

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

A HYSORE investigation of bimetallic titanium-vanadium microporous catalysts: elucidating the nature of the active sites

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/117862> since

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



UNIVERSITÀ DEGLI STUDI DI TORINO

This is an author version of the contribution published on:

Questa è la versione dell'autore dell'opera:

[Chem. Commun 48, 2012, DOI: 10.1039/c2cc33997h]

The definitive version is available at:

La versione definitiva è disponibile alla URL:

www.rsc.org/chemcomm

A HYSCORE Investigation of Bimetallic Titanium-Vanadium Microporous Catalysts: Elucidating the Nature of the Active Sites.

Sara Maurelli,^a Mario Chiesa,^{a,*} Elio Giamello,^a Rebecca M. Leithall^b and Robert Raja^b

5 Vanadium and titanium bimetallic AIPO-5 molecular sieves have been synthesized and characterized by means of Electron Spin Echo detected EPR and Hyperfine Sublevel Correlation (HYSCORE) spectroscopy. Direct evidence for framework substitution of redox-active Ti ions and VO²⁺ units at Al sites is provided through the detection of large ³¹P hyperfine couplings.

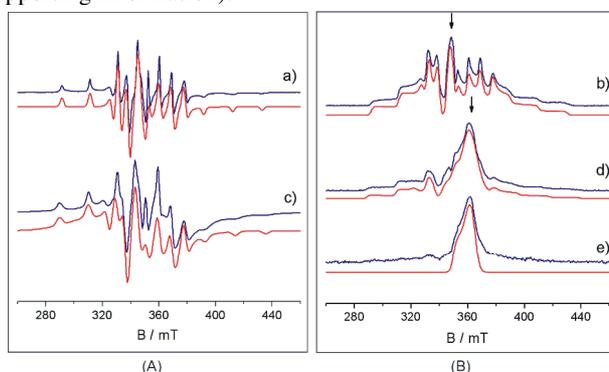
Porous aluminophosphate architectures, (AIPO-*n*), where *n* denotes a particular structure type, represent a class of microporous crystalline materials that are akin to the well-known zeolites and characterized by neutral lattices constituted by alternating PO₄ and AlO₄ tetrahedra.¹ Their uniform and molecular sized pores can be specifically tailored towards shape-selectivity for various catalytic transformations.²⁻⁴ Moreover, beside their structural features, the chemical reactivity of these materials can be suitably modified by the isomorphous incorporation of various transition metal ions (TMIs). The strength and the reactivity of these active sites that are important for catalysis, will ultimately depend on their local coordination and oxidation states. As an example, titanium insertion in tetrahedral sites of open framework materials has been found particularly effective in enabling catalysts with superior conversions and selectivities in many important reactions,^{5,6} the catalytic activity being associated to the coordinatively unsaturated tetrahedral Ti(IV) ions⁷⁻¹¹. Vanadium doped AIPOs yet provide another compelling example of size- and shape-selective oxidation catalysts¹² that are used in processes including alkane ammoxidation and alkene epoxidation.¹³⁻¹⁵

Recently it has been proposed that the activity of the catalytically active centers can be enhanced by simultaneous incorporation of different transition metal ions as reported by Paterson et al.¹⁶ in the case of titanium (IV) and cobalt (III) co-doped in the AIPO-5 framework. Clearly, subtle control of such systems requires reliable characterization methods allowing to monitor in detail the local structural environment and the chemistry (catalytic potential) of the dopant ions.

We have recently shown that Electron Paramagnetic Resonance (EPR) spectroscopy and the associated hyperfine techniques of Electron Spin Echo Envelope Modulation (ESEEM) and Electron Nuclear Double Resonance (ENDOR) can be particularly effective in characterizing the structural localization and chemical reactivity of paramagnetic TMIs in the AIPO's structure.^{17,18}

In this letter we report on the advanced EPR characterization of a vanadium-titanium bimetallic substituted AIPO-5, demonstrating the framework localization of the two active metals, whilst simultaneously monitoring their redox behaviour.

