Insight into the construction of open-framework aluminophosphates

Jihong Yu and Ruren Xu

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Over the past twenty five years, a class of open-framework aluminophosphates, denoted AlPOs, has been prepared with neutral zeolitic frameworks and anionic frameworks showing wonderfully complex structural and compositional diversity. An insight into the construction of open-framework AlPOs revealing their general structural features and topological chemistry is provided in this *tutorial review*, and the role of templating and the designed construction and synthesis of AlPOs are discussed.

1. Introduction

Traditionally, a zeolite is a crystalline aluminosilicate or silica polymorph based on corner-sharing TO_4 (T = Si and Al) tetrahedra to form a three-dimensional four-connected framework with uniformly sized pores of molecular dimensions.[1] Zeolite materials are very important in industrial technologies such as catalysis, sorption, and ion-exchange. At the beginning of the 1980's, a novel class of crystalline, microporous aluminophosphates was reported by Wilson *et al.* at Union Carbide that represented the first family of framework oxide molecular sieves synthesized without silica.[2] This discovery opened the door to a new era in open-framework inorganic materials.[3]

The novel aluminophosphate molecular sieves, designated $AlPO_4$-*n*, were prepared with a wide range of pore sizes by using a hydrothermal synthetic technique in the presence of organic amines or quaternary ammonium cations as templates or structure-directing agents.[4,5] The structures of $AlPO_4$-*n* are based on strict alternation of AlO_4 and PO_4 tetrahedra forming a neutral open-framework. The lattice Al and/or P atoms can be partially replaced by silicon and/or other elements to form frameworks with Brønsted acid sites and/or catalytically active metal centers.[6,7] Some $AlPO_4$-based molecular sieves are analogous to zeolites, but many $AlPO_4$-*n* compounds have a unique structure with no zeolite counterpart, for example VPI-5 with extra-large 18-ring channels.[8] In recent decades, the employment of new synthetic techniques, such as the solvothermal synthetic route[9] and the very recent ionothermal synthetic route involving using an ionic liquid as both the solvent and template,[10] has opened up many new possibilities in the preparation of new compounds with previously unseen compositional and structural diversity. To date, at least 200 structure-types of open-framework aluminophosphates (hereafter designated AlPOs) have been identified. These include neutral open-framework $AlPO_4$-*n* molecular sieves and their isomorphic substitute analogues, and anionic framework AlPOs. The anionic framework AlPOs comprise three-dimensional and low-dimensional frameworks made up of alternate Al-centered polyhedra (AlO_4, AlO_5, AlO_6) and P-centered tetrahedra $P(O_b)_n(O_t)_{4-n}$ (b: bridging, t: terminal, n = 1,2,3,4) forming diverse stoichiometries such as $AlPO_4(OH)^-$, $AlP_4O_{16}{}^{9-}$, $AlP_2O_8{}^{3-}$, $Al_2P_3O_{12}{}^{3-}$, $Al_3P_4O_{16}{}^{3-}$, $Al_3P_5O_{20}{}^{6-}$, $Al_4P_5O_{20}{}^{3-}$, $Al_5P_6O_{24}{}^{3-}$, $Al_{11}P_{12}O_{48}{}^{3-}$, $Al_{12}P_{13}O_{52}{}^{3-}$, $Al_{13}P_{18}O_{72}{}^{15-}$ and so forth.[11] Recently, we

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: jihong@jlu.edu.cn; rrxu@jlu.edu.cn

Jihong Yu

Jihong Yu, was born in 1967 in Liaoning. She obtained BS, MS, and PhD degrees from Jilin University, and has worked at the Hong Kong Science and Technology University and Tohoku University. Since 1999 she has been a Professor in the Chemistry Department, Jilin University. Her research interest is in the design and synthesis of zeolite and related open-framework inorganic materials. She received an award from the National Outstanding Youth Fund of China in 2001. She serves as an editorial board member of the journal of Microporous and Mesoporous Materials.

Ruren Xu

Ruren Xu was born in 1932 in Zhejiang. He obtained a BS degree from the National Shanghai Jiaotong University, and has worked at Fu Dan University and Hamburg University. Since 1979, he has been a Professor in the Chemistry Department, Jilin University. His research interest is in molecular engineering of zeolite and porous materials. He is an academician of the Chinese Academy of Sciences and an academician of the Third World Academy of Sciences. He has been the Councillor of the International Zeolite Association since 1998.

have built up a structure database containing detailed structural information on open-framework AlPOs reported in the literature.[12]

The discovery of open-framework AlPOs has brought some conceptual breakthrough for traditional microporous compounds, *e.g.*, the framework elements not only limited to Al and Si atoms; the upper-limit of pore size not only delimited to 12-ring; the primary building units not only defined to tetrahedra; particularly the on-going search for new structures provides some mechanism clues on the formation of open-framework materials. The discovery of AlPOs also improves the current application areas of microporous materials.[13] One of the important promising areas of application of AlPOs shown very recently is in catalysis where aerial oxidations are possible using linear and cyclic hydrocarbons.[14] The nanosized channels of $AlPO_4$-*n* also present suitable host systems for the fabrication of advanced functional materials, *e.g.* monosized single-walled carbon nanotubes.[15]

In this review, we aim to provide an insight into the construction of open-framework aluminophosphates and further to develop a basis for their designed construction. We believe that the understanding of the structural chemistry of open-framework materials will play an essential role in rationalization of the extended solid structures and further assist in the development of the molecular engineering of crystalline inorganic materials.

2. General structural aspects of AlPOs

2.1 Classification

The open-framework AlPOs reported to date comprise a wide range of structures and compositions. In terms of the electrostatic properties and Al/P ratios of the frameworks, they can be classified as two major categories: i) neutral framework $AlPO_4$-*n* with Al/P = 1, and ii) anionic framework AlPOs with Al/P $\leqslant$ 1.

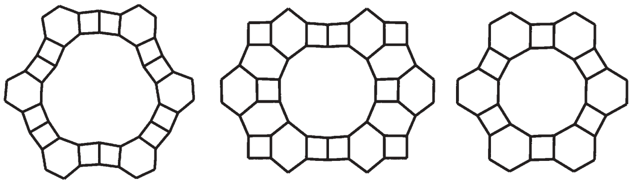
2.1.1 Neutral framework $AlPO_4$-*n* with Al/P = 1. The characters of $AlPO_4$-*n* include a neutral framework and a univariant framework composition with Al/P = 1.[16] Subsequent efforts to incorporate other elements have led the formation of $AlPO_4$-based molecular sieves with catalytic properties, such as SAPO (S: Si), ELAPO (El: Li, Be, B, Ga, Ge, As, Ti…..), ElAPSO, MeAPO (Me: metal), and MeAPSO. Even though some of them have been found no pure $AlPO_4$-*n* counterpart yet, these structures can be ideally described using a hypothetical $AlPO_4$-*n* lattice with alternate Al and P sites as a basis. To date, 167 zeolite framework type codes have been identified.[17] The $AlPO_4$-based molecular sieves include 51 unique structure types with extra-large pores (>12-ring), large pores (12-ring), intermediate pores (10-ring), small pores (8-ring), and very small pores (6-ring). These structures include 16 zeolite analogues, such as CHA ($AlPO_4$-34), ERI ($AlPO_4$-17), and 35 novel structures, such as VFI (VPI-5) and AEL ($AlPO_4$-11). Fig. 1 illustrates several representative $AlPO_4$-*n* molecular sieves with different pore openings and dimensions, including VPI-5 (VFI): 18-ring (1.27 × 1.27 nm), $AlPO_4$-8 (AET): 14-ring (0.79 × 0.87 nm), $AlPO_4$-5 (AFI): 12-ring (0.73 × 0.73 nm), $AlPO_4$-11 (AEL): 10-ring (0.40 × 0.65 nm), $AlPO_4$-41 (AFO): 10-ring (0.43 × 0.70 nm), and $AlPO_4$-25 (ATV): 8-ring (0.30 × 0.49 nm).

