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Computational Prediction of the Phase Transformation of Two As-Synthesized Oxyfluorinated Compounds into the Zeotype CHA Forms

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The numerous syntheses of templated inorganic open frameworks in hydrothermal conditions[1] were the starting point for the development of porous solids obtained by calcination, with applications as molecular sieves, for adsorption or catalytic purposes. Indeed the structure-directing agents, used during the synthesis of such compounds, are often incorporated in the final structure. Upon thermal treatment (calcination), these template molecules can usually be removed, along with other species, such as water molecules and hydroxy groups. However, whereas the crystal structures of as-synthesized solids are well characterized, those of calcined solids, which are of crucial interest, are scarcely described, this is because of their powder form and a result of the difficulties of ab initio resolution from powder data.

Fortunately, in the last ten years, computational tools have proved their efficiency for simulating the structures and energetics of inorganic solids.[2] Recently, we have successfully investigated the dehydroxylation process and organic-template extraction of two as-synthesized aluminophosphates, namely $AlPO_4$-14,[3] and MIL-34.[4] Starting from the knowledge of the as-synthesized structure only, all the atoms that are known to be eliminated upon calcination are removed. The so-modified $AlPO_4$-14 and MIL-34 model frameworks were then submitted to energy minimizations. This way, we predicted the calcined $AlPO_4$-14 structure in excellent agreement with the experimentally calcined $AlPO_4$-14,[3] which had already been obtained before our calculations. Above all, we successfully anticipated the structures and energetics of the calcined form of MIL-34, before it was actually experimentally calcined. The cell parameters and atomic coordinates predicted from the simulation were used to perform the Rietveld refinement of the calcined sample powder pattern. The present work aims at developing a computational approach of the calcination process of fluorinated templated structures.

Indeed, fluoride ions can belong to the framework or act as template. In the continuously expanding number of synthetic oxyfluorinated AlPOs[5, 6] and GaPOs, which include three-dimensional (3D) frameworks with very large pores such as cloverite[7] or MIL-31,[8] fluoride ions may occupy one or two vertices of the Al/Ga polyhedra in terminal or bridging positions, such as in ULM-6[5] or CJ2[5] respectively, or act as anionic template, such as in cloverite,[7] $GaPO_4$-LTA,[9] and ULM-18,[10] where they are encapsulated in D4R cages (Figure 1).

Regarding calcination, fluorine anions are deemed to play a specific role in the stabilization of the as-synthesized structure. This function is strongly related to their position in the framework and their high electronegativity, which often leads to strong hydrogen bonding and therefore a tighter amine – framework interaction. However, the mechanisms involved at the atomic scale during the calcination process are complex and still not clearly elucidated.

Here, we present the first attempt to use a computational approach to study the structural evolution during the dehydrofluorination process and template extraction of two isotypic as-synthesized oxyfluorinated open-framework structures, an aluminophosphate UT-6, $(Al_6P_6O_{24}F)_2$-$(C_5H_5NH)_2$-$(H_2O)_{0.3}$,[6] and a gallophosphate GaPO-tricl.CHA, $(Ga_6P_6O_{24}F_2)$-$(C_4N_2H_6)_2$-(H_2O).[11] As shown from their X-ray diffraction (XRD) patterns, both structures adopt upon calcination the CHA zeotype,[12] which correspond to the chabazite structure.

Herein, the experimental structures of the as-synthesized UT-6 and GaPO-tricl.CHA were taken as starting points for our simulations. UT-6 and GaPO-tricl.CHA are isostructural

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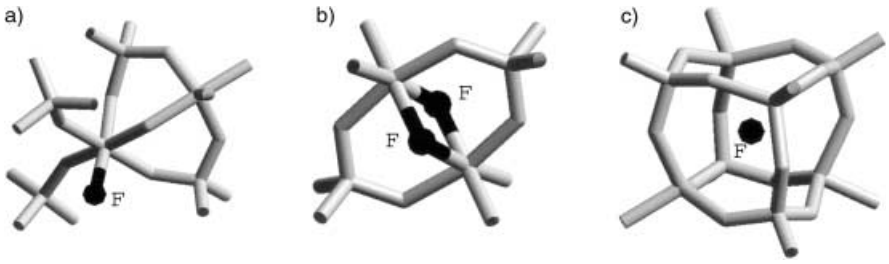

