



Cite this: DOI: 10.1039/c7cp06786k

Cobalt-to-vanadium charge transfer in polyoxometalate water oxidation catalysts revealed by 2p3d resonant inelastic X-ray scattering†

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Two isostructural cobalt containing polyoxometalate water oxidation catalysts, $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ (Co_4P_2) and $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-VW}_9\text{O}_{34})_2]^{10-}$ (Co_4V_2), exhibit large differences in their catalytic performance. The substitution of phosphorus centers in Co_4P_2 with redox-active vanadium centers in Co_4V_2 leads to electronic structure modifications. Evidence for the significance of the vanadium centers to catalysis, predicted by theory, was found from soft X-ray absorption (XAS) and resonant inelastic X-ray scattering (RIXS). The XAS and RIXS spectra determine the electronic structure of the cobalt and vanadium sites in the pre-reaction state of both Co_4V_2 and Co_4P_2 . High-energy resolution RIXS results reveal that Co_4V_2 possesses a smaller ligand field within the tetra-cobalt core and a cobalt-to-vanadium charge transfer band. The differences in electronic structures offer insights into the enhanced catalysis of Co_4V_2 .

Received 4th October 2017,
Accepted 22nd January 2018

DOI: 10.1039/c7cp06786k

rsc.li/pccp

Introduction

Transition metal based materials, containing partially filled 3d bands, exhibit redox chemistry that leads to their extensive investigation as candidates for new catalytic routes. For example, various supported iron and cobalt materials are used as catalysts for Fischer–Tropsch synthesis.^{1,2} The roles of catalysts in breaking and forming intermolecular bonds can be correlated to the electronic structures of the transition metal ions,³ which makes it important to understand the influence of transition metal sites in a catalyst. In catalysis, one consensus goal is harnessing solar energy to produce fuel, and water oxidation catalysis stays as a central thrust in the production of solar fuels *via* water splitting or carbon dioxide reduction.^{4–6} The oxidation of water ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$) is a highly demanding step that requires the coupling of four electron and proton transfers

together with the formation of the oxygen bond. Recently, a series of viable homogenous water oxidation catalysts (WOCs) with polyoxometalate (POM) ligands stabilizing transition metal cores have been developed.^{7–14} This family of WOCs are carbon-free, hydrolytically and oxidatively stable. Among them, the earth-abundant cobalt or nickel containing POM catalysts^{9,10,12–14} show potential for use on a realistic industrial scale. In particular, the tetra-cobalt POM catalyst $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ (Co_4P_2), first reported by Yin *et al.*,⁹ exhibits high photocatalytic performance with a turnover frequency (TOF) of $\sim 5 \text{ s}^{-1}$ and high O_2 evolution quantum yields.¹⁰ An isostructural vanadium-centered analogue, $[\text{Co}_4(\text{H}_2\text{O})_2(\alpha\text{-VW}_9\text{O}_{34})_2]^{10-}$ (Co_4V_2), was later reported to be a WOC with superior catalytic performances up to $\sim 10^3 \text{ s}^{-1}$ TOF.¹⁴ Both Co_4P_2 and Co_4V_2 have been established to be the dominant active catalysts, with reasonable hydrolytic and very high oxidative stabilities in aqueous conditions.^{14–16} Such a large catalytic difference intriguingly calls for examining the significance of substituting phosphorus centers in Co_4P_2 with vanadium centers in Co_4V_2 . Importantly, phosphorus and vanadium are in the centers of each catalyst and do not serve a direct role in water oxidation, which is understood to occur at the tetra-cobalt core.¹⁷ Therefore, a deep comparison of the ground state electronic structures of both catalysts may provide new insights into their relative catalytic properties.

The electronic structures of Co_4P_2 and Co_4V_2 have been discussed in previous work based on experimental results of UV-vis spectra and magnetism studies.^{9,14} Density functional

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† Electronic supplementary information (ESI) available: UV-vis & IR data, simulations, and experimental spectra comparisons. See DOI: 10.1039/c7cp06786k

theory (DFT) calculations suggested the role of the VO_4 orbitals in the molecular orbitals of Co_4V_2 . These observations, however, raise further questions: (1) are there relevant differences in the electronic structure of the tetra-cobalt core as a whole in these two POMs? (2) Can the theoretically predicted metal-to-metal charge transfer (MMCT) between the cobalt and vanadium 3d orbitals in Co_4V_2 be experimentally observed? The value of point (1) is emphasized in the original work on Co_4P_2 ,⁹ in which other cobalt containing POMs with different cobalt core structures were found to be catalytically inactive, suggesting the structural motif of the POM is important, not just the tetra-cobalt core. In Co_4P_2 and Co_4V_2 , the geometric structures of both tetra-cobalt cores are nearly identical, albeit with small deviations in Co–O bond lengths and Co–O–Co bond angles,^{9,14} but connections with heteroatoms (phosphorus or vanadium) may also affect the ligand-field-related cobalt 3d electronic states of the tetra-cobalt core. For point (2), charge transfer between partially filled cobalt 3d orbitals and empty vanadium 3d orbitals in Co_4V_2 , if observable, should support the predicted role of vanadium centers in the redox chemistry of the enhanced catalyst. To answer these two questions, we propose to investigate transition metal sites in both POMs (cobalt in Co_4P_2 and cobalt, vanadium in Co_4V_2), by XAS and RIXS. Specifically, the 2p ($L_{2,3}$ edge) XAS and the corresponding 2p3d RIXS with smaller final state lifetime broadenings at this edge and better instrumental resolution are selected.^{18–20}

