On the Necessity of Heteroatoms for Realizing Hypothetical Aluminophosphate Zeolites: A High-Throughput Computational Approach

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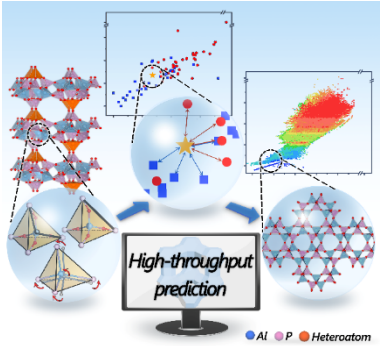
ABSTRACT

Aluminophosphate zeolites, including pure aluminophosphate (AlPO) and heteroatom-stabilized AlPO zeolites, have important applications in adsorption, separation and heterogeneous catalysis. Thus far, millions of hypothetical zeolite structures have been predicted, providing a large number of candidates to be synthetically targeted. However, their realization in experiment still requires *a priori* knowledge on whether heteroatoms are necessary in the synthetic preparation in order to stabilize a specific zeolite topology. To this end, many computational efforts have been made to compare the differences in framework energies and distortions before and after heteroatom incorporation. However, such an approach is not generally applicable for high-throughput computations, because of the combinatorial explosion of potential heteroatom incorporation sites in a hypothetical zeolite framework. Here, we establish a quantitative model to estimate the probability of a hypothetical framework being realizable as a pure AlPO or a heteroatom-stabilized AlPO zeolite. This model is based on Mahalanobis distances between hypothetical structures and their neighboring reference structures in distortion–energy plots. Our approach only requires one-step geometry optimization on zeolite frameworks as pure AlPO polymorphs without building many heteroatom-containing models, ensuring its applications in high-throughput structure evaluation and screening. We employed this approach on 84,292 hypothetical ABC-6 zeolite structures, and discovered that 17,050 of them could be realizable as pure AlPOs and 12,039 only realizable via heteroatom incorporation. Our results will provide important guidance toward the synthesis of new aluminophosphate zeolites.

TOC GRAPHICS



KEYWORDS

zeolite, aluminophosphate, heteroatom, high-throughput prediction, structure distortion

Zeolites are a class of crystalline microporous materials comprised of corner-sharing TO_4 tetrahedra (T: tetrahedrally coordinated Si, Al, P for example), which have been widely used in many important physical and chemical processes, such as adsorption, separation, and shape-selective catalysis.[1-4] Since their first discovery in 1982,[5] more than 70 types of aluminophosphate (AlPO) zeolites have been reported to date. Among them, pure AlPOs, which can be realized without introducing hetero-framework-atoms other than Al and P, have shown promising applications in adsorption and separation.[6,7] Although a small amount of heteroatoms can be introduced into pure AlPO frameworks, the contents of heteroatoms are usually quite low (e.g., 5% among all Al sites in CoAPO-18 (AEI topology)[8] and 10% in MnAPO-11 (AEL topology)[9]) and the framework topologies of pure AlPOs are not affected by heteroatom incorporation. As another kind of AlPO zeolites, the heteroatom-stabilized AlPOs, in which a considerable amount of heteroatoms occupy the Al sites (e.g., 25% of the Al sites are occupied by Mg in JU-92 (JNT topology),[10] 50% of the Al sites are occupied by Co in UCSB-8Co (SBE topology),[11] and all Al sites are occupied by Co in DAF-2 (DFT topology)[12]), can only be realized via heteroatom incorporation. Such zeolites usually exhibit distorted framework structures, which cannot be realized solely by the rigid AlO_4 tetrahedra. In comparison, heteroatom-centered tetrahedra with a much wider O–T–O angle range are more flexible, so introducing heteroatoms into AlPO zeolites can release the stress caused by framework distortions, enabling the realization of such kind of zeolites.[13,14] Heteroatom-stabilized AlPO zeolites have exhibited a large variety of topological structures different from AlPOs, and excellent performance in heterogeneous catalysis and ion exchange.[15-18] Therefore, predicting whether heteroatoms are necessary for the realization of hypothetical structures is of great importance for the synthesis of new aluminophosphate zeolites.

