Influence of the geometric structure on the V L₃ near edge X-ray absorption fine structure from vanadium phosphorus oxide catalysts


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Abstract
We present the V L₃ near edge X-ray absorption fine structure (NEXAFS) of a vanadium phosphorus oxide (VPO) catalyst. The spectrum is related to the V₃d-O₂p hybridised unoccupied states. The overall peak position at the V L₃-absorption edge is determined by the formal oxidation state of the absorbing vanadium atom. Details of the absorption fine structure are influenced by the geometric structure of the compound. Empirically we found a linear relationship between the energy position of several absorption resonances and the V-O bond length of the participating atoms. This allows to identify the contribution of specific V-O bonds to the near edge X-ray absorption fine structure. The bond length / resonance position relationship will be discussed under consideration of relations between geometric structure and NEXAFS features observed in X-ray absorption experiments and theory.

Keywords: vanadium phosphorus oxide; X-ray absorption spectroscopy; vanadium L₃-edge; VPO catalyst; electronic and geometric structure

Introduction
Vanadium phosphorus oxides (VPO) are well known to be efficient catalysts in the selective oxidation of n-butane to maleic anhydride [1]. It is believed that vanadyl pyrophosphate (VO)₂P₂O₇ is the active phase in this process [2]. Structural nuances of the catalyst seem to be of great importance for the catalytic performance. The material undergoes strong structural rearrangements during the activation process from the precursor to the equilibrated catalyst. Differently prepared catalysts have significant performance differences. The VPO surface offers a large variety of differently co-ordinated oxygen atoms due to the low symmetry of the supposed bulk structure. One can find oxygen that is singly co-ordinated to vanadium or phosphorus (V=O or P=O), doubly co-ordinated bridging oxygen (V-O-V, V-O-P, P-O-P) and triply co-ordinated bridging oxygen (V > O-P). The V⁺⁺-VPO-phase vanadyl pyrophosphate (VO)₂P₂O₇ possesses a structure in which two highly distorted VO₆ octahedra are joined by the edges (Fig. 1A). The structure is built up by layers parallel to the (100) plane in which pairs of octahedra are connected by PO₄ tetrahedra. The V=O bonds in the octahedra pairs are in trans position and the layers are connected by pyrophosphate groups [3]. A detailed view of the distorted VO₆ octahedra is shown in Fig. 1B. Three groups of oxygen bound to vanadium can be distinguished: apical oxygen atoms O(1) with a short V-O bond O(1a) and a long bond O(1b), planar oxygen atoms O(2) with one V atom and one P atom as nearest neighbours, and planar oxygen atoms O(3) with two V and one P as nearest neighbours.

In the literature different models of the details of the vanadyl pyrophosphate bulk structure obtained by XRD are discussed. Gorbunova et al. reported a orthorhombic crystal system with the lattice parameters a=7.725 Å, b=16.576 Å, c=9.573 Å [4], while Nguyen et al. re-examined this material and solved the structure as mono-
A structural model of vanadyl pyrophosphate according to Nguyen et al. [5]. A: View onto the (100) plane. The (b, c) planes are stacked along the a axis. Vanadium, oxygen and phosphorus atoms are represented as balls as indicated. Twinned VO$_6$ octahedra isolated and connected to other octahedra pairs by P$_2$O$_7$ double tetrahedra are shown. In the centre of the Figure the atomic arrangement of a central vanadium atom surrounded by oxygen atoms inside the highly distorted octahedra is displayed. B: Detailed view of the V-O octahedra. Three groups of oxygen bond to vanadium can be distinguished: apical oxygen atoms with a short V-O bond O(1a) and a long bond O(1b), planar oxygen atoms O(2) with one V atom and one P atom as nearest neighbours, and planar oxygen atoms O(3) with two V and one P as nearest neighbours.