The combined advantages of using transition metal 2p XAS and 2p3d RIXS to address the two targeted issues are: (a) both X-ray spectra are element-specific, enabling separate probes of transition metal elements of interest. As a result, a direct comparison of the electronic structures of the tetra-cobalt core in Co_4P_2 and Co_4V_2 is achievable. (b) Both techniques are independently sensitive to the ligand field. In particular, 2p3d RIXS is capable of observing the ligand field influenced 3d-orbital rich states with high accuracy.^{18,20–22} (c) 2p3d RIXS permits the clear observation of d–d, ligand-to-metal charge transfer (LMCT), and MMCT transitions.^{23–25} We note that MMCT features assigned in UV-vis spectra²⁶ are often either not well understood or misassigned ligand-to-metal charge transfer or d–d transition features. (d) Transition-metal 2p XAS and 2p3d RIXS spectra can be reliably interpreted by multi-electron theories.^{27–34} In this work, we measure the cobalt and vanadium 2p XAS and 2p3d RIXS spectra with high experimental energy resolution (*vide infra*). Cobalt experimental spectra are simulated *via* ligand field multiplet (LFM) methods, by which the detailed cobalt 3d electronic states can be approached. The vanadium data of Co_4V_2 confirms the previously reported¹⁴ valence state ($5+$, $3d^0$) of the two symmetry-equivalent vanadium centers. The possible beam induced effects on vanadium XAS and RIXS spectra are discussed. From the vanadium 2p3d RIXS spectra, the cobalt–vanadium charge transfer in Co_4V_2 is rationalized by combining a model calculation on the $3d^1$ (vanadium $4+$) ion. Finally, the cobalt and vanadium spectra provide complementary information on the differences of ground state electronic structures in Co_4P_2 and Co_4V_2 . These results are discussed with respect to the notable difference in catalytic rates between Co_4P_2 and Co_4V_2 , whereupon

the electronic spectra offer insights into contributing factors for water oxidation catalysis.

Experimental

Materials

$\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 27\text{H}_2\text{O}$ (Co_4P_2) and $\text{Na}_{10}[\text{Co}_4(\text{H}_2\text{O})_2(\text{VW}_9\text{O}_{34})_2] \cdot 35\text{H}_2\text{O}$ (Co_4V_2) were synthesized according to the published procedures.^{9,14} The obtained Co_4P_2 sample consisted of purple needle-like crystals and the Co_4V_2 sample of greenish-brown needle-like crystals. The identities and purities of each POM were confirmed by UV-vis and infrared spectroscopy. Infrared spectra (2% by weight in KBr) were recorded on a Nicolet 6700 FT-IR spectrometer. UV-vis spectra were acquired of ~ 1 mM aqueous solutions using an Agilent 8453 spectrophotometer equipped with a diode-array detector and Agilent 89090A cell temperature controller unit. Characterizations by UV-vis and FT-IR are provided in Fig. S1 and S2 in the ESI.†

XAS and RIXS measurements

Cobalt and vanadium 2p XAS spectra were acquired at the soft X-ray WERA beamline, ANKA synchrotron, Germany. Sample colors were confirmed to be identical prior to and after affixing to the sample holder as well as after XAS measurements. Before the XAS acquisition, the instrumental resolution was calibrated to be ~ 280 meV full width at half-maximum (fwhm) at 780 eV and ~ 150 meV fwhm at 510 eV. The cobalt 2p XAS spectra were measured with the total electron yield (TEY) method at room temperature (RT, ~ 300 K) and the partial fluorescence yield (PFY) method at 50 K. The vanadium 2p XAS spectra were obtained with the TEY method at RT. For both TEY and PFY acquisition, the normal incidence was used. All XAS spectra presented are averaged from multiple spectra. Each single spectrum was acquired at a new pristine sample position. For vanadium XAS acquisitions, the defocused mode with a large beam spot size ($500 \times 500 \mu\text{m}^2$) was used in order to reduce possible beam-induced damage to the sample.^{35–37} No visible beam damage effects were found by comparing spectral shapes of each single spectrum.

Cobalt RIXS spectra were measured at beamline 05A1, National Synchrotron Radiation Research Center (NSRRC), Taiwan.³⁸ The powdered samples were pressed into pellets and attached to copper sample holders. FT-IR spectra of both pellet samples prior-post pellet formation indicated no molecular structural change. Cobalt 2p XAS spectrum was acquired in a low energy resolution (~ 0.5 eV fwhm) PFY mode to match ANKA data for RIXS excitation energy determinations. The energy resolution of the RIXS elastic (zero energy transfer) peak was calibrated to be ~ 90 meV fwhm around the cobalt $2p_{3/2}$ edge (~ 780 eV). The linear horizontally (LH) polarized beam with incident angle $\sim 70^\circ$ with respect to the sample surface was used. The scattering angle between incoming and outgoing X-rays was set to be 90° . The present cobalt RIXS spectra consist of the sum of 60–90 RIXS spectra (1 minute acquisition time each). A new pristine sample position was changed for every 30 min, a time frame in which no

beam damage effects were observed in prior-post comparative RIXS measurements. The pressure and temperature during all data acquisition were $<1.0 \times 10^{-8}$ mbar and 16 K respectively.

