

Ionicity and Framework Stability of Crystalline Aluminophosphates

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First-principles quantum chemical techniques are applied to characterize the bonding properties of crystalline aluminophosphates (ALPOs) and to compare them with the isostructural silica-based zeolites. Results of the calculations agree with the available structural and calorimetric experimental data. By population and topological analyses of the calculated electronic density, the bonding in ALPOs is shown to be of molecular–ionic character and comprised of discrete Al^{3+} and PO_4^{3-} ions. The latter finding rationalizes the hydrophilicity and the defect chemistry of microporous ALPO frameworks in heterogeneous catalysis.

The exceptional structural and chemical diversity of microporous solids arises in part from the growing range of chemical building blocks from which these materials are constructed. The original family of aluminosilicate and silica-based zeolites has been greatly extended in recent decades, so “zeotypes” now include aluminophosphates (AIPOs) and gallophosphates (GaPOs), as well as metal-modified versions of these compounds (MeAIPOs).¹ Such materials open up new catalytic opportunities, especially in the field of selective and partial oxidation catalysis.^{2,3} It is known, however, that despite their structural similarity to zeolites AIPOs have crucial differences in their chemical behavior, relating both to their thermal stability and to their ability to accommodate high concentrations of framework heteroatoms. In this paper, we show how these vital features of AIPO chemistry relate to fundamental features of the bonding in the framework, which are qualitatively different in silica and metal phosphates. To investigate this topic, we have performed a detailed quantum-mechanical (QM) study of dense and microporous AIPO polymorphs and shall contrast the results with the isostructural SiO_2 zeolites.

The calculations reported have been performed employing two computer codes, CRYSTAL⁴ and DMOL.^{3,5} In both cases, we described the solid using periodic boundary conditions and employed a local basis set of split-valence plus polarization functions for each atom of the structure. With CRYSTAL, we compared the performance of different Hamiltonians, ranging from the Hartree–Fock (HF) to local⁶ or gradient-corrected⁷ density functionals (DF) to the HF–DF hybrid scheme (B3LYP) proposed by Becke.⁸ All Hamiltonians provide results in good overall agreement; in this paper, we focus mostly on the B3LYP calculations, which have proven very accurate in molecular calculations and of which the recent implementation in CRYSTAL makes the scheme available for solid-state applications. Here, we shall highlight the results needed to understand the chemical properties of AIPO frameworks; a more detailed description of the theoretical work will be given elsewhere.⁹ Only gradient-corrected DF calculations have been performed with DMOL.³

We studied four different AIPO frameworks, isostructural to the α -quartz, sodalite, chabazite, and ATN polymorphs of silica (in the following we refer to them as QUA, SOD, CHA, and ATN, respectively), which combine a relatively small unit cell

(a maximum of 36 atoms) and a direct relevance to catalysis. With the exception of one earlier density functional–local-density approximation (DF–LDA) work on berlinite,¹⁰ our study represents the first investigation of crystalline AIPOs performed with periodic ab initio QM methods. Earlier QM investigations were reported on AIPOs (see, for instance, refs 11–14), but were performed using small molecular clusters cut out from the microporous framework. In the latter case, the fragments are saturated with hydrogen or pseudo-hydrogen atoms (the latter have a different effective nuclear charge, to represent the nonequivalence of framework Al and P ions¹⁵). Especially for small molecular fragments, the saturation of the cluster can impose important boundary conditions, which are able to alter the calculated solution. This shortcoming of the model is overcome in our calculations, in which the extended nature of the AIPO framework is correctly described via the periodic boundary conditions. Our work represents therefore a substantial methodological improvement from the earlier cluster-based descriptions of the AIPO frameworks.

In Table 1, we report the geometry-optimized structure of berlinite, the crystal for which the most accurate experimental structural studies are available.^{16,17} The excellent agreement between calculated and experimental values gives confidence in the quality of our calculations. Only the DF calculations in the local density approximation yield a noticeable structural difference, with the usual underestimation (~ 1 – 2%) of the lattice parameters due to an overestimation of the nonbonded (van der Waals) interactions. The latter interactions, however, modify the Al–O–P angles but not the equilibrium bond distances.

The framework properties of microporous AIPOs are often assumed to match closely those of the isostructural SiO_2 polymorph; the long-range ordered alternance of Al^{3+} and P^{5+} cations can in fact balance their chemical difference, leaving similar framework properties in AlPO_4 and SiO_2 materials. The results of our calculations challenge the above idea, especially with respect to the bonding features of the framework aluminum, silicon, and phosphorus atoms with the oxygens.