clinic with the unit cell dimensions $a=7.7276$ Å, $b=16.5885$ Å, $c=9.5796$ Å, $\beta=89.97^\circ$ [5]. As a result, different bond length distributions for the ideal bulk structure of vanadyl pyrophosphate are assumed. In Fig. 2 the bond length distribution obtained by Nguyen et al. (model A) and Gorbunova et al. (model B) are compared. A tentative assignment of V-O bonds to the different groups of apical (O(1a), O(1b)) and planar (O(2), O(3)) oxygen atoms of the VO$_6$ octahedra (compare to Fig. 1B) are given. Interestingly, Gorbunova et al. reported a vanadyl bond length of about 1.70-1.72 Å which is completely absent in the structure solved by Nguyen et al. This interatomic distance seems to be unreasonable and therefore Thompson and Ebner re-determined the structure and found good R values only if they include disorder in their model [6]. Ebner and Thompson as well as Nguyen et al. pointed out that they obtained material with different colours during their preparation of single crystaline vanadyl pyrophosphate. They got emerald green and red brown crystals. A photograph of a (VO)$_2$P$_2$O$_7$ crystal is displayed in Fig. 3. The freshly cleaved surface is shown where macroscopic areas of different colour can be identified. This might be a hint for the heterogeneity of the prepared material and may explain the problems to determine an unique bulk structure of vanadyl pyrophosphate.

Single crystalline (VO)$_2$P$_2$O$_7$ did not show any detectable conversion of n-butane to maleic anhydride. Therefore we studied VPO catalyst powder. The material was investigated by means of X-ray absorption spectroscopy (XAS) in the soft energy range between 100 eV and 600 eV, which represents a surface sensitive method if applied in the electron yield mode. XAS probes the unoccupied density of states (DOS). Since the process is local and governed by dipole selection rules the data are related to the site- and symmetry selected DOS. No long range order is necessary and the method is therefore extremely useful to characterise amorphous or disordered material. In contrast to the large amount of work which has been done with a number of techniques on VPO catalyst to investigate their catalytic behaviour, geometry, morphology and electronic structure, only very few investigations have been reported on applying X-ray absorption in the soft energy range. This is unlike to the situation for binary vanadium oxides where a number of studies exist. Recently, Gerhold et al. investigated macroscopic single crystalline (VO)$_2$P$_2$O$_7$ at the vanadium L- and oxygen K-edge [7]. By using the polarisation of synchrotron light they assigned the different absorption fine structure resonances at the O K-edge to specific V-O and O-P hybridised orbitals. The authors do not discuss the V 2p absorption features.

![Figure 1](image1.jpg)

**Figure 1** Structural model of vanadyl pyrophosphate according to Nguyen et al. [5]. A: View onto the (100) plane. The (b, c) planes are stacked along the a axis. Vanadium, oxygen and phosphorus atoms are represented as balls as indicated. Twinned VO$_6$ octahedra isolated and connected to other octahedra pairs by P$_2$O$_7$ double tetrahedra are shown. In the centre of the Figure the atomic arrangement of a central vanadium atom surrounded by oxygen atoms inside the highly distorted octahedra is displayed. B: Detailed view of the V-O octahedra. Three groups of oxygen bond to vanadium can be distinguished: apical oxygen atoms with a short V-O bond O(1a) and a long bond O(1b), planar oxygen atoms O(2) with one V atom and one P atom as nearest neighbours, and planar oxygen atoms O(3) with two V and one P as nearest neighbours.

![Figure 2](image2.jpg)

**Figure 2** Comparison of the V-O bond length distribution for vanadyl pyrophosphate resulting from the structural models of Nguyen et al. (model A) [5] and Gorbunova et al. (model B) [4]. Every bond length found is represented by a filled triangle and dot, respectively. A tentative assignment of V-O bonds to the different groups of apical (O(1a), O(1b)) and planar (O(2), O(3)) oxygen atoms of the VO$_6$ octahedra (compare to Fig. 1B) are given. The assignment of bond lengths to resonances $\gamma_p^a$-$\gamma_p^b$ labelled in Fig. 4 and used in Fig. 6 is indicated by arrows.

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Figure 3 Photograph of the surface of a freshly cleaved (VO)2P2O7 crystal. The arrows indicate areas of different colour.

VPO is a highly electrically insulating material and it is difficult to apply successfully standard surface sensitive methods (e.g. STM, LEED) to explore its surface structure. In this work X-ray absorption spectroscopy was applied to gain information about the local geometric structure of the catalyst. In addition to the difficulties of getting information of the surface structure with other methods, XAS in the soft energy range can be applied in situ, i.e. under working conditions of the catalyst [8 - 10].