Vanadium XAS and RIXS spectra of Co_4V_2 were measured at the HORNET endstation,³⁹ BL07LSU,⁴⁰ SPring-8 synchrotron, Japan. The powdered sample was pressed into a pellet and attached to sample holders. Vanadium 2p XAS spectra were obtained with the TEY mode. The beam spot size used was $20 \times 40 \mu\text{m}^2$. The XAS spectrum was used to match the data acquired in ANKA to determine excitation energies. Beam induced effects observed from vanadium XAS spectra are discussed as shown in Fig. S3 (ESI†). For RIXS measurements, the X-rays with LH polarization were applied and the scattering angle between incoming and outgoing X-rays was 90° . The incident angle of X-rays with respect to the sample surface was 45° . The energy resolution of the RIXS elastic peak was fit to be ~ 204 meV fwhm at 510 eV. The vanadium RIXS spectra present were acquired in 5400–7200 s. During RIXS measurements, a scan mode was used under which the sample surface illuminated by X-rays shifted to a previously non-irradiated spot every 10 s. The pressure and temperature during XAS and RIXS acquisition were $<5.0 \times 10^{-9}$ mbar and RT respectively.

Results and discussion

The X-ray crystal structures of Co_4P_2 and Co_4V_2 in polyhedral representations are shown in Fig. 1. The corresponding ball-and-stick representations are shown in Fig. S4 (ESI†). Previous crystallographic characterizations have established that the two POMs are isostructural.^{9,14} In both POMs, two trilacunar B-type $[\text{XW}_9\text{O}_{34}]^{9-}$ ($\text{X} = \text{P}^{\text{V}}$ or V^{V}) ligands sandwich a tetra-cobalt core, $[\text{Co}_4(\text{H}_2\text{O})_2]^{8+}$, by bonding to fourteen oxygen atoms. All four cobalt centers in the tetra-cobalt core are octahedrally (O_h) coordinated, albeit with small tetragonal (D_{4h}) distortions. The four cobalt centers can be divided into two equivalent inner and outer atoms. The two inner centers connect to both heteroatoms (P or V) *via* μ_4 -O bridges and four tungsten octahedra *via* two *cis*- μ_2 -O and two *trans*- μ_3 -O bridges. In contrast, each outer center connects to only one heteroatom

via a μ_4 -O bridge and four tungsten octahedra *via* two *cis*- μ_2 -O and two *cis*- μ_3 -O bridges; the remaining bond is to an exchangeable aqua (water) ligand. Connections between the inner and outer centers are mediated by the aforementioned oxygen bridges: inner cobalt centers are two bonds away from all three adjacent cobalt centers, while outer centers are adjacent to only two centers. Moreover, the PO_4 (or VO_4) units are equivalent with approximately tetrahedral structures. This symmetric geometry simplifies the element-specific XAS and RIXS spectra, as the 3d electronic states will be reflective of (1) the average of the two unique cobalt centers from cobalt spectra, and (2) a single vanadium center from vanadium spectra.

Cobalt 2p XAS spectra of both POMs from the ANKA synchrotron are analyzed and Fig. 2 shows the $2p_{3/2}$ edge of the experimental and calculated results (see Fig. S5 and S6 (ESI†) for full experimental spectra). The noticeable shape deviations between experimental TEY (Fig. 2, left) and PFY (Fig. 2, right) spectra, *e.g.* the lower peak intensity of the second peak (~ 778.4 eV), are primarily caused by the large variations in intermediate state fluorescence decay probabilities.^{41,42} Measuring at low temperature (50 K in this case) directly probes the lowest lying ground state; while measuring at RT, contributions of Boltzmann weighted excited states are also included. In general, cobalt XAS spectral shapes of both Co_4P_2 and Co_4V_2 measured with either TEY or PFY mode are highly similar, consistent with the isostructural tetra-cobalt core geometries. Small variations in peak position in the TEY spectra, such as the second (~ 778.4 eV) or fourth (~ 779.8 eV) peak, are observed that may imply symmetry or ligand field related differences of multiplet states; these differences are less visible in PFY spectra. It is noted that (1) XAS spectra alone are often inadequate to demonstrate different electronic structures accurately (see the example shown in Fig. S7, ESI†) and (2) the same XAS spectrum can be justified theoretically with different LFM parameter values.²¹ The calculation of XAS spectra use the same set of parameters determined from calculations of $2p3d$ RIXS spectra, as listed in Table S1 (ESI†). Here, the calculated results adequately reproduce the experimental spectra, in particular the peak positions as compared in TEY spectra, suggesting the validity of electronic structure parameters found. Since $2p3d$ RIXS is known to be more sensitive to d-orbital rich states and our calculations of RIXS spectra set the LFM parameters, we focus more on discussing the cobalt 3d electronic states as derived from RIXS results.

The experimental cobalt $2p3d$ RIXS spectra acquired at NSRRC are present together with the calculated results in Fig. 3. Excitation energies a and b, shown in Fig. 2, were chosen for the RIXS acquisition of both POMs. Here, exciting at these two energies, the cobalt $2p3d$ RIXS probes both the d–d and the charge transfer transitions.⁴³ In general, the intrinsic final state lifetime broadening (fwhm) of $2p3d$ RIXS for late transition metals is much smaller (<0.1 eV) than that of $2p_{3/2}$ XAS (~ 0.5 eV). When measuring with high experimental energy resolution, *e.g.* here ~ 90 meV (at 780 eV), $2p3d$ RIXS spectra show richer multiplet states that permit more accurate determination of the ligand field strengths than from 2p XAS spectra (also see Fig. S7, ESI†). The RIXS spectral shapes and features of Co_4V_2 and Co_4P_2 , similar to the XAS spectra, resemble each

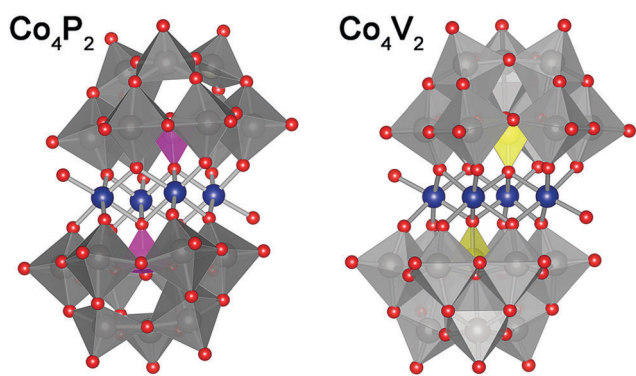


Fig. 1 X-ray crystal structures of Co_4P_2 (left) and Co_4V_2 (right) in polyhedral representations. Color scheme: red: oxygen; blue: cobalt; purple: PO_4 ; yellow: VO_4 ; gray: WO_6 .

