solution of structures combined with NMR and X-ray diffraction (XRD) Rietveld refinements.

Computational Methodology

The AASBU method proposed by Férey et al. could be summarized by the following key steps: (1) choose suitable building units; (2) define a force field which controls the possible assembly of the building units; (3) generate the trial arrangements of the building units through simulated annealing; and (4) assemble the building units under the control of the defined force field through energy optimization.[18−21] As the preliminary step of the whole simulation, selecting of the suitable building units is prerequisite.

In open-framework aluminophosphate structures, there exist two kinds of framework O atoms, that is, the bridging O atoms (denoted as O_b) and the terminal O atoms (denoted as O_t). The O_b atom is shared by a pair of atoms, that is, one Al atom and one P atom, while the O_t atom only connects with a single P atom. In the known aluminophosphate frameworks, three kinds of Al-centered polyhedra could be found, including $Al(O_b)_4$, $Al(O_b)_5$, and $Al(O_b)_6$, while four kinds of P-centered tetrahedra could be found, including $P(O_b)_4$, $P(O_b)_3(O_t)$, $P(O_b)_2(O_t)_2$, and $P(O_b)(O_t)_3$. In a typical zeotype aluminophosphate structure, all the Al atoms are four-coordinated in the form of $Al(O_b)_4$, and all the P atoms are four-coordinated in the form of $P(O_b)_4$. In anionic framework aluminophosphates, however, the structures are more complicated which are usually constructed by different kinds of Al- and P-centered polyhedra. For example, in the structure of AlPO−CJ19,[22] there exist all three kinds of Al atoms, that is, $Al(O_b)_4$, $Al(O_b)_5$, and $Al(O_b)_6$, and two kinds of P atoms, including $P(O_b)_4$ and $P(O_b)_3(O_t)$. All the possible combinations of different kinds of Al and P atoms could be easily calculated for a given content of Al and P atoms in the unit cell. Only the combinations of Al and P atoms which obey the Lowenstein's rule will be introduced in future simulations. According to the Lowenstein's rule, two criteria must be satisfied during the calculation of the possible combinations:

(1) The sum of the numbers of each kind of Al atom must be equal to the number of Al atoms in the unit cell, and similarly, the sum of the numbers of each kind of P atom must be equal to the number of P atoms in the unit cell;

(2) The number of $Al-O_b$ bonds must be equal to the number of $P-O_b$ bonds.

These two rules could also be summarized in eq 1:

$$\sum_{i=1}^{I} m_i = \sum_{j=1}^{J} n_j \tag{1}$$

where I (J) is the number of Al (P) atoms in the unit cell and m_i (n_j) is the number of O_b atoms connected with the ith (jth) Al (P) atom.

After all the possible combinations of different kinds of Al and P atoms are calculated, the exact number of O atoms in each combination, especially the number of O_b atoms, is figured out. For a typical zeotype aluminophosphate structure with an Al/P ratio of unity, because every O_b atom is shared by a pair of Al and P atoms and every Al or P atom is shared by four O_b atoms, the number of O_b atoms should always be the double of the sum of the numbers of Al and P atoms, that is, the $O_b/(Al + P)$ ratio should be 2. For an aluminophosphate structure with an Al/P ratio of nonunity, this $O_b/(Al + P)$ ratio may be less or higher than 2. In a structure with an $O_b/(Al + P)$ ratio less than 2, there are fewer connections between the Al and P atoms, that is, the O_b atoms are "under-saturated" to the frameworks. This causes the structures with large apertures or highly interrupted frameworks. In a structure with $O_b/(Al + P)$ ratio higher than 2, there are more connections between framework atoms, that is, the O_b atoms are "over-saturated" to the frameworks. This causes the structures with dense frameworks. Thus, the calculation of the $O_b/(Al + P)$ ratio for a structure might provide some useful clues to its framework.

Considering the combinations of different kinds of Al and P atoms, appropriate building units could be selected for further AASBU simulation. For example, two AlO_4, one AlO_5, one PO_4, and one $Al(O-PO_3)_4$ cluster could be

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Table 1. Force Field Parameters Used in the AASBU Simulation[a]

bond-stretching term		k_{BS} [kcal/(mol·Å^2)]	r_{BS}*/(Å)
Al_4	O_al	1000.0	1.73
Al_4	O_b	1000.0	1.73
Al_5	O_al	1000.0	1.77
Al_5	O_b	1000.0	1.77
Al_6	O_al	1000.0	1.83
Al_6	O_b	1000.0	1.83
P_4	O_p	1000.0	1.50
P_4	O_b	1000.0	1.50

bond-angle-bending terms			k_{BB} [kcal/(mol·Å^2)]	r_{BB}*/(Å)
O_*x*	Al_4	O_*x*	1000.0	2.70
O_*x*	Al_5	O_*x*	1000.0	2.65
O_*x*	Al_6	O_*x*	1000.0	2.65
O_*x*	P_4	O_*x*	1000.0	2.50
Al_4	O_b	P_4	100.0	3.10
Al_5	O_b	P_4	100.0	3.70
Al_6	O_b	P_4	100.0	3.60