To accelerate the discovery of new zeolitic materials, millions of hypothetical zeolite structures have been predicted via various computational methods.[19-25] Furthermore, many structure evaluation criteria have been proposed to predict the feasibility of the hypothetical structures.[26-31] However, their experimental realization still requires *a priori* knowledge on whether heteroatoms in addition to Al and P sources are necessary to be introduced into the synthetic system. Previous studies concerning the prediction of whether heteroatoms are necessary for specific AlPO structures are based on the substitution of Al atoms in pure AlPOs by heteroatoms. By comparing the difference in framework energies distortions between structure models with and without heteroatom incorporation, one can predict whether heteroatoms are required for the realization of specific AlPO structures.[13,14,32-34] Unfortunately, many AlPO structures consist of a large number of Al sites, and incorporating heteroatoms into every possible Al site will lead to many potential heteroatom-incorporated models to evaluate. For the vast number of candidate structures considered here, the computational overhead could be prohibitively high.

Here, we report for the first time a high-throughput approach to predict whether a hypothetical zeolite framework can be realized as a pure AlPO or a heteroatom-stabilized AlPO. Unlike previous studies, our approach does not involve the actual incorporation of heteroatoms for structure evaluation. We optimized 75 known reference aluminophosphate zeolite structures and 84,292 hypothetical ones as pure AlPO polymorphs, and obtained the relationship between their framework distortions and framework energies. By measuring the Mahalanobis distances from a hypothetical zeolite framework to its neighboring reference structures in distortion–energy plots, we predicted that 17,050 out of the 84,292 hypothetical zeolite frameworks could be realized as pure AlPOs, and 12,039 hypothetical frameworks could only be realized in experiment via the incorporation of heteroatoms. Our approach considers all zeolite frameworks as pure AlPO

Table 1. Reference aluminophosphate zeolite structures.

Pure AlPOs	AEI, AEL, AEN, AET, AFI, AFN, AFO, AFR, AFT, AHT, APC, APD, AST, ATN, ATO, ATS, ATT, ATV, AWO, AWW, CHA, ERI, EZT, GIS, LEV, LTA, MSO, OSI, PON, PSI, SAF, SFO, SOD, VFI, ZON, AlPO-78, PST-14
Heteroatom-stabilized AlPOs	ACO, AFS, AFV, AFX, AFY, ANA, AVL, BPH, CGF, CGS, CZP, DFO, DFT, EDI, FAU, GME, IFO, JNT, JRY, JSN, JSW, KFI, LAU, MER, OWE, PHI, RHO, SAO, SAS, SAT, SAV, SBE, SBS, SBT, SIV, SWY, THO, USI

polymorphs, thus avoiding the actual incorporation of heteroatoms into every possible Al site. The computational expense for our approach is much less than conventional methods, making our approach an important tool for high-throughput structure evaluation among the millions of hypothetical zeolite models.

First, 75 known aluminophosphate zeolites reported so far were chosen as the reference structures. As listed in Table 1, 37 zeolite framework types have been realized as pure AlPOs, and the other 38 can only be realized in experiment by the incorporation of heteroatoms other than Al. All of the 75 zeolite frameworks were fully optimized as pure AlPO polymorphs according to molecular mechanics method. Sanders-Leslie-Catlow (SLC) potentials and the program GULP were used throughout this study.[35,36] In an ideal tetrahedron, all bond lengths and bond angles should be equal. Distortions of rigid Al-centered tetrahedra in AlPO structures may induce framework stress, decreasing the framework stability. The stress can be alleviated by the incorporation of heteroatoms.[13] In this study, we considered two types of Al-centered tetrahedra, i.e., AlO_4 and AlP_4 tetrahedra. Several methods were used to quantify the distortions of these tetrahedra, including bond angle variances,[37] standard deviations of bond lengths, and continuous shape measure (CShM),[38] which reflects the deviation of a polyhedron from an ideal one. For AlO_4 tetrahedra, we calculated the O–Al–O angle variances, standard deviations of Al–O and O–O

distances, and CShM. For AlP_4 tetrahedra, P–Al–P angle variances, standard deviations of Al–P and P–P distances, and CShM were calculated. All these values were averaged among all of the tetrahedra in one unit cell. The correlations among framework energy relative to berlinite per T site (ΔE) and average distortion of each framework type are shown in Figures 1, S1, and S2.

Compared with that in AlO_4 tetrahedra, framework distortions in AlP_4 tetrahedra differ much more between pure AlPOs and heteroatom-stabilized AlPOs. So we employed P–Al–P angle variances, standard deviations of P–P distance, and CShM of AlP_4 tetrahedra hereafter in this work. As shown in Figure 1, heteroatom-stabilized AlPOs exhibit relatively higher framework distortions and energies than pure AlPOs. The correlation between framework density (FD) and ΔE of the 75 reference structures is shown in Figure S3. Pure AlPOs are generally denser than heteroatom-stabilized ones. According to the FD–ΔE correlation proposed by Foster et al.,[26] zeolite structures with higher relative energies are "less feasible", implying the necessity of heteroatom incorporation in these zeolites. By analyzing the single crystal structures of divalent-metal-containing aluminophosphate zeolites MAPO-CJ40 (JRY) and MAPO-CJ62 (JSW), we also found that hetero-metal-atoms preferentially occupied the most distorted Al sites to release the framework stress.[13,14] Therefore, structures on the upper-right part in Figure 1 should be unfeasible