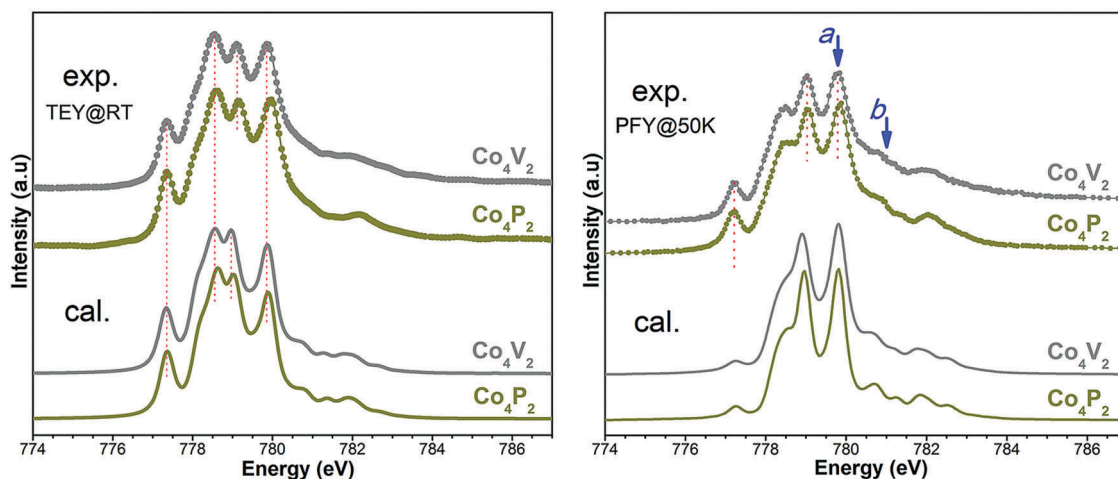


Fig. 2 Cobalt $2p_{3/2}$ XAS spectra of Co_4V_2 (gray) and Co_4P_2 (dark yellow). Left upper and lower: Experimental TEY spectra acquired at RT and corresponding calculated spectra. Right upper and lower: Experimental PFY spectra acquired at 50 K and corresponding calculated spectra. Arrows a and b indicate excitation energies of $2p3d$ RIXS spectra in Fig. 3. Red dotted lines indicate peak positions.

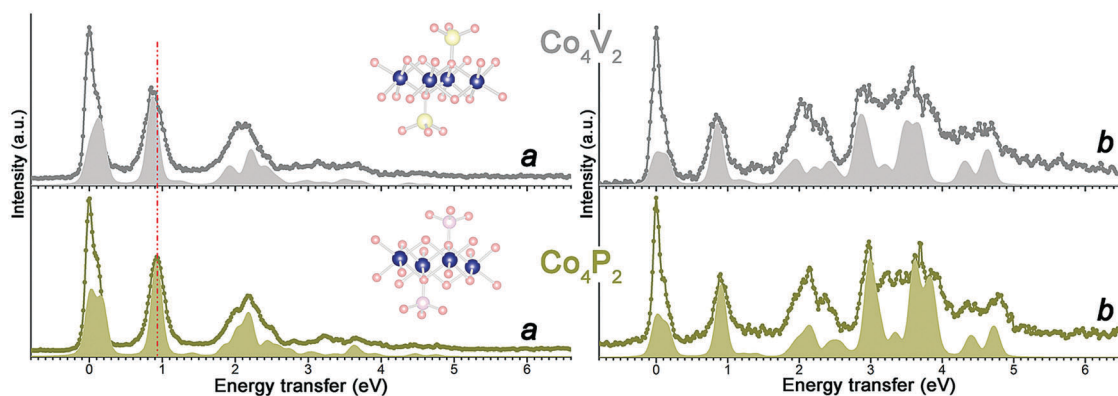


Fig. 3 Experimental (dots + line) and calculated (fillings) cobalt $2p3d$ RIXS spectra of Co_4V_2 (gray, upper panels) and Co_4P_2 (dark yellow, lower panels) acquired at excitation energies a (left panels) and b (right panels) as indicated in Fig. 2. Insets of left panels are the X-ray crystal structures of the tetra-cobalt core $[\text{Co}_4\text{O}_{14}(\text{H}_2\text{O})_2]$ together with two $[\text{VO}_4]$ or $[\text{PO}_4]$ units in ball-and-stick representations. Blue balls represent cobalt atoms and the faded red, yellow and pink balls represent oxygen, vanadium and phosphorus atoms, respectively. The red dot-dashed line in the left panels indicates the first d-d peak position.