Apart from aluminosilicate or silica zeolites, $AlPO_4$-based molecular sieves constitute a major class of zeolite materials. These $AlPO_4$-based materials are normally stable upon removal of the occluded template molecules, and exhibit excellent thermal stability up to 1000 °C. These materials are mildly hydrophilic.

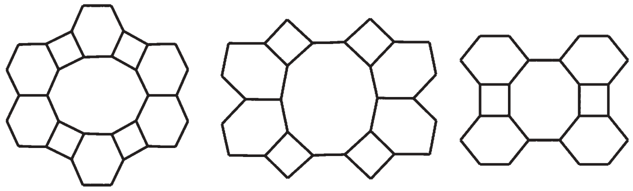
2.1.2 Anionic framework $AlPO_4$-*n* with Al/P $\leqslant$ 1. In contrast to neutral framework $AlPO_4$-*n* with Al/P = 1, most of the anionic framework AlPOs have an Al/P ratio less than unity.[11] The structures of anionic AlPOs are made up of alternation of Al-centered polyhedra (AlO_4, AlO_5, AlO_6) and P-centered tetrahedra $P(O_b)_n(O_t)_{4-n}$ (b: bridging, t: terminal, n = 1,2,3,4). The existence of terminal P–OH and/or P = O groups or $Al(OP)_n$ (n = 5, 6) polyhedra results in the deviation of Al/P ratio from unity in the framework. Their Al/P ratios are found as 1/1, 1/2, 2/3, 3/4, 3/5, 4/5, 5/6, 11/12, 12/13 and 13/18, and so forth. Their frameworks exhibit fascinating structural architectures. A notable example is JDF-20 with Al/P = 5/6,[18] which has the largest channel ring size of 20 among open-framework AlPOs (Fig. 2).

Anionic framework AlPOs have also been prepared with diverse low-dimensional framework structures, such as 2D layers with various porous sheets and sheet stacking sequences and 1D chains which might act as fundamental building blocks for complex structures. It is noteworthy that within each compositional family a wide variety of structure-types have been observed. For instance, the 2D frameworks with Al/P = 3/4 show diverse layered structures.

Most of the anionic framework AlPOs possess interrupted open-frameworks with terminal P–OH and/or P=O groups. They are unstable upon removal of the occluded protonated template molecules by calcination.



VPI-5:18-ring AlPO4-8:14-ring AlPO4-5:12-ring



AlPO4-11:10-ring AlPO4-41:10-ring AlPO4-25:8-ring

Fig. 1 Several representative $AlPO_4$-*n* molecule sieves with different pore openings.

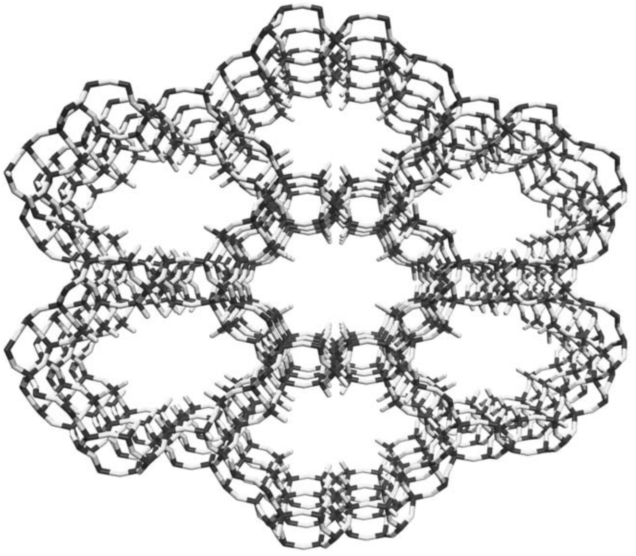


Fig. 2 JDF-20 with the largest channel ring size of 20.

2.2 Bonding patterns

2.2.1 Al–O–P bonding. As with aluminosilicate zeolites, open-framework AlPOs made up of Al–O–P bonds obey Löwenstein's Rule[19] with an avoidance of Al–O–Al bonds (only one exceptional case was reported in a layered AlPO containing Al–O–Al linkages[20]). The P–O–P bonds don't appear to be stable in these structures. Thus the avoidance of Al–O–Al and P–O–P bonds endows open-framework AlPOs featured by even-numbered rings. In interrupted anionic frameworks, a part of Al–O–P linkages are missed and terminal P–OH and/or P=O bonds are commonly observed that interact with the protonated templating molecules through H-bonds.[11]

By using first-principles quantum chemical techniques, Corà and Catlow characterized the bonding properties of crystalline AlPOs to compare them with the isostructural silica-based zeolites.[21] Their calculation results reveal that silica polymorphs and AlPOs differ in the nature of bonding. The silica polymorphs consist of covalently bonded SiO_4 units, while AlPOs are shown to be of molecular-ionic character and comprised of discrete Al^{3+} and $PO_4{}^{3-}$ ions. The ionicity of the AlPO frameworks might be responsible for the major contrast between the chemistry of AlPOs and that of aluminosilicates relative to the nature and concentration of dopants that can be introduced into the frameworks. In AlPOs, ionic substitutional dopants introduce minor perturbations to the host electric structure and therefore more readily replace Al in AlPOs than Si in zeolites.

2.2.2 Isomorphic substitutions. Flanigen *et al* elucidated the bonding concepts in $AlPO_4$-based molecular sieves.[6] The linkages of Al–O–P, Si–O–Si, Si–O–Al, Me–O–P, Me–O–P–O–Me have been observed, whilst the linkages of P–O–P, P–O–Si, Al–O–Al, Me–O–Al, Me–O–Me appear to be unlikely. Based on these patterns, they proposed rules for framework cation siting of metal and Si in AlPO frameworks: i) Me incorporation into a hypothetical Al site, ii) Si into a hypothetical P site, and iii) 2Si for Al + P.

Martens and Jacobs further elaborated the types of isomorphic substitutions according to various substitution mechanisms.[22] Fig. 3 shows different types of substitutions. The isomorphic substitution mechanism (SM) can be classified as: i) SM I—substitutions of Al atoms. SM I*a*, SM I*b*, and SM I*c* refer to monovalent, divalent and trivalent element substitutions of Al atoms, respectively, thus resulting in an M–O–P bond; ii) SM II—substitutions of P atoms. SM II*a* and SM II*b* refer to tetravalent and pentavalent element substitutions, respectively, thus resulting in an M–O–Al bond; iii) SM III—substitutions of pairs of adjacent Al and P atoms.

Si is the only element exhibiting the SM III. The avoidance of Si–O–P bonds precludes a "homogenous" substitution of 2Si for Al + P (SM III*ho*, Fig. 4a), and a "heterogeneous" substitution mechanism (SM III*he*, Fig. 4b) instead of SM III*ho* was proposed by Martens and Jacobs to reflect the presence of SiO_2 patches with only Si–O–Si and Si–O–Al bonds. The presence of additional Al within the SiO_2 patch produces a zeolite region.

In some cases, the incorporation of other elements into the $AlPO_4$ lattice represents combinations of substitution mechanisms.[22] The bonding concepts have remained valid for all stable, calcined structures describable as tetrahedral nets.

