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Influence of Organic Templates on the Structure and on the Concentration of Framework Metal Ions in Microporous Aluminophosphate Catalysts

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Energy minimization methods are used to investigate the packing energies of triethylamine and triethylammonium templates in two distinct aluminosilicate structures, $AlPO_4$-5 (AFI code) and the chabazitic $AlPO_4$-34 polymorph (CHA), both of which may be synthesized as Co-AlPOs from the same gel, depending on the concentration of Co^{2+} and template. We show that higher (cationic) concentrations of template, induced by higher (negatively charged) Co^{2+} substitution levels in the framework, favor the formation of a chabazitic structure. The $AlPO_4$-5 polymorph is, however, marginally more stable in the untemplated state, a result which is consistent with the reversion of the chabazitic phase to the $AlPO_4$-5 polymorph at higher temperatures or increased reaction time.

Introduction

In the synthesis of microporous solids, the choice of organic template is acknowledged to be of vital importance in directing synthesis toward particular structures. Moreover, in framework metal-substituted aluminophosphates and aluminosilicates they influence the degree of metal-ion substitution (of Si, Al, or P) of the framework itself. Developing an understanding of these factors is of major importance in generating new or improved solid acids. Such materials are of increasing catalytic significance, since a divalent metal M (M = Zn, Mg, Co, Mn, etc.) in the place of a framework Al ion, or Si^{4+} in place of a framework P ion, entails the inevitable introduction of a proton loosely attached to a framework oxygen in the vicinity of the substituent (Figure 1). A growing family of such solid acids (sometimes additionally possessing redox properties) has been reported, anionic frameworks being the key feature of the templated product.

There is, however, much uncertainty concerning the precise factors that influence the preparation of such solids. Why is it, for example, that some microporous solid acids seem capable of being formed only when a divalent metal ion is present in the framework? DAF-1,[1] a good catalyst for the acid-catalyzed isomerization of but-1-ene, idealized formula $Mg_xAl_{1-x}PO_4 \cdot nH_2O$ ($x = 0.22$ when prepared in an aqueous gel, although lower concentrations are possible when organic cosolvents are used[2]), is a notable example. And why is it that the presence or absence of a heteroatom ion in the precursor gel containing the organic template can quite radically influence the structure of the microporous product? For example, EU-1 is formed from a gel containing Al and hexamethonium as a template, while EU-2 is formed if the Al is absent from the same gel.[3] The dramatic nature of this effect is shown in Figure 2.

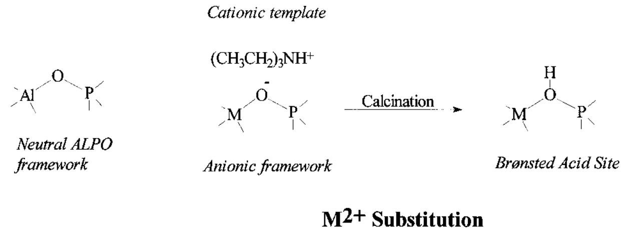

Figure 1. Schematic representation of M^{2+} substitution in AlPO frameworks. The neutral AlPO framework becomes anionic on substitution of divalent metal ions. Brønsted acid sites are formed on removal of the template by calcination.

In this paper, we explore the correlation between template and heteroatom concentration during synthesis by specific reference to a cobalt-containing aluminophosphate gel medium with triethylamine as the template. It is known that, in the absence of Co, $AlPO_4$-5 (AFI structure code) is formed rapidly from this gel[4] and no intermediate phase is noted. When Co(II) ions are added to the synthesis gel, the Co−$AlPO_4$-5 phase is still formed at low Co concentration, but at relatively high Co concentrations (0.08Co:Al) and in the presence of an excess of the template, triethylamine, an intermediate chabazitic (AlPO) phase is formed. This fact has been established both by ex situ[4,5] and in situ[6,7] diffraction studies. The chabazitic (CHA structure code) phase then redissolves at a rate determined by the

