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Elucidating the Nature and Reactivity of Ti Ions Incorporated in the Framework of AIPO-5 Molecular Sieves. New Evidences from ^{31}P HYSCORE Spectroscopy.

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ABSTRACT The incorporation of Ti ions within the framework of aluminophosphate zeotype AIPO-5 and their chemical reactivity is studied by means of CW-EPR, HYSCORE and UV-Vis spectroscopies. Upon reduction Ti^{3+} ions are formed, which exhibit large ^{31}P hyperfine couplings providing direct evidence for framework substitution of reducible Ti ions at Al sites.

The incorporation of transition metal ions (TMIs) into framework sites of porous and mesoporous materials is a key strategy in the quest for new materials with novel and controlled chemical and catalytic properties. A relevant example is that of aluminophosphate molecular sieves, AIPOs, which are microporous zeotype materials with neutral lattices and a wide range of structural diversity. Despite the structural analogy, AIPOs show a greater flexibility than zeolites toward chemical substitution, as shown by the large number of different incorporating TMIs which confer to these materials a peculiar bifunctional character due to the simultaneous presence of Brønsted and redox sites with great potential for application in catalytic processes.¹

Among the large variety of different TMIs, Ti-doped AIPOs (TiAIPO) are particularly interesting due to the specific activity of isolated tetrahedral Ti sites towards different chemical and photochemical processes.² Despite the importance of these Ti centers and the crucial role played by their local coordination, evidence for isomorphous substitution is often indirect. Conflicting views are present in the literature concerning a) the specific site (Al or P) for which Ti is being substituted; b) the number of sites actually participating to the redox chemistry and c) the chemical availability of these sites. The topic is

made more intriguing by the huge amount of experimental and theoretical results on the structure and reactivity of tetrahedral Ti sites in zeolite TS-1,³ allowing studying the influence of the matrix⁴ on the chemistry of isolated TMIs in well defined environment.

One of the most potent descriptors of the local environment of paramagnetic transition metal ions is Electron Paramagnetic Resonance (EPR) and the associated hyperfine techniques of ENDOR (Electron Nuclear Double Resonance) and HYSCORE (Hyperfine Sublevel Correlation) spectroscopies. In particular, for TMIs incorporated in various aluminosilicate or aluminophosphate molecular sieves, analysis of the hyperfine interactions due to ^{27}Al ($I=5/2$),^{5,6,7} ^{29}Si ($I=1/2$)⁸ and ^{31}P ($I=1/2$)⁹ nuclei from the framework allows obtaining direct information about the metal ion location.

In this work we employ EPR and HYSCORE spectroscopies complemented by UV-Vis spectroscopy to monitor the redox and coordination chemistry of $\text{Ti}^{4+}/\text{Ti}^{3+}$ ions in the TiAlPO-5 system. In particular we report the first observation of large ^{31}P hyperfine couplings, which, combined with the absence of specific ^{27}Al couplings, provide direct evidence for framework substitution of Ti at Al sites. Moreover we demonstrate that these very sites are coordinatively unsaturated and chemically accessible.

TiAlPO-5 (Ti 0.94 wt%) was prepared by hydrothermal synthesis following a standard procedure.^{10,11} Details on preparation and general properties are given in supporting information. The as prepared sample is EPR silent (Figure 1A (a)), while the corresponding UV-visible spectrum (Figure 1B (a)) is characterized by a strong absorption with maximum at 220 nm and a component at 270 nm. These features have been ascribed to ligand-to-metal charge-transfer transitions associated to Ti^{4+} ions incorporated at framework positions both as isolated and oligomeric species.¹²

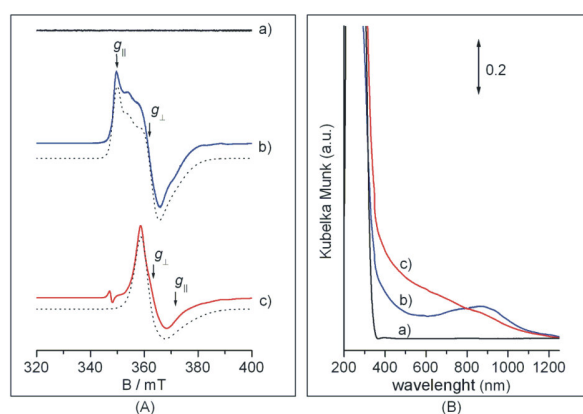


Figure 1. A) Experimental (solid line) and simulated (dotted line) CW-EPR spectra and B) corresponding optical absorption spectra of (a) oxidized, (b) reduced and (c) reduced upon water adsorption TiAlPO-5. The asterisk indicates a spurious radical-type signal. The arrows indicate the field positions at which HYSCORE experiments were performed.

