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in polyoxovanadate clusters Brittney E. Petel * and Ellen M. Matson * *

Oxygen-atom vacancy formation and reactivity

Reducible metal oxides (RMOs) are widely used materials in heterogeneous catalysis due to their ability to facilitate the conversion of energy-poor substrates to energy-rich chemical fuels and feedstocks. Theoretical investigations have modeled the role of RMOs in catalysis and found they traditionally follow a mechanism in which the generation of oxygen-atom vacancies is crucial for the high activity of these solid supports. However, limited spectroscopic techniques for in situ analysis renders the identification of the reactivity of individual oxygen-atom vacancies on RMOs challenging. These obstacles can be circumvented through the use of homogeneous complexes as molecular models for metal oxides, such as polyoxometalates. Summarized herein, a sub-class of polyoxometalates, polyoxovanadate-alkoxide clusters, $([V_6O_7(OR)_{12}]^n$; R = CH₃, C₂H₅; n = 2-, 1-, 0), are explored as homogeneous molecular models for bulk vanadium oxide. A series of synthetic strategies have been employed to access oxygen-deficient vanadium oxide assemblies, including addition of V(Mes)₃(thf), tertiary phosphanes, and organic acids to plenary Lindqvist motifs. We further detail investigations surrounding the ability of these oxygendeficient sites to mediate reductive transformations such as O_2 and NO_x^{1-} (x = 2, 3) activation.

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Introduction

Reducible metal oxides (RMOs) are materials composed of redox active metal centres (e.g., Ti, V, Fe, Ce) capable of fluctuating between multiple oxidation states. 1-3 These materials are widely used as functional components in

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industrially relevant processes, including energy-based applications, 4-6 biomass conversion to commodity chemicals, 7-9 and in the remediation of environmental contaminants. 10-14 Furthermore, owing to the modular nature of these metal oxides (i.e., tunable atomic composition which influences the chemical, physical, and electronic properties of these materials), these solid supports are



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Dr. Brittney Petel received her bachelor's degree in chemistry at the University of Delaware. She subsequently earned her PhD at the University of Rochester under the supervision of Prof. Ellen Matson. Her thesis focused on the development of vanadium oxide as atomically-precise models for bulk reducible metal oxides. Brittney Petel has earned several awards, including an ACS Women Chemist Committee Travel Award, Eli Huntington Hooker

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Prof. Ellen Matson received her PhD from Purdue University. Following a postdoctoral appointment at the University of Illinois at Urbana-Champaign, Matson began her independent career at the University of Rochester in 2015, where she is currently the Wilmot Assistant Professor of Chemistry. The Matson Laboratory studies the synthesis and reactivity of reduced, organofunctionalized polyoxovanadate clusters. Ellen Matson has earned several awards recognizing

early success in research and teaching, including a Sloan Fellowship, Cottrell Scholar Award, Camille Dreyfus Teaching-Scholar Award and the Edith Flanigen Award.

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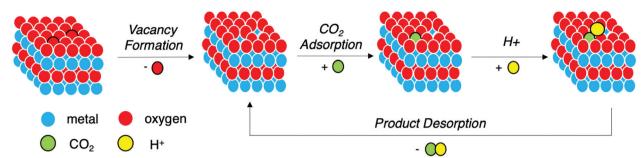


Fig. 1 Illustration of the Mars van Krevelen (MvK) mechanism. Key: O, red; transition metal, blue; CO₂, green; H⁺, yellow.¹⁹

well-established to catalyze various chemical transformations with high turnover numbers and/or selectivity.^{2,15,16}

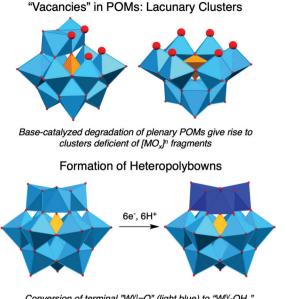
Given the widespread applicability of these extended solids, researchers have become interested in analyzing the reactive components of RMOs. Through this work, oxygen-atom vacancies, located at the surface of the material, have been identified as the active sites in catalysis. 2,17-19 These defects play a central role in the most commonly accepted mechanism for substrate activation with RMOs, the Mars van Krevelen (MvK) mechanism (Fig. 1). 19,20 In 1954, Mars and van Krevelen published a report detailing the oxidation of organic compounds over vanadium(v) oxide (V₂O₅). In this work, the authors noted that in the presence of heat, organic substrates with weak C-H bonds (e.g., anthracene) could be oxidized by the material under inert conditions. The authors invoke oxygen atom transfer (OAT) from the RMO to the substrate, resulting in the formation of an oxygen-deficient site at the surface of the material. Subsequent investigations of the reactivity of these oxygen-atom defects revealed that unsaturated metal cations are able to reduce substrates (e.g., O2, CO2), resulting in restoration of an oxygen atom at the surface of the material. 19,21-24

Certainly, compelling support for the MvK mechanism has been garnered through experimental analysis over the past 60 years. 19,20,25-31 However, it is important to note that these investigations provide only indirect evidence of oxygen-atom vacancy formation. Difficulties in gaining molecular-level insight into the formation and role of single oxygen vacancies using surface analytical techniques makes the in situ identification of these defect sites challenging. 32-38 Thus, to analyse the structural and electronic consequences of creating oxygen-deficient sites on the surface of RMOs during catalysis, researchers have turned to computational investigations, typically involving discreet models (i.e., clusters) to represent small sections of an extended solid. 39-41 These calculations have provided crucial information related to the influence of oxygen atom removal on the electronics of the RMO. For example, theoretical analysis of the oxidation state of vanadium ions within V₂O₅ show that excess charge, generated via V=O bond cleavage, is redistributed throughout the RMO, ultimately resulting in the reduction of neighboring redox-active metal ions (e.g., $V_2^V \rightarrow V^{III}V^V$ (comproportionation) $\rightarrow V_2^{IV}$).

