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Topotactic Oxidation of TiGaPO-1, a Pyridine-Templated Titanium Gallophosphate with a New Octahedral-Tetrahedral 3-D Framework Structure Containing Ti^{III}/Ti^{IV}

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The first 3-D open-framework TiGaPO complex, constructed from $Ti^{III}O_6$, $Ti^{IV}O_6$, GaO_4, and PO_4 polyhedra, contains pyridinium cations in a 1-D pore network and can be oxidized in air at 543 K with retention of the original framework structure.

Microporous materials attract tremendous research interest because of their applications as molecular sieves, ion exchangers, and catalysts in a range of technologically and commercially important processes.[1,2] Many attempts have been made over the past two decades to introduce transition-metal cations into microporous frameworks to confer redox activity, with its accompanying catalytic possibilities, on otherwise redox-inactive materials. Following success in preparing substituted aluminophosphate MeAPO phases,[3] the transition metals V,[4] Mn,[5] Fe,[5a] Co,[5a,6] and Zn[5a,5f,6a,6e,6f,7] have been incorporated into gallium phosphates, as low-level dopants and in more substantial concentrations, to produce MeGaPOs. By far, the majority of MeGaPO's produced so far have tetrahedral-based frameworks.[8] Some of these materials adopt the structures of known zeolites, e.g., MeGaPO analogues of sodalite,[6e,6f] gismondine,[6a,7a] and laumontite[5a] have been synthesized. Others, e.g., MeGaPO phases assigned the IUPAC framework-type codes CGS,[6g] CZP,[5f] and SBS,[6e] have structures not yet identified in other microporous systems. Far fewer examples of hybrid MeGaPO frameworks in which the transition-metal and gallium atoms have different coordination geometries are known. Most of these are MnGaPOs, where GaO_4 tetrahedra are found together with either MnO_5 square pyramids[5b] or $MnO_4(H_2O)_2$ octahedra,[5f] GaO_5 trigonal bipyramids with MO_6 octahedra (M = Mn, Fe, Co, Zn),[5c,6b] and both GaO_5 and GaO_6 units with MnO_4 tetrahedra.[5d] One of the notable absences from the list of metal cations incorporated with gallium into three-dimensional phosphate frameworks is titanium. Titanium is of great interest as a framework component because of its redox properties and photocatalytic activity. Microporous titanium(IV) silicates, such as ETS-4 and ETS-10, have already demonstrated good activity and selectivity as oxidation catalysts,[9] and there are a number of titanium phosphates (TiPOs) with open-framework structures with potentially similar properties.[10] Recently, the first TiGaPO, $[TH_2]_3[Ti_{2.5}(H_2O)_4Ga_{5.5}(PO_4)_{10}]\cdot 2H_2O$ (T = piperazine), which has a layered structure containing Ti^{III}, was

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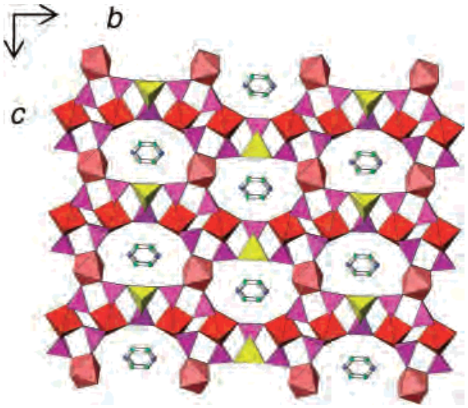

Figure 1. Polyhedral representation of TiGaPO-1 viewed along the *a* axis. $Ti^{III}O_4(H_2O)_2$ (pink), $Ti^{IV}O_6$ (red), GaO_4 (yellow), and PO_4 (magenta) units link to form a 3-D octahedral-tetrahedral hybrid framework containing a 1-D pore network in which pyridinium cations reside. Hydrogen atoms have been omitted for clarity.