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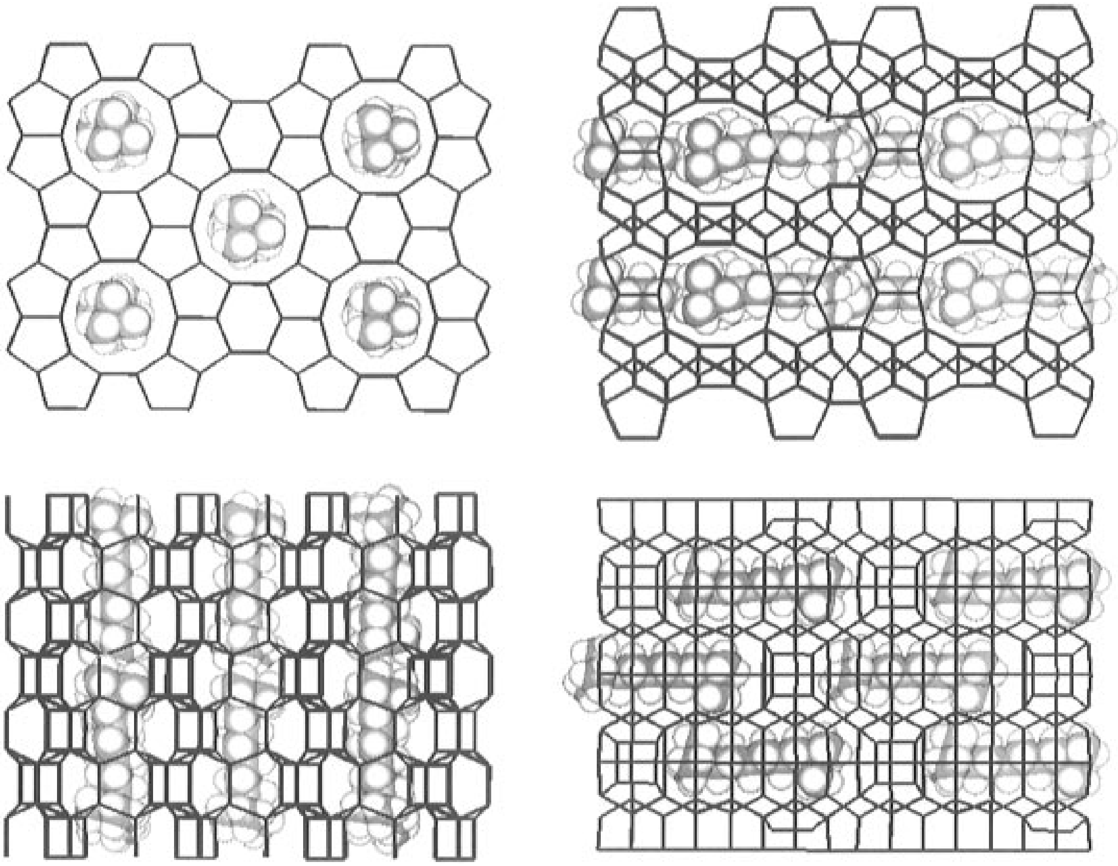

Figure 2. EU-2 (left) and EU-1 (right) framework structures viewed along (top) and perpendicular (bottom) to the channel direction. These two structures are formed under the same conditions using the same gel composition with the exception of the presence (in the case of EU-1) or otherwise (EU-2) of a small amount of aluminum. Note the dramatic change in channel structure (although pore dimensions are similar) and of the orientation of the template (hexamethonium in both cases). The positions of the template were calculated using the same procedure used in this work.

temperature until phase-pure Co–$AlPO_4$-5 is formed.[7] Indeed, at still higher temperatures this same gel does not yield any chabazitic phase at all, suggesting that this chabazitic AlPO cannot form as rapidly as the corresponding AFI structure. Furthermore, it is generally observed that when stable chabazitic AlPOs are formed (in the present regime $CoAlPO_4$-34 is produced), the syntheses are typified by high heteroatom and template concentrations and usually low preparation temperatures. For example, higher Mg and Si concentration favor formation of MgAPO-34 and SAPO-44 over MgAPO-5 and SAPO-5 respectively; low temperatures favor MAPO-34 over MAPO-5.[8] The formation of the CHA phase appears to be strongly correlated to the presence of Co since simply increasing the template concentration does not induce its formation.