Figure 1. Various environments for the fluorine atoms in microporous inorganic structures. Typical fragments are extracted from existing crystal structures, F atoms in black. a) Terminal position (CJ2, MIL-14, ULM-13), b) bridging position (UT-6, $GaPO_4$-tricl.CHA), c) encapsulated position (cloverite, $GaPO_4$-LTA).

3D structures containing cages and three independent eight-membered-ring channel systems, with two template molecules trapped in each cage (Figure 2). The framework topology for each of the two as-synthesized compounds is closely related to that of neutral $AlPO_4$-CHA, which is constructed from D6R cages connected by four-ring windows. In the case of the fluorinated structures, each six-ring of the D6R cages contains one octahedral aluminum or gallium atom that connects to that of another hexagonal prism through two Al-F-Al or two Ga-F-Ga bridges, respectively (Figure 3a). Among the three inequivalent aluminum or gallium atoms present in the asymmetric unit, only one belongs to such an AlO_4F_2 or GaO_4F_2 octahedron, while the two others belong to AlO_4 or GaO_4 tetrahedra, as indicated on Figure 3a.

Prior to energy minimizations, all the atoms which are thought to leave the structures upon calcination were removed in both structures, that is, the bridging fluorine anions, the water molecules, and the pyridinium template cations (UT-6) and the 1-methylimidazole cations (GaPO-tricl.CHA). This approach results in "virtually" calcined neutral structures, with $Al(Ga)PO_4$ compositions, where all Al (Ga) and P atoms are tetracoordinate. However, these artificially modified structures retain the Al2 or Ga1 atoms from the original structures in highly distorted environments that emanate from the elimination of the bridging fluorine anions in both structures (Figure 3b). In a final step, both modified structures were submitted to constant pressure energy minimizations in the original space group $P\bar{1}$.

The calculations were carried out using the GULP code.[13] The interatomic potentials used for UT-6 were those developed by Gale and Henson for aluminophosphates[14] and, for GaPO-tricl.CHA, those developed by us for simulating microporous gallophosphates.[15] These force fields have been shown to reproduce experimentally determined structures of a series of alumino-[16] and gallophosphates,[15] respectively, with a good accuracy.

The key result of energy minimizations is that the initial models of calcined UT-6 and GaPO-tricl.CHA rapidly converge towards the CHA zeotype, that is, $Al(Ga)PO_4$-CHA, with all the metal atoms in regular tetrahedral environments (Figure 3c). Fig-

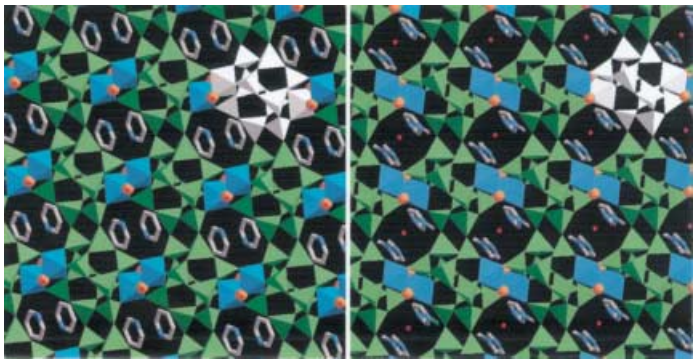

Figure 2. Polyhedral representation of the as-synthesized UT-6 (left) and GaPO-tricl.CHA (right) structures along the [010] and [100] directions, respectively. All AlO_4, GaO_4, and PO_4 tetrahedra are represented in green, while AlO_4F_2 and GaO_4F_2 polyhedra are shown in blue. F atoms: orange spheres, water molecules: red, and template molecules: gray cylinders. A hexagonal prism (D6R cage) is highlighted in white on each structure.