In Table 1, we report the calculated atomic charges in berlinite, defined via a Mulliken partition scheme; for each Hamiltonian employed, the other polymorphs examined show only minor differences, of less than 0.01 e, suggesting that the

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TABLE 1: Comparison of the Calculated and Experimental Crystal Structure of Berlinite (QUA-structured AlPO).^a

	exptl ¹⁶	exptl ¹⁷	B3LYP	HF	LDA ^d	GGA ^d
<i>a</i> (Å)	4.9429	4.9423	4.9442	4.9430	4.8161	4.9444
<i>c</i> (Å)	10.9476	10.9446	10.9463	10.9452	10.9115	10.9470
<i>x</i> (Al)	0.4660	0.4664	0.4644	0.4659	0.4584	0.4631
<i>x</i> (P)	0.4675	0.4669	0.4636	0.4652	0.4537	0.4627
<i>x</i> (O1)	0.4220	0.4163	0.4135	0.4186	0.4114	0.4114
<i>y</i> (O1)	0.2960	0.2922	0.2965	0.2953	0.3107	0.2994
<i>z</i> (O1)	0.3964	0.3977	0.3950	0.3976	0.3917	0.3933
<i>x</i> (O2)	0.4090	0.4156	0.4130	0.4166	0.4039	0.4106
<i>y</i> (O2)	0.2520	0.2576	0.2637	0.2592	0.2754	0.2663
<i>z</i> (O2)	0.8868	0.8837	0.8811	0.8830	0.8769	0.8795
<i>Q</i> (Al) ^b			+1.95	+2.19	+1.80	+1.90
<i>Q</i> (P) ^b			+2.25	+2.85	+1.94	+2.11
<i>Q</i> (O1) ^b			−1.04	−1.26	−0.93	−1.00
<i>Q</i> (O2) ^b			−1.05	−1.26	−0.94	−1.01
<i>r</i> ^c ; <i>q</i> ^b (Al–O)			1.745; 0.17	1.740; 0.14	1.738; 0.18	1.753; 0.17
<i>r</i> ^c ; <i>q</i> ^b (P–O)			1.539; 0.27	1.518; 0.27	1.537; 0.26	1.549; 0.26

^a Space group is $P3_121$; the *y* and *z* fractional coordinates of the Al and P atoms are (0,1/3) and (0,5/6), respectively. ^b Calculated net atomic charges (*Q*) and T–O bond populations (*q*), in e, defined via a Mulliken partition scheme. ^c Average T–O bond distance, *r*, in Å. ^d The columns LDA and GGA refer to local⁶ and gradient-corrected⁷ density functional calculations.