However, we should note that these syntheses are typically carried out in an excess of template. Conversely it is observed that the CHA phase does not appear when a pure AlPO gel is used or at very low Co concentrations. Recent work has shown that this behavior is also manifested during the synthesis of other $MeAlPO_4$-5 materials.[9] Diffuse reflectance spectroscopy has also suggested that at the gel stage the role of the template is as a pH regulator, modifying the Co chemistry[5] and not as a structure-directing agent. Furthermore, these authors suggest that Co species are strongly bound to crystallization nuclei during formation of a chabazitic phase while in $AlPO_4$-5 synthesis this interaction is much weaker. By seeking to understand the role of the template in the synthesis of these materials and the relationship between the template and the heteroatom in the framework, we hope to gain insights into the key factors involving the role of both cations and templates in the synthesis of microporous materials.

Methodology

Our approach involves computational techniques which have been successfully applied to the study of template–zeolite interactions.[10–12] Specifically, the approach of Freeman et al.,[13] originally developed to locate sorbate molecules within zeolites, is used to determine possible low-energy sites for individual template mol-

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ecules. A library of conformations of the sorbate molecule is generated by a molecular dynamics (MD) run and these conformations are then inserted, using a Monte Carlo method into the host framework. Suitable candidate structures are accepted according to supplied geometric and energetic constraints and subsequently energy-minimized using standard techniques. The methodology is implemented in the Catalysis module of the InsightII software,[14] and energy minimizations are carried out using the Discover code.[15] Once low-energy conformations of the template are calculated, the calculations are repeated with higher template concentration by replicating the single template in a supercell of the framework.

We have previously used this methodology[10,11] in studying templating and have demonstrated that the templating action can be correlated with the nonbonded interactions between the template and the framework. Our prior work has shown that the methodology reproduces experimental template geometries and that it is possible using these techniques to select the most suitable templates for a given framework. Others have shown that this method provides a useful correlation between template–framework interactions and crystallization times for siliceous systems.[12]

All initial docking calculations were performed using periodic boundary conditions with a rigid framework. We note that experimental unit-cell dimensions change little when templates are removed, and therefore we conclude that this assumption has little effect on the interactions of the templates and the framework. The microporous frameworks were treated as their siliceous analogues, i.e., $2Si^{4+} \equiv Al^{3+} + P^{5+}$. For AlPOs this approximation is justified first by the strict Al and P alternation, but more importantly by the fact that the oxygen of the framework is the dominant atom involved in nonbonding interactions with the template. We further note that suitable molecular mechanics descriptions of aluminophosphate materials are not as well developed as those for aluminosilicates. Cobalt is not considered explicitly in these calculations owing first to the absence of any suitable potential parameters and second to the lack of experimental indications of preferential siting of the Co in the framework. However, we are mainly concerned with the possible concentrations of templates rather than their specific interactions with Co (or other metal atoms). Although the charge interactions between the framework and the template will be significant, we have previously shown[8] that it is the van der Waals interactions which are the dominant forces in determining template geometry and binding. The long-range electrostatic forces between the framework and the template control the relative *concentration* of the template and the framework substituent via the criterion of electroneutrality. But, they do *not* greatly influence the magnitude of the template/host binding energy or the geometry. Therefore, neglecting the Co charge will have little effect on conclusions drawn regarding the relative binding of templates in different framework structures. The ab initio derived force field cff91_czeo[16,17] was used for these calculations, with the parameters summarized in Table 1.

Table 1. Nonbonding Parameters from the cff91_czeo Force Field[a]

type	r/Å	ϵ/kcal
sp^3 C	4.0100	0.0540
sp^3 N	4.0700	0.0650
sp^3 N in protonated amines	3.2620	0.0650
H bonded to C, N	2.9950	0.0200
Si in zeolite	0.0001	0.0000
O in zeolite	3.4506	0.1622

[a] Bonding parameters are given in detail by Hagler et al.[16] and Hill and Sauer.[17] Nonbonding energy between atoms i and j separated by distance r_{ij} is given by $E = e_{ij}[2(r_{ij}^*/r_{ij})^9 - 3(r_{ij}^*/r_{ij})^6]$, where $r_{ij}^* = [(r_i^6 + r_j^9)/2]^{1/6}$ and $\epsilon_{ij} = 2\sqrt{\epsilon_i \epsilon_j}(r_i^3 r_j^3)/(r_i^6 r_j^6)$.