Lennard-Jones terms		k_{LJ} [kcal/(mol·Å^2)]	r_{LJ}*/(Å)
O_al	O_p	1000.0	0.20
Al_4	Al_4	1.0	3.90
Al_5	Al_5	1.0	4.10
Al_6	Al_6	1.0	4.30
P_4	P_4	1.0	3.90

repulsive exponential terms		k_{RE} (kcal/mol)	r_{RE}*/(Å)
O_al	O_al	0.15	2.00
O_p	O_p	0.15	2.00

[a] Note: Al_4, Al_5, and Al_6 denote the Al atoms with coordination numbers of 4, 5, and 6, respectively; P_4 denotes a four-coordinated P atom; O_b denotes a bridging O atom linking a pair of Al and P atoms; O_al (O_p) denotes a terminal O atom connecting with only one Al (P) atom; and O_*x* denotes any kind of O atom.

selected as building units for the generation of the aluminophosphate structures with the Al/P stoichiometry of 4/5.

In addition to the building units, a force field which controls the assembly of the building units is also a prerequisite for the AASBU simulation.[18−21] The atom types and the force field parameters used in our assembly procedure are listed in Table 1. The "energy" of the whole system consists of two parts: the bonding interactions which control the sizes and shapes of the building units and the nonbonding interactions which control the assembly of building units during the simulations. The bonding interactions include bond stretchings and bond angle bendings. Bond-stretching energy (E_{BS}) is calculated from the distance between two atoms connecting with each other through a chemical bond. Bond-angle-bending energy (E_{BB}) is calculated from the distance between two atoms that are bonded to a common atom. Their expressions are both in a harmonic form and listed in eqs 2 and 3:

$$E_{BS} = k_{BS}(r_{BS} - r_{BS}^*)^2 \quad (2)$$

$$E_{BB} = k_{BB}(r_{BB} - r_{BB}^*)^2 \quad (3)$$

where the subscript "BS" denotes the bond-stretching term, the subscript "BB" denotes the bond-bending term, the superscript "*" denotes the equilibrium value, "*k*" denotes the force constant, and "*r*" denotes the distance between any two atoms. As shown in Table 1, to maintain the rigidity of the polyhedra in building units, the force constants for bond stretchings and O−Al(P)−O angle bendings are set to be very large. However, because a little flexibility on the building units is necessary, the force constants for the O-centered angle bendings are set to be relatively smaller. Compared with the bonding interactions, the assembly of building units is controlled by two nonbonding terms, including a Lennard-Jones expression and a repulsive exponential expression (eqs 4 and 5):

$$E_{LJ} = k_{LJ}[(r_{LJ}^*/r_{LJ})^{12} - 2(r_{LJ}^*/r_{LJ})^6] \quad (4)$$

$$E_{RE} = k_{RE}\exp[12.5(1 - r_{RE}/r_{RE}^*)] \quad (5)$$

where the subscript "LJ" denotes the Lennard-Jones term and the subscript "RE" denotes the repulsive exponential term. The Lennard-Jones expression is parametrized to attract O_al and O_p atoms into a close distance (0.2 Å in this work) to form a "sticky pair" and could be further "glued" together to form an Al−O−P linkage. The repulsive exponential expression is parametrized to repulse the O_al atom from its neighbor O_al atoms and O_p atom from its neighbor O_p atoms (Table 1). Thus, the Al−O−Al and the P−O−P linkages between building units could be avoided during the assembly simulation.

After the building units and the force field have been defined, the candidate structures could be generated by the AASBU method. At the beginning of the simulation, trial arrangements of the building units should be generated. In the AASBU approach by Férey et al., the simulated annealing method is used to generate the trial arrangements of the building units.[18−21] Because our aim is not to enumerate all the possible arrangements of the building units, we generate the trial arrangements of the building units by simple random sampling instead of simulated annealing in our approach to speed up the simulation. Furthermore, for the same reason, the unit cell is fixed during the assembly procedure in our approach, which is fully relaxed in the existing AASBU approach by Férey et al. The predefined cell parameters are selected on the basis of the approximate values of the known structures. Another advantage of fixing the unit cell during the assembly procedure is to control the framework dimensionality. For example, when generating 2D layered structures, the lattice length could be fixed to a large value along the direction perpendicular to the layers to avoid the connections of the building units along that direction. The detailed procedures of our approach are as follows:

(1) Determine what kinds of building units need to be included in the simulation and their numbers in the unit cell.

(2) Generate the required number of building units in a specified unit cell randomly.

(3) Optimize the "energy" of the system using our predefined force field. After this step, the building units are assembled together by the attractions between O_al and O_p atoms, that is, "sticky pairs". It should be noted that, in this step, the linkages between the building units are nonbonding interactions between O_al and O_p atoms.