Upon reduction of the sample under H_2 at 673 K the CW-EPR spectrum reported in Figure 1A (b) is observed. The spectrum is dominated by an $S=1/2$ species with a nearly axial g tensor (Table 1). The exact line shape of the experimental EPR spectrum could only be reproduced in the simulation by adding a second species with lower abundance (about $35\pm 5\%$ as estimated from the computer simulation) and axial g tensor ($g_{||}=1.969$, $g_{\perp}=1.90$) suggesting that more than one Ti^{3+} species, differing in the local coordination geometry, are contributing to the overall ESR powder spectrum. The g values of both species are typical for Ti^{3+} in a tetrahedral crystal field as in the case of tetrahedral titanium in TS-1¹³ or in TiMCM-41.¹⁴ This assignment is corroborated by the appearance of a broad band centered around 870 nm in the corresponding UV-Vis spectrum (Figure 1B (b)), that can be ascribed to ligand field $d-d$ transition of Ti^{3+} sites in Td coordination.^{15,16} Analysis of the EPR and UV-Vis spectra thus provides convincing evidence that upon reduction isolated Ti^{3+} ions occupy a framework position. Quantitation of the EPR signal in Figure 1A, indicates that the amount of reduced Ti is of the order of $20\pm 5\%$ of the Ti present in the sample. This is in accord with other literature reports concerning different TMIs incorporated in the AlPO-5 structure.¹⁷

Further insights into the local coordination environment of the Ti^{3+} ions is provided by HYSCORE spectroscopy, which allows probing the interaction of the unpaired electron of Ti^{3+} with neighbouring magnetic nuclei of the framework (^{27}Al and ^{31}P). The HYSCORE spectrum recorded at a field position corresponding to g_{\perp} is shown in Figure 2(a) and contains different pairs of cross peaks indicated with P(1)-P(4) which stem from the superhyperfine interaction between the unpaired electron of Ti^{3+} and different ^{31}P nuclei. Two sets of cross-peaks (P(1) and P(2)) appear in the (+,+) quadrant approximately centered around the ^{31}P nuclear Larmor frequency ($\nu(^{31}P) = 6.24$ MHz). The first set (P(1)) is characterized by a ridge shape with maximum extension of about 3 MHz, while the second set (P(2)) appears at *ca.* (11.3, 1.8) (1.8, 11.3) MHz along the diagonal of the (+,+) quadrant, The other cross peaks (P(3) and P(4)) appear in the (-,+) quadrant separated by $2\nu(^{31}P)$ and positioned at approximately (-14.2, +2.1) (-2.1 +14.2) MHz and (-16.5, +4.1) (-4.1 +16.5). In the (+,+) quadrant a diagonal peak centred at the ^{27}Al nuclear Larmor frequency ($\nu(^{27}Al) = 4.02$ MHz) is also present, which is due to remote (matrix) ^{27}Al nuclei. Similar HYSCORE spectra were observed at different magnetic fields across the EPR spectrum (also at the outer field settings where only one species is contributing), indicating that the different species, which contribute to the overall spectrum, share a similar phosphorous-rich local environment and that the observed differences in the g tensor may be due to small alterations in local coordination geometry.

The ^{31}P HYSCORE spectra taken at different magnetic field positions could be well reproduced by simulation (see supporting information) using four different ^{31}P nuclei with hyperfine parameters listed in

Table 1, where a positive sign was assumed based on the positive ^{31}P nuclear g factor. The ^{31}P coupling characterized by $a_{\text{iso}} \approx 9$ MHz agrees with the coupling reported by Arieli et al. for Mn^{2+} doped AlPO_n systems⁹ and all ^{31}P hyperfine couplings correlate with those observed in the case of Ti^{3+} centers in potassium tytanil phosphates (KTiOPO_4) single crystals,¹⁸ characterized by interatomic Ti-P distances comparable with those of TiAlPO_5 .¹⁹ Moreover, similar ^{31}P couplings have been reported for vanadyl phosphate molecular complexes.²⁰