An alternative approach to studying the surface chemistry of metal oxides is through the use homogeneous cluster complexes as molecular models for these materials. In particular, polyoxometalates (POMs) have emerged as promising candidates for modelling extended solids due to their comparmetal oxide surface structure and properties. 42-45 These polynuclear inorganic molecular assemblies are comprised of multiple transition metal oxyanions connected through bridging oxygen atoms, with general formulas of $[M_xO_y]^{n-}$, where M is commonly a high-valent, early-transition metal (e.g., W^{VI}, Mo^{VI}, or V^V). One of the most noteworthy characteristics of these polynuclear assemblies is that their composition and delocalized electronic structure often manifests in rich redox properties. 46,47 Indeed, the electrochemical profile of these polynuclear assemblies have resulted in their applicability in catalysis, 48,49 nanotechnology, 50,51 medicine, 52,53 energy storage, 47,54-57 and materials science. 49,58

Given the similar surface structure and delocalized electronic nature of POMs and metal oxide materials, researchers have targeted an improved understanding of the mechanism of substrate activation at the surface of RMOs via the use of these homogeneous cluster complexes. Extensive studies analyzing the oxidation of organic molecules, catalyzed by a Keggin phosphovanadomolybdate cluster (e.g., $[PV_2Mo_{10}O_{40}]^{5-}$), reveals a noteworthy resemblance to the proposed oxidative MvK mechanism. These seminal contributions have revealed that these reactions likely proceed through OAT from the surface of the cluster to the substrate. 59-67 Additional support of a POM-mediated MvK-type mechanism was garnered from theoretical calculations which revealed that the overall free energy of OAT from the heteropolyanion to the organic substrate is energetically favorable (i.e., $\Delta G_{298,Anthrancene}$ = -17.1 kcal mol⁻¹).⁶¹ However, to date, isolation and characterization of the expected oxygen-deficient clustercontaining product, complex [PV2Mo10O39]ⁿ⁻, remains elusive.

Despite the established OAT reactivity of POMs, there is relatively few examples of isolated clusters with surface oxygenatom defects. This is mainly credited to the difficulties in controlling the metal-to-oxygen ratios within self-assembled POMs, as well as the lack of literature featuring methods for the post-synthetic oxygen-atom abstraction from these discreet metal oxide assemblies. Indeed, "vacancy formation" in POMs has traditionally been relegated to the removal of entire $[MO_x]^n$ subunits (Fig. 2, top). 45,68 Prior to our studies, only a single example of an "oxygen-deficient" POM had been reported;



Conversion of terminal "WVI=O" (light blue) to "WIV-OH2" (dark blue) mediated by proton coupled electron transfer

Fig. 2 "Vacancies" in polyoxometalate research. Lacunary clusters derived from the addition of base to plenary motifs, picture are the mono-(top, left) and tri- (top, right) lacunary assemblies of the Keggin ion; the vacant site(s) in lacunary structures are highlighted by large spherical oxygen atoms (red). The 6 e⁻ reduction of the Keggin ion in the presence of acid results in the formation of three metal-aqua moieties at the surface of the polyoxotungstate (bottom). Light blue polyhedral: W^{VI} ; dark blue polyhedral: W^{IV}; red spheres: oxygen; orange polyhedral: Si.^{69,70}

Pope and Pipegrass found that cluster reduction was possible following the proton-assisted reduction of the Keggin ion, [SiW₁₂O₄₀]⁶⁻.69,70 Labelling studies confirmed that these reductive conditions resulted in the conversion of three tungsten(vi)oxo moieties to three tungsten(IV)-aqua species at the surface of the metal oxide core (Fig. 2, bottom).

To further extend our understanding of oxygen atom vacancy formation in POMs, our research group has been investigating defect formation via post synthetic modification of a unique class of these metal oxide assemblies, namely

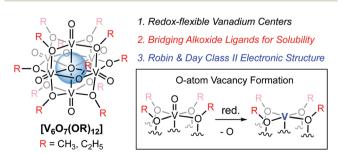


Fig. 3 Polyoxovanadate-alkoxide (POV-alkoxide) clusters as models for surface reactivity of metal oxides. Oxygen-atom vacancy formation is observed at vanadyl sites within the Lindqvist assembly upon addition of stochiometric reductant or acid. POV-alkoxide clusters serve as excellent models for this transformation due to their physicochemical properties. Figure reprinted with permission from B. E. Petel, et al., Inorg. Chem. 2019, 58, 10462-10471. Copyright 2019 American Chemical Society.

Lindqvist-type polyoxovanadate-alkoxide (POV-alkoxide) clusters $([V_6O_7(OR)_{12}]^n$; Fig. 3).⁷¹⁻⁷³ We have found that the structural composition and tunable electronic properties of these alkoxovanadium clusters makes them promising molecular candidates for studying the formation of surface defects in RMOs. These vanadium oxide assemblies have fewer sites available for reduction in comparison to the surface of bulk materials (i.e., only six terminal vanadyl ions, surrounded by inaccessible alkoxide-bridged moieties), presenting a more controlled system that allows for the unambiguous determination of the consequences of removal of a terminal oxido ligand from the surface of the cluster. Furthermore, the bridging alkoxide ligands increase the solubility of these clusters in organic solvents, and provide the opportunity to use homogeneous spectroscopic handles for probing defect formation on these model complexes (e.g., ¹H NMR spectroscopy).

It is important to note that while there are similarities between POV-alkoxides and bulk vanadium oxide systems, variations in the physical and chemical properties of these clusters and their heterogeneous congeners limits our ability to directly compare the two systems. For example, while the introduction of bridging alkoxide moieties aids in the selfassembly and solubility of our POV-alkoxide clusters, V_xO_y materials typically lack surface ligands. 40,74 Furthermore, significant variation of the electronic structure of POMs and RMOs (i.e., discreet frontier orbitals and continuum of states, respectively) challenges the ability to electronically compare the clusters and extended solids. 72,75,76 Nonetheless, the molecular composition has driven our laboratory to investigate these molecular clusters as models for extended solids.