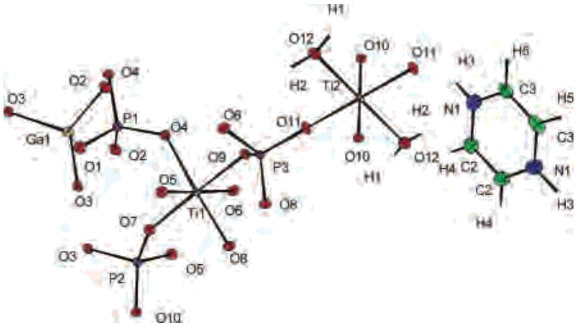

Figure 2. Local coordination of TiGaPO-1 with thermal ellipsoids (50% probability). Average Ga−O and P−O bond lengths are 1.826 and 1.536 Å, respectively. For Ti(1), in the 4+ oxidation state, Ti(1)−O bond lengths lie in the range 1.908(2)−1.988(2) Å. For Ti(2), in the 3+ oxidation state, Ti(2)−O bond lengths are 1.933(2) and 2.069(2) Å in the Ti(2)−O-P bridges and 2.107(2) Å in the $Ti(2)-OH_2$ group. The pyridinium cations are disordered over two positions by symmetry.

reported.[11] In this Communication, however, we report the preparation of the first templated TiGaPO with a 3-D framework structure (designated TiGaPO-1). TiGaPO-1 contains mixed-valence $Ti^{III/IV}$ and has an octahedral-tetrahedral structure in which the Ti^{III}, Ti^{IV}, and Ga^{III} cations lie on distinct, identifiable sites. Heating the material in air oxidizes the Ti^{III} to Ti^{IV} with retention of the framework structure. Remarkably, single crystals of TiGaPO-1 remain intact even on heating to 753 K, providing a rare opportunity to determine the structures of both oxidized and reduced forms by single-crystal X-ray diffraction.

TiGaPO-1 was prepared as single crystals and pure polycrystalline powder under hydrothermal conditions using pyridine as the structure-directing agent.[12] The dusky-pink color of the products provided preliminary evidence that at least some of the titanium in TiGaPO-1 was present as Ti^{III}, most probably in an octahedral site. The structure[13] is assembled from Ti-centered octahedra in combination with Ga- and P-centered tetrahedra linked to form an open, 3-D framework of formula $[Ti_3Ga(PO_4)_5(H_2O)_2]^-$. The framework charge is balanced by pyridinium cations, which reside in the resulting pores (Figure 1). Within the asymmetric unit, there are three crystallographically distinct metal sites, two octahedral and one tetrahedral, and three tetrahedral phosphorus sites (Figure 2). Unlike the majority of MeGaPOs characterized to date, in which the transition metal and gallium are disordered over the same framework sites,[7c,14] the gallium cation in TiGaPO-1 has exclusively four coordination, as GaO_4, whereas the two titanium cations, Ti(1) and Ti(2), are octahedrally coordinated as TiO_6, reflecting the difference in size of the metal cations. In the case of $Ti(1)O_6$, all six oxygen atoms coordinate to phosphorus, whereas for Ti(2), which lies on an inversion center, only four oxygen atoms bridge to phosphorus, and the two remaining oxygens belong to coordinated water molecules that lie trans to each other and complete a $Ti(2)O_4(H_2O)_2$ polyhedron. The hydrogen atoms of the water molecules were located in difference Fourier maps in the single-crystal X-ray diffraction analysis. Bond-valence calculations[15] for Ti(1) and Ti(2) yield valence sums of 4.34 and 3.16, suggesting that their oxidation states are 4+ and 3+, respectively, and that TiGaPO-1 is a mixed-valence material.

The framework of TiGaPO-1 contains isolated, irregular-shaped channels running parallel to the *a* axis bounded by 10-membered rings of alternating metal- and phosphorus-based polyhedra [cross-pore distances O(3)⋯O(4) and O(6)⋯O(10) of 6.80(1) and 8.74(1) Å, respectively]. Pyridinium cations, which are disordered over two symmetry-related positions, reside in the channels and interact with the inorganic framework via a network of hydrogen bonds [N⋯O distances lie in the range 2.98(1)−3.22(1) Å].