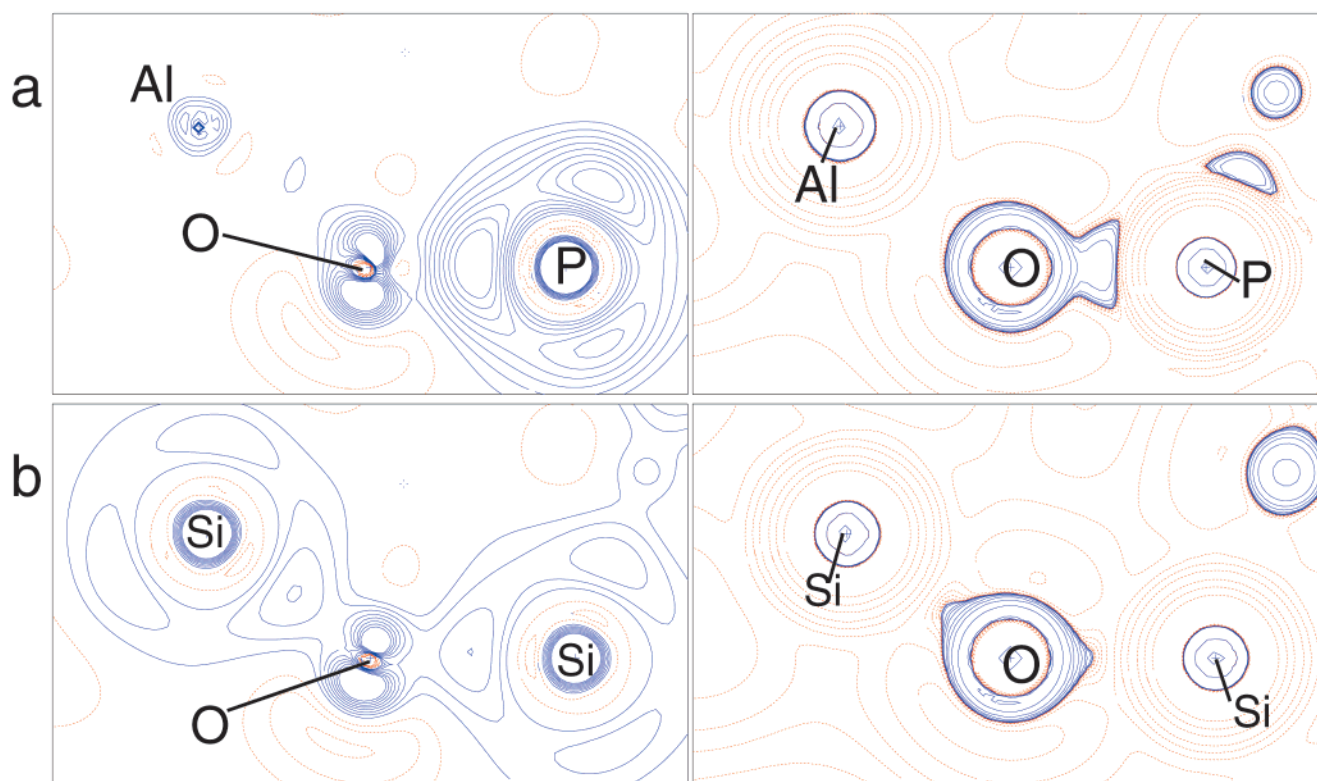


Figure 1. Difference electron density map (solid minus isolated formal ions, left plots) and Laplacian, *L*, of the electron density (right plots) in a plane containing one Al–O–P (a) or Si–O–Si (b) unit in QUA-structured materials. Continuous, dashed, and dot–dashed lines in the left plots correspond to positive, negative, and zero densities; in the right plots, continuous lines define the regions of negative *L* and covalent T–O interaction and dashed lines correspond to zones of positive *L* and ionic interaction. In both left and right plots, zones of covalent bonding are colored in blue and zones of ionic bonding in red.

bonding features are a local property of the solid, which are only marginally affected by the crystalline environment. Net charges and bond populations indicate that the P–O bond is strongly covalent, while the Al–O interaction in AlPOs is essentially ionic. The net charge of P is less than half the formal value of +5, and the P–O bond has an overlap population of 0.27 e, twice the value of the Al–O bonds. The values calculated for the Si–O bonds in silica ($Q_{\text{Si}} = +1.50$, $q_b = 0.31$ e at the B3LYP level) are similar to those of the P–O bonds in AlPOs and suggest an important component of covalence in the bonding. To support this finding, in the left column of Figure 1, we show two difference density maps obtained by subtracting

the density of isolated formal ions from the total electron density of the solid. The maps are drawn in a plane containing one Al–O–P, or the corresponding Si–O–Si unit, in QUA-structured materials. Via these maps, we can compare the population of the valence atomic orbitals on the tetrahedral (T) species (T = Al, Si, and P) with a perfectly ionic solution: the more electrons are associated with the T ion, the more its bonding with the oxygens is covalent. In the figure, we clearly see that, while the difference density shows almost no feature on Al, which can be described as ionic, an important fraction of the valence electron density is associated with Si, and even more so with P. Moreover, the electronic redistribution shows