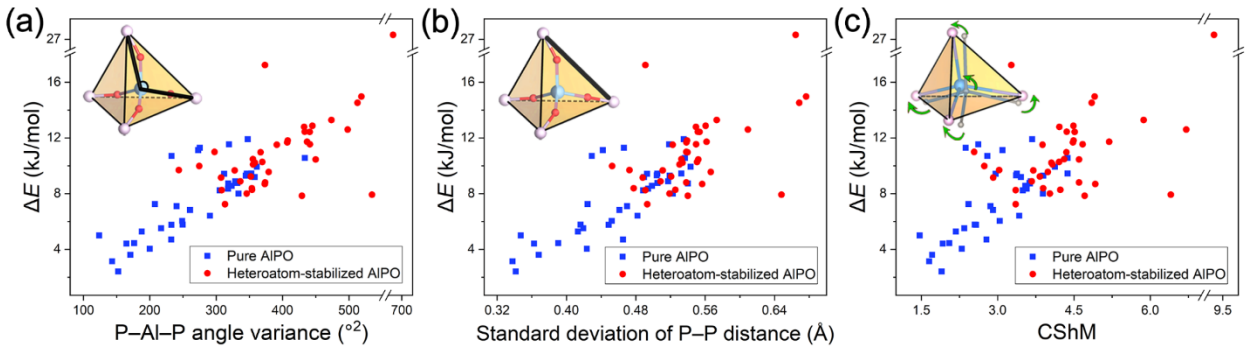


Figure 1. ΔE versus framework distortions measured by the average (a) P–Al–P angle variance, (b) standard deviation of P–P distance, and (c) CShM of AlP_4 tetrahedra in 75 known reference aluminophosphate zeolites.

as pure AlPOs and need to be stabilized via heteroatom incorporation. CZP is the most distorted structure because of its unusual helical ribbon structure, in which all 4-rings are edge-sharing, causing significant tetrahedral distortions in central T sites.[39]

To confirm the reliability of our molecular mechanics calculations, we chose eight zeolite frameworks from the 75 reference structures with an energy gap of 2 kJ/mol from one another. These zeolite frameworks were further optimized by periodic DFT calculations using the generalized gradient approximation[40] and the PBEsol functional[41]. Dispersion correction was accounted for with the method proposed by Tkatchenko and Scheffler.[42] Both lattice parameters and atomic positions were relaxed during geometry optimization. The corresponding average P–Al–P angle variances, standard deviations of P–P distances, and CShM values of AlP_4 tetrahedra were calculated on these DFT-optimized structures (Table S2), which exhibited excellent linear correlation with molecular mechanics results. Therefore, our molecular mechanics calculations are reliable, and we will not perform expensive periodic DFT calculations for the following calculations.

Next, we optimized 84,292 hypothetical zeolite models as pure AlPO polymorphs. These models were derived from our previous studies in the systematic enumeration of ABC-6 zeolite structures reported.[23,43] Since there is no clear boundary separating pure AlPOs and heteroatom-stabilized AlPOs in Figure 1, we cannot directly determine whether a hypothetical model can be realized as pure AlPOs or heteroatom-stabilized AlPOs. However, from Figure 1, we can calculate how far a hypothetical model is from the reference structures. Here, we propose a quantitative model based on the weighted Mahalanobis distances of hypothetical structures to their neighboring reference structures to predict the probability of hypothetical structures being pure AlPOs or heteroatom-stabilized AlPOs (Figure 2). Mahalanobis distances (D) were calculated using the inverse of the

covariance matrix of framework distortions and energies (see method section). The reason we chose Mahalanobis distance instead of Euclidean distance is that Mahalanobis distance is unitless and scale-invariant, which takes into account the correlation between framework distortions and energies in different scales.[44] For each hypothetical zeolite framework type, we calculated its Mahalanobis distance from each of the 75 reference structures. The probability of a hypothetical structure being pure AlPO, P_A, can be calculated from its weighted distances from M nearest reference structures:

$$P_A = \sum_{i=1}^{N} D^{-1} \Big/ \sum_{i=1}^{M} D^{-1} \times 100\% \qquad (1)$$