Some examples of using X-ray absorption spectra for this purpose are discussed in the literature. Oscillations of the absorption coefficient far away from the onset of the absorption edge are regularly used in EXAFS analysis to obtain structural information. But also the variation of the absorption coefficient just at the edge can be used. An important example can be found in the NEXAFS of small molecules adsorbed on surfaces. By analysing the energy difference between the ionisation threshold and the σ* ("shape") resonance it is possible to determine the internuclear distance between the pairs of atoms giving rise to the resonance [11 - 13]. One finds in almost all cases a linear relationship between the so defined position of the σ* ("shape") resonance and the bond length. The higher the photon energy of this resonance the smaller the internuclear distance between the participating atoms.

In the case of solid state materials, examples of identifying the influence of the geometric structure on features of the NEXAFS can be found in literature, too. Some NEXAFS resonances at the K-edges of high Tc superconductors of the YBaCuO type and of NiO have been assigned by Lytle to specific inter-atomic distances in the compounds [14]. Wong et al. compared various vanadium K-edge spectra where they paid attention in particular to the trends in the dependence of the pre-edge fine structure on the local vanadium coordination [15]. They concluded that the distinct pre-peak in the near edge spectrum of V2O5 originates from 1s → 3d transitions, which become dipole allowed if the full local octahedral O6 symmetry is decreased. Wong et al. argued that the pre-edge structure originates from states generated by a cage formed by the central vanadium and nearest-neighbour oxygen atoms ("cage effect"). Šipr et al. compared experimental and theoretical polarised V K-edge spectra of V2O5 [16]. They found that the presence of the nearest vanadyl oxygen atom is significant for the shape of the distinct pre-peak and that both the short bond length and deviations from inversion symmetry are crucial.

Experimental details

V2O5 powder was of commercially available grade (Merck) while the VPO powder was prepared by subsequent transformation of the precursor compound VOHPO4 · 0.5H2O under n-butane oxidation conditions (feed gas: 1.5vol% butane in air) at 400°C for 75h. The crystalline hemihydrate precursor was prepared by the alcoholic preparation route [2]. In brief V2O5 (Merck) was refluxed with H3PO4 (85% Aldrich) in isobutanol for 16 h. The light blue solid was recovered by filtration, washed with isobutanol and ethanol, refluxed in water for 1 h, filtered hot, and dried in air (110°C, 16h).

The XAS experiments were performed with a special reactor cell designed for in situ X-ray absorption investigation consisting of two stainless-steel chambers. Details about the set-up and the data processing can be found in the literature [8, 9]. Experiments were carried out at the undulator beamline UE/56-2 at the third generation synchrotron radiation facility BESSY in Berlin [17]. The powder samples were fixed on an alumina sample holder by a double adhesive conductive tape (Plano). To get the desired information we analysed the near edge X-ray absorption fine structure (NEXAFS), i.e. the strong variations of the absorption coefficient just at the absorption edge. The data were collected in the total electron yield mode (TEY) under vacuum conditions. The photon energy of the NEXAFS spectra was calibrated by the π*-resonance of molecular oxygen at 530.8 eV [18]. The resolving power E/ΔE was about 3000. Vanadium L3-edge spectra were normalised to the same maximum peak height and analysed by a least squares fit, using Gauss-Lorentz profiles considering experimental and intrinsic broadening.

Results and discussion

In Fig. 4 the vanadium L3 X-ray absorption edge of V2O5 and VPO powder are displayed. The V L3-absorption edge corresponds to the V2P3/2 → V3d electronic transition. Both samples show a very detailed absorption fine structure with a number of distinct resonances that are labelled in the Figure. The resonance positions have been extracted by an unconstrained least squares fit. The number of assumed resonances for V2O5 was obtained by an additional experiment. In this investigation single crystalline V2O5 was measured at different incident angles of the polarised synchrotron radiation with respect to the sample surface similar to the study of Goering et al. [19]. Only the NEXAFS of V2O5 powder is presented here in order to compare it to the polycrystalline VPO catalyst. The minimum number of fitting profiles that are necessary for a satisfactory fit is assumed for VPO.