For the calculation of lattice energies two approaches were used. Energy minimizations using the same molecular mechanics methods described above with the addition of full framework minimization were performed on the unit cells with the template in place. However, molecular mechanic energies have no clear thermodynamic interpretation as the energy zero is system specific. We therefore also calculated the lattice energy of the (calcined) frameworks using Born model potentials, where the potential functions used are defined so that the energy is zero when all ions are infinitely separated, permitting meaningful comparison between different systems. Further details of the methodology are given in ref 18. The GULP code[19] was used with potential parameters from the work of Jackson and Catlow[20] and Gale and Henson[21] for the siliceous and AlPO systems, respectively.

Under the pH conditions of the synthesis, the template is protonated and is the source of the charge compensation arising from the presence of Co in the framework (see Figure 1). We have therefore considered both the neutral and protonated form of the template. However, since we would have to provide a charge balance for the protonated form, the calculations on triethylammonium (and other cationic templates) have been performed without charge interactions, an approximation which as discussed above will not lead to substantial errors in the relative template-framework geometries and binding energies.

Results and Discussion

Siliceous unit cells of the CHA and AFI with a variety of template concentrations have been considered. For the CHA structure, either one or two molecules of triethylamine may be accommodated within the structure. Table 2 gives the results (in terms of binding energy per template molecule) for the CHA structure for both cases, and Figure 3 illustrates the optimum template geometry within the structure. It is clear that the presence of two templates in the unit cell provides a much greater stabilization than is calculated for just one template. Even higher concentrations resulted in unfeasible geometries and large strains. In the AFI structure, once a suitable low-energy configuration for a single template is identified, the concentration of the

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Table 2. Results for the Triethylamine/Chabazite Structure[a]

			E_{inter}/template (kJ mol^{-1})	
template	template concn (per unit cell)	T site: template	no charges	with charges
triethylamine	1	12	−47.3	−71.6
triethylamine	2	6	−61.1	−83.7
triethylammonium	1	12	−33.3	
triethylammonium	2	6	−77.0	

[a] $E_{\text{inter}} = E_{\text{host}} - E_{\text{free}}$, where E_{host} is the total energy of the framework/template combination, E_{free} is the energy of an isolated gas-phase template molecule. The results are normalized to give an E_{inter} per template. Due to the charge on the unit cell when triethylammonium is included and the lack of detailed knowledge of the location of the charge compensating Co, charge interactions have not been included in calculations on these systems.

template within the framework is increased from 0.25 to 1.0 molecule/unit cell (12T sites) using a supercell. Table 3 gives the results for this structure, and Figure 4 shows the arrangement of the highest template concentration considered. In contrast to the results obtained for the CHA structure, E_{inter} does not increase significantly with the template concentration. Evidently, the template−template interactions are less prominent here, and thus we conclude that the formation of the AFI structure can also occur with lower template concentrations than with an optimal "fully occupied" template concentration. Moreover, we note that in addition to the pronounced difference in the variation of stability with template loading, we also find that the binding of the template to the CHA framework is significantly higher than in the AFI structure. Overall, the effect of the template on the stability of the framework is clearly greater in the CHA structure.

If we now assume that the maximum concentration of the template is equal to the concentration of Co—the template providing the charge compensation for the incorporation of the Co in the framework—then these results clearly demonstrate how different Co concentrations are attainable in the two structures. Furthermore, if we consider that the uptake of Co is dominated by kinetic and not thermodynamic factors—not unreasonable given the large range of Co content which can be included in $AlPO_4$ structures—it is now apparent why the CHA structure forms only in the presence of high Co *and* high template concentrations. Our calculations have shown that to form the CHA structure the concentration and orientation of template molecules is more critical. For CHA to form with triethylamine, we calculate that it is energetically preferential for 2 template molecules/unit cell to be accommodated per unit cell, providing a significant increase in stability over a single template. The CHA phase is unlikely to form at lower template concentrations. But for the higher template concentration, two Co cations must also be present, for charge neutrality; therefore, the CHA structure is only likely to form if there is a Co:T site ratio of 1:6; lower Co levels do not result in the CHA phase since they do not allow the required Co (and hence template) concentration per cage to be attained. We also note that only MAPO (and SAPO) phases with the chabazite phase have been formed, further demonstrating the role of the heteroatom−template interaction in making this structure accessible. Therefore, it is the availability of Co (and M^{2+}) in the gel which determines whether CHA phases form.