where N is the number of pure AlPOs among M neighbors. Note that the reciprocal of D was used to account for its corresponding weight in the population. The probability of a hypothetical structure being heteroatom-stabilized aluminophosphate, P_H, can thus be calculated as:

$$P_H = 100\% - P_A \qquad (2)$$

The values of P_A and P_H were calculated separately on three distortion–energy plots shown in Figure 1. For each structure, if the calculated P_A (or P_H) on two or more plots exceeded 75%, the lowest accepted confidence level adopted in this study, we categorized it as pure AlPO (or heteroatom-stabilized AlPO). In this study, we tested different M values ranging from 3 to 15 on 75 reference AlPOs. When $M = 10$, 82.6% of the reference pure AlPO and 90.5% of the reference heteroatom-stabilized AlPOs could be correctly categorized (Table S3). These were the best accuracy rates we obtained and so we set $M = 10$ hereafter in this study.

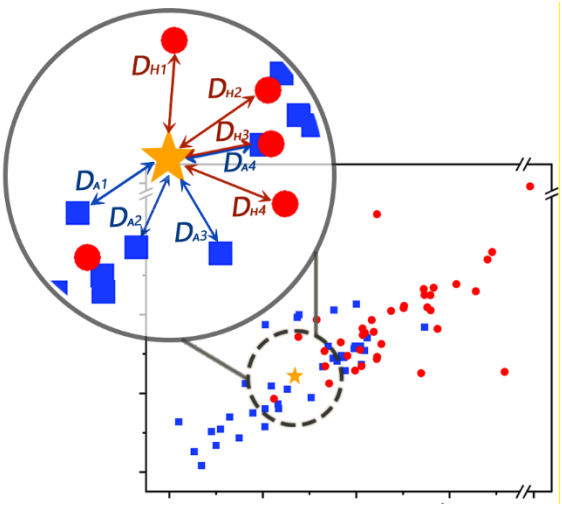


Figure 2. Illustration of the Mahalanobis distances between a hypothetical structure (the yellow star) and its neighboring reference structures (blue squares and red circle dots).

Finally, we employed this approach for the high-throughput prediction on whether heteroatoms are necessary for the realization of 84,292 hypothetical ABC-6 structures as AlPOs. After geometry optimization, we calculated the P–Al–P angle variances, standard deviations of P–P distance and CShM values of AlP_4 tetrahedra for all hypothetical structure models. Then, their probability of being pure AlPOs or heteroatom-stabilized AlPOs were calculated according to equations (1) and (2). As shown in Figure 3, the predicted results were in good consistency with that in Figure 1. Similar to reference AlPOs, among the 84,292 hypothetical models, those with lower framework energies and less distortions are more likely to be realizable as pure AlPOs, whereas those with higher energies and more distortions may only be realized via the incorporation of heteroatoms. In particular, taking 75.0% as the lowest acceptable confidence level, 17,050 hypothetical models were predicted to be realizable as pure AlPOs, and 12,039 as heteroatom-stabilized AlPOs. We could not categorize the remaining structures because their calculation results did not achieve the accepted confidence level. Among the 1,127 most realizable ABC-6 structures which were comprised of no more than four types of polyhedral cages, the numbers of pure and heteroatom-stabilized AlPOs were 690 and 122, respectively. Gratifyingly, we recently

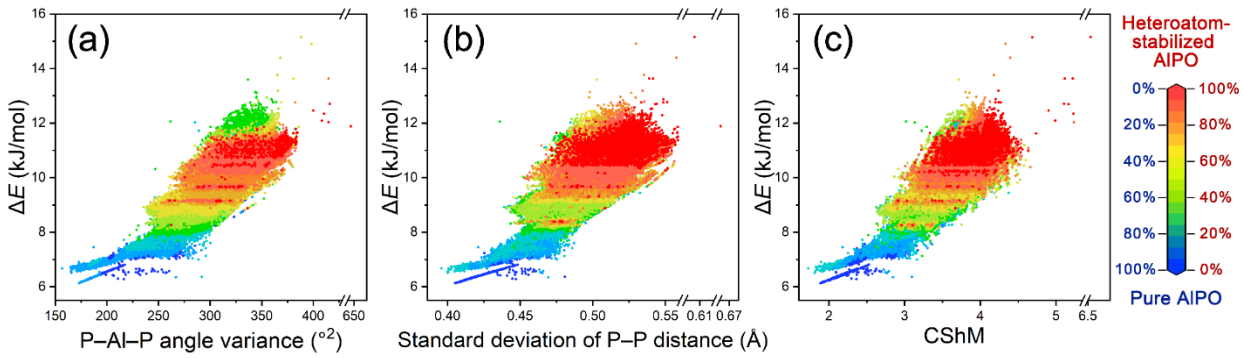


Figure 3. Δ*E* versus framework distortions measured by the average (a) P–Al–P angle variance, (b) standard deviation of P–P distance, and (c) CShM of AlP_4 tetrahedra in 84,292 hypothetical ABC-6 structures. Calculated probability of each structure as pure AlPO or heteroatom-stabilized AlPO is highlighted in different colors.