On first sight the overall spectral shape is quite similar for VPO and V2O5. A detailed analysis shows spe-
specific differences in position and intensity ratio of the features. The absorption maximum is shifted to lower photon energies for VPO compared to V$_2$O$_5$. It is a well known fact that the overall peak position at the vanadium L$_3$-edges is sensitive to the valence of the metal atom [20 - 22]. With increasing oxidation state the overall spectral weight is shifting to higher photon energies quite similar to the chemical shift observed in XPS, although NEXAFS is a resonant process. This shift is caused by the different electrostatic potential at the vanadium site. The positive shift with increasing valence can be understood conceptually to be due to an increase in the attractive potential of the nucleus and a reduction in the repulsive core Coulomb interaction with the other electrons in the compound. In order to transfer this relationship to high resolution spectra of VPO compounds with their asymmetric shape, the 1st momentum $E_{\text{center}} = |E \cdot \text{TEY}(E)e\text{d}E$ of the area normalised spectral distribution at the V L$_3$-edge was calculated. $E$ is the photon energy and TEY the total electron yield. By determining $E_{\text{center}}$ for reference compounds with a known oxidation state (V$^{5+}$: VOPO$_4$ · 2H$_2$O, β-VOPO$_4$; V$^{4+}$: VOHPO$_4$ · 0.5H$_2$O) and catalysts with independently determined oxidation state (by titration [23]) (VPO$_x$, VPO$_b$) and from the position of the pre-peak at the V K-edge [15] (VPO$_b$) a linear correlation between $E_{\text{center}}$ and the average oxidation state of the material is found (Fig. 5).

To get a deeper understanding of the NEXAFS it would be useful to compare the experimental data with simulations of the absorption structures. Unfortunately no such calculations have been published yet for vanadyl pyrophosphate, which is believed to be the active phase of VPO catalysts. This is probably due to the high complexity of its geometric structure displayed in Fig. 1. Keeping in mind that XAS is a local method it should be possible to conclude upon an unknown system from a model system with similar local structure but different long range order. V$_2$O$_5$ shows a very similar distortion of the VO$_6$ octahedra (Fig. 1B) although there is no continuous network of V-O bonds in the (100) plane for vanadyl pyrophosphate (compare to Fig. 1A) and the configuration is 3d to 3d$^0$ in contrast to the 3d$^2$ state of the binary oxide [24].

Nevertheless the NEXAFS of the reference compound V$_2$O$_5$ and the VPO catalyst is quite similar at the V L$_3$-edge, which can be seen in Fig. 4. This suggests that band-structure calculations available for V$_2$O$_5$ may help to understand the underlying principles of the V L$_3$-NEXFAS of the VPO catalyst, too. Eyert and Höck presented first-principles augmented spherical wave calculations for the real structure of V$_2$O$_5$ as well as for different hypothetical, less distorted geometries of the VO$_6$ octahedra [25]. They found that in addition to the crystal field splitting of the electronic V 3d states into $t_{2g}$ and $e_g$ states there exists a splitting into different features at the V L$_3$-edge. This is due to deviations of the VO$_6$ octahedra from cubic symmetry which is reflected in both the V and O density of states. A different bonding-antibonding splitting of the V-O hybridised orbitals causes a shift in energy of the corresponding states relative to the valence-band maximum. The short V-O$_{\text{vanadyl}}$ (1.577 Å) and V-O$_{\text{edge}}$ bonds (1.779 Å) cause a larger bonding-antibonding splitting and therefore they are represented at higher energies in the DOS than the longer V-O$_{\text{chain}}$ bonds (1.878 Å and 2.017Å).