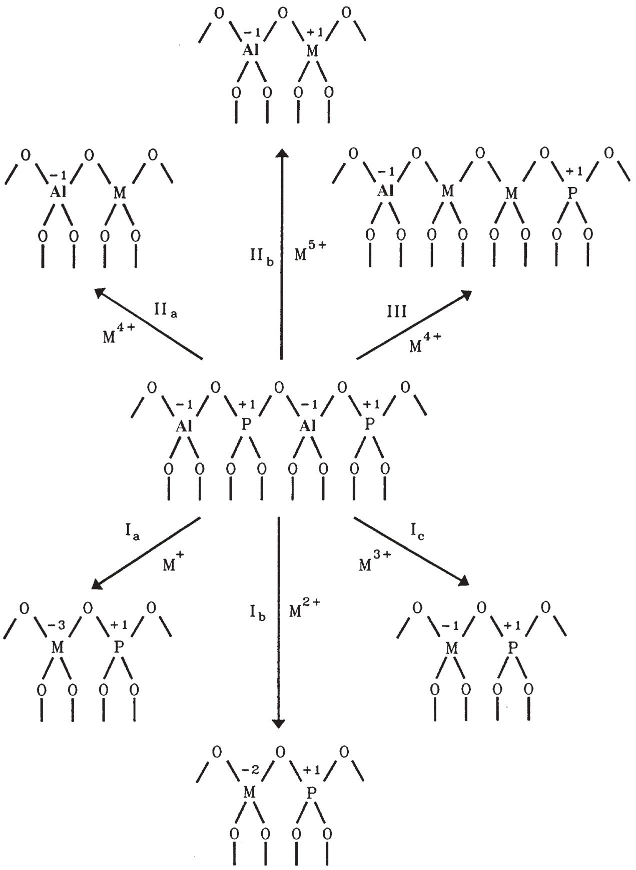


Fig. 3 Isomorphic substitution mechanisms in $AlPO_4$-based frameworks. Reproduced with permission from ref. 22, copyright Elsevier 1994.

3. Topological chemistry of AlPOs

3.1 Building units

The complex structures of open-framework AlPOs can be understood on the basis of their construction from fundamental building units. The essential topochemical features of open-framework AlPOs are described in this section. Topologically, the neutral framework $AlPO_4$-*n* molecular sieves can be described as four-connected 3D frameworks since the Al and P atoms occupy the 4-connected vertices of a 3D net; most of the anionic framework AlPOs can be described as interrupted frameworks because a part of the Al–O–P linkages are missed.

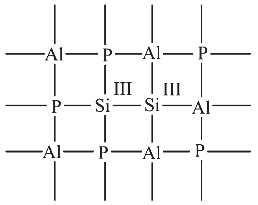
3.1.1 Four-connected 3D frameworks.

3.1.1.1Secondary building units (SBU's). The four-connected 3D frameworks, typically for zeolite frameworks, can be thought to be constructed of finite secondary building units (SBU's).[17] The SBU's, which contain up to 16 T-atoms, are derived assuming that the entire framework is made up of one type of SBU only. It should be noted that SBU's are invariably non-chiral. This means that SBU's in the isolated state of highest possible symmetry are neither left- nor right-handed. A unit cell always contains an integral number of SBU's. 18 SBU's have been listed for zeolites in the 5th edition of the ATLAS,[17] among which 8 occur in four-connected 3D $AlPO_4$-*n* frameworks (Fig. 5). In some cases combinations of SBU's have been encountered, *i.e.*, the respective framework cannot be generated from one type of SBU only. The SBU's are only theoretical topological building units and should not be considered to be or equated with species that may be in the solution/gel during the crystallization of a synthetic material.

3.1.1.2 Infinite 2D nets and linkage into 3D frameworks. The four-connected 3D frameworks of $AlPO_4$-*n* can also be thought to be constructed of infinite component units, like chains and layers.[23] Some AlPO structures can be constructed from a parallel stack of simple three-connected 2D nets. A 2D net is denoted with the size of the three circuits that meet at the different types of nodes. For instance, as seen in Fig. 6a, $(4.4.18)(4.6.18)_2$ 2D net in VFI framework associates with two 4-rings and an 18-ring meet at one type of node, a 4-ring, a 6-ring and an 18-ring at the second one. The abundance of the (4.6.18) type of nodes is twice that of the (4.4.18) nodes. The most obvious way to generate a four-connected 3D framework from a 2D net is to arrange one type of 3-connected 2D net into a parallel stack and to link each vertex to only one other vertex. To form a 3D net, some of the new edges must point upward and some downward from each 2D net. This variability explains the diversity of structures that can be constructed starting from a stacking of one type of 2D nets.

Martens and Jacobs described several $AlPO_4$-*n* structures with tubular pores that can be rationalized by the 2D net approach.[22] In the topologies of VFI: $(4.4.18)(4.6.18)_2$-2D net, AET: $(4.6.6)(4.4.14)(4.6.14)_2(6.6.14)$-2D net, AEL: $(4.6.10)_4(6.6.10)$-2D net, AFO: (4.6.6)(4.6.10)(4.10.10)-2D net, and ATV: $(4.6.8)_2(6.8.8)$-2D net (see also Fig. 1), interlinking of the 2D nets occurs through a same pattern: each 2D net is linked with the previous 2D net through Al atoms, and with the subsequent 2D net through P atoms. This strict alternation of linking results in the structures possessing a monodimensional tubular micropore system with the pores running in the direction perpendicular to the 2D nets. Fig. 6b shows the VFI framework linked by the 2D net. Interestingly, such a linkage would give rise to particular dipolar properties. This polar property is unique for the above group of $AlPO_4$-*n* frameworks, but less pronounced in other $AlPO_4$ topologies which are not based on 2D nets and the alternate linkage mode.

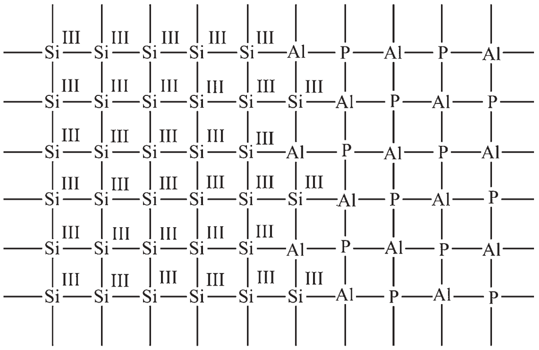
SM III ho



Si(1Si3P); Si(1Si3Al)

(a)

SM III he



Si(4Si); Si(1Si3Al); Si(3Si1Al)

(b)

Fig. 4 Two-dimensional representation of Si substitution in an $AlPO_4$ framework (a) homogeneous substitution and (b) heterogeneous substitution. Reproduced with permission from ref. 22, copyright Elsevier 1994.

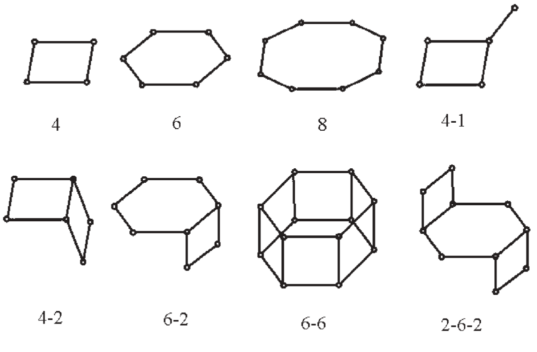


Fig. 5 Secondary building units (SBU's) found in $AlPO_4$-*n* based frameworks and their symbols.