other and from these spectra the high spin (cobalt $3d^7$, $S = 3/2$) ground state of the cobalt centers are confirmed.^{43,44} A change of the lowest ($^4T_{2g}$) peak position is visible from 881 ± 1 meV (Co_4V_2) to 925 ± 1 meV (Co_4P_2), as determined from a Gaussian peak fit (Fig. S8, ESI†). This indicates the different ligand field strength of the tetra-cobalt core in two POMs. The ligand field strengths of Co_4V_2 and Co_4P_2 are described by the respective $10Dq$ values of 870 meV and 930 meV, slightly modified from the $^4T_{2g}$ peak position due to the $3d$ spin-orbit coupling (66 meV). A small distortion is used for Co_4V_2 with -0.005 eV Dt value for (see Table S1, ESI†). The slightly tetragonal distortions shown in both tetra-cobalt cores are described by the Ds and Dt parameters used in LFM calculations. The tetragonal distortions mainly determined by the geometries between cobalt and oxygen atoms, including bond distances and angles, have been revealed in the X-ray crystallographic data.^{9,14} The ligand field strength and the related cobalt $3d$ electronic states, however, were less effectively

shown in the cobalt $2p$ XAS spectra (*vide supra*) in this work. In $2p3d$ RIXS spectra, due to the ionic nature of cobalt $2+$ atoms, d-d transitions are considerably probed with few (ligand-to-metal or metal-to-metal) charge transfer contributions to the spectral features, from which a more accurate ligand field strength and $3d$ electronic states can be obtained. The d-d transitions that represent a type of long-lived recombination center and, further, involve charge carriers localized to the metal center, are expected to be important for photocatalytic processes.⁴⁵ Compared to Co_4P_2 , a smaller effective ligand field strength of the tetra-cobalt core in Co_4V_2 suggests that the attraction of vanadium centers in Co_4V_2 to $\mu\text{-O}$ bridges is larger than that of phosphorus centers in Co_4P_2 , which would imply that the cobalt $3d$ character in the oxygen $2p$ bands is reduced in Co_4V_2 than the analogue of Co_4P_2 ; in other words, we pose that the cobalt $3d$ electrons are more localized in Co_4V_2 .

In the LFM calculations of cobalt RIXS spectra, the super-exchange values used are from the modeling results on previous

magnetic studies.¹⁴ The exchange interactions between cobalt centers are different, corresponding to the different types of mediated oxygen bridges, and the values are also slightly different in Co_4V_2 and Co_4P_2 due to variations of geometries. Effects of such subtle deviations (e.g. 2.61×10^{-4} eV for Co_4V_2 and 2.99×10^{-4} eV for Co_4P_2) on the X-ray spectra, however, are too minor to be detected. Thus, the same values are used for both POMs. Atomic values of spin-orbit coupling (both $L\text{-S}_p$ and $L\text{-S}_d$) for cobalt 2+ ions are used for both tetra-cobalt cores. The ligand field parameters (10Dq, Ds and Dt) are determined mainly based on the position of the first d-d excitation peak ~ 0.9 eV, similar to a few other cobalt 2p3d RIXS studies.^{22,44} The Slater integrals that describe the multi-electron coulomb and exchange interactions are optimized to the experiment, where the values are close to the atomic values as indicated in Table S1 in the ESI†. The reductions of F_{dd}^2 and F_{dd}^4 coulomb Slater integrals are respectively 86% and 93% of the atomic values for Co^{2+} ion, following the arguments offered by Schmidtke.^{46,47} The calculated RIXS 2D maps of Co_4V_2 and Co_4P_2 are presented in Fig. S9 (ESI†).

To understand the role of vanadium centers in Co_4V_2 , they are also investigated by the XAS and RIXS spectra as shown in Fig. 4. Previous bond valence sum (BVS) calculations¹⁴ revealed that the vanadium centers are in the 5+ oxidation state with empty valence orbitals. Clearly, the spectral shape of transition metal 2p XAS is strongly correlated to the coordination environment and number of 3d electrons of the metal center.⁴⁸ The 2p XAS spectrum of two iso-pseudotetrahedral vanadium centers in Co_4V_2 (in Fig. 2) is, indeed, remarkably similar to $3d^0$ transition metal counterparts in literature,^{36,49–51} which supports the BVS calculation result. We note that vanadium 5+ centers can suffer from soft X-ray induced effects, such as photoreduction that causes the vanadium oxidation state to change to 4+.⁵² In the current work, we compare the XAS spectra measured at ANKA with a defocus mode and the spectra at SPring-8 with the smaller beam size normal mode (Fig. S3, ESI†). Considering the difference in flux density ($\text{photon s}^{-1} \mu\text{m}^2$)³⁷ at the two beamlines and the prominent change of spectral shape, we believe that spectra acquired at SPring-8 include features of vanadium 4+ due to beam induced photoreduction. While it is hard to fully exclude photoreduction effects, the ANKA XAS data in Fig. 4 is dominated by features of the vanadium 5+ ions.

The vanadium sites in Co_4V_2 , unlike the cobalt centers, are highly covalent, where charge transfer effects between oxygen ligand and metal centers are non-negligible. The ground state can be effectively described as a mixture of $3d^0$ and $3d^1\bar{L}$ configurations, where $\bar{L}$ represents a hole in the oxygen ligand 2p band. Note that the $3d^2\bar{L}^2$ configuration is ignored here. Similar configuration mixtures are also present in the intermediate and final states of the 2p3d RIXS process. Within the configuration interaction model, four main peaks (corresponding to excitation energies a–d) in the XAS spectrum have mostly e_g (peak a and c) and t_{2g} (peak b and d) character.^{36,53} For vanadium 5+ ions, the 2p XAS final state has $2p^5 3d^1$ and $2p^5 3d^1\bar{L}$ configurations in which multiplet effects must be taken into account; on the contrary, the initial and final states of the 2p3d RIXS