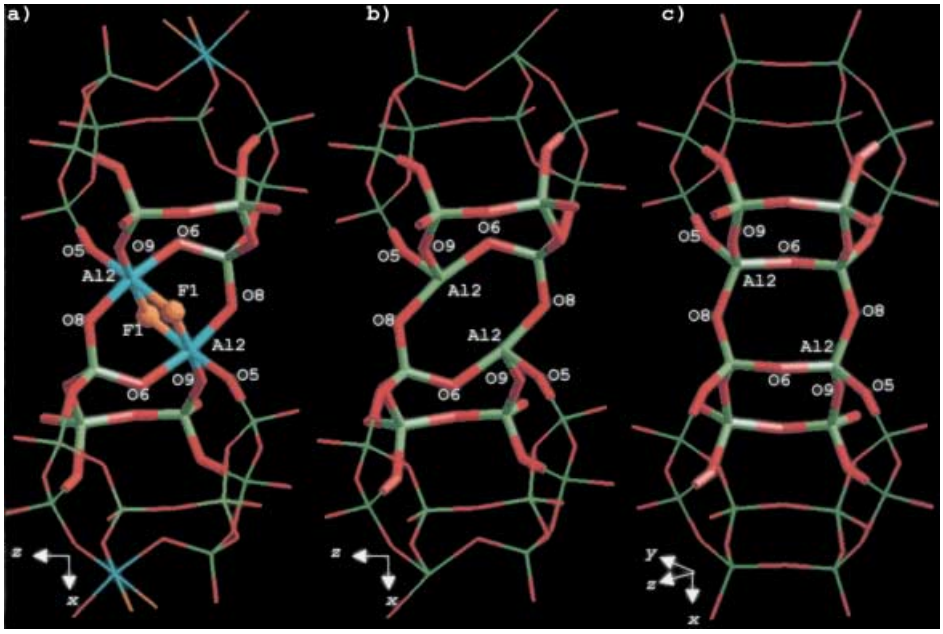

Figure 3. Framework fragment extracted from UT-6 which represents, up and down, two different D6R cages linked by two Al2 octahedra (hexacoordinate metal atoms are shown in blue, tetracoordinate in green, oxygen atoms in red, fluorine atoms in orange). a) In the as-synthesized structure, Al2 atoms are hexacoordinate at the center of AlO_4F_2 octahedra. b) After the removal of F atoms and prior to the calculations, Al2 atoms are in highly distorted tetrahedral environment. c) After energy minimizations, the predicted calcined UT-6 shows all Al atoms in regular tetrahedral environments. Selected bond lengths [Å] and angles [°] are also given for both the as-synthesized: Al2-O5 1.824, Al2-O6 1.874, Al2-O8 1.900, Al2-O9 1.824; O8-Al2-O9 90.8, O8-Al2-O6 169.9; predicted calcined structures Al2-O5 1.726, Al2-O6 1.721, Al2-O8 1.734, Al2-O9 1.716; O8-Al2-O9 107.2, O8-Al2-O6 112.5.

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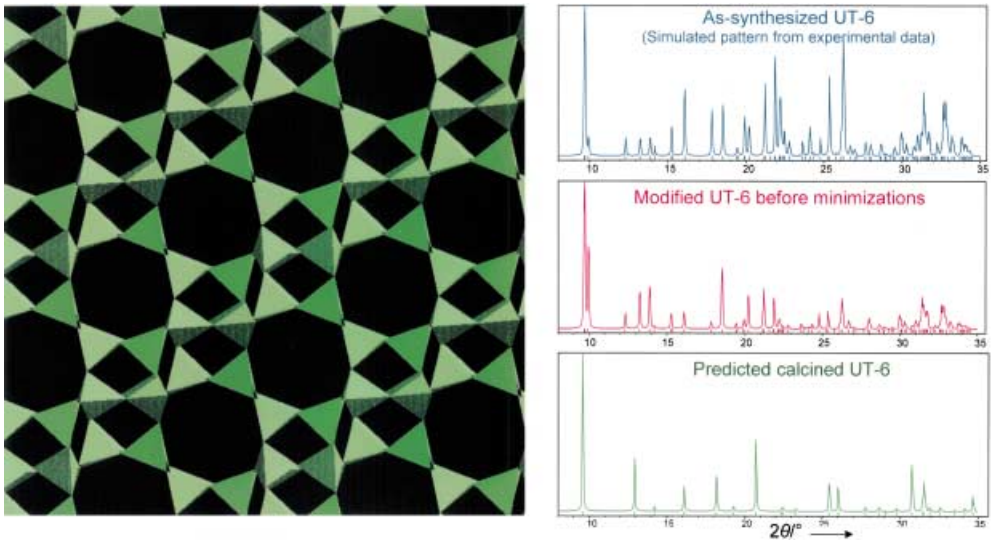