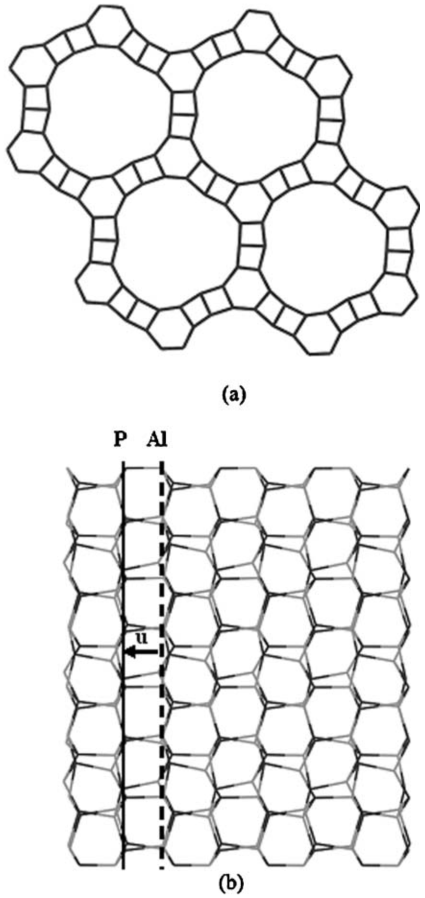


Fig. 6 (a) $(4.4.18)(4.6.18)_2$ 2D net of the VFI framework and (b) VFI framework viewed perpendicular to the *c* axis. Layers of Al atoms (dotted line) and P atoms (solid line) alternate in the structure giving rise to permanent dipoles. Reproduced with permission from ref. 22, copyright Elsevier 1994.

Details about the 2D nets and linkages into 3D nets can be found in the comprehensive review by Smith.[23]

3.1.2 Interrupted three-dimensional and low-dimensional frameworks. The existence of terminal P–OH and/or P=O groups results in the interruption of 3D frameworks and the low dimensionality of the frameworks.

Similar to the above four-connected 3D frameworks, some complex 3D interrupted frameworks can be also described based on simple 2D nets. An example from AlPO-DETA,[24] $[H_3N(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}[Al_2P_3O_{12}]^{3-}$ with Al/P = 2/3, is presented to illustrate the construction of 3D interrupted frameworks from 2D nets.

AlPO-DETA is constructed from strict alternation of AlO_4 and PO_4 tetrahedra. However, differently from the four-connected $AlPO_4$-*n* frameworks in which all the Al and P vertices are shared, AlPO-DETA possesses doubly and triply bridged PO_4 tetrahedra, resulting in a highly interrupted open-framework. As seen in Fig. 7a, the structure consists of parallel 12- and 8-ring channels along the *c* direction, with terminal P=O groups protruding into the channels. The framework can be constructed from a parallel stack of the (4.8^2)-2D net in which each node is three-connected (Fig. 7b).The fourth linkages of each Al node in the 2D net connect adjacent layers (previous and subsequent layers) through extra doubly bridged PO_4 tetrahedra to form the 3D interrupted open-framework, leaving the fourth linkage of each P node in the 2D net terminal. The structure of AlPO-DETA implies that diverse interrupted 3D open-frameworks can be also built up starting from a stacking of one type of 2D nets as with four-connected zeolite frameworks.

A large fraction of terminal P–O bonds gives an effect that the Al–O–P connections cannot be extended three dimensionally, thus resulting in low-dimensional networks including 2D layers, 1D chains, and 0D clusters.[11]

A variety of 2D layered networks with different Al and P stoichiometries is noteworthy in open-framework AlPOs. 2D layered AlPOs are found as $AlPO_4(OH)^-$, $AlP_2O_8^{3-}$, $Al_2P_3O_{12}^{3-}$, $Al_3P_4O_{16}^{3-}$, $Al_4P_5O_{20}^{3-}$, and $Al_{13}P_{18}O_{72}^{15-}$, *etc.*, among which the stoichiometry of $Al_3P_4O_{16}^{3-}$ is known in a large number of 2D layered compounds. With the exception of $[C_3N_2H_5]_2[Al_3P_4O_{15}(OH)]$ which contains AlO_5 units, the anionic sheets of $Al_3P_4O_{16}^{3-}$ are typically made up of alternation of AlO_4 and PO_4 tetrahedra in which the Al vertices are shared but not all the P vertices. Each PO_4 tetrahedron shares three oxygen atoms with adjacent Al atoms, leaving one oxygen atom terminal. Different linkages of these tetrahedral units lead to various sheet topologies. Fig. 8 shows eight distinct 2D sheet structures. Five types of

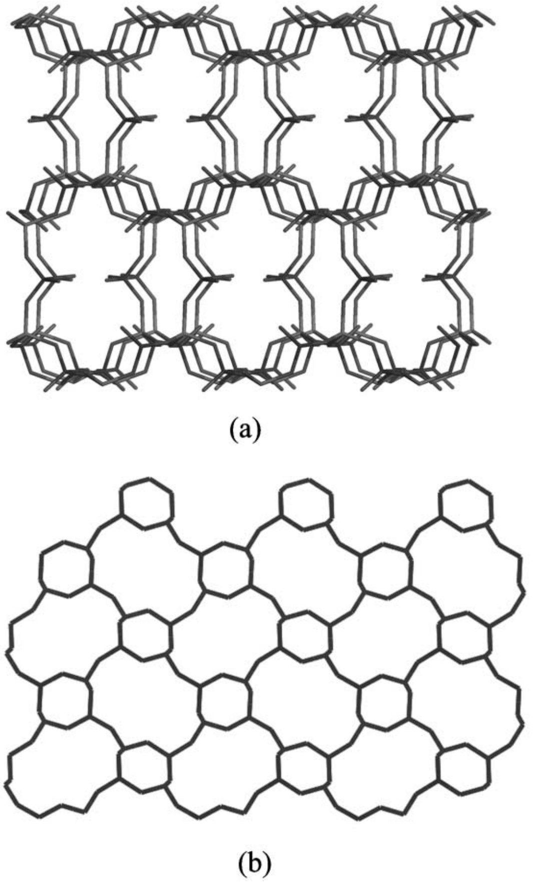


Fig. 7 (a) Framework of AlPO-DETA consisting of parallel 12- and 8-ring channels along the *c* axis and (b) (4.8^2) 2D net in the framework of AlPO-DETA.

SBU's constructing the sheets are also shown. Topologically, these 2D sheets can be described as 3.4-connected 2D nets in which the P atoms occupy 3-connected nodes and the Al atoms occupy 4-connected nodes.

A number of AlPOs also occur as 1D infinite chains with stoichiometry of $AlP_2O_8^{3-}$ and $Al_3P_5O_{20}^{6-}$. The chains are made up of alternation of AlO_4 tetrahedra and $P(O–Al)_nO_{4-n}$ (n = 1, 2, 3) tetrahedra with terminal P–OH and/or P=O groups. The corner-sharing 4-ring chains (AlPO-CSC) and edge-sharing 4-ring chains (AlPO-ESC) with Al/P = 1/2 have the simplest chain structures. AlPO-CSC is made up of alternation of quadruply bridged AlO_4 tetrahedra and doubly bridged PO_4 tetrahedra to form linear corner-sharing Al_2P_2 4-ring chain (Fig. 9a). AlPO-ESC is made up of quadruply bridged AlO_4 units and triply and singly bridged PO_4 units through Al–O–P linkages to form a zigzag ladder of fused Al_2P_2 4-rings with pendant PO_4H side groups (Fig. 9b). Oliver *et al.* proposed that the corner-sharing 4-ring chains, on hydrolysis and rotation of bonds, may transform to higher dimensional structures.[25] Experimentally, by using AlPO-CSC as a building unit, we have successfully built up the 3-D open-frameworks $MAlP_2O_8{\cdot}C_2N_2H_9$ *via* transition metal cations (M = Ni^{2+}, Co^{2+}, Fe^{2+}). The intact AlPO-CSC chains are kept in the 3D frameworks.[11]

3.2 Al and P coordinations and stoichiometries

The structural and compositional richness of AlPOs are attributed to the diverse coordinations of Al and P atoms. The majority of $AlPO_4$-*n* molecular sieves are based on a four-connected network of corner sharing tetrahedra, *i.e.*, AlO_{4b} and PO_{4b} (b: bridging oxygen between Al and P). There is a number of $AlPO_4$-*n* with mixed-bonded frameworks containing five- or six-coordinated Al atoms with one or two extra-framework oxygen species, such as OH and H_2O.[26] For instance, both VPI-5 and $AlPO_4$-8 contain $AlO_{4b}(H_2O)_2$ units; $AlPO_4$-17, -18, -20, -21 and -31 contain $AlO_{4b}(OH)$ units. By omitting the OH and H_2O species, these frameworks can be idealized as a four-connected framework.