The sample was synthesized using previously reported methods¹³ with a gel ratio of: 0.97Al : 1.5P : 0.03V : 0.03Ti : 0.8SDA : 50H₂O, employing N-methyl dicyclohexylamine, as the structure-directing agent (SDA).¹⁹ Powder X-ray diffraction (PXRD) confirmed the phase purity affording diffraction patterns characteristic for the AFI framework,²⁰ with high crystallinity and no secondary phase impurities. EPR and HYSCORE spectra were recorded prior and after reduction of the sample in the presence of H₂ at 673 K (details are given as supporting information).



35 **Figure 1.** Experimental (blue) and simulated (red) CW (a) and ESE detected (b) EPR spectra of oxidized VTiAIPO-5, (c) CW and (d, e) ESE spectra of the reduced sample. Spectra (b) and (d) were recorded with an interpulse delay $\tau = 200$ ns while for spectrum (e) $\tau = 400$ ns. All spectra were recorded at 10K. The arrows indicate the field position at which HYSCORE experiments were performed.

The Continuous Wave (CW) and Electron Spin Echo (ESE) detected-EPR spectra of the calcined VTiAIPO-5 sample are shown in Figure 1(a) and 1(b), respectively. The field swept spectra are characterized by an axially symmetric powder pattern typical of V⁴⁺ in a vanadyl environment with distorted octahedral coordination. The EPR parameters deduced from computer simulation of the spectra (supporting information) are consistent with those reported in the literature for square pyramidal oxovanadium-(IV) complexes²¹⁻²⁴. Spectra reported in Figure 1 indicates thus that, despite the oxidative treatment (via calcination at 823 K in the presence of O₂), part of the vanadium present in the sample remains in the EPR active +4 oxidation state (*d*¹ electronic configuration) in agreement with previous reports.²⁵ In order to probe in detail the local environment of the EPR active VO²⁺ ions HYSCORE experiments have been performed. The HYSCORE spectrum of the oxidized sample recorded at the so-called "powder like position" ($B_0 = 347.4$ mT, arrow in Figure 1b) is reported in Figure 2a.

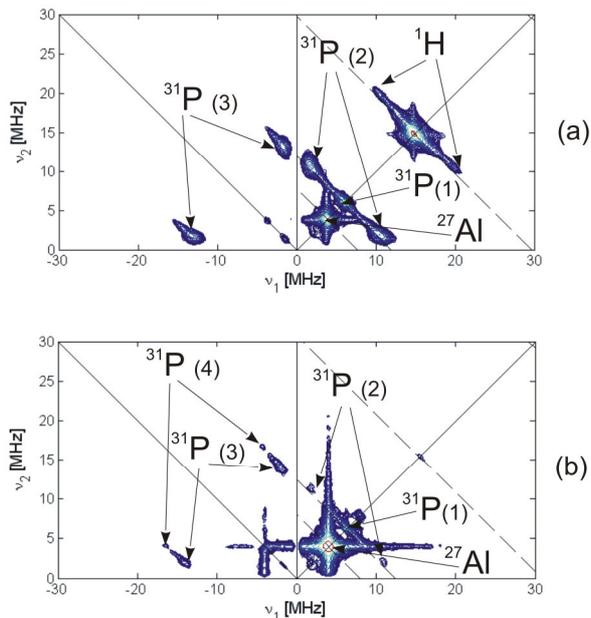
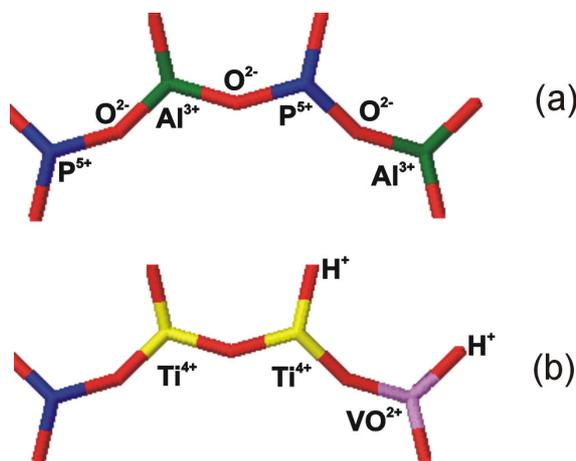


Figure 2. HSCORE spectra of (a) oxidized VTiAlPO-5 sample at the observer position indicated in Figure 1(b); (b) reduced VTiAlPO-5 sample at the observer position indicated in Figure 1(d). Four spectra with different τ values (96, 128, 176 and 216 ns) are added together after Fourier transform in order to eliminate blind spots. All spectra were recorded at 10 K.

