

A predictive computational study of AlPO₄-14: crystal structure and framework stability of the template-free AlPO₄-14 from its as-synthesised templated form

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The crystal structure of AlPO₄-14 in its calcined form was predicted using lattice energy minimisation and an initial model derived from its as-synthesised templated form, highlighting the possibility of using computational approaches for exploring thermodynamic stabilities of as-synthesised open-framework structures upon template extraction.

The evergrowing field of open-framework inorganic materials is in part related to the extensive development of synthetic routes involving organic amines.¹ The template molecules or structure-directing agents are incorporated in the final structure, acting as compensating charges or allowing the production of micropores with tailored size and shape. In a number of cases, for example aluminophosphates (AlPOs), the non-framework species may be removed, leaving behind an open-framework structure with potential adsorption or catalytic properties. However, the removal of the template is often a critical step and the production of the related stable open-framework compound cannot be easily anticipated.

In the recent years, computational tools have played a key role in the study of the structure and energetics of open-framework materials,² with the widespread use of energy minimisation techniques. For example, in the field of zeolites, energy minimisations have made it possible to locate extra-framework cations,³ elucidate the adsorption sites of sorbate molecules⁴ and to solve structures.⁵ Also, the relative thermodynamic framework stabilities of various inorganic systems, such as silica polymorphs⁶ and aluminophosphates,⁷ have been successfully studied using appropriate forcefields.

Here we present an attempt to use energy minimisation to anticipate the calcined crystal structure of an as-synthesised aluminophosphate structure. Our main interest is to predict the stability and the crystal structure of the inorganic framework in the absence of the structure directing agent or template, starting from the knowledge of the as-synthesised structure only. We describe illustrative results for the AlPO₄-14 system, for which validating experimental structural data are available, both for the as-synthesised and calcined forms, from a synchrotron powder X-ray diffraction study.⁸

Diffraction results⁸ show that the as-synthesised AlPO₄-14 structure comprises alternating Al and P atoms, linked by bridging oxygen atoms, with P atoms in a tetrahedral environment and the Al atoms possessing various coordinations (IV, V and VI) as a consequence of the extra-framework species becoming bonded. While two of the four inequivalent Al atoms are in tetrahedral coordination, one is in fivefold coordination and the other in octahedral coordination. The arrangement of AlO_x and PO₄ polyhedra constructs a three-dimensional 8-ring channel system in the *a* and *b* directions. The structure also contains hydroxy groups and non-framework species, *i.e.* protonated isopropylamine templating agents and water molecules. Each hydroxy group bridges three Al atoms: a five coordinate one and two six coordinate aluminium atoms. The isopropylamine template is protonated and balances the charge

on the hydroxy group. Fig. 1 shows the above features in a selected view of the as-synthesised AlPO₄-14. The calcination of AlPO₄-14 leads to a zeotype open-framework structure where all Al and P atoms are in tetrahedral coordination, that retains the three-dimensional 8-ring channel system.

Our calculations were carried out using the lattice energy minimisation code GULP.⁹ The interatomic potentials used were those developed by Gale and Henson using an empirical fit to the crystal structure plus elastic and dielectric properties of berlinite.¹⁰ This formal charge shell model forcefield has been shown to reproduce the experimentally determined structures of aluminophosphates with good accuracy and to yield estimates of their relative framework stabilities that are consistent with thermodynamic data.⁷

The experimental crystal structure of the as-synthesised AlPO₄-14, Al₈P₈O₃₂(OH)₂(C₃H₁₀N)₂(H₂O)₂, proposed by Wilson *et al.*⁸ was taken as a starting point for our calculations. This structure was then modified prior to energy minimisation as follows: atoms that are presumed to evacuate upon calcination, *i.e.* bridging hydroxy groups, isopropylamine templates and water molecules, were removed, leaving behind a neutral open-framework structure, namely, Al₈P₈O₃₂. This results in a structure where all four inequivalent Al atoms are in tetrahedral coordination, retaining two Al atoms in highly distorted environments (with O–Al–O angles ranging from 90 to 167°) that emanate from the two six-fold and five-fold coordinated Al atoms of the as-synthesised structure (see Fig. 2). In a final step, the modified structure was submitted to a constant pressure (*i.e.* allowing both cell parameters and fractional coordinates to relax) minimisation in space group *P*-1 since this was the space group of the as-synthesised structure.

In Fig. 3(a), we show the calcined structure of AlPO₄-14 as predicted by our energy minimisation. Clearly, the agreement with the observed calcined structure [Fig. 3(b)] proposed by Wilson *et al.*⁸ is very good. In Table 1, we show a comparison

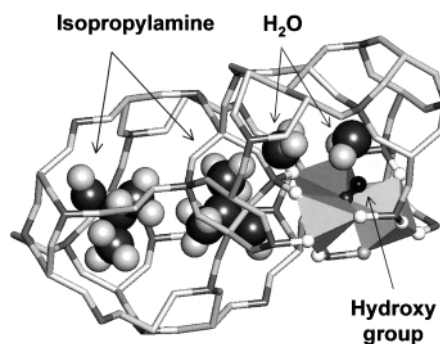


Fig. 1 Partial view of the as-synthesised AlPO₄-14 structure, Al₈P₈O₃₂(OH)₂(C₃H₁₀N)₂(H₂O)₂ from crystal data in ref. 7. Water molecules and organic template molecules are trapped in adjacent cages. A selection of three Al atoms with bipyramidal and sixfold coordination is represented with solid polyhedra, where the bridging hydroxy group participates in the coordination of all three Al atoms.