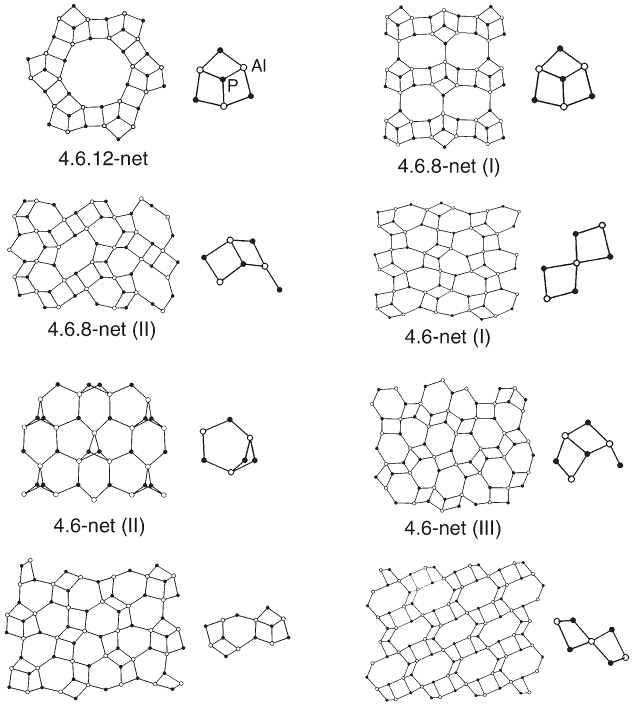


Fig. 8 Eight distinct 2D sheet structures. SBU's constructing the sheets are also shown. Reproduced with permission from ref. 16, copyright American Chemical Society 1986.

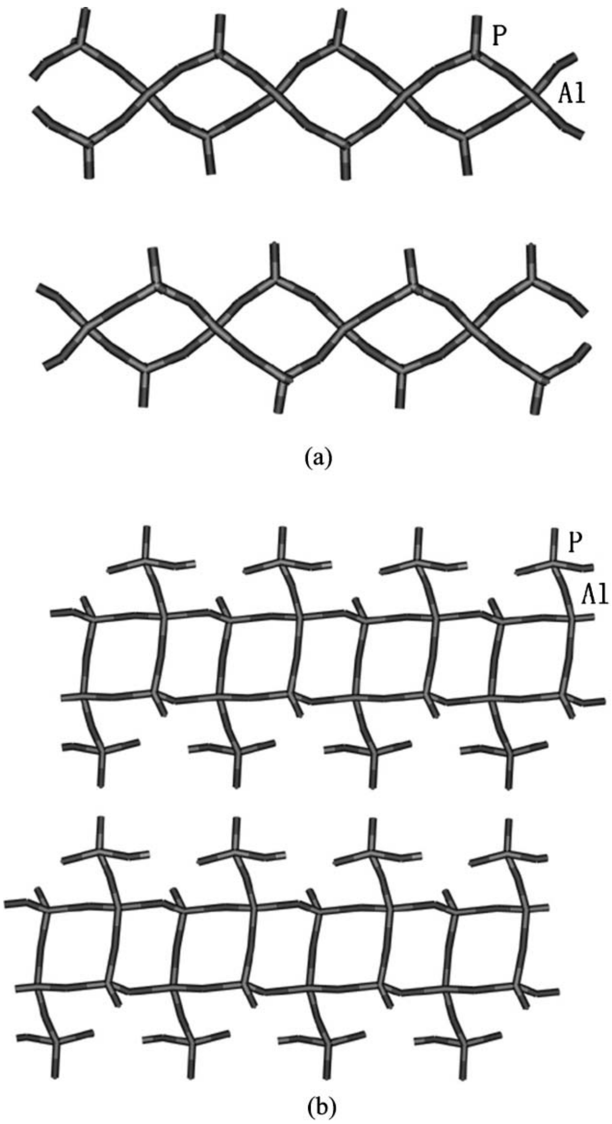


Fig. 9 Two 1D chains with $AlP_2O_8^{3-}$ stoichiometry (a) corner-sharing 4-ring chains (AlPO-CSC) and (b) edge-sharing 4-ring chains (AlPO-ESC).

The anionic open-framework AlPOs display a wide range of Al and P coordinations. The Al coordinations occurring in these AlPOs are four, five and six in the forms of $AlO_{3b}(OH)$, AlO_{4b}, AlO_{5b}, $AlO_{4b}(OH)$, $AlO_{4b}(OH)_2$, $AlO_{4b}(H_2O)_2$, $AlO_{4b}(OH)(H_2O)$, $AlO_{5b}(OH)$ and AlO_{6b}, while the P coordinations are solely four in the forms of PO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$, PO_bO_{3t} (b: bridging O between Al and P; t: terminal O). Detailed information about the Al and P coordinations can be found in the AlPO database in ref. 12.

Combinations of alternate Al and P atoms give rise to various framework structures and Al and P stoichiometries. According to the Löwenstein's Rule, the number of Al–O_b bonds must be equal to the number of P–O_b bonds in open-framework AlPOs. Consequently, the correlation of coordination environments of Al and P can be described in the following eqn (1):[11]

$$\sum_i m_{\mathrm{AlO}i\mathrm{b}} \times i_{\mathrm{AlO}i\mathrm{b}} = \sum_j n_{\mathrm{PO}j\mathrm{b}} \times j_{\mathrm{PO}j\mathrm{b}} \qquad (1)$$

where *i(j)* is the number of bridging oxygens coordinated to Al (P), *m(n)* is the number of AlO_{ib} (PO_{jb}) coordination, $\sum m_{\mathrm{AlO}i\mathrm{b}}/\sum n_{\mathrm{PO}j\mathrm{b}}$ = Al/P, i = 3, 4, 5, and 6 corresponding to AlO_{3b}, AlO_{4b}, AlO_{5b} and AlO_{6b} units, respectively, j = 1, 2, 3, and 4 corresponding PO_4 units with one, two, three and four bridging oxygens, respectively. Based on this equation, the detailed Al and P coordinations for a given stoichiometry can be enumerated.

By applying advanced solid-state NMR techniques, the detailed Al and P coordinations can be determined. We have recently investigated a series of anionic framework AlPOs with different Al and P coordinations by various solid-state NMR techniques, including ^{27}Al, ^{31}P magic angle spinning (MAS), ^{27}Al → ^{31}P cross polarization (CP), ^{27}Al{^{31}P} rotational echo double resonance (REDOR), and ^{31}P{^{27}Al} transfer of population double resonance (TRAPDOR). Different Al coordinations (AlO_{4b}, AlO_{5b}, and AlO_{6b}) and P coordinations (PO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$, and PO_bO_{3t}), where b represents bridging oxygens and t represents terminal oxygens, can be unambiguously distinguished. Furthermore, a new method to determine the Al/P ratio of open-framework AlPOs based on eqn (1) as well as NMR studies has been established,[27] which is useful for the understanding of unknown AlPO structures.

4. Templating in the construction of AlPOs

Open-framework AlPOs are synthesized by hydrothermal or solvothermal crystallization of reactive aluminophosphate gels in the presence of an organic base as the templating agent (or structure-directing agent) as in the synthesis of high-silica zeolites. These template species occupy the pore and cages of the structures and play an important role in directing the formation of a specific structure.