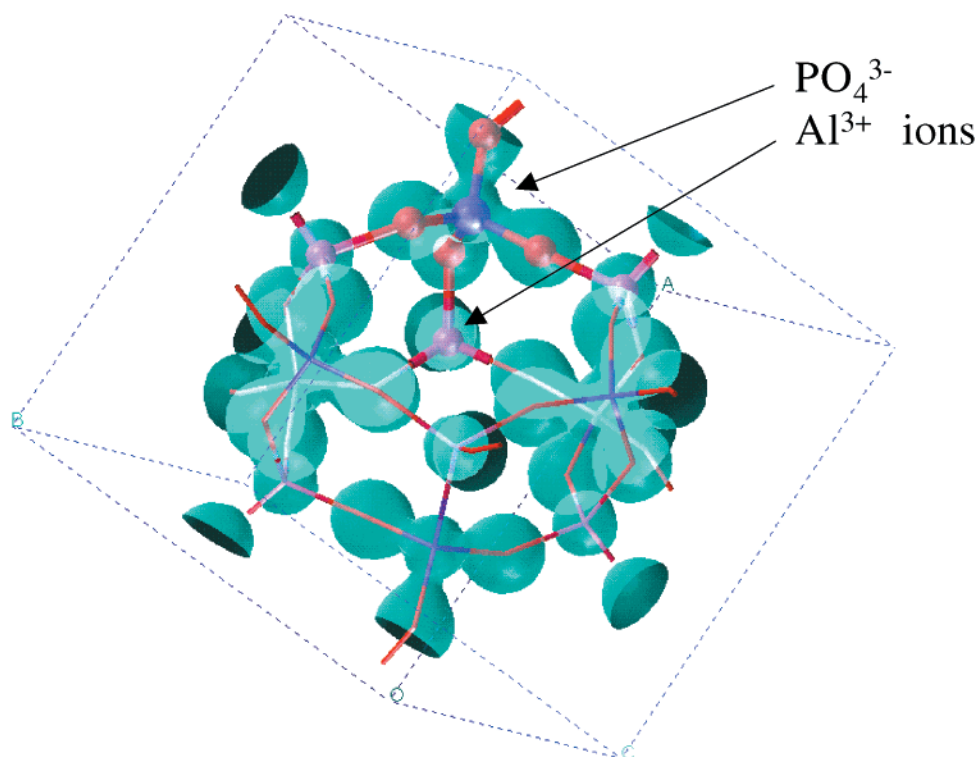


Figure 2. Three-dimensional isodensity plot ($\rho = 0.12 \text{ e/b}^3$) of the electron density in the unit cell of AIPO-34 (CHA) calculated with DMOL³. Note the natural separation of the framework into discrete Al^{3+} and PO_4^{3-} ions.

clear maxima in the Si–O and P–O directions, indicative of their covalent bonding.

A similar result is obtained in the calculations performed with DMOL³. In Figure 2, we report a three-dimensional plot of the calculated electron density for the CHA AIPO polymorph. The isodensity level chosen, 0.12 e/b^3 , corresponds to the valence density in the solid and shows again a separation of the framework into discrete Al^{3+} and PO_4^{3-} units.

An alternative, and more accurate, description of the bonding features in the solid can be achieved by means of the quantum theory of atoms in molecules proposed by Bader.¹⁸ In regions of ionic interaction, the (calculated) electron density, ρ , shows minima along the bonds and has a positive curvature; the regions of covalent bonding, instead, correspond to local maxima of ρ , where the curvature is negative. By calculating and mapping the Laplacian of the calculated electronic density ($L = \nabla^2\rho$) along the T–O bonds, we can therefore easily detect the regions of ionic and covalent interaction in the solid. This feature is illustrated in the right column of Figure 1, in which we report the Laplacian of the calculated electronic density from our B3LYP study. We see in the figure that in AIPOs there is an ample zone of negative L along the P–O bond; again, therefore, the P–O interaction is described as covalent. The Al–O bond, instead, has positive L , with only a minor distortion of the electronic shell on the oxygen toward Al. The Si–O bond in zeolites has intermediate behavior between the Al–O and P–O bonds but still causes an appreciable distortion of the electron density around the oxygen. A small area of negative L is present along the Si–O directions.

All of the above arguments give unambiguous information on the nature of the bonding in AIPOs: the Al–O and P–O bonds are such that *the AIPO frameworks comprise discrete Al^{3+} and PO_4^{3-} ionic units*, i.e., the bonding is molecular-ionic, rather than the continuous semicovalent network present in silica and aluminosilicates.

TABLE 2: Relative Stability of the Polymorphs Examined, as Obtained from the CRYSTAL Calculations^a

material//Hamiltonian	QUA	SOD	ATN	CHA
SiO_2 //HF ²⁰	0.00	+4.6		+6.3
AIPO//HF	0.00	+11.8	+12.2	+13.9
AIPO//B3LYP	0.00	+6.0	+7.5	+9.7

^a Results are reported in kJ per mole of TO_2 units; the energy values for the silica polymorphs are from ref 20, using the 6-31G(d) basis set and the HF Hamiltonian. Our calculations on AIPOs are reported at both the B3LYP and HF levels, the latter for comparison with ref 20, in which no geometry optimization was performed with the B3LYP Hamiltonian.