Further evidence for the presence of Ti^{III} in TiGaPO-1 is obtained from the UV−visible reflectance spectrum. The single broad band centered at ∼21600 cm^{-1} can be assigned to the spin-allowed transition $^2T_{2g} \rightarrow {}^2E_g$ anticipated for a $3d^1$ ion in an octahedral crystal field.[16] The corresponding band for the hexaaquo ion, $[Ti(H_2O)_6]^{3+}$, is at ∼20300 cm^{-1}. In addition, magnetic susceptibility data for a phase-pure sample of TiGaPO-1, determined after cooling of the sample in the measuring field of 1000 G, demonstrate that the sample

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(12) Ga_2O_3 (120.3 mg), H_2O (10 mL), pyridine (0.25 mL), and H_3PO_4(aq) (1 mL, 85%) were added in order to a 23-mL Teflon-lined autoclave. Titanium powder (325 mesh, 108.3 mg) was added with stirring to produce a gel of molar composition 1.00 Ga_2O_3:3.52 Ti:4.81 py:22.26 H_3PO_4(aq):865 H_2O, which was then heated at 453 K for 12 days. The solid product, recovered by filtration and washed with distilled water, consisted of dusky-pink platelike single crystals of TiGaPO-1, contaminated with small quantities of blue and white unidentified polycrystalline material. A pure polycrystalline sample of TiGaPO-1 was subsequently prepared from a similar gel in which 123.4 mg of titanium was added to the same mixture as above using the same heating and workup procedures. The powder XRD pattern of the product could be fully indexed on the basis of the unit cell determined in the single-crystal study.[13] CHN analysis: found C 7.60, H 1.45, N 1.85; calcd for $[C_5NH_6][Ti_3Ga(PO_4)_5(H_2O)_2]$ C 7.47, H 1.25, N 1.74%. The IR spectrum shows several bands in the region 3334−3100 cm^{-1} and sharp bands at 1643, 1610, 1541, and 1494 cm^{-1}, confirming the presence of pyridinium cations.

(13) TiGaPO-1: $[C_5NH_6][Ti_3Ga(PO_4)_5(H_2O)_2]$, $M = 804.32$, monoclinic, $P2_1/m$, $a = 5.0996(1)$ Å, $b = 21.2595(6)$ Å, $c = 8.9209(3)$ Å, $\beta = 90.239(1)°$, $V = 967.15(5)$ Å^3, $Z = 2$, $T = 150(2)$ K, $R(F) = 0.0347$ and $R_w(F) = 0.0368$ using 1789 reflections with $I > 2\sigma(I)$.

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is paramagnetic throughout the temperature range $5 \leq T$/K ≤ 295, providing strong support for the presence of Ti^{III} in the framework. The data do not follow Curie−Weiss behavior, as the plot of reciprocal susceptibility as a function of temperature shows a pronounced curvature. However, an estimate of the effective magnetic moment per formula unit can be obtained from the quantity $(8\chi_{mol}T)^{1/2}$, which varies from 1.63 μ_B at 295 K to 1.27 μ_B at 5 K. The room-temperature value is similar to those determined for $Ti_2(SO_4)_3$ (1.61 μ_B)[17] and $TiCl_3(NC_5H_5)_3$ (1.63 μ_B)[17] and is consistent with a Ti^{III}/Ti^{IV} ratio of 1:2. The temperature variation might be due to the effects of spin−orbit coupling associated with the ^2T ground state of Ti^{III}.

Thermogravimetric analysis of TiGaPO-1, performed under dry flowing O_2 over the temperature range 298−1273 K, shows a weight loss of 4.2%, occurring in two approximately equal steps over the ranges 543−643 and 643−790 K, which corresponds to the loss of two water molecules (calcd 4.48%). A further weight loss of 9.77%, observed in two steps over the ranges 790−1000 K (4.81%) and 1000−1200 K (4.96%) is attributed to the loss of pyridine (calcd 9.84%). The final product is white and amorphous.