(4) "Glue" each "sticky" atom pair into one atom, that is, combine each pair of O_al and O_p atoms into one O_b atom. Any O_al or O_p atom which has not found its "sticky" opposite is turned into an O_t atom. In this step, the building units are linked together through Al−O−P bonds, and the hypothetical frameworks are built up.

Table 2. Space Groups, Coordination Environments, and $O_b/(Al + P)$ Ratios for the Known and the Hypothetical Structures with the $Al_8P_{10}O_{40}$ Stoichiometry

		number of each kind of Al and P atom in a unit cell								
name	space group	No.	$Al(O_b)_4$	$Al(O_b)_5$	$Al(O_b)_6$	$P(O_b)_4$	$P(O_b)_3(O_t)$	$P(O_b)_2(O_t)_2$	$P(O_b)(O_t)_3$	$O_b/(Al + P)$
SIZ-1	$P\bar{1}$	51	6	2		6	2	2		1.89
Mu-4	$P\bar{1}$	51	6	2		6	2	2		1.89
AlPO-HDA	Cc	24	4	4		8		2		2.00
AlPO-CJ19	$P2_1$	17	4	2	2	8	2			2.11
H-1	$P\bar{1}$	49	6	2		4	6			1.89
H-2	$P\bar{1}$	49	6	2		4	6			1.89
H-3	$P\bar{1}$	22	4	4		6	4			2.00
H-4	$P\bar{1}$	73	8			4	4	2		1.78
H-5	$P2_1$	24	4	4		8		2		2.00
H-6	Cc	22	8	8		12	8			2.00

At the end of the simulation, further refinements using the Burchart force field[23] are carried out for the generated aluminophosphate structures. During this procedure, both the cell parameters and the atomic coordinates are relaxed to obtain feasible framework geometries. The framework energy of every generated structure is also calculated. Any structure with higher framework energy than that of the existing ones is removed.

Results and Discussion

1. Combinations of Al and P Atoms of Various Coordinations for $Al_8P_{10}O_{40}$ Stoichiometry. In this paper, we will take the calculation of all the possible combinations of 8 Al atoms and 10 P atoms in a unit cell with an $Al_8P_{10}O_{40}$ stoichiometry as an example to illustrate our method. According to the known open-framework aluminophosphate structures, three kinds of Al atoms, including $Al(O_b)_4$, $Al(O_b)_5$, and $Al(O_b)_6$, and four kinds of P atoms, including $P(O_b)_4$, $P(O_b)_3(O_t)$, $P(O_b)_2(O_t)_2$, and $P(O_b)(O_t)_3$, are chosen for the calculation. On the basis of our two calculation rules, there are 80 possible combinations of these seven kinds of atoms for the $Al_8P_{10}O_{40}$ stoichiometry. All these combinations are listed in Table 1 in Supporting Information, together with their $O_b/(Al + P)$ ratios.

For all of the 80 possible combinations of 8 Al atoms and 10 P atoms, the $O_b/(Al + P)$ ratio ranges from 1.78 to 2.22. For the purpose of comparison, the $O_b/(Al + P)$ ratios for all of the over 200 already-known aluminophosphate structures are also calculated. The mean $O_b/(Al + P)$ values for 1D, 2D, and 3D open-framework aluminophosphates are 1.433, 1.676, and 1.982, respectively. The distribution of the $O_b/(Al + P)$ ratios in three dimensionalities is illustrated in Figure 1 in Supporting Information. It is found that the $O_b/(Al + P)$ ratios for the 1D frameworks are usually below 1.60; the $O_b/(Al + P)$ ratios for the 3D frameworks are usually above 1.80, while the $O_b/(Al + P)$ ratios for the 2D frameworks cover a wide range from 1.50 to 1.80. It should be noted that some 2D frameworks with thick slablike layers may have high $O_b/(Al + P)$ ratios as 3D frameworks, and some 3D frameworks with highly interrupted structures may have low $O_b/(Al + P)$ ratios as 2D frameworks. Although there is no exact mathematical relation between this ratio and the framework dimensionality, the statistics results on more than 200 known aluminophosphate structures are still very useful for the prediction of the framework feature of a hypothetical structure. Because the $O_b/(Al + P)$ ratios for our hypothetical structures range from 1.78 to 2.22, we could deduce that these $O_b/(Al + P)$ ratios represent structures with 2D layers or 3D frameworks, that is, aluminophosphate structures with $Al_8P_{10}O_{40}$ stoichiometry have little possibility to be with 1D chain networks.