This feature article summarizes our efforts to understand OAT in polyoxovanadate assemblies, in an attempt to model the surface reactivity of RMOs. Beginning with the initial step of the MvK mechanism (i.e., oxygen-atom vacancy generation), we outline synthetic methodologies toward isolating reduced POV-alkoxide clusters via V=O bond cleavage.77-80 These investigations have resulted in the isolation of a family of oxygen-deficient polyoxometalate clusters, namely [V6O6 $(OR)_{12}$ ⁿ $(n = -1, 0, 1+; R = CH_3, C_2H_5)$ and $[V_6O_5(OCH_3)_{12}]^0$. Notably, characterization of the resultant clusters show similar structural and electronic perturbations to that of oxygendeficient vanadium oxides (e.g., V2O5, VO2). Next, a summary of the exploration of these metal oxide surrogates as functional models for the extended solids is presented, revealing that the oxygen-deficient clusters are capable of mediating small molecule activation (e.g., O_2 and NO_x^{1-} ; x = 2, 3). 77,81,82

Metal oxygen bond cleavage on Lindqvist POV-alkoxides using V(Mes)₃(thf)

Synthesis of oxygen-deficient vanadium oxide clusters

With the ultimate goal of using POV-alkoxides to analyse the consequence of vacancy formation on metal oxide surfaces, the discovery of synthetic methods to access oxygen-deficient

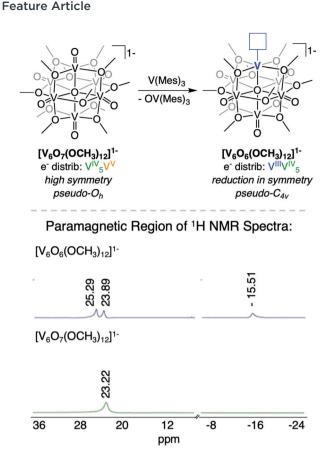


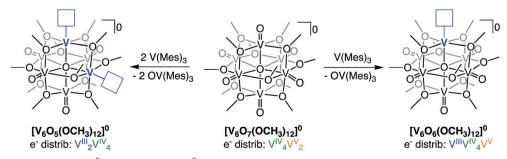
Fig. 4 Top, synthesis of oxygen-deficient POV-alkoxide cluster. Bottom, paramagnetic region of ¹H NMR spectra of fully-oxygenated POV-alkoxide cluster (bottom, green) and mono-vacant cluster (top, blue) in CD₃CN. Figure reprinted with permission from B. E. Petel, et al., J. Am. Chem. Soc. 2018, 140, 8424-8428. Copyright 2018 American Chemical Society.

vanadium oxide assemblies was required. As such, we began our investigations by targeting vacancy generation on the homometallic, Lindqvist POV-alkoxide cluster, $[V_6O_7(OCH_3)_{12}]^{1-.77}$ We hypothesized that addition of $V(Mes)_3(thf)$ (Mes = 2,4,6-trimethylphenyl), a potent reductant and OAT reagent, 83 to $[V_6O_7(OCH_3)_{12}]^{1-}$ might promote V=O bond cleavage and result in the formation of a cluster bearing a single oxygen-deficient site. Indeed, addition of V(Mes)₃(thf) to the fully oxygenated cluster resulted in an immediate color change from green to brown/yellow (Fig. 4, top).

Given the aforementioned solubility of these POV-alkoxides in organic solvents, ¹H NMR spectroscopy has proven to be an exceptional tool for analyzing modifications to the cluster surface. The parent, fully-oxygenated cluster has a single, broad resonance located at ~ 23 ppm in acetronitrile- d_3 (CD₃CN), corresponding to the protons of the twelve, symmetryequivalent methoxide ligands of the hexavanadate cluster (Fig. 4, bottom). However, removal of a single oxygen atom from the surface of the cluster lowers its symmetry from pseudo- O_h to pseudo- C_{4v} , yielding a spectrum with three resonances (δ (CD₃CN) = 25.3, 23.9, -15.5 ppm). Further analysis of the cluster containing product by electrospray ionization mass spectrometry (ESI-MS; (-)ve mode, carrier solvent: MeOH) revealed formation of a new parent ion with a mass-to-charge ratio (m/z) consistent with the molecular weight of an oxygendeficient POV-alkoxide cluster, $[V_6O_6(OCH_3)_{12}]^{1-}$, plus an equivalent of methanol.

Characterization of $[V_6O_6(OCH_3)_{12}]^{1-}$ by electronic absorption spectroscopy presented crucial electronic information toward understanding the change in vanadium oxidation state distribution following OAT. The absorption spectra of the mixed-valent parent POV-alkoxide complex (ox. state distribution: V^{IV}₅V^V) features two intervalence charge transfer (IVCT) bands located 398 nm (ε = 3542 M⁻¹ cm⁻¹) and 1000 nm $(\varepsilon = 814 \text{ M}^{-1} \text{ cm}^{-1})$; these features are indicative of charge transfer between V^{IV} (d¹) and V^V (d⁰) metal centres within the Lindqvist core.⁷³ However, following oxygen-atom abstraction, these absorption features disappear, suggesting reduction of the V^V ion to V^{III} (ox. state distribution: V^{III}V^{IV}₅). Notably, the change in the oxidation state of vanadyl ions within the reduced POV-alkoxide cluster is similar to the theorized electronic consequences of oxygen-atom vacancy formation in V_2O_5 . 39-41

The change in the oxidation state distribution between the parent and mono-vacant clusters (i.e., $V^V \rightarrow V^{III}$) suggested that the availability of do vanadyl ions is crucial for the POV-alkoxide to undergo this two-electron redox reaction. Indeed, the reduction of VIV ions embedded within the POValkoxide is unlikely as no reports, to date, feature an electronrich VII ion within a POM. As such, we hypothesized that repeating this reaction with the parent POV-alkoxide cluster in its neutral charge-state, $[V_6O_7(OCH_3)_{12}]^0$ (ox. state distribution: V^{IV}₄V^V₂), would afford an additional site for OAT, ultimately resulting in the ability to form up to two oxygen



Scheme 1 Synthesis of $[V_6O_5(OCH_3)_{12}]^0$ and $[V_6O_6(OCH_3)_{12}]^0$.