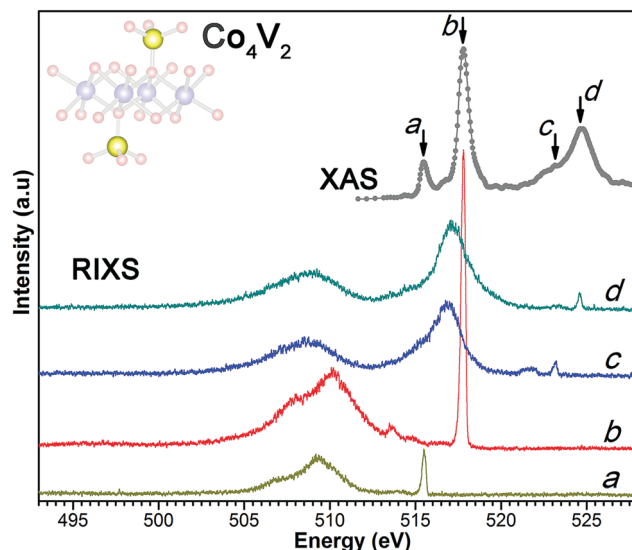


Fig. 4 Experimental vanadium 2p XAS and 2p3d RIXS spectra of Co_4V_2 . Excitation energies a–d of RIXS spectra are indicated by arrows on the XAS spectrum. Inset is the X-ray crystal structure of the tetra-cobalt core $[\text{Co}_4\text{O}_{14}(\text{H}_2\text{O})_2]$ and two $[\text{VO}_4]$ units in ball-and-stick representation. Yellow balls represent vanadium atoms and the faded red and blue balls represent oxygen and cobalt atoms respectively. The XAS spectrum was acquired at ANKA and RIXS spectra were measured at SPring-8.

process have either zero or one electron ($3d^0$, $3d^1\bar{L}$) where multiplet effects are not present. Moreover, the absence of filled 3d states implies the absence of d–d transitions features. Thus, a more transparent observation on the bound electronic states, e.g. charge transfer, of vanadium 5+ is expected from RIXS results than from the XAS spectrum.

For both RIXS spectra acquired with excitation energies a (515.5 eV) and b (517.8 eV) at $2p_{3/2}$ absorption edge, a broad inelastic feature can be observed, with a respective energy transfer maximum of ~ 6.3 eV and ~ 7.5 eV (Fig. 5). Similarly, a shoulder is shown on the lower energy side of each inelastic feature with an emission energy of ~ 507.2 eV and ~ 508 eV, respectively (Fig. 4). When excitation energies move to c

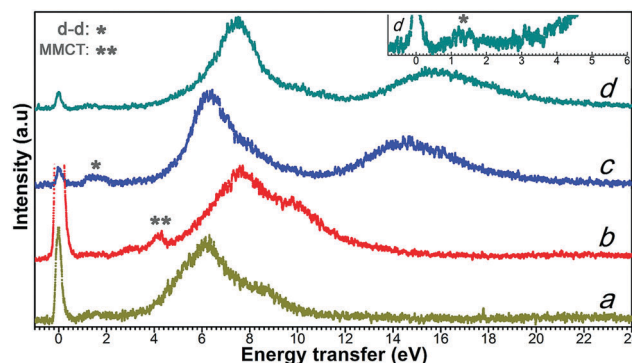


Fig. 5 Vanadium 2p3d RIXS spectra acquired at excitation energies a–d, plotted as the energy transfer spectra. The inset shows the low energy transfer range of the RIXS spectrum acquired at the excitation energy d. One grey asterisk indicates the d–d excitation. Two grey asterisks indicate the MMCT.

(523.1 eV) and d (524.6 eV) at the $2p_{1/2}$ absorption edge, RIXS spectra show prominent double inelastic features. Inelastic peaks: (I) at the lower emission energy (Fig. 4), are between 506 and 512 eV in both spectra, with a ~ 0.2 eV maximum difference; (II) at the lower energy transfer (Fig. 5), are with energy transfer maximum of ~ 6.3 eV and ~ 7.5 eV in spectra c and d, respectively.

In all four RIXS spectra, the inelastic features with energy transfers of ~ 6.3 eV and ~ 7.5 eV correspond to the nonbonding $3d^1\bar{L}$ configuration.⁵³ The 3d states with e_g symmetry are selectively excited to intermediate states with energies a and c, and similarly t_{2g} symmetry with energies b and d. The nonbonding peaks in RIXS spectra c and d are drastically enhanced w.r.t. the elastic peak intensity, when compared to their counterparts in spectra a and b. Similar enhancements and their relaxation mechanism were found in titanium ($4+$, $3d^0$) RIXS spectra of $TiCl_4$ by Hague *et al.*⁵³ With energies c and d, the $2p_{1/2}$ core-level is resonantly excited, and the subsequent Coster–Kronig transition yields the $3d^1c\bar{L}$ and $3d^0c$ configurations (c represents an electron in the continuum). Radiative decay can occur between these two configurations, the emission energy of which may coincide with the energy of nonbonding features. Therefore, the presence of an extra decay channel explains the intensity enhancement of corresponding nonbonding peaks.

The shoulders on the lower energy side of inelastic features in spectra a and b, as well as the lower energy inelastic peaks in both spectra c and d, correspond to the antibonding state. In Fig. 4, it can be seen that all transitions to the antibonding state remain almost at the fixed emission energy. This is because the antibonding state has a broad band-like structure, and decay from the intermediate antibonding state to the final antibonding state maintains symmetry and energies. This makes features corresponding to the antibonding state appear similar to a fluorescence peak with constant emission energy.