Figure 4. Calcined UT-6 as predicted by our energy minimizations in tetrahedral representation along with its simulated X-ray powder pattern (in green), the pattern of the as-synthesized structure after the removal of template molecules, water molecules, and F atoms and before minimizations (in red) and the pattern of the full original as-synthesized UT-6 (in blue).

ure 4 shows the whole predicted calcined $AlPO_4$-CHA zeotype structure. A careful examination of the minimized structures shows that both compounds undergo a change of symmetry from $P\bar{1}$ in their as-synthesized forms, into $R\bar{3}$ in their calcined forms. Table 1 gathers the simulated and experimental data when available, with a comparison of the atomic coordinates between the predicted and experimental calcined $AlPO_4$-CHA. Our results are in excellent agreement with the experimental findings.[6, 11, 17, 18]

Table 1. Comparison between the simulated and experimental data (for the aluminophosphate only) for the predicted calcined forms of $AlPO_4$-CHA and $GaPO_4$-CHA.[a]

	$AlPO_4$-CHA			
Space group	a [Å]	b [Å]	c [Å]	Method
$R\bar{3}$	13.8381(1)	13.8381(1)	14.9365(1)	exp
$R\bar{3}$	13.6932	13.6932	14.6411	calcd
atoms	x/a	y/b	z/c	
P	0.89155	0.56139	0.44112	exp
	0.89777	0.55726	0.43533	calcd
Al	0.66282	0.55810	0.43589	exp
	0.67451	0.56410	0.44544	calcd
O1	0.59272	0.67019	0.65639	exp
	0.58619	0.65853	0.67858	calcd
O2	0.64871	0.01042	0.50019	exp
	0.64564	0.98722	0.49595	calcd
O3	0.79166	0.57395	0.46494	exp
	0.78435	0.57024	0.47006	calcd
O4	0.91205	0.80410	0.12282	exp
	0.88928	0.80054	0.12860	calcd
$GaPO_4$-CHA				
space group	a [Å]	b [Å]	c [Å]	
$R\bar{3}$	unknown	unknown	unknown	exp
$R\bar{3}$	13.845	13.845	13.849	calcd

[a] Experimental calcined $AlPO_4$-CHA was obtained upon calcination of its triclinic templated form, and the latter was synthesized in the fluoride medium using piperidine as templating molecule. The structure of experimental calcined $AlPO_4$–34 has been solved by Rietveld refinement of the X-ray powder diffraction pattern. This is described in details elsewhere.[17]

Our simulations not only successfully capture the experimental change of symmetry ($P\bar{1} \rightarrow R\bar{3}$) upon calcination, but also give its atomic-scale interpretation. Indeed, such higher symmetry emanates mainly from the regularization of the four-rings, $T_2P_2O_{12}$ (T = Al or Ga), because of both local and cooperative readjustment of the framework upon lattice energy minimizations (Figure 3b,c).