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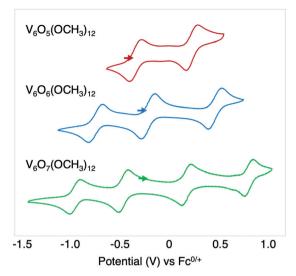


Fig. 5 Cyclic voltammograms of fully-oxygenated (bottom, green), mono-vacant (middle, blue), and di-vacant (top, red) POV-alkoxide clusters. CV collected in dichloromethane with 0.1 M [^Bu₄N][PF₆] as supporting electrolyte.⁷⁹

vacancies. Through manipulating the equivalence of reductant added [i.e., 1-2 equiv. V(Mes)₃(thf)], we were able to control the metal-to-oxygen ratio within the cluster, isolating a neutral, mono- and di-vacant POV-alkoxide cluster, [V₆O₆(OCH₃)₁₂]⁰ $(V^{III}V^{IV}_{4}V^{V})$ and $[V_{6}O_{5}(OCH_{3})_{12}]^{0}$ $(V^{III}_{2}V^{IV}_{4})$, respectively (Scheme 1).79

Striking changes in the electrochemical profiles of the resultant oxygen-deficient POV-alkoxide clusters were observed via cyclic voltammetry (CV; Fig. 5). The CV of the parent, fullyoxygenated Lindqvist POV-alkoxide cluster, $[V_6O_7(OCH_3)_{12}]^0$, features four, quasi-reversible, one-electron redox events, located at +0.83, +0.20, -0.40, and -0.93 V in dichloromethane (vs. $Fc^{0/+}$).⁷² These redox processes encompass five redoxmers of the vanadium oxide assembly, ranging from the di-anionic (ox. state distribution: V_6^{IV}) to di-cationic (ox. state distribution: VIV2V4) charge-states. However, the CV of the mono-vacant cluster, [V₆O₆(OCH₃)₁₂]⁰, only possesses three quasi-reversible redox events ($E_{1/2} = -0.70$, -0.16, and 0.52 V vs. Fc^{0/+} in DCM), assigned to sequential oxidation of vanadyl ions.⁷⁹ A fourth, irreversible redox event was observed at $E_{\rm p,a}$ = +1.16 V, suggesting that vacancy formation translates to oxidative instability of the POV at high potentials.

Similar perturbations were observed in the voltammogram of the di-vacant cluster; in this case, the removal of a second oxygen-atom results in the retention of only two quasireversible redox events. We hypothesize that these electronic changes are due to the decoupled nature of the resultant VIII ions within the POV-alkoxide, which limits electron transfer to the remaining VIV/VV vanadyl ions within the oxygen-vacant POVs (i.e., only 5 and 4 vanadium ions able to participate in electron transfer in $[V_6O_6(OCH_3)_{12}]^0$ and $[V_6O_5(OCH_3)_{12}]^0$, respectively).

Structural characterization of oxygen-deficient POV-alkoxides

With electronic evidence supporting the formation of $[V_6O_6(OCH_3)_{12}]^n$ (n = 1-, 0) and $[V_6O_5(OCH_3)_{12}]^0$ in hand, we next set out to investigate the structural influence of O-atom removal from the POV-alkoxide surface via singlecrystal X-ray diffraction (SCXRD; Fig. 6 and Table 1). In addition to unambiguously confirming the formation of the oxygen-deficient species, SCXRD can provide insight into the structural perturbations that occur across the Lindqvist framework upon defect formation. Furthermore, the growth of crystals with site-differentiated metal ions can provide insight into the valency of the vanadium ions that compose the cluster core via bond valence sum (BVS) calculations. 71,84 Such investigations would provide atomic-level insight into the structural and electronic consequences of vacancy formation in metal oxides; analyses that accentuate the value of using homogeneous inorganic complexes to model heterogenous metal oxides.

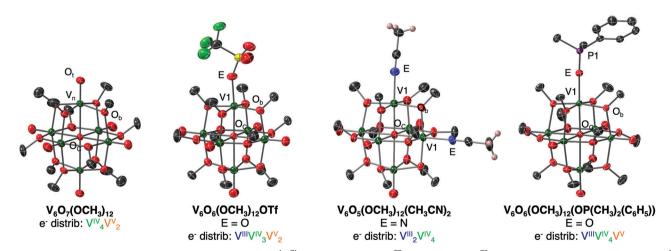


Fig. 6 Molecular structures of complexes $[V_6O_7(OCH_3)_{12}]^{1-,71}$ $[V_6O_6(OCH_3)_{12}]OTf_1$, $[V_6O_5(OCH_3)_{12}]OTf_2$ and $[V_6O_6(OCH_3)_{12}(OP(CH_3))_2(OP(CH_3))_2]OTf_3$. Structures are depicted with 30% probability ellipsoids. Hydrogen atoms, counter ions and solvent molecules have been omitted for clarity. Key: O, red; V, dark green; C, grey; S, yellow; F, light green; N, blue; P, purple; H, pink.

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[V₆O₆(OCH₃)₁₂]OTf,⁷⁷ [V₆O₅(OCH₃)₁₂]^{0,79} $[V_6O_6(OCH_3)_{12}(OP(CH_3)_3)]^{0,78}$ $[V_6O_7(OCH_3)_{12}]^{1-71}$ 1 Structural parameters $[V_6O_6(OCH_3)_{12}(OP(CH_3))_2(C_6H_5)]^{0.78}$

	Compound						
Bond	V ₆ O ₇ (OCH ₃) ₁₂ ⁷	$[V_6O_6(OCH_3)_{12}]OTf^{77}$ [E=O)	$V_6O_5(OCH_3)_{12}(CH_3CN)_2^{79}$ (E=N)	$V_6O_6(OCH_3)_{12}(OP(CH_3)_3)^{78} \ (E=O)$	$V_6O_6(OCH_3)_{12}$ $(OP(CH_3)_2(C_6H_5))^{78}$ (E=O)		
V1-E	_	2.052(8) Å	2.112(2) Å, 2.104(3) Å	2.062(5) Å	2.0403(19) Å		
$V1-O_c$	_	2.079(4) Å	2.0666(17) Å, 2.0760(17) Å	2.120(5) Å	2.0982(17) Å		
O1-P1	_	_ ` `	_	1.467(6) Å	1.5032(19) Å		
$V1-O_b-V_n$	_	105°	105°	105.1°	105.3°		
V1-O _b -V1	_	_	96.9°	_	_		
V_n - O_c (avg.)	2.25 Å	2.32 Å	2.37 Å	2.31 Å	2.32 Å		
V_n -O _t (avg.)	1.60 Å	1.59 Å	1.61 Å	1.59 Å	1.60 Å		
V_n -O _b - V_n (avg.)	110°	_	_	_	_		

Key: V1 = apical V^{III} centre; O_c = central μ^6 -oxygen atom; O_t = terminal oxygen atom of the vanadyl moieties; V_n = vanadium centres, n = 2-5; O_b = oxygen atom of the bridging methoxide ligands.