In the context of the above arguments, we note the work of Urbina de Navarro et al.,[22] who found strong Co gradients across phases when AFI and CHA are formed together. These authors found that the CHA phase contained up to 10 mol % Co while the AFI had 0−4 mol % Co. However, when AFI alone is formed, from a gel with lower Co concentration, the subsequent $AlPO_4$-5 had up to 8 mol % CO, while synthesis of the pure CHA phase again resulted in Co concentrations of 10 mol %—an observation which suggests that uptake of Co into the CHA phase is rapid which has also been suggested elsewhere.[5] Moreover, in line with our arguments concerning the need for 2 triethylamine molecules/unit cell of CHA, we note that Urbina de Navarro et al.[22] also find a significantly higher concentration of template in the mixed phase than in pure AFI, an effect which would not be apparent if the CHA phase had only 1 template molecule/unit cell as in AFI. Therefore, we conclude that for CHA to form, higher (triethylamine) template concentrations are required in the nucleation stage, suggesting that the template has more than the pH regulating role proposed by Uytterhoeven and Schoonheydt.[5] We are currently investigating the interactions of gel species with templates to provide further details as to the mechanism of the synthesis.

We have also determined the siting and maximum concentration of other templates which form a chabazitic AlPO in order to establish if our method compares well with experimental compositional analyses (as no compositional analysis exists for the triethylamine templated material). Table 4 shows the maximum calculated concentration of three templates in a chabazitic unit cell and the experimental compositions.[23] We see that for each template, the calculated and experimental ratio of template to TO_2 unit is in good agreement, satisfying us that the conclusions drawn above regarding the concentration of triethylamine in the same CHA structure are correct. Note that for diethylethanolamine, 2 templates/cage is possible (this being sterically impossible for the other templates), although such configurations are much less energetically favored than in the case for one per cage. Therefore, it is suggested than metal concentration will again play a major role in the formation of this chabazitic structure (Co−$AlPO_4$-47): at high Co concentration, Co uptake will allow maximum template concentration, while lower Co concentration may result in some singly occupied cages. This results would explain the intermediate Co:template ratio (1:8.3) found experimentally for pure Co−$AlPO_4$-47. However, we note that the more readily synthesized Co−$APSO_4$-47 has a concentration of 2 templates/cage, which is required to compensate the framework charge deficiency of −2.0/cage assuming that Co replaces Al, that Si replaces P, and that the template is protonated.[24]

The maximum possible Co concentration in the $AlPO_4$-5 structure is calculated to be 1:12 (if the Co:

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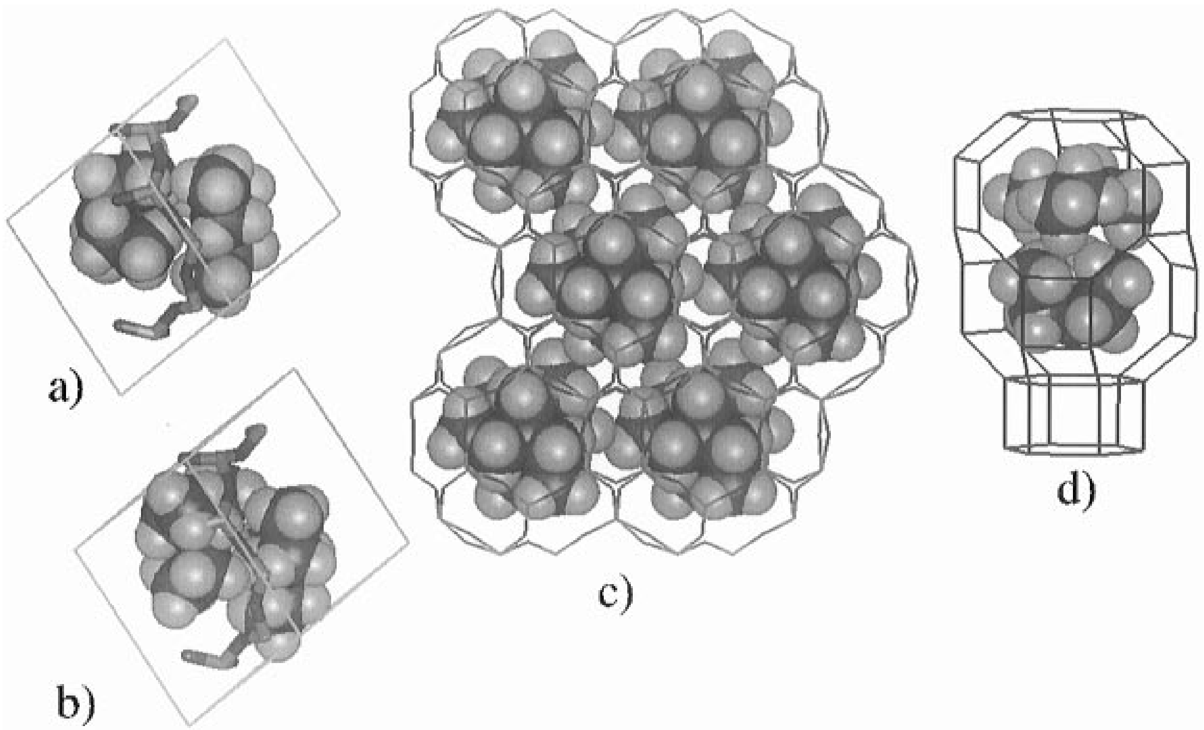