4.1 Types of templates

A large variety of organic templates can facilitate the synthesis of open-framework AlPOs. So far, over 100 species have been seen successfully as templates, typically involving quaternary ammonium cations and various organic amines including primary, secondary, tertiary, and cyclic amines, and alkanolamines. Some stable metal–ligand complexes such as Cp_2Co^{2+} and $Co(en)_3{}^{3+}$, have also been used in the synthesis of AlPO materials. Very recently, ion liquids have been used as both the solvent and template for the preparation of SIZ-*n* type AlPO materials by Morris and coworkers.[10]

The one-template-multiple-structure and multiple-template-one-structure phenomena are remarkable in open-framework AlPOs. For example, di-*n*-propylamine (Pr_2NH) has been used in the synthesis of at least ten different AlPO structure types, such as $AlPO_4$-11, -31, -39, -41, -43, -46, -47, -50, H3/MCM-1, and H1/VPI-5/MCM-9, exhibiting low structure specificity. On the other hand, some structures readily form from many different templates, *e.g.*, $AlPO_4$-5 is much less template specific, and can be synthesized with >25 different templates. Tetrapropylammonium hydroxide is a typical template for the synthesis of $AlPO_4$-5, which is stacked in a tripod arrangement with the head of one TPA ion suspended between the three feet of the next TPA ion with a hydroxyl group neatly suspended between them.[16] As seen in Fig. 10, although this tripod arrangement is such a good geometrical fit with the cylindrical wall, the TPAOH is not a template in the true sense because of the inconsistency of the three-fold molecular symmetry and six-fold channel symmetry.

A few AlPO structures exhibit high template specificity. For example, $AlPO_4$-20 can be crystallized only with TMAOH. The spherical TMAOH molecule with a 0.62 nm diameter fits neatly into the sodalite cage.

In some AlPOs, a mixture of templates appears to cooperatively direct the formation of the structures. For instance, SAPO-37 is prepared by a mixture of TPAOH and TMAOH. Structural characterizations show the presence of TMA in the sodalite cages, and TPA in the supercages. In the synthesis of $AlPO_4$-52, both Pr_3N and TEAOH appear to be necessary, but only TEAOH is occluded in the structure.

As with organic amine, water can also play an important structure-directing role. A notable example has been seen in VPI-5. Even though VPI-5 is preferentially prepared in the presence of organic amines, the organic species are not occluded into the extra-large 18-ring pores. Instead, water molecules form an intriguing H-bonded triple helix inside the channel.[28]

In the family of anionic framework AlPOs, the occluded organic amines in the products are exclusively protonated and

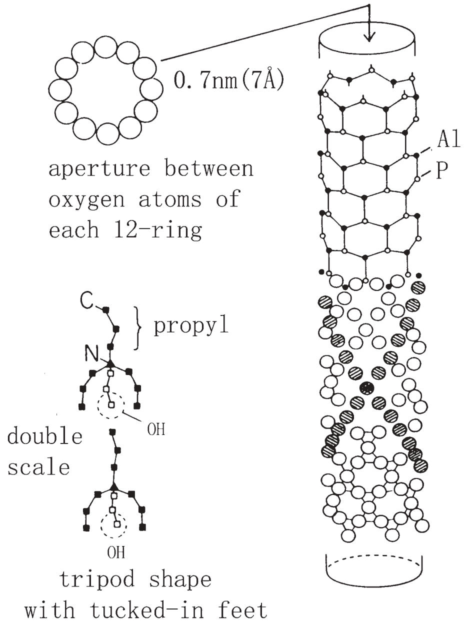


Fig. 10 Cylindrical channel in $AlPO_4$-5 and the stacking of the encapsulated tetrapropylammonium hydroxide species. Reproduced with permission from ref. 16, copyright Elsevier 1994.

play a charge balancing role as well. The protonated amine molecules interact with lattice oxygen atoms of the host framework through H-bonds and thus stabilize the frameworks. Fig. 11 shows the interaction of Et_3NH^+ cations with the interrupted framework of extra-large pore JDF-20. Each 20-ring accommodates four Et_3NH^+ cations. It is interesting to note that the structure with the largest pore opening is not templated by a particularly large template, but in fact multiple organic cations in the pore.

4.2 Role of templating

Templating has been a frequently discussed phenomenon in the synthesis of zeolite and related open-framework materials.[29,30] So far, the relationship between the templating agents and the structures, usually known as templating effect, is still not fully understood. The term templating has been frequently used in the context of synthesizing high-silica zeolites. One definition about templating was described by Lok *et al.* as "the phenomenon occurring during either the gelation or the nucleation process whereby the organic species organizes oxide tetrahedra into a particular geometric topology around itself and thus provides the initial building block for a particular structure type."[31] Gel chemistry is also essential to the formation of microporous aluminophosphates. With the addition of organic base, the gel chemistry of aluminophosphate is altered, and the templating becomes operative only in the gel with right gel chemistry. Therefore the dual role of the organic templates in the synthesis of open-framework AlPOs is evident. It serves the important role of modifying the gel chemistry, and it also has a structure-directing effect.

The organic template plays at least two additional roles in the product, *i.e.*, stabilizing voids and balancing the framework charge. By packing the cages and channels the organic can increase the overall thermodynamic stability of the template/lattice composite, so that the metastablility of the lattice alone is less critical.[4] The stabilizing and charge balance role of organic templates is quite evident in anionic framework AlPOs. After removing the occluded template molecules by calcination, the anionic frameworks normally collapse. On investigation of the formation of 2D layered AlPOs with $Al_3P_4O_{16}{}^{3-}$ stoichiometry, our studies show that the protonated template cations, except for balancing the charge of macroanionic layers, interact with the host inorganic layers (*i.e.*, terminal P=O groups) through extensive H-bonds, which is believed to stabilize the 2D layered structures.[32] Furthermore, the templates also determine the stacking sequences of 2D layers. The template molecules interact with the host inorganic network with certain regularity and their interaction can be well described based on the interaction between SBUs and protonated amino groups. This allows the template molecules to be located with a reasonable success.

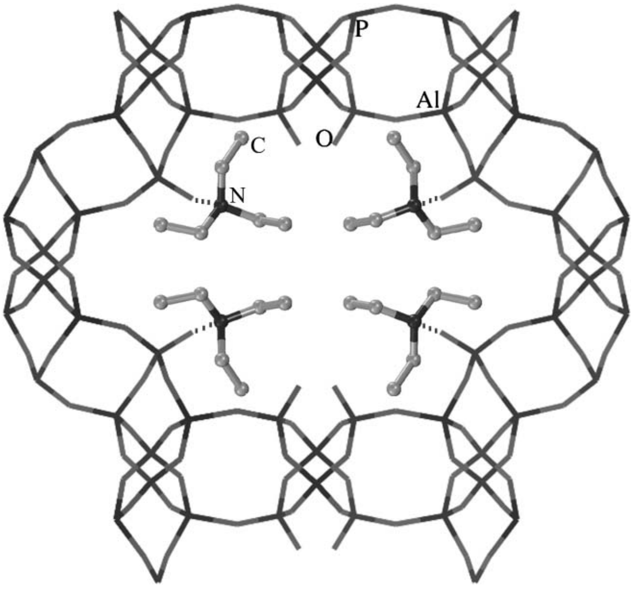


Fig. 11 Interaction of Et_3NH^+ templating molecules with the host framework of JDF-20 through N···O hydrogen bonds.