5 The spectrum contains signals stemming from the superhyperfine interaction between the unpaired electron hosted in the V orbitals and ^{31}P , ^{27}Al and ^1H nearby nuclei. In particular, two sets of cross-peaks ($^{31}\text{P}(1)$ and $^{31}\text{P}(2)$) appear in the (+,+) quadrant approximately centered at the ^{31}P nuclear Larmor frequency ($\nu(^{31}\text{P}) = 5.993$ MHz), while a third set of cross peaks ($^{31}\text{P}(3)$) appears in the (-,+) quadrant separated by $2\nu(^{31}\text{P})$ and positioned at approximately (-13.8, +1.8) (-1.8 +13.8) MHz. Analogous spectra were observed for the monometallic VAiPO-5 system (not shown). The characteristics of the cross-peaks $^{31}\text{P}(1)$ - $^{31}\text{P}(3)$ lead to their assignment to three phosphorus nuclei with maximum hyperfine couplings of 3, 11, and 16 MHz, respectively. In the (+,+) quadrant a diagonal peak centred at the ^{27}Al nuclear Larmor frequency ($\nu(^{27}\text{Al}) = 4.02$ MHz) is also present, which is due to remote (matrix) ^{27}Al nuclei. The observed ^{31}P couplings agree with values reported for vanadyl phosphate molecular complexes²⁶ and together with the absence of distinct ^{27}Al couplings provide unambiguous evidence for framework substitution of VO^{2+} units at Al^{3+} position. When a VO^{2+} substitutes for an Al^{3+} , a +1 charge compensation is required in order to maintain the electroneutrality of the system. Such a charge compensation is provided by a H^+ forming an OH^- group in the proximity of the VO^{2+} group. Direct evidence for the presence of such a proton is provided by the ridge centered at the ^1H nuclear Larmor frequency with maximum extension of about 15 MHz (Figure 2a). Analysis of the ^1H ridge and comparison with powder²⁷ and single crystal ENDOR²⁸ data for the $[\text{VO}(\text{H}_2\text{O})_5]^{2+}$ ion as well as hydrated vanadium exchanged zeolites^{22,29} indicates that such an hydroxyl is located in the first coordination sphere, laying in the VO^{2+} equatorial plane.

20 On reducing the system the overall intensity of the EPR spectrum increases due to reduction of previously EPR silent V^{5+} species. As a result, broadening of the vanadyl spectral features in the spectrum of Figure 1c is observed, associated with the onset of dipole-dipole interactions. The spin Hamiltonian parameters of the VO^{2+} spectral pattern of the reduced sample show minor changes with respect to the unreduced system (see supporting information), however, simulation of the central region of the spectrum is not possible by simply increasing the spectral linewidth, suggesting the presence of new, overlapping species, generated upon reduction. Disentanglement of the overlapping spectra is obtained by recording the ESE detected EPR spectrum at different time intervals (Figure 1(d) and (e)). The spectrum recorded with a pulse interval $\tau = 200$ ns (Figure 1(d)) shows together with the presence of the typical ^{51}V hyperfine pattern a second prominent species (indicated with an arrow) in Figure 1(d), which is isolated on recording the spectrum with $\tau = 400$ ns (Figure 1(e)). This species, characterized by a longer phase memory time (T_m), is assigned to Ti^{3+} in tetrahedral coordination on the basis of the \mathbf{g} tensor extracted by computer simulation ($g_{\parallel} = 1.991$ and $g_{\perp} = 1.908$), which coincides with values recently reported by some of us in the case of reduced TiAlPO-5.¹⁷



Scheme 1. Schematic illustration of a) AIPO-5 fragment and b) Ti/V framework insertion as deduced from the EPR experiments on the reduced sample. This scheme represents one possible situation whereby the doping species are placed as first neighbors for the sake of simplicity. It is well plausible that other configurations where the same sites are non first neighbors may also be possible.