We analysed the V L$_3$-absorption spectra with respect to the influence of the geometric structure on the NEXAFS by trying to find a correlation between the reso-
nance sequence and the bond lengths. In the case of $\text{V}_2\text{O}_5$ it is in fact possible to find a representation for all relevant vanadium oxygen distances that are present in the NEXAFS as suggested by the calculation [25]. The linear relation found between the bond length revealed by XRD and the NEXAFS resonance position obtained by the least squares fit is displayed in the inset of Fig. 6. The energy position of resonances $V_1-V_6$ is given relative to the position of the absorption feature $V_1$. A fit of the data points obtained by linear regression is shown as a solid line. Remarkably, no equivalent for the long interlayer vanadium-oxygen distance of 2.791 Å could be found. This can be explained by the very weak bond and therefore almost missing hybridisation between these atoms. This is in agreement with findings in vibrational spectroscopy studies of this material [26]. In this framework $V_1-V_4$ represent mainly the $t_{2g}$ states while $V_5$ is attributed to the broad $e_g$ states in the DOS. For the $e_g$ states the contribution of the different vanadium-oxygen bonds is overlapping and cannot be deconvoluted.

Two additional profiles between $V_1$ and $V_4e$ are needed to get a satisfying fit of the $V L_3$-NEXAFS of $V_2\text{O}_5$ (compare to Fig. 4). These components do not fit in the linear relationship between bond length and resonance position. On the one hand this may be caused by an incomplete separation between the $t_{2g}$ and $e_g$ states. In fact, the calculation presented in [25] indicated a strong contribution of $e_g$ states in the energy range of resonance $V_4$. On the other hand intra-atomic effects are certainly of importance for the strongly correlated 3d states of transition metal ions. Therefore multiplet effects caused by 2p-3d and 3d-3d Coulomb and exchange interactions could have an influence on the spectral shape at the $V L_3$-absorption edge.

Analysing the VPO NEXAFS in the same way is hindered by the fact that the details of the geometric structure of the supposed catalytic active phase vanadyl pyrophosphate are still a matter of debate. However, the general building principle of twinned octahedra isolated by phosphate groups as described in the introduction seems to be undoubted. In Fig. 6 the relationship between the position of the observed VPO NEXAFS resonances $V_{1*}^j-V_{6*}^j$ and the bond lengths obtained from the models of Nguyen et al. [5] ($\text{▲}$: model A in Fig. 2) and Gorbunova et al. [4] ($\bullet$: model B in Fig. 2) for vanadyl pyrophosphat is shown. The resonance positions are given relative to the energy position of $V_1$ of $\text{V}_2\text{O}_5$ (515.16 eV). The assignment of every NEXAFS resonance of VPO to a bond length can be found in Fig. 2 for both structural models A and B. All data points follow a linear relationship between assumed bond length and resonance position. A fit of the data points obtained by linear regression is also indicated. The regression fit parameters for model B (solid line) are slightly different than the ones for model A (dotted line). The correlation for structural data from model B is better than for model A. This is mainly due to the inclusion of a bond length of 1.72 Å which is solely present in the structural model of Gorbunova and Linde [4]. The data point with the largest deviation from the assumed linear relationship corresponds to resonance $V_5^*$ of VPO (compare to Fig. 4). No equivalent bond length in model A could be identified for this resonance. Interestingly, there would result a bond length of around 1.77 Å similar to the one indicated in the structural model B if one applies strictly the relation obtained by linear regression to the resonance energy. $V_{1}^*$ is attributed to the sum of $e_g$ states in the density of states equivalent to resonance $V_1$ of $\text{V}_2\text{O}_5$. Comparing the slopes of the regression lines obtained for the data of VPO and $\text{V}_2\text{O}_5$ displayed in Fig. 6 reveals slightly different values. This is probably due to differences in the bonding, e.g. a variation in the degree of hybridisation between vanadium and oxygen in both compounds.