Apart from inelastic peaks corresponding to nonbonding and antibonding states, two other inelastic features are also observed in RIXS spectra b and c, with energy transfer 4.2 eV and 1.5 eV, respectively (see Fig. 5). The 1.5 eV inelastic feature, which is conspicuous in spectrum c, also appears in the spectrum d (see the inset in Fig. 5), but at lower intensity. The fact that $2p3d$ RIXS efficaciously probes d–d excitations and 1.5 eV represents a typical ligand field strength of transition metal ions, reasonably suggests this feature to be the result of d–d excitation of vanadium $4+$ ions, a consequence of beam induced photoreduction. While a fast scan mode was used during RIXS acquisitions to minimize the photoreduction effects, beam induced modifications on the sample are difficult to fully eliminate.

Importantly, the observed spectral features most likely arise from vanadium $5+$ ions, the dominant species, while the photoreduced vanadium $4+$ ions contribute only minor components. The observation of the d–d excitation in spectrum c, and less so in the spectrum a and d, but its apparent absence in spectra b is to be expected by referring to the corresponding absorption cross section. A comparison of the XAS spectral shape (in Fig. S3, ESI†) shows the varied absorption cross section ratio between the two components at

these four excitation energies. The vanadium $4+$ ion resonates more at excitation energy c, where the d–d excitation feature is more obvious in the corresponding RIXS spectrum. At excitation energy b, the resonances of vanadium $5+$ ions are most dominant, and in the corresponding RIXS spectrum no evidence of d–d excitations from vanadium $4+$ ions is observed. Therefore, the d–d excitation from photoreduction of vanadium is most visible in the RIXS spectrum c, but still just remains a minor spectral feature. Note that although photoreduction effects in RIXS spectra should be quite different from those shown in XAS spectra due to the different acquisition methods, these effects in RIXS are best judged by comparison to XAS results. In the left panel of Fig. 6, a simplified single-electron schematic representation of vanadium $4+$ d–d excitation in $2p3d$ RIXS processes is shown. A model LFM RIXS calculation result of vanadium $4+$ ions, in which only the single d–d excitation feature can be observed, is shown in Fig. S10 (ESI†). The symmetry of vanadium $4+$ ions in this calculation is assumed to be tetrahedral, without consideration of changes that may occur due to photoreduction.

In addition to the 1.5 eV d–d excitation, another inelastic feature with 4.2 eV energy transfer is clearly seen in the spectrum b, but is absent in the other three spectra. This inelastic feature cannot be due to a d–d excitation because the 4.2 eV value greatly exceeds the ligand field strength of any known transition metal ions. Likewise, it cannot represent charge transfer between oxygen ligand and vanadium metal centers (LMCT), since in that scenario the feature should be observed in all four RIXS spectra. Therefore, the only logical source of this feature is MMCT between cobalt ions and vanadium ions in Co_4V_2 . The MMCT, a.k.a. intersite d–d charge transfer, has been observed in manganese RIXS spectra of manganite⁵⁴ and in titanium RIXS spectra of a $MTiO_3$ series,^{24,25} where M is manganese, iron, cobalt, or nickel. In Co_4V_2 , each vanadium tetrahedron shares one oxygen atom with three cobalt ions in the tetra-cobalt core. The 3d orbitals of cobalt and vanadium can interact *via* the mediation of the hybridized oxygen 2p orbital, promoting charge transfer between cobalt and vanadium ions. The right panel of Fig. 6 shows schematically an energy diagram of the lowest bases of the vanadium initial state, where the state corresponding to the cobalt 3d and vanadium 3d charge transfer (d^6d^1) is located between the bonding and nonbonding states. The spectral intensity of this state, comparing with those

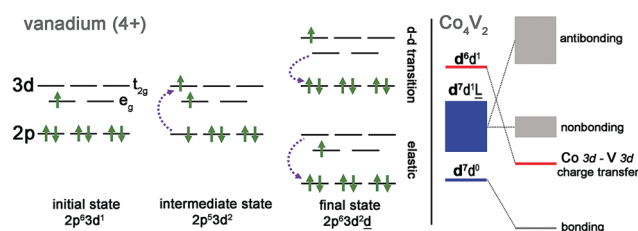


Fig. 6 Left panel: A simplified single-electron schematic representation of $2p3d$ RIXS processes for the vanadium $4+$ ion. Right panel: The energy diagram of lowest bases for the vanadium initial state of Co_4V_2 . The bold d^n and narrow d^m or $d^m\bar{L}$ indicate the cobalt and vanadium configurations, respectively.

of nonbonding and/or antibonding states, is relatively weak due to the indirect nature of the cobalt-to-vanadium charge transfer path *via* the mediator oxygen, while the charge transfer path between ligand oxygen and vanadium is direct. We note that in principle this MMCT peak should also be visible in the cobalt 2p3d RIXS. But the cobalt spectra are dominated by d-d transitions, the MMCT peak is largely hidden. When exciting at energy b, the large absorption cross section gives rise to enhancement of the total RIXS cross section, which allows direct observation of the 3d orbital admixture between cobalt and vanadium centers. At the other three excitation energies (a, c and d), however, other strong transition channels overwhelm and obscure the weak cobalt-to-vanadium charge transfer channel, rendering it invisible in RIXS spectra. Spectroscopic evidence of cobalt-to-vanadium charge transfer in Co_4V_2 , revealed by vanadium 2p3d RIXS spectra, experimentally supports the previous DFT calculated orbital mixture between VO_4 and Co_4O_x .¹⁴

Overall, the results from 2p XAS and 2p3d RIXS spectra indicate that despite being isostructural and possessing heteroatoms with the same oxidation state, there are two notable differences in the electronic structures of Co_4P_2 and Co_4V_2 . First, the smaller ligand field strength of the tetra-cobalt core in Co_4V_2 indicates shorter V–O bonds and correspondingly longer Co–O bonds. The net result of this change is that the cobalt 3d electrons are more localized on the cobalt atoms in Co_4V_2 . Second, an MMCT band observed in Co_4V_2 indicates significant interaction between the cobalt atoms of the catalytic core and the vanadium heteroatom. This MMCT, putatively $\text{V:3d}^0\text{–Co:3d}^7 \rightarrow \text{V:3d}^1\text{–Co:3d}^6$, results in a greater degree of electron delocalization across the tetra-cobalt core than in Co_4P_2 , where no low-lying empty 3d states are available.