5 The HYSORE spectrum recorded at an observer position coinciding with the maximum echo intensity of the Ti^{3+} species is shown in Figure 2(b). The spectrum is analogous to that reported¹⁷ for Ti^{3+} ions substituted in the monometallic TiAlPO-5 structure and is characterized by a series of cross peaks due to the interaction between the unpaired electron with nearby ^{31}P ions, having maximum hyperfine couplings of 3, 11, 16 and 26 MHz. These values together with the absence of distinct ^{27}Al couplings provide a direct evidence for framework substitution of Ti^{3+} at an Al site. It is important to note that in this case, at variance with the VO^{2+} case, no charge compensation is needed for a Ti^{3+} substituting for an Al^{3+} . This is reflected by the absence of the pronounced ^1H signal observed in the case of VO^{2+} . It should also be noted that no evidence is found for ^{51}V superhyperfine couplings suggesting that no Ti^{3+} -O-V species are present, at least at the metal loadings employed in the present study.

Taking into account the neutral character of the AIPO lattice and based on our previous findings relative to the monometallic TiAlPO-5 system,^{17,18} a schematic representation of the bimetallic Ti/V system, as emerges from this study, is proposed in 15 Scheme 1. Here two Ti ions replace an Al^{3+} - P^{5+} pair; whereby only the Ti substituting for the Al is reducible to Ti^{3+} and thus EPR active. The EPR experiments provide direct evidence for VO^{2+} units substituting for Al^{3+} species, while no evidence is found for V species at P sites, which explains why no Ti^{3+} - ^{51}V superhyperfine interaction is detected. We wish to reiterate that this state of affairs does not exclude the presence of Ti^{4+} -O-V framework species, which cannot be directly detected by EPR due to the low natural abundance of Ti magnetically active isotopes. The presence of these species may well explain the synergic effects of the 20 two dopants in catalytic transformations where the tetrahedral (under-coordinated and redox inactive) Ti^{4+} ions at P sites act as coordinative centers (*e.g.* for oxygen binding), while the oxovanadium species can be involved in the redox activity (for hydrocarbon and olefin oxidations).¹³ Preliminary catalytic results reveal indeed that the bimetallic VTiAlPO-5 catalysts are more active (TON 575) than their corresponding monometallic analogues (TONs 148 and 395 respectively for TiAlPO-5 and VAlPO-5) in the oxidation of benzyl alcohol at 100 °C using molecular oxygen as oxidant. Similar trends were also observed in the 25 epoxidation of cyclohexene, with selectivities approaching 99% for cyclohexene epoxide.

In summary, we report herein for the first time direct experimental evidence for the simultaneous isomorphous substitution of VO^{2+} and Ti^{3+} in the framework of AIPO-5 architecture. Large ^{31}P hyperfine coupling similar to those observed in vanadyl²⁶ and titanyl³⁰ phosphates demonstrate that VO^{2+} and redox active Ti ions are substituting for Al^{3+} framework sites. These results provide the first detailed experimental description of the local structural environment of bimetallic V-Ti substituted 30 aluminophosphates, which is of crucial importance for evoking structure-property relationships that will play a pivotal role in the design of active sites for engineering higher activities and selectivities in industrially-significant catalytic transformations.

We wish to thank Honeywell Nylons, Morristown, New Jersey (USA) for financial assistance.

Notes and references

^a Dipartimento di Chimica, Università di Torino, Via Giuria, 7. 10125-Torino, Italy. E-mail: m.chiesa@unito.it

^b School of Chemistry, University of Southampton, Southampton, SO17 1BJ, UK.

† Electronic Supplementary Information (ESI) available: Experimental details on sample synthesis and EPR measurements, PXRD and cell parameter refinement values, statistical distribution of the active sites, HYSORE spectra at g_{\parallel} position. See DOI: 10.1039/b000000x/

- 1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
- 2 S. O. Lee, R. Raja, K. D. M. Harris, J. M. Thomas, B. F. G. Johnson and G. Sankar, *Angew. Chem. Int. Ed. Engl.*, 2003, **42**, 1520.
- 3 R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.*, 1999, **121**, 11926.
- 4 J. M. Thomas, R. Raja, G. Sankar and R. G. Bell, *Acc. Chem. Res.*, 2001, **34**, 191.
- 5 I. W. C. E. Arends, R. A. Sheldon, M. Wallau and U. Schuchardt, *Angew. Chem. Int. Ed. Engl.*, 1997, **36**, 1144.
- 6 R. D. Oldroyd, G. Sankar, J. M. Thomas and D. Ozkaya, *J. Phys. Chem. B*, 1998, **102**, 1849.