Such a result confirms the indication arising from earlier experimental studies¹⁶ and has important consequences for our understanding of the chemistry of AIPO catalysts. The ionicity of the framework can effectively explain the less pronounced resistance of AIPOs than that of zeolites when steamed; while the covalent Si–O backbone is resistant to this treatment, the ionic AIPOs dissolve. The ionicity of the Al–O interaction is also likely to control the defect chemistry of the Al site; ionic substitutional dopants introduce minor perturbations to the host electronic structure and therefore more readily replace Al in AIPOs than Si in zeolites. In particular, late transition metal cations, such as those of Ni, Co, Fe, and Mn, which form ionic oxides with relatively small cation radii,¹⁹ would be expected easily to substitute for Al, as is indeed observed in the metal-modified catalytic materials.^{1–3}

In Table 2, we further report the calculated internal energy for the four polymorphs, relative to the stable QUA structure. Results for AIPOs have been obtained using both the B3LYP and HF Hamiltonians: the former because it provides the most accurate energetics, the latter to compare our results with a recent paper on zeolites,²⁰ in which no geometry optimization was performed with the B3LYP Hamiltonian. For AIPO materials, we find the same order of stability as obtained in ref 20 for zeolites. The parallel behavior indicates that long-range

effects in the crystal have a qualitatively similar influence on isostructural materials with different chemical composition. The chemical composition of the framework, however, has a strong quantitative effect on the energetics, and the energy difference between the AIPO polymorphs is substantially greater than that in zeolites. From the results of our calculations, we attribute the higher energy difference to the oxygen net charge, which is larger in AIPOs than in zeolites, mostly because of the ionic Al–O bond. The higher ionicity increases the energy toll to pay when the density of the crystal decreases from the dense to the microporous polymorphs.

The calculated energetic stability of the different AIPO polymorphs compares well with the results of thermochemical studies,²¹ in which the relative energy of microporous AIPOs compared to berlinite (QUA) covers the range of 11–17 kJ/mol (of AIPO₄ units; i.e., 5.5–8.5 kJ/mol of TO₂ sites in the units of Table 2). Experimental calorimetric work^{21,22} disagrees instead with our findings when comparing the relative (in-)stability of microporous AIPOs and zeolites from the stable QUA polymorph. In particular, the experimental energy range of zeolites extends to 14 kJ/mol (of TO₂ units), higher than that calculated in ref 20 and higher than the experimental range derived for AIPOs. In this respect, we note that the calculations, both those presented here and in ref 20, refer to a defect-free material of pure SiO₂ or AIPO₄ composition. Experimentally, microporous zeolites and AIPOs are usually obtained with a templated synthesis,¹ which requires the inclusion of dopant ions in the framework to charge-balance the positive charge of the organic template. The presence of defects, either introduced during the synthesis or in postsynthetic treatments such as dealumination,²³ can effectively alter the energetic content of the solid. This effect is particularly pronounced when the energy difference between polymorphs is small, as is the case for zeolites. The microporous SiO₂ samples employed in the calorimetric study of ref 22 contain a residual amount of Al and extraframework Na, K, and Ca ions, detected by chemical analysis. We consider that these framework defects may effectively increase the energy of the microporous frameworks with respect to quartz (which is easier to obtain in defect-free forms) derived experimentally, thus explaining the disagreement between calculated and experimental values.

Our findings concerning the ionicity of the AIPO framework, and the higher energy of the microporous polymorphs (in defect-free forms) relative to the stable QUA structure, concur in explaining the lower stability of microporous AIPOs compared to their isostructural zeolites. This feature is a direct consequence of the bonding nature in the materials. As noted, the framework ionicity is also responsible for the major contrast between the chemistry of AIPOs and that of aluminosilicates, relative to the nature and concentration of dopants that can be introduced into the materials. Mastering the degree of covalence in zeotypic

materials, for instance, via appropriate framework substitutions, may prove an effective route toward the synthesis of improved catalysts, which combine the structural stability of zeolites with the wider range of dopants, including the redox-active ions, allowed by AIPOs. Quantum mechanical calculations of the kind proposed here may provide an effective tool to discriminate the effect of each substitutional dopant on the bonding and hence on the framework strength, so as to complement and direct future experimental efforts.

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