To analyse these new oxygen-deficient complexes by SCXRD, we explored crystallization methods toward growing crystals suitable for X-ray analysis.⁷⁷ Unfortunately, all crystallization attempts of the monoanionic and neutral, mono-vacant clusters, $\left[V_6O_6(OCH_3)_{12}\right]^{1-}$ and $\left[V_6O_6(OCH_3)_{12}\right]^0$, respectively, resulted in significant disorder within the unit cell, presenting challenges in performing the desired bond metric analyses. Thus, to modify the mode of crystallization of the POValkoxide, we oxidized complex $[V_6O_6(OCH_3)_{12}]^{1-}$ with silver triflate, resulting in formation of the triflate-bound POV-alkoxide, $[V_6O_6(OCH_3)_{12}]OTf$. The use of this weakly coordinating anion presented an opportunity to have a large functional group bind to the electron-rich vanadium(III) ion, reducing the overall symmetry of the unit cell. Indeed, crystals that featured site-differentiated vanadyl ions were obtained via cooling methanolic solutions of the cluster to -35 °C, permitting bond metric analyses.

Significant changes in V-O bond lengths and V-O-V bond angles were observed; removal of a surface oxygen atom resulted in a shortened V1-O_c (O_c = central μ_6 -oxygen atom) bond length and truncated V1– O_b – V_n (O_b = bridging methoxide oxygen atom; n = 2, 3, 4, 5) bond angles, relative to that of the

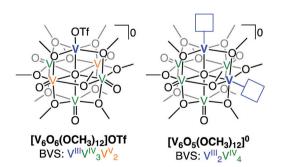


Fig. 7 Bond valence sum (BVS) calculations for the crystallographically independent vanadium ions in $[V_6O_6(OCH_3)_{12}]OTf$ (left)⁷⁷ and $[V_6O_5(OCH_3)_{12}]OTf$ $(OCH_3)_{12}$ $]^0$ (right). ⁷⁹ BVS calculated using eqn (1) and (2), where R_0 = 1.762 (V^{III} -O), 1.770 (V^{IV} -O) and 1.791 (V^{V} -O), and where N = 5.1 (V^{III}) or 5.2 (V^{IV}, V^V).

parent, fully-oxygenated metal oxide cluster (Fig. 6 and Table 1).⁷¹ Taken together, these structural variations between the parent and oxygen-deficient POV-alkoxides reveal that the reduced vanadium ion is pulled toward the centre of the cluster in the oxygen-deficient assemblies.

Similar structural perturbations have been predicted for O-atom removal from the surface of vanadium(v) oxide. Using density functional theory (DFT), Hermann and coworkers found that generation of vacant sites on V2O5 results in a substantial reorganization of vanadium ions within the lattice.³⁹⁻⁴¹ Ultimately, these structural changes are predicted to result in the formation of new V-O-V linkages throughout the extended solid which are hypothesized to stabilize the oxygen-deficient metal oxide. While the geometry of vanadyl ions within vanadium(v) oxide is clearly different from that of the Lindqvist cluster (i.e., V_2O_5 , square pyramidal; $V_6O_7(OCH_3)_{12}$, octahedral), the similar movement of the reduced vanadium(III) ion presents further evidence that these vanadium oxide clusters are reasonable models for that of the nanocrystalline material.

Analysis of the molecular structure of the di-vacant species revealed that the two oxygen-deficient sites are located on adjacent vanadium ions within the Lindqvist core (Fig. 6).⁷⁹ The sole formation of the *cis*-isomer of $[V_6O_5(OCH_3)_{12}]^0$ is likely a result of the structural perturbations observed upon O-atom removal. Similar to the changes observed in bond metric analyses of the triflate-bound species described above, the VIII (V1) ions within the di-vacant cluster are pulled toward the central, μ₆-oxygen atom, manifesting in decreased V1-O_c bond lengths and V1-O- V_n bond angles. Indeed, while the transisomer could form following the second O-atom abstraction, the subsequent 0.2 Å truncation of trans-V-O_c moieties would result in greater structural perturbations relative to that of the cis-vacant molecule, destabilizing the assembly.

the X-ray data for $[V_6O_6(OCH_3)_{12}]OTf$ and [V₆O₅(OCH₃)₁₂]⁰ in hand, we next turned our attention to analyzing the oxidation state of vanadyl ions within the hexanuclear core via BVS calculations. 84-86 According to this valence

sum rule, the valence of a metal ion can be calculated by summation of the individual bond valences surrounding the atom (eqn (1) and (2)):

$$Valence = \sum v_{ij}$$
 (1)

$$v_{ij} = \left(\frac{R_{ij}}{R_0}\right)^{-N} \tag{2}$$

where v_{ii} is the individual bond valencies, R_0 , 85 and N^{85} are calculated parameters for the ideal bond length of M^n -E bonds $(M^n = metal \ of 'n' \ charge \ state, E = element) \ and \ R_{ij} \ is \ the$ experimentally determined bond length(s) in Angstroms (Å). The BVS calculations of complex [V₆O₆(OCH₃)₁₂OTf] indicate an overall oxidization state distribution of V^{III}V^{IV}₃V^V₂ (Fig. 7).⁷⁷ These results not only confirm that O-atom removal results in the two-electron reduction of a VV ion within the parent POV-alkoxide cluster, but also reveals that the electron-rich V^{III} ion retains its trivalent oxidation state upon oxidation. The retention of the VIII ion confirms that the apical vanadium ion is decoupled from the remainder of the V=O moieties within the Lindqvist core, as a completely delocalized metal oxide cluster would likely result in comproportionation between V^V and VIII ions. Notably, DFT calculations describing the electronic perturbations of vacancy generation on V2O5 suggest that comproportionation of a VV=O moiety neighboring the reduced VIII ion results in the formation of a VIV-O-VIV linkage. 39-41 These results showcase the electronic differences between the Lindqvist cluster and V2O5. Similar electronic perturbations were observed in the BVS calculations of the divacant complex, which show that the two d⁰ vanadyl ions were reduced by two-electrons, resulting in an overall oxidation state distribution of VIII2VIV4.79

Alternative methods for oxygen-atom vacancy formation in POV-alkoxides

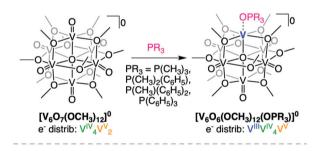
Oxygen-atom transfer to tertiary phosphanes