Figure 3. Optimal calculated template geometries for the CHA structure with two templates per unit cell shown for (a) triethylamine and (b) triethylammonium. We also show (c) the extended template structure and (d) the location of the templates in the chabazitic cage structure (here, oxygen atoms are omitted for clarity, being located approximately halfway between the tetrahedral atoms shown).

Table 3. Calculated Binding Energies for the Triethylamine/$AlPO_4$-5 Structure[a]

			E_{inter}/template ($kJ\ mol^{-1}$)	
template	template concn (per unit cell)	T site: template	no charges	with charges
triethylamine	$^{1}/_{4}$	48	−32.7	−62.7
triethylamine	$^{1}/_{2}$	24	−35.4	−64.1
triethylamine	1	12	−37.0	−66.8
triethylammonium	1	12	−37.2	

[a] E_{inter} is as defined for Table 2. Calculations were performed on a supercell of $AlPO_4$-5 so that in the system with 1 template/unit cell, the calculation is performed on 16 template molecules.

template ratio is unity as discussed above), suggesting that higher Co concentrations are not possible in the AFI structure. Again, higher concentrations result in unfeasible geometries and energies. This template concentration is in good agreement with a typical template concentration of 1.2/unit cell in $AlPO_4$-5[23] and with typical M^{2+} concentrations. However, since we find that the binding energy of triethylamine does not significantly decrease at lower template concentrations, this results suggests that AFI can still form at these low template concentrations. Furthermore, we note that in a great number of $CoAlPO_4$-5 syntheses[5,8,22,24,25] the Co concentration is lower than would be expected if full template occupancy (as calculated here) and Co:template parity is attained, thereby providing support for our conclusion that templating effects are not as critical for the formation of AFI as for other frameworks. The rapid depletion of Co from gels and subsequent formation of very low Co concentrations or pure $AlPO_4$-5[22] further suggests that template−framework interactions are relatively unimportant in $AlPO_4$-5 formation. Conversely our conclusion regarding the necessity for inclusion of high template concentration in the CHA phase is supported by the formation of mixed phases; strong interaction between Co species and the template resulting in formation first of the CHA phase and subsequently of the Co-depleted gel forms $AlPO_4$-5.

We now return to the fact that chabazitic AlPO in this synthesis regime can be an intermediate phase which redissolves, giving way to only the Co-$AlPO_4$-5 phase.[6,7] Can this be accounted for by considering the lattice energy of the two structures? First, we consider the stability of the two microporous lattices in the absence of templates (i.e., conditions relevant to calcined materials) using Born model potentials, a technique which gives thermodynamically comparable lattice energies. We see (Table 5) that the CHA structure is thermodynamically less stable than the $AlPO_4$-5 structure, when considered both as an AlPO framework and as the SiO_2 analogue. Although this results does not account for the influence of the Co or the template on the stability of the framework, it does provide a thermodynamic basis for the metastability of the phase. However, this calculated difference in energy is small, a result also noted from experimental determinations of the formation enthalpy of a large number of microporous materials.[26] Thus, it is clear that small changes in the energetics of the synthesis, such as those brought about by template−framework and template−heteroatom interactions can bring about substantial changes in the products as seen here.