Figure 4 shows the simulated pattern of calcined $AlPO_4$-CHA. It is in excellent agreement with the experimental[6, 17] one. For completeness, the simulated pattern of the experimental as-synthesized UT-6 compound is given, as well as the simulated pattern of the same structure after removal of F atoms and extra-frameworks species prior to energy minimizations, further illustrating the phase transformation occurring upon calcination. A similar agreement was obtained in the case of $GaPO_4$-CHA.[11]

Then, the lattice energies per tetrahedral site (T site) of our initial ($-12\,455.75$ kJ mol^{-1} for UT-6 and $-12\,402.83$ kJ mol^{-1} for $GaPO_4$-tricl.CHA) and final models are compared with the energies of the related dense structures, that is, α-berlinite ($-12\,936.40$ kJ mol^{-1}) and $GaPO_4$-quartz ($-12\,925.56$ kJ mol^{-1}). The calcined UT-6 ($-12\,927.84$ kJ mol^{-1}) is 8.56 kJ mol^{-1} per T site less stable than α-berlinite, while the calcined GaPO-tricl.CHA ($-12\,913.72$ kJ mol^{-1}) is 11.84 kJ mol^{-1} less stable than $GaPO_4$-quartz per T site, which makes them relatively stable compounds. For comparison, the work of Henson et al. demonstrates that aluminophosphates are between 4 and 13 kJ mol^{-1} less stable than the thermodynamically favored dense polymorph, α-berlinite, under ambient conditions.[16]

Herein, we have validated our computational "calcination" method on two isotypic structures containing fluorine atoms in their as-synthesized structures. This result shows that one may capture in one simple simulation step, the complex

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successive processes involved during calcination of oxyfluorinated templated compounds, such as defluorination, dehydration, and template decomposition, and predict the related calcined microporous structure. In these cases, we show that there is no need to describe the whole thermodynamic cycle to gain valuable information concerning the phase transformation of an as-synthesized compound into its related neutral framework in terms of energetics and structures. Such a method may not be applied to the specific cases where the calcination involves complex atomic rearrangements such as topotactic transformations, but in many cases, simulation is able to anticipate the solid-state transformation of an anionic molecular sieve into its related neutral framework. This is also the first time that our method gives accurate prediction of the solid-state transformation on a gallophosphate structure.

Received: November 2, 2001 [Z18147]

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Assembly of a Face-to-Face Tetranuclear Copper(I) Complex as a Host for an Anthracene Guest**

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The tailoring of sophisticated multitopic ligands that undergo metal-induced self-organization into well-defined architectures opens ways to the construction of organized supramolecular entities.[1] Such systems may display, at the molecular level, useful recognition and catalytic properties[2] and, at the macroscopic level, unusual mesomorphic[3] and electronic behavior.[4] Along these lines, it has been shown that rigid and linear polytopic ligands bearing bidentate chelating sites might self-assemble into well defined square-matrix arrays of metal centers without apparent defects following the general principle of maximum coordination.[5, 6] However, when flexible ligands are used the previous ideal situation is not effective anymore, instead, host – guest complexes have been characterized, in which an uncomplexed ligand is embedded into the structure.[7] The inclusion of a guest in a metal-containing architecture is an attractive property because it provides unique opportunities to study bimolecular reactions in microenvironments.[2, 8]

As a first step toward the catalytic transformation of guest molecules encapsulated in a macrocyclic groove containing photo- or electroactive metals, we report that the use of a ditopic phenanthroline (phen) ligand bearing a spiro[5.5]undecane spacer provides, upon complexation with copper(I) cations, a face-to-face arrangement together with an intertwined texture as minor species.

Here the self-inclusion of a free ligand is not observed but motion around the methylene linkage provides two types of supramolecular organization based on a linear or orthogonal arrangement of the phenanthroline subunits. Furthermore, the capability of the complex to exhibit an ideal cleft for flat polycyclic hydrocarbons prompted us to study the inclusion of

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[**] This work was supported by the Centre National de la Recherche Scientifique and by the Engineering School of Chemistry (ECPM). Professor Randy Thummel is acknowledged for providing us a sample of ligand **L** (see ref. [9]) and Dr. Alain Van Dorsselaer for research facilities. We thank Dr. Mike Craig for reading the manuscript prior to publication and also Dr. Marc Ledoux for his expertise in the numeric processing of Figure 5.