Natoli tried to give a theoretical justification for the sensitivity of certain features in the NEXAFS to inter-atomic distances in the framework of multiple scattering theory [27]. He obtained an EXAFS like relationship $k^-|r = \text{const.}$ ($k$: photoelectron wave vector, $r$: nearest neighbour distance). This can be rewritten as $(E_r-V_0)^2 = C \cdot E_r$ is the energy of the resonance relative to an interstitial potential $V_0$ of muffin-tin type in the material which defines the zero of energy of the photoelectron, $r$ is the bond length between the absorbing atom and its nearest neighbours. $C$ is determined by the atomic scattering phases and taken as constant. $C$ could be energy dependent in the resonant region due to the non-negligible energy dependence of the atomic phase shifts [27]. Originally applied to the case of continuum resonances ("shape resonance"), Natoli suggested the use of this relation for bound molecular or atomic-like localised resonances as well [27]. In general muffin-tin atomic potentials and scattering phase shifts change with the electronic structure. Sette et al.
already remarked that \( V \) must vary with \( r \) to hold the linear relationship found for \( E \) and \( r \) in the case of free [13] and surface adsorbed molecules [28, 29]. Although the small \( r \) interval investigated by Sette et al. did not really allow to distinguish a linear correlation and the \( 1/r^2 \) relationship between the resonance position and the intra-molecular bond length, applying the \( \left( E_r - V_0 \right) \cdot r^2 = \text{const.} \) rule gave much worse correlation coefficients than the linear relationship. Therefore they suggested a dependence of the potential \( V \) on \( r \) of the form \( V(r) = A + \frac{B}{r} + C \cdot r \). Shneerson et al. developed an analytical theory for the position of NEXAFS resonances for diatomic molecules [30]. They pointed out that both the muffin-tin zero potential \( V \) and the phase shifts depend on the internuclear distance, so that a direct interpretation of Natoli’s rule is not valid. They suggested a relation of the form \( E_r = A + \frac{B}{r} + C \cdot \frac{1}{r^2} \) for the relation between resonance position and bond length. They found that this function is rather linear within the range of experimental data. This can also be shown for our data of the V L\(_3\)-edge of VPO. In Fig. 6 in addition to the linear regression line (solid line) a fit for model B with the expression given by Shneerson et al. is displayed as a dashed line. Within the range of our data there is only a very slight deviation from the linear relationship assumed.

Applying the theoretical results for free or adsorbed molecules to solids is of course not a straightforward task. But one should take into account that the V L\(_3\)-edge spectra reflect mainly the density of the narrow sharp structured d-states around vanadium, which bear more atomic character than the more delocalised p states probed by XAS at the V K-edge. Successful calculations of L\(_3\)-edge spectra of some transition metal compounds using an atomic multiplet description including the crystal field indicate that intraatomic effects may indeed dominate for transition metal compounds in octahedral symmetry [31]. Furthermore the structural building units of vanadyl pyrophosphate, the twinned octahedra are highly isolated from each other by the pyrophosphate groups (Fig. 1A). This “site isolation” effect is assumed to be crucial for the use of this material for selective n-butane oxidation [3, 32]. It is believed that the total oxidation of n-butane is suppressed by this structural peculiarity. This may attribute to the surprising comparability of the bond length / resonance position relationship presented here to the “bond lengths with a ruler” framework successfully established for free and surface adsorbed molecules [28, 29].

Summary and conclusions

We have presented vanadium L\(_3\)-edge X-ray absorption spectra of a VPO catalyst and compared it to the NEXAFS of \( \text{V}_2\text{O}_5 \). We have shown that the overall peak position defined by the 1\(^\text{st} \) moment of the spectral distribution at the vanadium L\(_3\)-absorption edge of VPO changes linearly with the formal valence of the vanadium atom. Furthermore we found empirically a linear relationship between the position of particular NEXAFS resonances and the geometric structure of vanadyl pyrophosphate determined by XRD. Therefore it is concluded that details of the NEXAFS are related to structural peculiarities of the material. The discussion above indicates that the association between particular spectral and geometric features is not a straightforward task in the general case. For solid state materials it is expected that the position of the near edge features is influenced both by a “bond length effect” and by the valence of the absorbing atom.

We are well aware that there is the need for further investigation as well as theoretical support of the findings presented in this paper. Nevertheless we could show that X-ray absorption spectroscopy can be a very useful tool for the study of complex materials. Identifying the contribution of specific vanadium-oxygen bonds to the NEXAFS at the V L\(_3\)-edge of VPO allows a detailed study of this important material for catalysis. In particular investigating the catalyst under working conditions rendered possible by means of in situ NEXAFS [8 - 10] might provide valuable information about the electronic structure of the active surface. The results presented in this paper indicate that it might be possible to study the changes of specific vanadium-oxygen bonds at different levels of activity of the catalyst.

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