To investigate the role of the template sublattice in stabilizing the framework structures, we have energy minimized the unit cells including the templates using the molecular mechanics force field described earlier (Table 6). We see that again the AFI (treated here as

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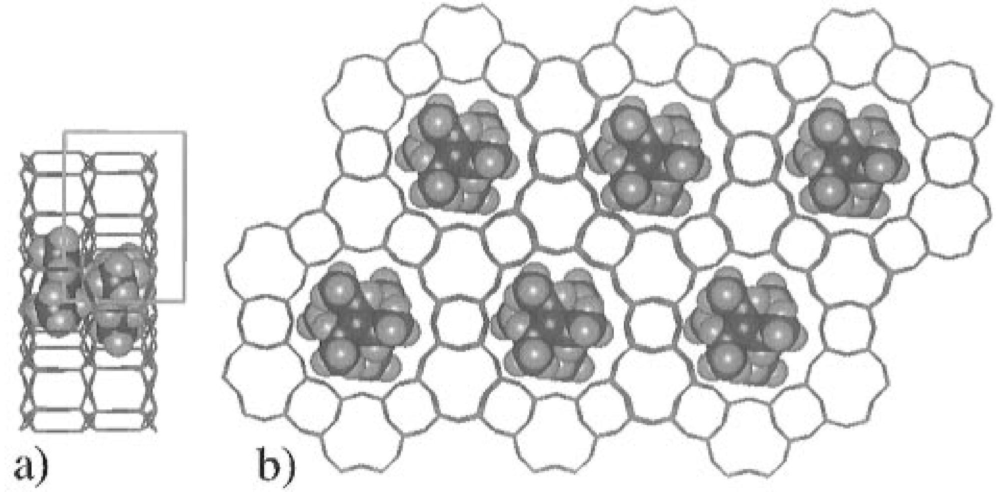

Figure 4. Optimal calculated template geometries for triethylamine at the highest template concentration considered in the ALPO$_4$-5 structure. Views are shown (a) perpendicular and (b) along the channel direction, showing the packing of the templates at the highest concentration considered.

Table 4. Binding Energies of Other Experimental Templates in the CHA Structure[a]

template	E_{inter}/template (kJ mol^{-1})	R concn per unit cell (and R:TO$_2$ ratio)	exptl compositions (and R:TO$_2$ ratio)
tetraethylammonium	−80.6	1 (1:12)	0.08R $Co_{0.09}Al_{0.41}P_{0.51}O_2$ (1:12.5)
diethylethanolamine	−66.3	1 (1:12)	0.12R $Co_{0.11}Al_{0.39}P_{0.5}O_2$ (1:8.3)
	−37.4	2 (1:6)	0.17R $Co_{0.07}Al_{0.42}Si_{0.13}P_{0.38}O_2$ (1:6)[24]
cyclohexylamine	−61.9	1 (1:12)	0.1R $Co_{0.1}Al_{0.39}P_{0.5}O_2$ (1:10)

[a] R is the particular template in question. Each calculation was performed with all Coulombic interactions excluded. Experimental compositions from ref 23 unless otherwise noted.

Table 5. Calculated Lattice Energies for Both Siliceous and Aluminophosphate Analogues of the AlPO$_4$-5 and Chabazitic Structures[a]

		$E_{lattice}$ per unit cell/eV	$E_{lattice}$ per TO$_2$/eV
AlPO$_4$-5 ($T_{24}O_{48}$)	siliceous	−3085.9390	−128.581
	AlPO	−3216.5053	−134.021
chabazite ($T_{12}O_{24}$)	siliceous	−1607.8597	−128.554
	AlPO	−1542.6508	−133.988

[a] The (P1) unit cells were energy minimized to zero force on all cell parameters and internal coordinates.