Even though a true templating effect, *i.e.*, hand-in-glove fit between organic and inorganic lattice, is less pronounced in the synthesis of open-framework AlPOs, it seems that an encapsulated organic species in the void space of the inorganic host can adopt configuration that conforms best with the surrounding aluminophosphate framework. For example, $AlPO_4$-12, -21 and -EN3 were all synthesized with encapsulated ethylenediamine. It is stabilized into optical isomers of the *gauche* form by intramolecular bonding in $AlPO_4$-12 and -21, while it occurs in $AlPO_4$-EN3 as the *trans* configuration with N–C–C–N extended along a straight eight-ring channel. The empirical evidence is that for a template to be successful there must be a 'good fit' between the guest molecule and the host framework formed.

The importance of the template molecules appears not only in its role of structure directing but also of orientating the distribution of Si in the frameworks. Barthomeuf and co-workers demonstrated the role of the template in directing Si distribution in the lattice of SAPO materials.[33]

In metal-substituted AlPOs, the template molecules also influence the degree of metal-ion substitution of the frameworks. Lewis *et al.* studied the influence of organic templates on the structure and on the concentration of framework metal ions in microporous AlPO catalysts.[34] Their calculations demonstrate that the degree of metal-ion substitution of the framework is controlled not only by the relative stability of the framework but also by the need to accommodate the structure-directing and charge-compensating template molecules. Templates with higher charge/size ratios will allow a greater control over the ratio of metal substitution or heteroatom incorporation in the framework.

5. Designed construction of AlPOs

A better understanding of the structural construction of open-framework AlPOs will allow a designed construction. Recently, computational modeling techniques have substantially aided in the prediction of crystal structures of zeolite and related open-framework materials.[35–37] The desired structures with predefined pore structures, building units and compositions can be designed based on constrained assembly of atoms or automated assembly of secondary building units.

5.1 Design of zeolite frameworks with predefined pore geometry through constrained assembly of atoms

Recently, we have developed a simple and straightforward computational method for the generation of zeolite frameworks with specified pore structures by introducing an additional constraint, *i.e.*, *forbidden zones*, in the simulation input.[38] Using this methodology, one is able to generate new hypothetical zeolite frameworks with desired pore geometries.

In this method, the channel structure represented as four cylinders, called *forbidden zones* (Fig. 12), is first defined in a unit cell and then *T* atoms are placed outside of the forbidden zones based on specified symmetry and distance constraints. 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 structural model is built using Cerius^2 software package. Bridging oxygen atoms can be automatically added on the basis of the distances between the nearest atoms. The structures are further refined using a DLS refinement or energy minimizations. Details about the simulation steps can be found in ref. 38.

This method allows a user to specify the pore size, the number of unique atoms, the unit cell and the space group. It can be applied to generate 4-connected zeolite frameworks by defining any desired porous pattern, such as cross-linked channels and chiral channels. It should be noted that the generated frameworks by this method are assumed with a SiO_2 composition. The $AlPO_4$ frameworks correspond to those generated structures containing even-numbered ring channels made up of alternation of Al and P atoms. The thermodynamic feasibility of hypothetical frameworks can be evaluated based on some characteristic properties such as relative lattice energies and average bond distances and angles, *etc*.

5.2 Design of zeolite structures with predefined building units through automated assembly of secondary building units (AASBU)

Draznieks and Férey *et al.* developed a computational method for the *de novo* prediction of inorganic crystal structures through automated assembly of secondary building units (AASBU).[39] This method has been further applied to the design of AlPOs with predefined double-four (D4R) units. The key feature of this method lies in the use of predefined D4R units and in the exploration of their periodical autoassembly in 3-D space through a cascade of simulated annealing/minimization steps.

The preliminary step consists of building the D4R unit, *i.e.*, $M_8B_{12}L_8$ (M, central metal atom; B, bridging atoms between M atoms; L, ligand atoms) shown in Fig. 13. The rules that control the possible assembly of the D4R units are encapsulated in a cost function consisting of a Lennard–Jones-like term with a force field that essentially favors the attraction of ligand atoms to one another, *i.e.*, favors the formation of ligand···ligand ''sticky-atom'' pairs that allow two D4R units to assembly through L···L linkages, and avoids unwanted configurations of D4Rs. The candidate structures based on D4R units are then generated by using a cascade of simulations. Lattice energy minimizations are performed to estimate the viability of the hypothetical frameworks as AlPO candidates as compared to those existing related compounds. Details about the simulation steps can be found in ref. 39.

The AASBU method allows not only the organization of the known structures to be rationalized but also the search for new topologies based on the same building units.

5.3 Design of open-framework AlPOs with predefined stoichiometries using the AASBU method with Löwenstein's constraints

Recently we have described an approach to generate hypothetical open-framework AlPOs with predefined Al/P stoichiometry using AASBU method with additional Löwenstein's constraints.[40]As presented in Section 3.2, for each specified Al/P stoichiometry, all the possible combinations of Al and P atoms with different coordination states could be calculated according to Löwenstein'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 Löwenstein's Rule, additional constraints are introduced into the simulation. The force field which controls the assembly of the building units is

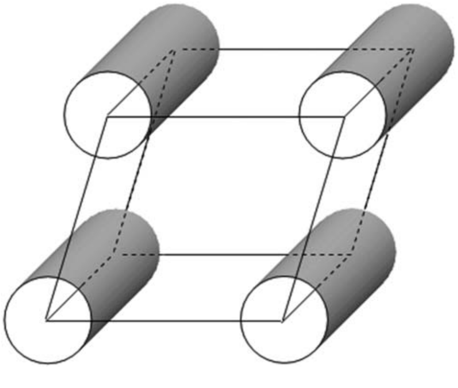


Fig. 12 The forbidden zones defined as cylinders in one unit cell as used in the method of constrained assembly of atoms. Reproduced with permission from ref. 38, copyright American Chemical Society 2003.

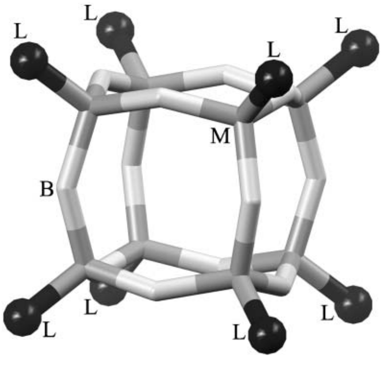


Fig. 13 Representation of the D4R unit as used in the AASBU method. L: ligand atom; B: bridging atom; M: metal atom. Reproduced with permission from ref. 39, copyright American Chemical Society 2002.

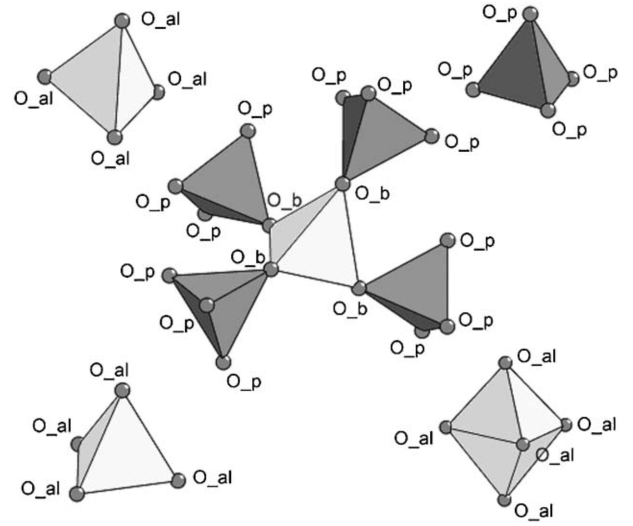


Fig. 14 The initial building units with 3 × $Al(O_b)_4$, 1 × $Al(O_b)_5$, 2 × $P(O_b)_4$, and 3 × $P(O_b)_3(O_t)$ atoms in an asymmetric unit for the generation of AlPOs with $Al_8P_{10}O_{40}{}^{6-}$ stoichiometry under space group $P\bar{1}$. Reproduced with permission from ref. 40, copyright American Chemical Society 2005.

parameterized to favor the formation of Al–O–P linkages while avoiding the formation of Al–O–Al or P–O–P linkages. Fig. 14 illustrates the initial building units including 3 × $Al(O_b)_4$, 1 × $Al(O_b)_5$, 2 × $P(O_b)_4$ and 3 × $P(O_b)_3(O_t)$ atoms for the generation of AlPOs with $Al_8P_{10}O_{40}{}^{3-}$ stoichiometry. They are assembled through the attraction between the O_al and O_p atoms under the control of the force field; at the end of the simulation, the building units are assembled together and the 'sticky atom' pairs are formed. After the simulation terminates, 'sticky atom' pairs are glued into single O_b atoms, and the hypothetical structures are generated and are further refined using Burchart force field. Details about the simulation steps can be found in ref. 40.