Up to now, there have been four unique aluminophosphate structures reported which could be seen as members of the $Al_8P_{10}O_{40}$ family, including SIZ-1,[24] Mu-4,[25] AlPO-HDA,[26] and AlPO-CJ19.[22] Their space groups, coordination environments, and the $O_b/(Al + P)$ ratios are listed in Table 2. Among these four aluminophosphates, Mu-4 is a 2D layered structure, while the other three are 3D open-framework structures. Mu-4 and SIZ-1 are constructed from the linkages of six $Al(O_b)_4$, two $Al(O_b)_5$, six $P(O_b)_4$, two $P(O_b)_3(O_t)$, and two $P(O_b)_2(O_t)_2$ in the unit cell, corresponding to the No. 51 combination of 8 Al and 10 P atoms in our calculation result; AlPO-CJ19 is constructed from the linkages of four $Al(O_b)_4$, two $Al(O_b)_5$, two $Al(O_b)_6$, eight $P(O_b)_4$, and two $P(O_b)_3(O_t)$ in the unit cell, corresponding to the No. 17 combination of 8 Al and 10 P atoms in our calculation result; and AlPO-HDA is constructed from the linkages of 8 $Al(O_b)_4$, 8 $Al(O_b)_5$, 16 $P(O_b)_4$, and 4 $P(O_b)_2(O_t)_2$ in the unit cell, corresponding to the No. 24 combination of 8 Al and 10 P atoms in our calculation result, except for the different multiplicities (see Table 1 in Supporting Information).

2. Generation of Hypothetical Structures with $Al_8P_{10}O_{40}$ Stoichiometry Using the AASBU Method with Lowenstein's Constraints. According to our calculation results, appropriate combinations of different numbers of building units could be selected for the AASBU simulation. In this paper, we will take the generation of hypothetical aluminophosphate structures with $Al_8P_{10}O_{40}$ stoichiometry as an example to illustrate our method. For instance, six $Al(O_b)_4$, two $Al(O_b)_5$, four $P(O_b)_4$, and six $P(O_b)_3(O_t)$ atoms could be a possible combination for an aluminophosphate structure with $Al_8P_{10}O_{40}$ stoichiometry (see Table 1 in the Supporting Information, result No. 49). The $O_b/(Al + P)$ ratio of this

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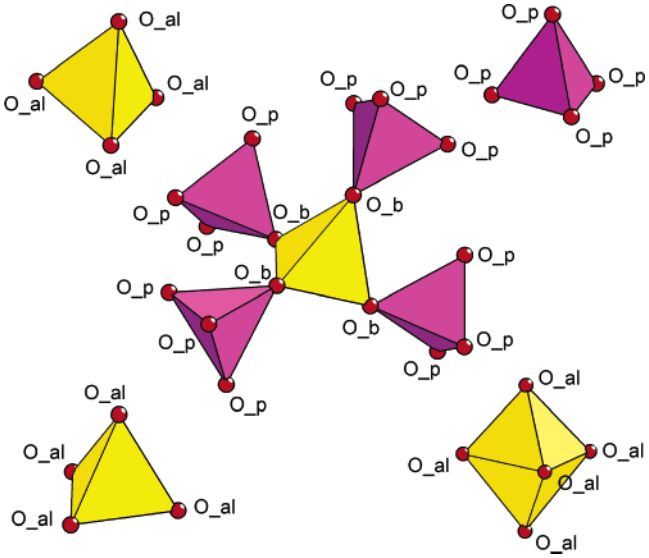

Figure 1. Building units for the generation of aluminophosphate structures with six $Al(O_b)_4$, two $Al(O_b)_5$, four $P(O_b)_4$, and six $P(O_b)_3(O_t)$ atoms in a unit cell. The yellow polyhedra denote the AlO_4 and AlO_5 polyhedra, the pink tetrahedra denote the PO_4 tetrahedra, and the red balls denote the oxygen atoms. The force field types for oxygen atoms are also labeled. It should be noted that only half of the required number of building units are needed because of the symmetric operations under space group $P\bar{1}$.

structure is 1.89, suggesting that structures with such coordination environments might possess 2D frameworks with thick layers or 3D highly interrupted frameworks with large apertures, according to our statistics on the known structures. Assuming a space group with two symmetric operations, such as space group $P\bar{1}$, only half of the atoms, that is, three $Al(O_b)_4$, one $Al(O_b)_5$, two $P(O_b)_4$, and three $P(O_b)_3(O_t)$ atoms, are needed to be introduced in the asymmetric unit. All the building units used in this example are shown in Figure 1, together with the labels of the force field atom types for the oxygen atoms. The simulation is carried out in a unit cell with $a = b = c = 10$ Å and $\alpha = \beta = \gamma = 90°$. Here, we take the generation of hypothetical structure H-1 as an example to illustrate the general assembly procedure. First, the building units are randomly introduced in the unit cell (Figure 2a); then, they are assembled through the attraction between the O_al and O_p atoms under the control of our force field (Figure 2b), and at the end of the simulation, the building units are assembled together and the "sticky atom" pairs are formed (Figure 2c). After the simulation terminates, "sticky atom" pairs are glued into single O_b atoms, and the hypothetical structure H-1 is formed. Both the atomic coordinates and the cell parameters of H-1 are further refined using the Burchart force field. As shown in Figure 3, this structure has a 3D open framework. Along the [100] direction, there are distorted 16-MR channels in which pairs of terminal O atoms protrude (Figure 3a). In addition to the 16-MR channels, there exist 8-MR channels running along the [010] direction (Figure 3b). This structure could also be viewed as exclusively constructed by the Al_4P_5 building blocks (Figure 3c).