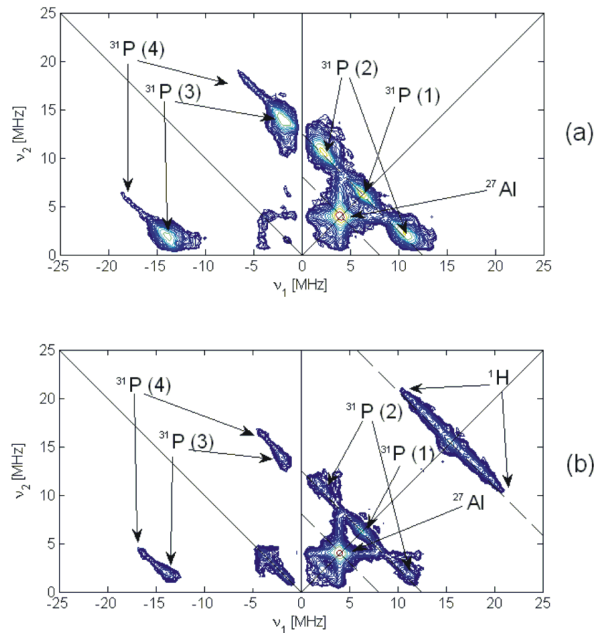


Figure 2. Experimental HYSORE spectra recorded at 5K of (a) reduced and (b) reduced with coordinated water TiAlPO_5 taken at an observer position (362.0 mT) corresponding to g_{\perp} . Three τ values (104, 136 and 250 ns) are summed together after Fourier transform. Spectra at other magnetic field settings, together with the corresponding computer simulations, are given as supporting information.

In all cases the distinctive feature of phosphate groups directly bound to the paramagnetic metal ion (M) is represented by distinct and relatively large a_{iso} values comparable to those reported in Table 1. Such isotropic couplings are found to be induced by spin density transfer to ^{31}P through the directly coordinated oxygen and are particularly sensitive to structural variations, the values depending markedly on the M-O-P bond angle.^{20,21} The presence of large ^{31}P couplings typical for phosphate coordination in the HYSORE spectrum, combined with the absence of such a coupling due to ^{27}Al provides thus a unique and direct proof for framework substitution of Ti^{3+} for the isovalent Al^{3+} . Considering the neutral nature of the AlPO lattice, a possible mechanism explaining the formation of Ti^{3+} sites at Al^{3+} position is presented in Chart 1, whereby the replacement of a Al^{3+} and P^{5+} couple by two Ti^{4+} ions is proposed, in analogy with the well known mechanism for incorporation of Si in SAPO materials.²²

Sample	^{31}P							^1H					
	g_x	g_y	g_z	a_{iso}	T_{xx}	T_{yy}	T_{zz}	α, β, γ	a_{iso}	T_{xx}	T_{yy}	T_{zz}	α, β, γ
re- duced TiAlP O-5	1.898±0.005	1.918±0.005	1.991±0.002	P(1) 1.7±0.5	- 0.67±0.5	- 0.67±0.5	+1.34±0.8	0,90, 0					
				P(2) 9.3±0.5	- 0.3±0.5	- 2.3±0.5	+2.7±0.5	0,90, 0					
				P(3) 13.6±0.5	- 0.7±0.5	- 1.7±0.5	+2.3±0.5	90,90, ,0					
				P(4) 19.3±0.5	- 2.3±0.5	- 3.3±0.5	+5.7±0.5	0,90, 0					
hy- drated TiAlP O-5	1.938±0.005	1.918±0.005	1.865±0.002	P(1) 1.7±0.5	- 0.67±0.5	- 0.67±0.5	+1.34±0.8	0,90, 0					
				P(2) 9.3±0.5	- 0.3±0.5	- 2.3±0.5	+2.7±0.5	0,90, 0	6± 1	- 7±0.5	5±0.5	2±0.5	20±10,30 ±10,0
				P(3) 13.6±0.5	- 0.7±0.5	- 1.7±0.5	+2.3±0.5	90,90, ,0					
				P(4) 19.3±0.5	- 2.3±0.5	- 3.3±0.5	+5.7±0.5	0,90, 0					

Table 1. Spin-Hamiltonian parameters of reduced TiAlPO-5. The parameters are obtained from simulation of the EPR and HYSCORE spectra reported in Figures 1 and 2. Hyperfine couplings are given in MHz. The Euler angles α , β , γ are given in degrees.