synthesized two of these ABC-6 structures as heteroatom-stabilized AlPO zeolites in our experiment: magnesium aluminophosphate JU-60 and zinc aluminophosphate JU-61.[43] According to the three distortion–energy plots in Figure 1, both JU-60 and JU-61 exhibited quite high probability being heteroatom-stabilized AlPO zeolites (88.3%, 100%, and 100% for JU-60; 93.8%, 94.3%, and 94.6% for JU-61), which agreed well with our experimental results. The positions of JU-60 and JU-61 in three distortion–energy plots are shown in Figure S4. These results validate the feasibility of our method on the prediction of whether a hypothetical aluminophosphate structure should be a pure or heteroatom-stabilized AlPO zeolite.

According to a new quantitative model based on the Mahalanobis distances between hypothetical AlPOs and reference AlPOs in distortion–energy plots, we are able to predict whether heteroatoms are necessary for the realization of hypothetical AlPO zeolites. Unlike previous studies that need to build many heteroatom-stabilized AlPO models by incorporating heteroatoms into every possible Al site, our method needs only one-step geometry optimization on zeolite frameworks as pure AlPO models. By avoiding the incorporation of heteroatoms and the high computational cost caused by that, our approach is highly applicable for high-throughput

evaluation on a vast number of hypothetical structures. Meanwhile, tests on 75 known aluminophosphate structures exhibit accuracy rates of >80% for pure AlPOs and >90% for heteroatom-stabilized AlPOs, indicating the reliability of our high-throughput approach. More importantly, our quantitative model based on Mahalanobis distances does not involve any particular information of zeolite structures, so it will also be applicable to other materials. Our next step is to predict the organic structure-directing agents that will lead the formation of these target zeolites. All these computational efforts will provide important guidance for the realization of hypothetical zeolites and reduce the time and resource and the associated expenses of trial-and-error, serendipity-led experiments.

Computational Methods

Building AlPO models. The initial structure models were obtained from the database of International Zeolite Association[45] and the Hypothetical Zeolite Database[23]. All non-framework species such as structure-directing agents and extraframework ions were removed. Pure AlPO models were built according to Löwenstein's rule,[46] where Al and P atoms were strictly alternated over adjacent tetrahedral sites. Molecular mechanics geometry optimizations were carried out using GULP program with the Sanders-Leslie-Catlow (SLC) interatomic.[35,36] Periodic DFT geometry optimizations were carried out using the generalized gradient approximation[40] and the PBEsol functional[41] provided by the DMol^3 module in Materials Studio[47]. Dispersion correction was accounted for with the method proposed by Tkatchenko and Scheffler.[42] The cell parameters and atomic positions were all relaxed during molecular mechanics and DFT geometry optimization.

Distortion calculation. Both AlO_4 and AlP_4 tetrahedra were considered in the distortion calculation. Distortions of tetrahedra were characterized using bond angle (O–Al–O angle for

AlO_4, and P–Al–P angle for AlP_4 tetrahedra) variances,[37] standard deviations of bond distances (Al–O bond and O–O distances for AlO_4 tetrahedra, Al–P bond and P–P distances for AlP_4 tetrahedra, respectively), and continuous shape measure (CShM)[38] of both AlO_4 and AlP_4 tetrahedra. Distortion of a framework structure was described by the mean distortion values of all Al-centered AlO_4 or AlP_4 tetrahedra. Calculations of the bond angle variances and standard deviations of bond distances were performed using perl script implemented in Materials Studio.[47]

Calculation of Mahalanobis distances. Mahalanobis distances between hypothetical and reference structures were calculated according to the following equation,

$$D = \sqrt{(\vec{x_i} - \vec{x_j})^{\mathrm{T}} S^{-1} (\vec{x_i} - \vec{x_j})} \qquad (3)$$

where $\vec{x_i}$ and $\vec{x_j}$ are the two-dimensional vectors of the hypothetical and reference structures on distortion–energy plots, respectively, and S is the covariance matrix.

SUPPORTING INFORMATION

Tables S1–3, Figures S1–4. Detailed data of ΔE, framework distortion and corresponding P_A and P_H values of 84,292 hypothetical ABC-6 structures.

ACKNOWLEDGMENT

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