Like H-1, many hypothetical structures, as well as all of the four existing structures with the $Al_8P_{10}O_{40}$ stoichiometry, could be generated, if other combinations of different kinds of Al and P atoms are introduced in the simulation. Some

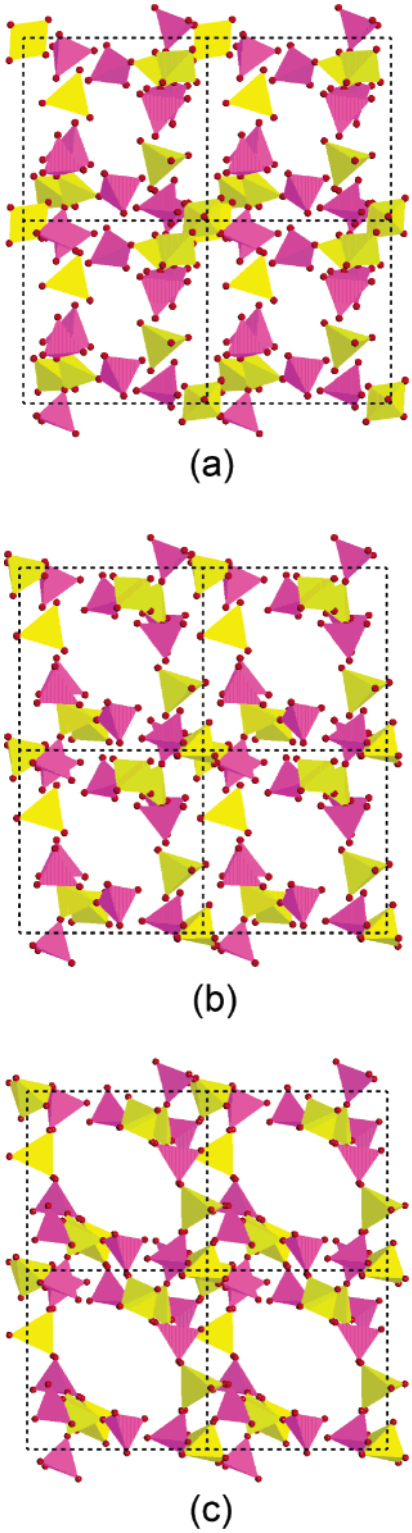

Figure 2. Generation process of H-1 using the AASBU simulation. (a) The initial building units are randomly generated in the unit cell; (b) the building units are assembled together through the attraction of O_al and O_p atoms; (c) the "sticky atom" pairs are "glued" together to form the structure. The yellow polyhedra denote the Al-centered polyhedra, the pink tetrahedra denote the PO_4 tetrahedra, and the red balls denote the oxygen atoms.

of the hypothetical structures are listed in Table 2, together with their space groups, types of Al and P atoms which are introduced, and the $O_b/(Al + P)$ ratios. The unit cell parameters and the atomic coordinates of these structures are presented in Supporting Information.