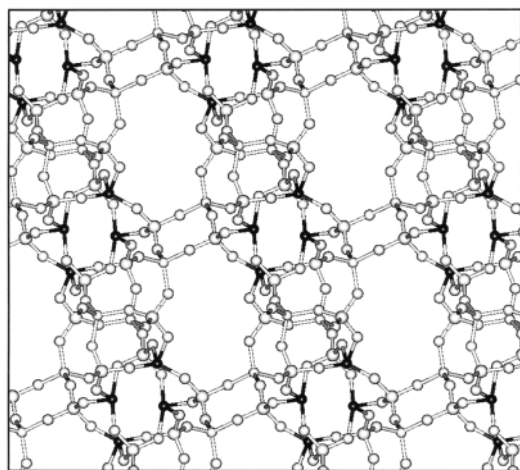


Fig. 2 Initial model for calcined $\text{AlPO}_4\text{-14}$, $\text{Al}_8\text{P}_8\text{O}_{32}$, used in our calculations and constructed from its as-synthesised form, removing the templating agent, water molecules and bridging hydroxy groups. The so-modified structure is left with Al atoms in highly distorted tetrahedral environment (shown in black).

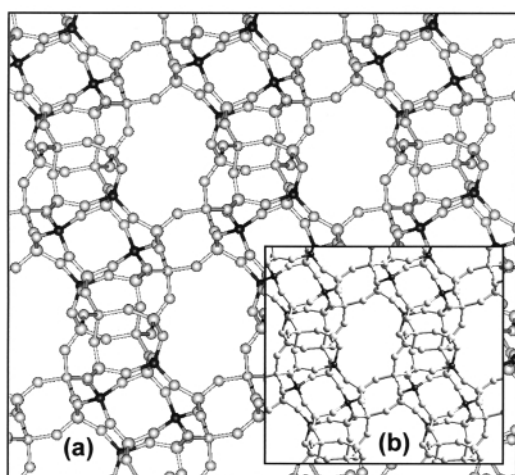


Fig. 3 (a) Predicted structure for calcined $\text{AlPO}_4\text{-14}$ from energy minimisation of the initial model, $\text{Al}_8\text{P}_8\text{O}_{32}$. (b) Observed structure of calcined $\text{AlPO}_4\text{-14}$ proposed by Wilson *et al.*⁸

Table 1 Cell dimensions of the observed and predicted $\text{AlPO}_4\text{-14}$ structure in its calcined form

| | Observed structure of calcined $\text{AlPO}_4\text{-14}$ from diffraction ⁸ | Predicted structure of calcined $\text{AlPO}_4\text{-14}$ from its as-synthesised form ^a |
|--------------------------------|--|---|
| Cell dimensions ($P\bar{1}$) | | |
| $a/\text{\AA}$ | 9.704 | 9.674 |
| $b/\text{\AA}$ | 9.736 | 9.751 |
| $c/\text{\AA}$ | 10.202 | 10.269 |
| α° | 77.81 | 77.46 |
| β° | 77.50 | 76.50 |
| γ° | 87.69 | 87.14 |

^a This work

of our calculated lattice parameters for the predicted calcined $\text{AlPO}_4\text{-14}$ with those of the observed structure. Interestingly, our initial model of calcined $\text{AlPO}_4\text{-14}$, with an initial lattice

energy of $12374.8 \text{ kJ mol}^{-1}$ per tetrahedral unit, converged rapidly towards the structure where all Al atoms are in regular tetrahedral environment, with a final lattice energy of $12924.9 \text{ kJ mol}^{-1}$ per tetrahedral unit. This makes the structure of $\text{AlPO}_4\text{-14}$ 11.7 kJ mol^{-1} less stable than α -berlinite per T site. For comparison, the work of Henson *et al.*⁷ demonstrates that the most pure aluminophosphates are between 4 and 13 kJ mol^{-1} less stable than the thermodynamically favoured polymorph under ambient conditions, making $\text{AlPO}_4\text{-14}$ a relatively unstable structure. Our energy minimisation predicts the observed structure of $\text{AlPO}_4\text{-14}$ remarkably well, especially as the initial model had large distortions arising from the deletion of ligand atoms in the coordination spheres of the Al atoms from the as-synthesised form. Also, we checked that minimisations from both points, the initial model of calcined $\text{AlPO}_4\text{-14}$ or the observed calcined structure, lead to the same structure.

Another important use of potentials is that they can test space groups for possible lower symmetry distortions, as found for other AlPOs.⁷ The phonon spectrum at the Γ point of the calcined structure of $\text{AlPO}_4\text{-14}$ was calculated to check the space group as $P\bar{1}$. The structure was found to be phonon stable in this space group verifying that the symmetry is at least $P\bar{1}$.

In summary, energy minimisation allows us to estimate the thermodynamic stability of calcined $\text{AlPO}_4\text{-14}$ and to predict its crystal structure, starting with the knowledge of the as-synthesised structure and anticipating the species removed during the calcination process. The further viability of this approach has been recently demonstrated through the prediction of the calcined form of a newly synthesised templated aluminophosphate, where atomic coordinates of the calcined form, which has a structure different from the as-synthesised form, were obtained from the simulation, allowing their direct use for future powder diffraction refinement.¹¹

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