Table 6. Calculated Lattice Energies (kJ mol^{-1}) for Both Templated Siliceous AFI and CHA Structures Using the Molecular Mechanics Methodology[a]

	Framework in the absence of template		Templated framework		template stabilization energy per TO$_2$ unit
	E_{latt} per unit cell	E_{latt} per TO$_2$ unit	E_{latt} per unit cell	E_{latt} per TO$_2$ unit	
AFI $T_{24}O_{48}\cdot(C_6H_{15}N)_2$	−4394	−183	−4643	−193	−10
CHA $T_{12}O_{24}\cdot(C_6H_{15}N)_2$	−1801	−150	−2040	−170	−20

[a] The (P1) unit cells were energy minimized to zero force on all cell parameters and internal coordinates. The template stabilization energy is the energy gained per TO$_2$ unit when the structure is templated and is therefore directly related to E_{inter} previously defined.

a purely siliceous system) is more stable than CHA. However, it is not strictly valid to compare different systems since the energy function used to describe different unit cells is not the same (different numbers of atoms and interactions modify the energy function). Nevertheless, given that the energy of the framework is dominant and that the template−framework interactions contribute only a fraction of the total energy, it is clear that the AFI structure is again more stable than the CHA structure, as determined above using the Born model potentials. More importantly, we again note a higher stabilization of the structure on inclusion of the template in CHA than AFI, as we previously found for the binding energy of the templates. Nevertheless, it is unlikely that lattice energy differences are decisive in determining the relative stabilities of microporous frameworks.[26] Other considerations such as relative growth rates of the two structures are likely to be important. The CHA structured MeAlPOs also generally form much slower than AlPO$_4$-5,[27,28] which we suggest is a consequence of the requirement for a greater extent of ordering of the template in CHA. We further note that the AlPO$_4$-5 appears to be highly stable: not only is it readily formed in a large range of gel conditions but also it survives thermal treatment.[23] These factors will influence the transformation of the CHA phase to the AFI phase in the synthesis gel.

In our previous work[10] we demonstrated how the templates that are most effective experimentally for a given structure are those which have the maximum binding energy to the framework. Thus, we should be able to determine if indeed the AFI and CHA phases are more likely to be formed by triethylamine than other AlPO phases. We have therefore determined the binding energy of triethylamine in a number of AlPO frameworks using the same methodology described above for CHA and AFI. We see (Table 7) that the binding energy of triethylamine is lower in these structures than in CHA (Table 2), and so it comes as no surprise that the CHA phase is formed with this

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(27) Ashtekar, S.; Chilukuri, S. V. V.; Prakash, A. M.; Harendranath, C. S.; Chakrabarty, D. K. *J. Phys. Chem.* **1995**, *99*, 6937.

(28) Barrett, P. A.; Sankar, G.; Catlow, C. R. A.; Thomas, J. M. *J. Phys. Chem. Solids* **1995**, *56*, 1395.

Table 7. Binding Energies of Triethylamine in a Variety of AlPO Frameworks[a]

framework (IZA code)	E_{inter} (per template)/kJ mol^{-1}
$AlPO_4$-41 (AFO)	−57.0
$AlPO_4$-18 (AEI)	−46.5
$AlPO_4$-11 (AEL)	−69.4
$AlPO_4$-36 (ATS)	−24.0
$AlPO_4$-17 (ERI)	−75.7

[a] E_{inter} as defined in Table 2.

template rather than any of these other structures. However, the binding energy of triethylamine in the AFI structure is lower than in both $AlPO_4$-11 and $AlPO_4$-37. Thus, other factors must dominate the synthesis of these phases. Future work will investigate whether the preferential formation of AFI can be explained by kinetic and other factors pertaining to the synthesis conditions.

Conclusions

The competitive formation of the AFI and CHA structures from a CoAlPO gel is explained by the uptake of template and of Co(II) ions from the gel, the more stable AFI structure being accessible at low template concentration. Furthermore, a limit of 1 Co atom/unit cell of AFI is imposed by the maximum template concentration possible in the structure given that the template charge compensates for this heteroatom. To form the thermodynamically less stable CHA phase, it is necessary to increase the relative template concentration such that there are 2 template species/unit cell. This, in turn, requires that sufficient Co is present. Thus we conclude that the CHA phase forms as a consequence of the correlation and interaction of the Co and the template and will not form if the concentration of either Co or template is insufficient. Future work will consider the nature of this Co−template interaction and the mechanism of nucleation.

Our calculations demonstrate how the concentration of heteroatoms in a microporous 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. They provide information that may be used to design new templates with higher charge/size ratios, which, if they retain their structure-directing abilities, will allow a greater control over the range of heteroatom incorporation in the resulting microporous framework. Our calculations can also assist in pointing to possible modifications in synthesis procedures that permit fine tuning of the properties of microporous materials.[2]

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