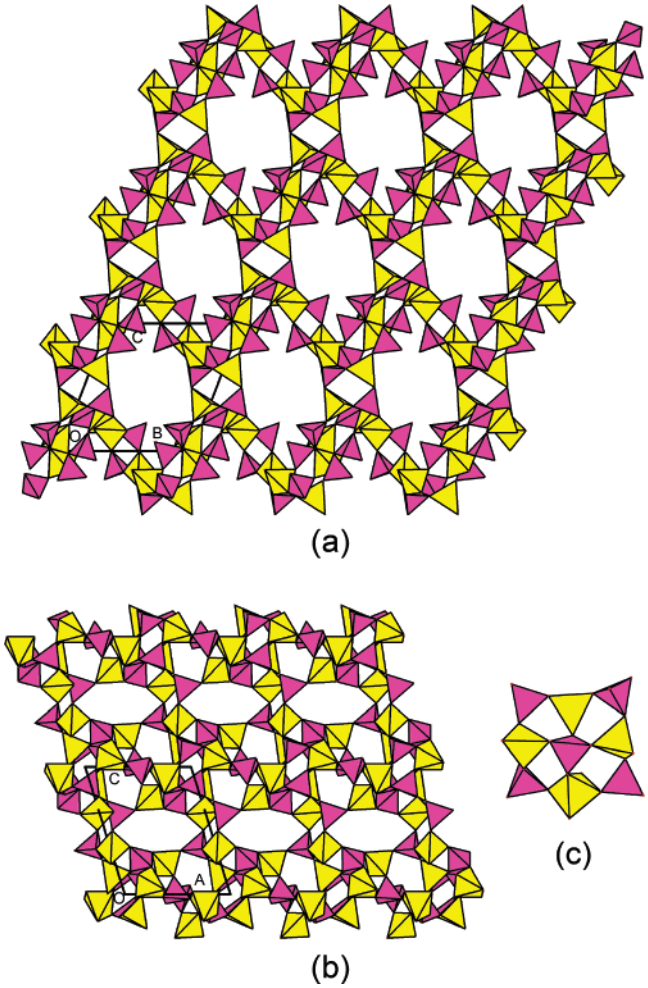

Figure 3. Hypothetical aluminophosphate structure H-1. This structure has a distorted 16-MR channel along [100] direction (a) and an 8-MR channel along [010] direction (b). This structure could also be seen as constructed by the Al_4P_5 building blocks (c). The yellow polyhedra denote the Al-centered polyhedra; the pink tetrahedra denote the P-centered tetrahedra.

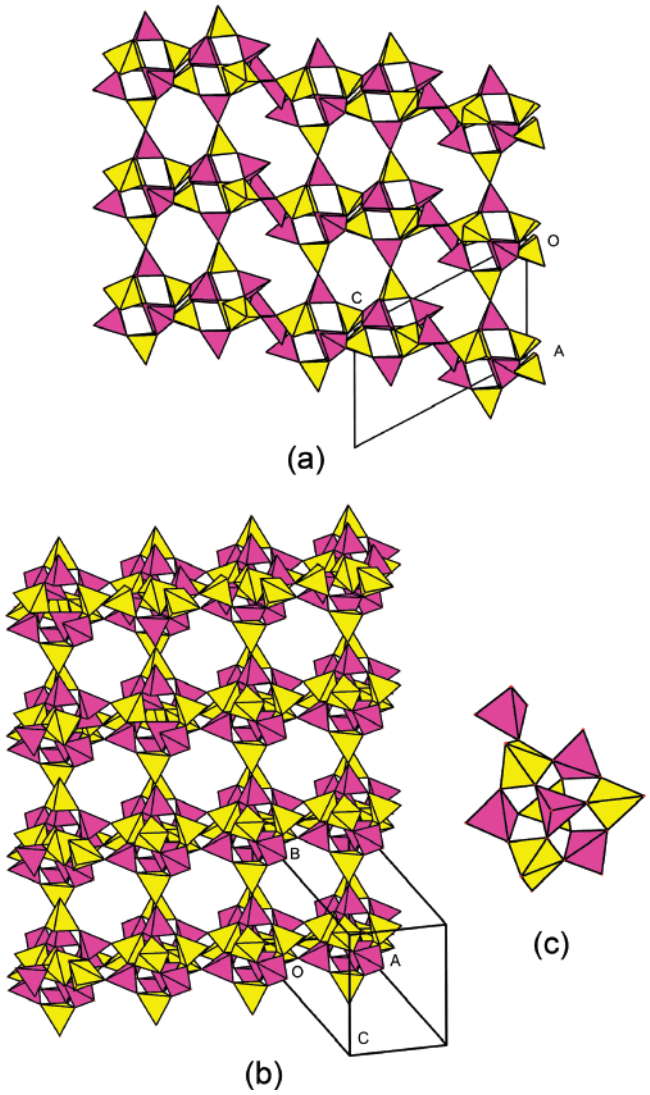

Figure 4. Hypothetical framework of structure H-3 with 12-MR channels and 8-MR channels along the [010] direction (a) and 10-MR channels along the [$\bar{1}$11] direction (b). This structure could also be seen as constructed by the branched D4R building blocks (c). The yellow polyhedra denote the Al-centered polyhedra; the pink tetrahedra denote the P-centered tetrahedra.

Hypothetical structure H-3 has four $Al(O_b)_4$, four $Al(O_b)_5$, six $P(O_b)_4$, and four $P(O_b)_3(O_t)$ atoms in its unit cell. It is also generated in space group $P\bar{1}$, and its $O_b/(Al + P)$ ratio is 2.0. As illustrated in Figure 4, there are three kinds of channels in this framework, including the 12-MR channels and the 8-MR channels running along the [010] direction (Figure 4a) and the 10-MR channels running along the [$\bar{1}$11] direction (Figure 4b). This framework could also be regarded as being constructed by the branched D4Rs (Figure 4c).

Hypothetical structure H-5 is generated in the space group $P2_1$ which has the same number of symmetric operations as $P\bar{1}$. It consists of four $Al(O_b)_4$, four $Al(O_b)_5$, eight $P(O_b)_4$, and two $P(O_b)_2(O_t)_2$ atoms in its unit cell, which corresponds to the No. 24 combination of Al and P atoms in our calculation results. As illustrated in Figure 5a, this structure could be viewed as being constructed by linking of 4.8^2-net layers through a certain up−down scheme, which forms the 8-MR channels along the [100] direction. Interestingly, this kind of 8-MR channel and 4.8^2-net framework are closely related to the known zeolite framework GIS.[27] In the framework of GIS, the 8-MR channels run along two perpendicular directions to form a 2D intersecting channel system. However, in hypothetical structure H-5, the 8-MR channels run along only one direction, while those along the other direction are blocked by additional P atoms (the blue tetrahedra in Figure 5b).