Tertiary phosphanes (PR₃; R = aliphatic, aromatic) have been demonstrated to efficiently remove oxygen atoms from a variety of transition metal-oxo complexes via OAT.87-94 The prevalent application of phosphanes as oxygen-atom acceptors is credited to the strong P=O bond generated following OAT (e.g., $(CH_3)_3PO$; 139 kcal mol⁻¹, $(C_6H_5)_3PO$; 127 kcal mol⁻¹). 95 As such, we began our efforts toward probing OAT from POV-alkoxide clusters to phosphanes by adding trimethylphosphine $(P(CH_3)_3)$ to complex $[V_6O_7(OCH_3)_{12}]^{1-}$. We posed that in analogy to the OAT chemistry observed with V(Mes)₃(thf), OAT to the phosphane would result in the formation of the previously reported oxygen-deficient POV-alkoxide cluster. Unfortunately, despite exhaustive modifications to the experimental conditions, no reactivity was observed between the monoanionic, fully-oxygenated cluster and P(CH₃)₃. We justified this observation by the fact that the reduced character of the complex requires a more potent reductant for successful OAT. Thus, we turned our attention to the reactivity of P(CH₃)₃

with the more-oxidized, neutral POV-alkoxide cluster, $[V_6O_7(OCH_3)_{12}]^{0.78}$

Addition of excess P(CH₃)₃ to [V₆O₇(OCH₃)₁₂]⁰ resulted in complete consumption of the fully-oxygenated cluster after 19 hours at 70 °C (Fig. 8, top). Analysis of the resultant reaction mixture by ¹H NMR and electronic absorption did not match that of the previously isolated monovacant cluster.⁷⁹ Although the ¹H NMR spectra of the product of $[V_6O_7(OCH_3)_{12}]^0$ and P(CH₃)₃ was comprised of three paramagnetically shifted and broadened signals, consistent with the expected reduction of cluster symmetry (i.e., pseudo- O_h to pseudo- C_{4v}), the resonances obtained were shifted from those expected for $[V_6O_6(OCH_3)_{12}]^0$ (Fig. 8, bottom). We hypothesized that these inconsistencies were a result of coordination of the byproduct of the reaction, OP(CH₃)₃, to the oxygen-deficient site of the reduced POV-alkoxide (i.e., $[V_6O_6(OCH_3)_{12}(OP(CH_3))_3]^0$).

Crystals suitable for SCXRD unambiguously confirmed that the trimethylphosphine oxide byproduct was indeed coordinated to the site-differentiated VIII ion (Table 1). Similar to that observed in $[V_6O_6(OCH_3)_{12}]OTf$ and $[V_6O_5(OCH_3)_{12}]^0$, the V1-O_c bond length was decreased by ~ 0.2 Å. Furthermore, the V1–O1 bond in [V₆O₆(OCH₃)₁₂(OP(CH₃)₃)] was significantly lengthened in comparison to the average V=Ot bond length within the parent cluster.⁷¹ This lengthened V1-O1 bond, coupled to the



Paramagnetic Region of ¹H NMR Spectra:

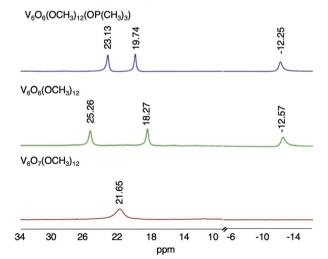


Fig. 8 Top, reduction of POV-methoxide cluster with P(CH₃)₃. Bottom, paramagnetic region of ¹H NMR spectra of fully-oxygenated POV-alkoxide cluster (red), mono-vacant cluster (green), and phosphine oxide-bound cluster (blue) in CD₃CN.⁷⁸

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Table 2 Relationship between phosphane nucleophilicity (pKa or an electronic parameter derived from $\nu(CO)$ of a nickel compound), cone angle, and reaction time for formation of all (OPR3)-bound clusters^a

	P(CH ₃) ₃	P(CH ₃) ₂ (C ₆ H ₅)	$P(CH_3)(C_6H_5)_2$	P(C ₆ H ₅) ₃
pK _a ⁹⁹	8.65	6.50	4.59	2.73
Electronic	2064.1	2065.3	2067.0	2068.9
parameter ¹⁰⁰				
Tolman Cone Angle ¹⁰⁰	118	122	136	145
Reaction time	19 h	7 h ^b	28 h	15 days
$[V_6O_7(OCH_3)_{12}]^0$				
Reaction time	4 days	4 days	>20 days	_
$[V_6O_7(OC_2H_5)_{12}]^0$	·	•	•	

 $[^]a$ General reaction conditions: 1 equiv. [V₆O₇(OCH $_3$)₁₂], 4 equiv. phosphane, 70 °C. b Only 2 equiv. P(CH $_3$)₂(C₆H $_5$) used. 78

similar P=O bond distances of free (1.48 Å, theoretically determined⁹⁶) and coordinated (1.467(6) Å) OP(CH₃)₃ in complex $[V_6O_6(OCH_3)_{12}(OP(CH_3)_3)]^0$ offered support for a dative interaction between the reduced VIII centre and the resultant phosphine oxide moiety. The oxidation state distribution of vanadyl ions within the product was analysed via BVS calculations, revealing the expected mixed-valent distribution for a neutral, oxygen-deficient cluster, VIIIVIV VV.

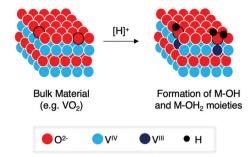
Previous investigations of the influence of phosphane identity on OAT with inorganic metal-oxo complexes have revealed that alteration of the phosphane nucleophilicity and/or cone angle can significantly affect the rate of these reductive transformations. 87,97-101 To investigate this phenomenon with POV-alkoxide clusters, a series of phosphanes, ranging in nucleophilicity and cone angle (i.e., P(CH₃)₂(C₆H₅), P(CH₃) $(C_6H_5)_2$, $P(C_6H_5)_3$, were added to $[V_6O_7(OCH_3)_{12}]^0$ (Table 2). In each case, phosphane addition resulted in formation of a mono-vacant POV-methoxide cluster with a dativelycoordinated phosphine oxide ligand. However, qualitative analysis of the reaction rate showed that the rate of OAT was significantly influenced by the identity of the phosphane. More nucleophilic phosphanes, which also have smaller cone angles, (i.e., P(CH₃)₃, P(CH₃)₂(C₆H₅)) facilitated OAT in less than 24 h, whereas the larger, less nucleophilic phosphanes, such as P(C₆H₅)₃, took significantly longer for complete consumption of $[V_6O_7(OCH_3)_{12}]^0$ (e.g., 15 days; Table 2). These results suggest that the sterics and/or basicity of PR3 significantly influence OAT from the surface of the cluster.