The mixed-valence compound is stable in air at room temperature over a period of several months. However, it is possible to oxidize the Ti^{III} centers in TiGaPO-1 by heating in air. At 543 K and above, this oxidation takes place rapidly, and the compound color changes from pink to white. Remarkably, single crystals heated as high as 753 K retain their integrity, and after being cooled in air, their structure, denoted TiGaPO-1a,[18] can be determined by single-crystal X-ray diffraction. TiGaPO-1a has the formula $[C_5NH_6][Ti_3Ga(PO_4)_5(H_2O)(OH)]$, and the metal-phosphate framework, closely related to that of TiGaPO-1, has pyridinium cations retained in the pores. The quality of the crystals was so high that the detailed coordination around the titanium atoms, including the proton positions on the coordinated $-OH_2$ and $-OH$ groups, could be determined, demonstrating that the $Ti(2)^{III}O_4(H_2O)_2$ unit in TiGaPO-1 transforms into a $Ti(2)^{IV}O_4(H_2O)(OH)$ unit in TiGaPO-1a (Figure 3). The asymmetry of coordination around this metal site is responsible for the change from the centrosymmetric space group $P2_1/m$ to noncentrosymmetric $P2_1$ upon oxidation: the remainder of the TiGaPO-1a framework is essentially unchanged from that of TiGaPO-1 and exhibits a high degree of pseudosymmetry. Bond-valence sums of 4.36, 4.29, and 4.12 confirm that the oxidation state of all the titanium species present is 4+.

The onset of oxidation of TiGaPO-1 at around 543 K involves the loss of a proton. This process appears from the TGA study to be associated with the loss of the first water molecule from the Ti^{III} center, $Ti^{III}O_4(H_2O)_2$, to form $Ti^{IV}O_4(OH)$. Protonation of the $-OH$ group must occur before the second water molecule can be lost. The pyridinium cations in the framework pores must provide the proton source in this case. Upon cooling of the complex in air, two water molecules per formula unit are taken back up to give the coordination around the redox-active Ti(2) centers shown in Figure 3b. Clearly, this system is worthy of further study, and we are currently investigating the dehydrated phases in an attempt to gain further insights into the structural changes occurring during the sequence of reactions seen in the TGA study. Unfortunately, heating TiGaPO-1 crystals above 773 K in air destroys them, suggesting that, as pyridine is lost, the framework collapses. As yet, we are unable to shed any light on why the pyridine is lost in two clear steps each of which corresponds to one-half of a pyridine per formula unit. We also have preliminary evidence that it is possible to reverse the oxidation process and reduce the Ti^{IV} centers in TiGaPO-1a back to Ti^{III} using *n*-BuLi in hexane with framework retention, and this is currently under further investigation.

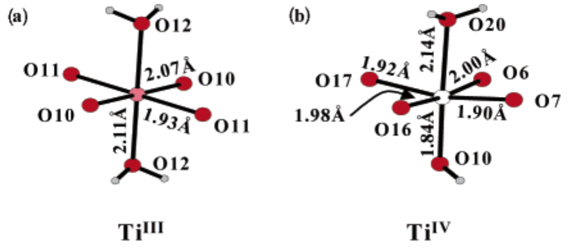

Figure 3. Coordination of Ti(2) (a) as Ti^{III} in TiGaPO-1, consisting of four bridging oxygens and two water molecules, and (b) as Ti^{IV} in TiGaPO-1a, with four bridging oxygens, one water molecule, and one hydroxyl group.

In summary, the first 3-D TiGaPO contains mixed-valence Ti^{III}/Ti^{IV} and exhibits interesting redox activity. Remarkably, heating in air results in oxidation to a material containing Ti exclusively in the 4+ oxidation state with retention of the octahedral-tetrahedral framework structure. The extraordinary stability of the single crystals of the TiGaPO, a very unusual occurrence in open-framework materials, has enabled the changes in the detailed structure occurring upon oxidation, primarily involving changes in the local coordination of Ti, to be followed by single-crystal X-ray diffraction.

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Supporting Information Available: CIF file, bond-valence calculations, powder XRD and TGA traces, magnetic data, and IR spectrum are available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for TiGaPO-1 and TiGaPO-1a are also available at the Cambridge Crystallographic Data Centre.

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(18) TiGaPO-1a: $[C_5NH_6][Ti_3Ga(PO_4)_5(H_2O)(OH)]$, $M = 803.31$, monoclinic, $P2_1$, $a = 5.1028(2)$ Å, $b = 21.1626(7)$ Å, $c = 8.8581(4)$ Å, $\beta = 89.997(1)°$, $V = 956.57(7)$ Å^3, $Z = 2$, $T = 150(2)$ K, $R(F) = 0.0456$ and $R_w(F) = 0.0510$ using 3305 reflections with $I > 2\sigma(I)$.