Upon reduction with H_2 a Ti^{3+} is formed replacing for the isovalent Al^{3+} ion, while a proton (in the form of an hydroxyl) will compensate the charge imbalance at the remaining site. The fact that no sign of proton coupling is observed in the HYSCORE spectrum of the reduced TiAlPO-5 suggests that the charge compensating proton is stabilized away from the Ti^{3+} centre. This does however not exclude the presence of Ti-O-Ti species at neighbouring sites, whose abundance is expected to increase with increasing Ti loading. Interestingly similar oligomeric species have been invoked as responsible for the 270 nm UV absorption band observed in TiAlPO.¹² The experimental results show thus that only a fraction (about 20%) of the total Ti is actually reduced and this fraction is composed of Ti ions at Al sites.

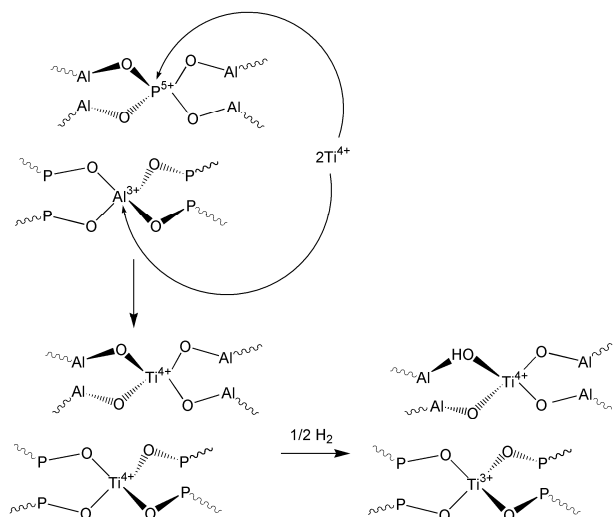


Chart 1 Schematic representation of the TiAlPO-5 reduction mechanism.

In order to assess the chemical accessibility of these Ti^{3+} species, H_2O molecules were adsorbed on the reduced sample. Upon water adsorption a new CW-EPR spectrum is observed (Figure 1A (c)) characterized by a different g tensor, typical of Ti^{3+} in distorted octahedral symmetry (Table 1). The spectrum of Figure 1A (b) could be restored by outgassing the sample at 400 K. Consistent with the modification of the EPR spectrum is the depletion of the $d-d$ band at 870 nm (Figure 1B (b)) with growth of a broad component at higher frequency, in the typical region of octahedrally coordinated Ti^{3+} species (Figure 1B (c)).¹⁵

The EPR and UV-Vis spectra reported in Figure 1 provide thus a textbook example of a reversible change in the crystal field experienced by isolated Ti^{3+} ions induced by water adsorption, proving the

chemical accessibility of these centres. The HYSORE spectrum recorded at the g_{\perp} position (Figure 2(b)) shows ^{31}P couplings which are analogous to those previously discussed for the dry system. Small differences between Figures 2a and 2b are mainly due to the different contour levels at which the two spectra are plotted. A major difference in the hydrated sample is found in the (+,+) quadrant where a ridge centered at the ^1H nuclear Larmor frequency ($\nu(^1\text{H}) = 15.41$ MHz) with maximum extension of about 11 MHz is present. This ^1H coupling correlates with the water proton coupling recently reported by some of us²³ in the case of the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ model system and unequivocally proves that Ti^{3+} ions substituting for Al^{3+} framework ions are chemically accessible and potentially reactive sites.

In summary we have reported the first observation of large ^{31}P hyperfine couplings in a TiAlPO-5 material demonstrating, at variance with existing reports,²⁴ that the fraction of Ti undergoing the redox chemistry (*i.e.* $\text{Ti}^{4+}/\text{Ti}^{3+}$) is limited to framework Ti ions at Al sites. We also demonstrate that these very sites are capable of water coordination and are thus chemically accessible. We believe that these results will be of importance in clarifying the role of Ti in AlPO materials and in designing new catalysts with specific functionalities.

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SUPPORTING INFORMATION PARAGRAPH. Details on the synthesis of the sample, powder X Ray diffraction, scanning electron microscopy, specific surface area and porosity. Simulations of the HYSORE spectra at different magnetic field positions.

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