In an effort to decouple the steric and electronic influences of OAT to PR3, we extended our investigations to Lindqvist architectures with longer bridging alkoxide ligands. Previously, it has been demonstrated that an increased alkoxide chain length of bridging oxides within the vanadium oxide assembly has no effect on the electronic structure of the hexavanadate core. 72,76,102 This suggests that similar OAT between the series of phosphanes and the neutral POV-ethoxide cluster, [V₆O₇ $(OC_2H_5)_{12}]^0$ (ox. state distribution: $V^{IV}_4V^V_2$), would be observed, providing a method to solely examine the correlation between sterics and OAT.

We initiated these efforts by investigating the reactivity of $P(CH_3)_3$ and $P(CH_3)_2(C_6H_5)$ with $[V_6O_7(OC_2H_5)_{12}]^{0.78}$ While

Acid-induced Metal Oxide Reduction

Electron Proton Co-Doping



Vacancy Formation on POV-ethoxide Cluster via **Addition of Organic Acids**

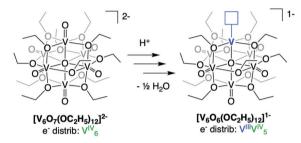


Fig. 9 Schematic representation of proton-induced activation on a metal oxide surface (top) and the comparable reactivity observed in POV-alkoxide clusters (bottom).80

complete OAT was indeed possible from the POV-ethoxide cluster to the more nucleophilic phosphanes, the increased steric bulk surrounding the vanadyl moieties resulted in a 4-fold increase in reaction time in comparison to the POV-methoxide analogues (Table 2). Furthermore, attempts to deoxygenate complex $[V_6O_7(OC_2H_5)_{12}]^0$ with more sterically encumbered phosphanes (i.e., $P(CH_3)(C_6H_5)_2$, $P(C_6H_5)_3$) resulted in limited OAT after prolonged heating (>2 weeks at 70 °C).

Acid-induced oxygen-atom vacancy formation

Interested in developing a "green" route for oxygen-atom vacancy formation at the surface of POV-alkoxide clusters, we next turned our attention to the reactivity of $[V_6O_7(OR)_{12}]^n$ with organic acids.80 Inspiration for these studies was derived from reports describing the electron-proton co-doping mechanism of surface activation of bulk VO2 (Fig. 9). 103,104 In these reports, formation of low valent vanadium centres were observed upon addition of electrons and protons to the material. While there is debate as to the location of these reduced ions within the material, the authors cite that reduction of the bond order of vanadium oxygen bonds via formation of hydroxyl and aqua ligands within the material.

To model the surface reactivity of VO2 with acid, we explored stochiometric reactions of our POV-alkoxide cluster in its mostreduced charge state with an organic acid.80 Following addition of triethylammonium tetrafluoroborate ([HNEt3]BF4, 1 equiv.) to the dianionic POV-ethoxide cluster, $[V_6O_7(OC_2H_5)_{12}]^{2-}$ (1 equiv.),

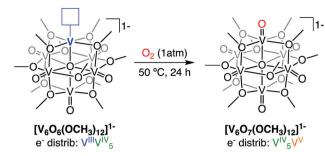
analysis of the crude reaction mixture by ¹H NMR spectroscopy revealed a series of resonances consistent with the formation of a mixture of products. Signals located at 26.07 and -2.00 ppm correspond to the protons of the bridging ethoxide moieties of the previously reported, monoanionic, POV-ethoxide cluster, [V₆O₇(OC₂H₅)₁₂]^{1-.76} The remaining paramagnetically shifted and broadened resonances, ($\delta = 29.56, 28.53, -1.30, -2.56,$ and -25.66 ppm) suggested formation of an oxygen-deficient organofunctionalized POV cluster, $[V_6O_6(OC_2H_5)_{12}]^{1-}$. The identity of this product was confirmed through independent synthesis of the monoanionic, oxygen-deficient assembly via reduction of the previously reported complex, [V₆O₆ $(OC_2H_5)_{12}^{0.78}$

The formation of an oxygen-deficient metal oxide assembly upon addition of acid is a rare observation in POM chemistry. Studies focused on interactions between POMs and protons typically involve acidification of an aqueous solution containing the polyoxoanion; results have predominantly shown cation exchange processes, yielding metal oxide assemblies with one or more protonated bridging oxido ligands. 105-109 This disparate reactivity of plenary POM motifs is likely due to the fact that these clusters are composed of metal centres with do electronic configurations (e.g., WVI, MoVI, VV, TaV, and Nb^V). In contrast the reduced POV-alkoxide possesses six, d¹ V^{IV} ions that provide electron density for proton reduction.

The reactivity of $[V_6O_7(OC_2H_5)_{12}]^{2-}$ with acid more aptly resembles the reported synthesis of reduced, "heteropolybrown" polyoxotungstate architectures, originally reported by Launay and coworkers (Fig. 2, bottom). 110-112 In this study, the authors propose that the six-electron reduction of the polyoxotungstate Keggin ion, $[(H_2)W_{12}O_{40}]^{6-}$, via controlled potential electrolysis under acidic conditions, results in the reduction of three terminal WVI=O moieties to WIV-OH2 groups.69 In a subsequent article, Piepgrass and Pope spectroscopically confirm the proposed structural configuration. 113

Small molecule activation by oxygendeficient POV-alkoxides

Computational investigations on RMO-catalyzed OAT processes have determined that substrate-surface interactions can enable the formation of deoxygenated products though multi-electron redox reactions at defect sites within bulk materials.²⁴ However, challenges in monitoring reaction progress using current in situ or in operando analytical techniques have hampered our understanding of the structural and electronic perturbations of RMO surfaces during heterogeneous OAT transformations.32-38 As such, with the aforementioned strategies in hand for oxygenatom removal from the surface of POV-alkoxide clusters, we turned our attention to the reactivity of the defect sites in these molecular assemblies. In this section, we explore the mediation of small molecule (e.g., O_2 , ⁷⁷ NO_x^{1-} ; x = 2, $3^{81,82}$) activation with oxygen-deficient POV-alkoxide clusters. Overall, the capability of the mono-vacant POV-alkoxide clusters to facilitate substrate coordination and activation confirms that Lindqvist metal



Scheme 2 Reactivity of [V₆O₆(OCH₃)₁₂]¹⁻ with O₂

oxide cluster complexes can serve as a functional model for RMO-catalyzed MvK transformations.