-
- 7 A. Corma, M. T. Navarro and J. Pérez Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 147.
- 8 R. D. Oldroyd, J. M. Thomas, T. Maschmeyer, P. A. MacFaul, D. W. Snelgrove, K. U. Ingold and D. D. M. Wayner, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2787.
- 9 T. Maschmeyer, F. Rey, G. Sankar and J. M. Thomas, *Nature*, 1995, **378**, 159.
- 5 10 E. Gianotti, V. Dellarocca, L. Marchese, G. Martra, S. Coluccia and T. Maschmeyer, *Phys. Chem. Chem. Phys.*, 2002, **4**, 6019.
- 11 M. Anpo and J. M. Thomas, *Chem. Commun.*, 2006, 3273.
- 12 P. Concepción, P. Corma, J. M. López Nieto and J. Pérez-Pariente, *Appl. Catal. A*, 1996, **143**, 17.
- 13 T. Itoh, K. Jitsukawa, K. Kaneda and S. Teranishi, *J. Am. Chem. Soc.*, 1979, **101**, 159.
- 14 K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.*, 1973, **95**, 6136.
- 10 15 H. Mimoun, M. Mignard, P. Brechot and L. Saussine, *J. Am. Chem. Soc.*, 1986, **108**, 3711.
- 16 J. Paterson, M. Potter, E. Gianotti and R. Raja, *Chem. Commun.*, 2011, **47**, 517.
- 17 S. Maurelli, M. Vishnuvarthan, M. Chiesa, G. Berlier and S. Van Doorslaer, *J. Am. Chem. Soc.*, 2011, **133**, 7340.
- 18 S. Maurelli, M. Vishnuvarthan, M. Chiesa and G. Berlier, *Phys. Chem. Chem. Phys.*, 2012, **14**, 987.
- 19 M. Sánchez-Sánchez, G. Sankar, A. Simperler, R. G. Bell, C. R. A. Catlow and J. M. Thomas, *Catalysis Letters* 2003, **88**, 163.
- 15 20 M. M. J. Treacy and J. B. Higgins, *Collection of Simulated XRD Powder Patterns for Zeolites* 5th Revised ed., Elsevier Science and Technology: Netherlands, 2007.
- 21 N. D. Chasteen in *Biological Magnetic Resonance* L. J. Berliner and J. Reuben Eds., Plenum Press: New York, 1981, **3**, 53.
- 22 J. Woodworth, M. K. Bowman and S. C. Larsen, *J. Phys. Chem. B* 2004, **108**, 16128.
- 23 M. Chiesa, V. Meynen, S. Van Doorslaer, P. Cool and E. Vansant, *J. Am. Chem. Soc.*, 2006, **128**, 8955.
- 20 24 D. Mustafi, M. Makinen, *Inorg. Chem.*, 1988, **27**, 3360.
- 25 C. Montes, M. E. Davis, B. Murray and M. Narayana, *J. Phys. Chem.* 1990, **94**, 6431.
- 26 S. A. Dikanov, B. D. Liboiron and C. Orvig, *J. Am. Chem. Soc.*, 2002, **124**, 2969; D. Mustafi, J. Telser and M. W. Makinen, *J. Am. Chem. Soc.*, 1992, **114**, 6219; J. Petersen, K. Fisher and D. J. Lowe, *J. Biol. Inorg. Chem.*, 2008, **13**, 623.
- 27 M. S. Rigutto and H. Van Bekkum, *J. Mol. Cat.*, 1993, **81**, 77.
- 25 28 N. M. Atherton and J. F. Shackleton, *Mol. Phys.*, 1980, **39**, 1471.
- 39 A. C. Saladino and S. C. Larsen, *Catalysis Today*, 2005, **105**, 122.
- 30 S. D. Setzler, K. T. Stevens, N. C. Fernelius, M. P. Scripsick, G. J. Edwards and L. E. Halliburton, *J. Phys.: Condens. Matter*, 2003, **15**, 3969.