Each of the two differences noted above may contribute to the enhanced catalytic activity observed in Co_4V_2 compared to Co_4P_2 . It is generally assumed that the mechanism of water oxidation in many materials, including cobalt-containing polyoxometalates, relies on a proton-coupled electron transfer (PCET) process, whereby the concerted transfer of protons and electrons lowers the energetic barrier to catalytic turnover.⁵⁵ Consequently, the pK_a of the complex is an important parameter in water oxidation, where up to four deprotonation events must likely occur within the catalytic cycle. As 3d electron density is more localized to Co atoms in Co_4V_2 , the associated water ligands will be bound more strongly to the complex, resulting in a higher pK_a for Co_4V_2 than Co_4P_2 . The first pK_a for Co_4P_2 was experimentally determined to be ~ 8 .⁵⁶ The greater O–H bond strength will make the first pK_a a little above the pK_a of Co_4P_2 , assumed to be >8 (as yet unreported, Y. Gueletii, personal communication). The pK_a of Co_4V_2 is therefore within the pH range under which these POMs catalyze the water oxidation. As a result, a small change in the pK_a may have an outsized effect on the overall catalytic rate due to the complex interactions of kinetics and thermodynamics associated with sequential and concerted electron transfer pathways. The nature of PCET within these POMs is a matter of active research, and future investigations will elucidate whether the spectroscopic results

reported herein have a measurable impact on the overall catalytic cycle.

The presence of a cobalt-to-vanadium MMCT band in Co_4V_2 may also be a contributing factor to the difference in catalytic activity. Observation of this band suggests a greater degree of electron delocalization across the tetra-cobalt core. This delocalization can result in a redox levelling effect, reducing the energetic barriers to successive oxidation events. This observation is speculative and consistent with a catalytic mechanism in which the first oxidation has the highest potential and is thus rate-limiting. If later events in the catalytic cycle are rate-limiting then the electronic structures of the oxidized states are most relevant, and inferences made based on the ground state are no longer valid. Nonetheless, a degree of interaction between the tetra-cobalt core and two nearby redox active heteroatoms is likely to influence the electronic structure in all oxidation states, a conclusion supported by recent computational analysis.¹⁷ To verify this hypothesis, an ambitious goal would be to isolate Co_4V_2 at higher oxidation states and evaluate the presence of MMCT bands in their corresponding RIXS spectra. We note that the present high-quality spectroscopic results on the pre-reaction electronic structure of both POMs are limited to address the issue about their different catalytic performances. A full study of the physiochemical differences for these two POMs under catalytic working condition will be definitively required to further understand the catalytic mechanisms.

Conclusion

We use element-specific 2p XAS and 2p3d RIXS spectra to separately investigate the 3d transition metal sites in Co_4P_2 and Co_4V_2 POM WOCs. Differences in the cobalt 3d electronic structures of each tetra-cobalt core are revealed by both XAS and RIXS. High energy resolution 2p3d RIXS results unveil small deviations of the ligand field strength between the two isostructural cobalt cores. From the vanadium 2p XAS and 2p3d RIXS spectra, the oxidation states and ligand field strengths of symmetry-equivalent vanadium centers are obtained. RIXS results effectively show the bound electronic states of vanadium with oxygen ligands and cobalt centers. Spectral evidence of vanadium and cobalt MMCT in Co_4V_2 supports previous theoretical predictions. Such charge transfer between transition metal centers suggests Co_4V_2 has unique redox properties, potentially influencing water oxidation catalysis. In Co_4P_2 , no analogous orbitals or charge transition channels assist redox properties of the tetra-cobalt core. However, we note that the different ground electronic structure of Co_4P_2 and Co_4V_2 , obtained here, are expected to be modified during catalytic reactions; further investigation into the electronic structures of the multiple oxidation states of Co_4V_2 is warranted. The observation of charge transfer between cobalt and vanadium in Co_4V_2 provides insight into the electronic structures of this POM WOC and may lead to a more complete understanding of electron transfer routes related to its enhanced catalytic properties.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work is financially supported by the China Scholarship Council (CSC) and the ERC advanced grant XRAYonACTIVE, number 340279. CLH thanks the DOE, Office of Basic Science, Solar Photochemistry program (grant DE-FG02-07ER15906) for support. The synchrotron radiation experiments at the HORNET end station of BL07LSU of SPring-8 were carried out by the joint research in the Synchrotron Radiation Research Organization and the Institute for Solid State Physics, the University of Tokyo (Proposal No. 2013B7458, 2014A7470). We are grateful to ANKA and to the Karlsruhe Nano Micro Facility (KNMF) for the provision of beamtime. We thank the onsite assistances by Meng-jie Huang, Peter Nagel, and Michael Merz in ANKA, Dr Jun Okamoto in NSRRRC and Dr Jun Miyawaki in SPring-8.

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