This method will not only serve as an effective tool for the design of hypothetical AlPO structures with predefined Al and P stoichiometry, but will also be an effective approach for setting up the initial structural models for the solution of structures combined with NMR and XRD Rietveld refinements.

6. Approaches toward rationalization of the synthesis

Rationalization of the synthesis of target materials with desired structures is a challenging task in materials sciences. Many efforts have been made to develop some strategies toward the rational synthesis of target microporous materials with predetermined pore structures, compositions and properties.[41]

In the synthesis of open-framework AlPO materials, the choice of templating molecules is believed to be crucial in directing the synthesis toward a particular structure. Recently, computer modeling techniques have been used to design templates for specified hosts.[35] The template-directed synthesis is an effective approach for a desired AlPO framework.

Lewis *et al.* developed the *de novo* design of template molecules for the synthesis of microporous materials.[42] This method allows the template molecules to be grown within the confines of the specific pore system. Growth is initiated from a seed molecule placed in the host followed by a number of random actions including i) build, ii) rotate, iii) shake, iv) rock, v) bond twist, vi) ring formation, and vii) energy minimization. The actions are controlled by the cost function and additional van der Waals overlap functions, which measures the effective fit of the molecule in the framework. Further details can be seen in ref. 42. This method has demonstrated its potential in designing new templates on different types of zeolite topologies.[13]

Fig. 15 illustrates the growth process involved in the formation of a candidate template, 1,2-dimethylcyclohexane in the LEV structure starting from a methane seed. Experimentally, using the amino analogue of this template, 2-methylcyclohexylamine, as the template, a microporous cobalt aluminophosphate DAF-4 with LEV structure type is formed.

The method of *de novo* design of templating molecules is a way of determining *a priori* the templates that will be successfully in directing a particular AlPO framework.

We have developed a method for investigating the templating ability of organic amines in the formation of 2D layered and 3D interrupted open-framework AlPOs in which H-bondings play a dominant role in stabilizing the frameworks.[32,43] In terms of nonbonding interactions of host inorganic framework and guest organic molecules, the templating ability of organic amines can be predicted by

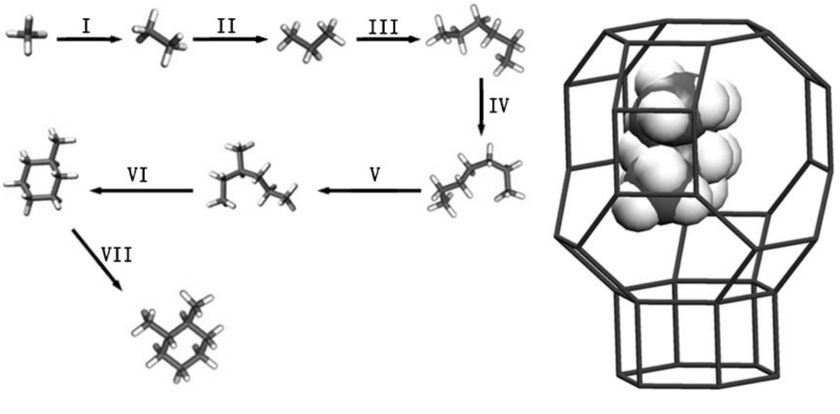


Fig. 15 The growth process involved in the formation of a candidate template, 1, 2-dimethylcyclohexane in the LEV structure starting from a methane seed. Reproduced with permission from ref. 42, copyright Macmillan Publishers Ltd. 1996.

molecular dynamic simulations. Burchart1.01–Dreiding2.21 force field is chosen for energy optimization and calculation. Some parameters which are not addressed in the force field are added. In terms of the energies of host–template nonbonding interactions, mainly H-bonding and van der Waals interactions, the templating ability of various organic amines for a particular inorganic host can be predicted. Some suitable templating candidates that have lower interaction energies with a given host can be selected in the synthesis. This method has successfully guided the synthesis of microporous aluminophosphates with framework structures analogous to that of AlPO-HDA, $[C_6H_{18}N_2]^{2+}[Al_4P_5O_{19}(OH)]^{2-}$, with main 12-ring channels.[43]

Wright *et al.* succeeded in the synthesis of AlPO-based microporous solids including STA-1 and STA-2 with rationally designed templates. The chosen template cations are linear diquinuclidinium ions of the form $[(C_7H_{13}N)–(CH_2)_n–(NC_7H_{13})]^{2+}$ which possess features of flexibility, charge and bulky end groups likely to form structures with interconnected pore space.[44]

Stucky *et al.* further showed the strategy for the preparation of metalloaluminophosphates with multidimensional large-pore structures based on charge-density matching of host framework and guest template molecule.[45,46] Following the survey of known zeolite structures in which large cages and multidimensional channel systems are associated with a relatively high framework charge density, the synthesis of open-frameworks with large cages interconnected by multidimensional large-pore channels has been successfully achieved by means of structure direction through host–guest charge-density matching in the highly charged phosphate system. The charge of the organic template determines the framework compositions and charge. The generation of configurations with large cages and pores requires additional domain separation of the charged wall from cage and core contents. Diamines of the general formula $H_2N(CH_2)_nNH_2$ with desired high charge density and spatially competing hydrophilic and hydrophobic regions have been proven effective in directing the formation of three novel structures with large-pore multidimensional 12-ring channels in a metalloaluminophosphate system including UCSB-6, -8, and -10.[46]

The above demonstrates how template-directed synthetic approach can be useful in the rational synthesis of target open-framework AlPOs with a particular structure. However, it must be kept in mind that the gel chemistry is also crucial and that the templating becomes operative only in the gel with right gel chemistry. Recently, a combinatorial approach has been successfully applied to the hydrothermal and solvothermal synthesis of open-framework AlPOs.[47] Using this approach, an extensive study of complex multi-component gel system is easily achieved. The combination of computational simulation and combinatorial chemistry approach will be an efficient route for the synthesis of open-framework AlPOs with desired frameworks.[48]

7. Conclusions

Open-framework AlPOs comprise wonderfully complex structures and compositions. They can be prepared with neutral zeolitic frameworks with different pore sizes and anionic frameworks with various architectures and Al and P stoichiometries. Their bonding characters and topological chemistry are different from silica-based zeolites. The open-frameworks of AlPOs are typically built up from Al-centered polyhedra and P-centered tetrahedra through Al–O–P linkages. The organic templating molecules play an important role of structure-directing, as well as modifying the gel chemistry in the formation of open-framework AlPOs. The diverse coordinations and connections of Al and P atoms are responsible for the remarkable diversity in both structure and composition of AlPOs promoted with the aid of various templating molecules. A better understanding of the structural construction, as well as the interaction between the host frameworks and guest templating molecules, has greatly enhanced our ability in the designed construction and synthesis of target open-framework AlPOs with the assistance of computer simulations. Ultimately, the crystallization mechanism of microporous materials must be understood in order to rationalize the synthesis of materials with desired structures, compositions and properties. We hope that the information provided here will stimulate further fundamental work in this area.

Acknowledgements

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