3. Generation of Hypothetical Structures with Other Stoichiometries Using the AASBU Method. In general, for this method, there is no restriction to the stoichiometry and the dimensionality of the hypothetical aluminophosphates to be generated. For example, in contrast to the 80 combinations Al and P atoms for the stoichiometry of $Al_8P_{10}O_{40}$, there are 77 combinations for the $Al_6P_8O_{32}$ stoichiometry (Table 2 in Supporting Information). Among these 77 results, No. 68 represents the combination of six $Al(O_b)_4$ and eight $P(O_b)_3(O_t)$. This is a common combination of Al and P atoms for a 2D layered aluminophosphate with $Al_6P_8O_{32}$ stoichiometry. The $O_b/(Al + P)$ ratio for this combination equals 1.71, which agrees well with the average value of 1.676 for the 2D

(27) Baerlocher, Ch.; McCusker, L. B. Database of Zeolite Structures. http://www.iza-structures.org/databases/ (accessed May 2005).

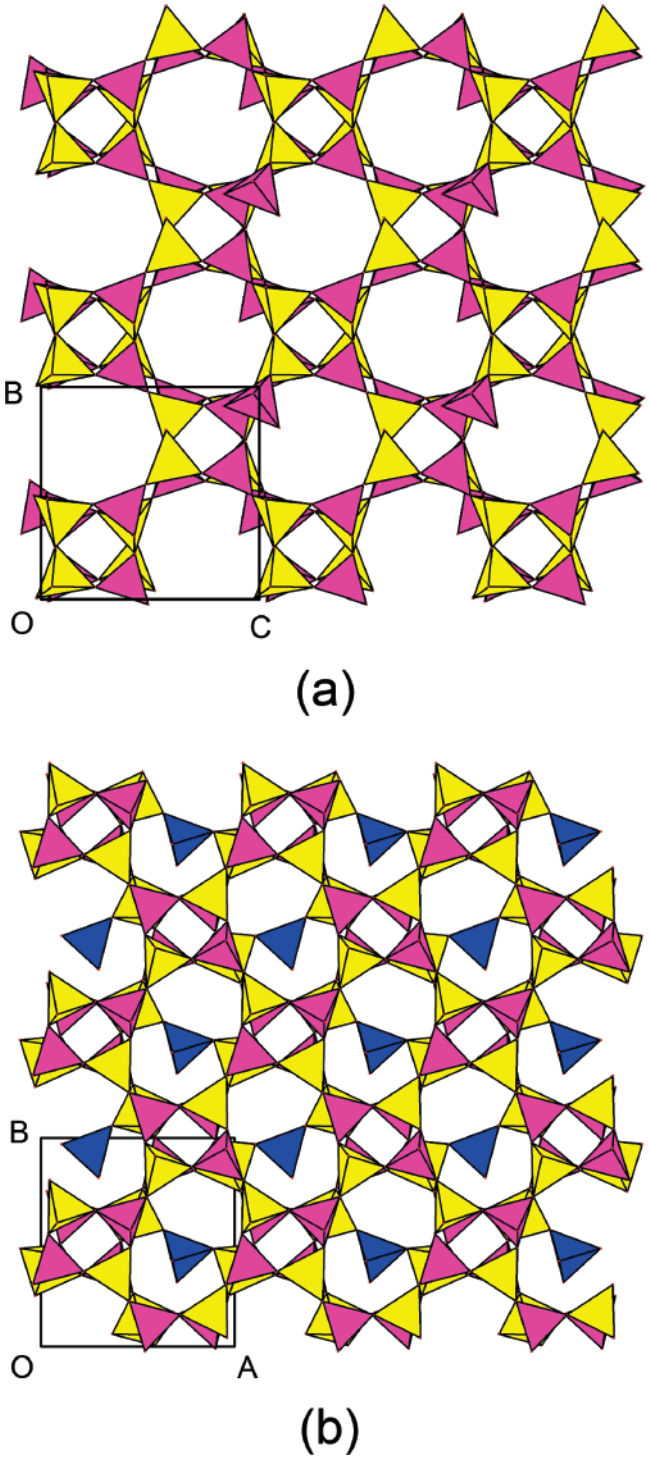

Figure 5. Framework of the hypothetical structure H-5. (a) The 8-MR channels and the 4.8^2-net layers viewed along [100] direction. (b) The blocked 8-MR channels viewed along the [001] direction. The yellow polyhedra denote the Al-centered polyhedra, the pink tetrahedra denote the P-centered tetrahedra, and the blue tetrahedra denote the blocking P atoms.

layered structures. This implies that such structures are likely to be 2D layered networks. When six $Al(O_b)_4$ and eight $P(O_b)_3(O_t)$ are used as the building units, several hypothetical 2D aluminophosphate layers with $Al_6P_8O_{32}$ stoichiometry could be generated. Figure 6 illustrates one of these hypothetical layers found in space group *Cmm*2. This layer could also be viewed as the combination of 4-MRs and 8-MRs to form a 4.8-net sheet.

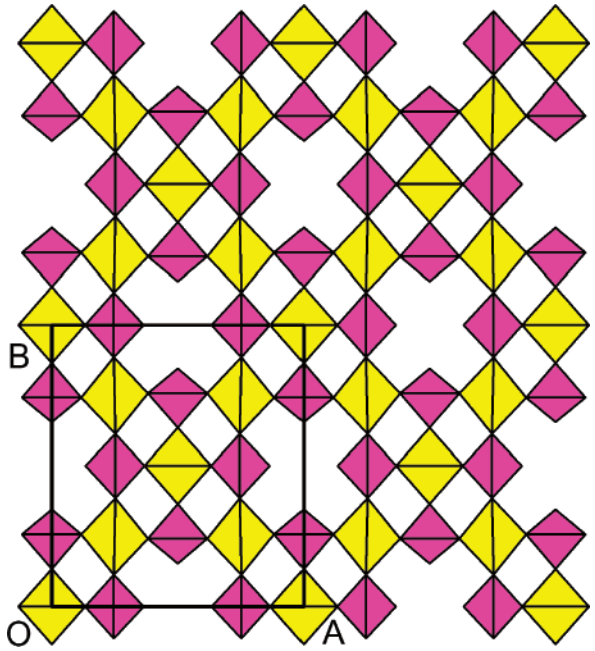

Figure 6. Hypothetical layer viewed along the [001] direction. The yellow tetrahedra denote the Al-centered tetrahedra; the pink tetrahedra denote the P-centered tetrahedra.

Conclusions

The approach we describe here provides an effective way to generate open-framework aluminophosphate structures with an Al/P ratio of nonunity on the basis of the AASBU method. During the simulation, two additional constraints are adopted because of the Lowenstein's rule for the open-framework aluminophosphate structures: (1) the building units for the simulation are decided on the basis of the calculation of all possible combinations of Al- and P-centered polyhedra according to the Lowenstein's rule and (2) the building units are encouraged to be connected with each other through Al−O−P bonds, while against the formation of Al−O−Al or P−O−P linkages. In general, there is no restriction to the stoichiometry and the space group for this method. Various structures could be generated by systemically changing the space groups and the cell parameters. It is particularly effective when the building units and the cell parameters are chosen appropriately, which grants its potential use in the structure solution of aluminophosphate structures. Férey et al. have reported some successful examples about the application of the AASBU method in the field of structure solution.[28,29] Using the AASBU method to solve the structure based on the powder XRD pattern requires the knowledge of its building units, which will be used to generate the initial structure model for further Rietveld refinement. In the field of aluminophosphates, the primary building units are AlO_m (m = 4, 5, 6) polyhedra and PO_4 tetrahedra, which could be easily identified by solid-state magic-angle spinning NMR. Furthermore, when advanced NMR techniques, such as $^{27}Al \rightarrow {}^{31}P$ cross polar-

(28) Dutour, J.; Guillou, N.; Huguenard, C.; Taulelle F.; Mellot-Draznieks, C.; Férey, G. *Solid State Sci.* **2004**, *6*, 1059−1067.
(29) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surblé, S.; Dutour, J.; Margiolaki, I. *Angew.* Chem., Int. Ed. **2004**, *43*, 6296−6301.

ization, $^{27}Al\{^{31}P\}$ rotational echo double resonance, and $^{31}P\{^{27}Al\}$ transfer of population double resonance are used, the detailed coordination environments of Al and P, such as the number of O_b and O_t atoms, could be unambiguously identified.[30] On the basis of the NMR experiments and our calculation results on the possible combinations of different kinds of Al and P atoms, the building units used in the AASBU method and their respective numbers could be obtained. Running the AASBU simulation with additional constraints in each possible space group suggested by powder index analysis will finally generate the best initial structure model for further Rietveld refinement. This approach will no doubt reduce the initial trials on starting models and facilitate further structure solution.

(30) Zhou, D.; Xu, J.; Yu, J.; Chen, L.; Deng, F.; Xu, R. *J. Am. Chem. Soc*, submitted.

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Supporting Information Available: The combinations of the various kinds of Al and P atoms for the stoichiometry of $A_8P_{10}O_{40}$ and $Al_6P_8O_{32}$, the distribution of $O_b/(Al + P)$ in three dimensionality, and the atomic coordinates for the hypothetical aluminophosphate structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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