Dioxygen reduction with oxygen-deficient POV-alkoxide clusters

The reduction of O2 is an important step in heterogenous catalysis. 114,115 Indeed, the addition of molecular oxygen to extended solids can influence both the chemical composition and reactivity of the solid support. For example, surface-O2 interactions are crucial in a wide variety of industrially important transformations such as chemical conversion (i.e., CO and hydrocarbon conversion)^{116–119} and electrocatalysis (i.e., oxygen reduction reaction in fuel cells). 120-122 Furthermore, molecular oxygen is typically added to reduced RMOs to restore surface oxygen atoms via oxygen exchange between the solid support and gaseous reactant. 19,21-23 This process makes RMO materirecyclable, often remaining operational for several years. 16,123,124

Given the importance of O2 interactions with RMOs, we decided to begin our investigations into the reactivity of

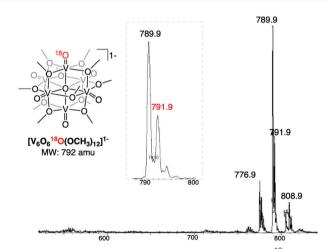


Fig. 10 ESI-MS (-)ve mode of control experiment using ¹⁸O₂ (1 atm). Inset highlights mass distribution resulting from incorporation of labeled oxygen atoms within the hexavanadate cluster (red), however the un-labeled cluster ($[V_6O_7(OCH_3)_{12}]^{1-}$; m/z 790), is observed in a relatively high quantity. This is likely due to exchange of $\rm H_2O$ with [V₆O₆¹⁸O(OCH₃)₁₂]¹⁻. Figure reprinted with permission from B. E. Petel, et al., J. Am. Chem. Soc. 2018, 140, 8424-8428. Copyright 2018 American Chemical Society.

$$\begin{bmatrix} V_6O_7(OCH_3)_{12} \end{bmatrix}^{2^-} \\ e^- \text{ distrib: } V^{\parallel V_6} \\ \end{bmatrix} \begin{bmatrix} V_6O_7(OCH_3)_{12} \end{bmatrix}^{1^-} \\ e^- \text{ distrib: } V^{\parallel V_6} \\ \end{bmatrix} \begin{bmatrix} V_6O_7(OCH_3)_{12} \end{bmatrix}^{1^-} \\ e^- \text{ distrib: } V^{\parallel V_6} \\ \end{bmatrix} \begin{bmatrix} V_6O_7(OCH_3)_{12} \end{bmatrix}^{1^-} \\ e^- \text{ distrib: } V^{\parallel V_6} \\ \end{bmatrix} \begin{bmatrix} V_6O_7(OCH_3)_{12} \end{bmatrix}^{1^-} \\ e^- \text{ distrib: } V^{\parallel V_6} \\ \end{bmatrix} \begin{bmatrix} V_6O_7(OCH_3)_{12} \end{bmatrix}^{1^-} \\ e^- \text{ distrib: } V^{\parallel V_6} \\ \end{bmatrix} \begin{bmatrix} V_6O_7(OCH_3)_{12} \end{bmatrix}^{1^-} \\ e^- \text{ distrib: } V^{\parallel V_6} \\ \end{bmatrix} \begin{bmatrix} V_6O_7(OCH_3)_{12} \end{bmatrix}^{1^-} \\ \end{bmatrix} \begin{bmatrix} V_6O_7(OCH_3)_{1$$

Scheme 3 Reactivity of $[V_6O_6(OCH_3)_{12}]^{1-}$ with NO_2^{1-} (left) and NO_3^{1-} (right).⁸¹

oxygen-deficient POV-alkoxide clusters with O2. Addition of 1 atm of O_2 to $\left[V_6O_6(OCH_3)_{12}\right]^{1-}$ resulted in quantitative formation of the fully-oxygenated cluster, $[V_6O_7(OCH_3)_{12}]^{1-}$, after 24 hours at 50 °C (Scheme 2). To probe the solution stability of the monovacant cluster at the relevant reaction conditions, a control experiment was conducted by heating $[V_6O_6(OCH_3)_{12}]^{1-}$ to 50 °C for 24 hours; no evidence of cluster degradation was observed. Furthermore, confirmation that the oxygen-atom participating in OAT was from O2 reduction was achieved via the addition of isotopically-enriched dioxygen (18O2). Analysis of the resulting product by ¹H NMR and electrospray ionization mass-spectrometry (ESI-MS) confirmed formation of the corresponding labelled product, $[V_6O_6^{18}O(OCH_3)_{12}]^{1-}$ (Fig. 10). Collectively, these results confirm that the oxygen-deficient cluster can reduce molecular oxygen, revealing the propensity of the surface-defect on the homogeneous molecular model to facilitate activation of oxygenated substrates.

Reduction of nitrogen-containing oxyanions with oxygendeficient POV-alkoxide clusters

To expand the reactivity profile of the mono-vacant POV-alkoxide cluster, we became interested in investigating whether $\left[V_6O_6(OCH_3)_{12}\right]^{1-}$ could mediate the reduction of oxyanions, specifically nitrite (NO₂¹⁻; one-electron reduction) and nitrate (NO₃¹⁻; two-electron reduction). Although POMs

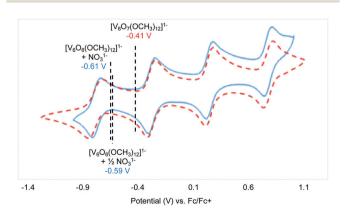


Fig. 11 Open circuit potential for the independently synthesized, fullyoxygenated cluster ([V₆O₇(OCH₃)₁₂] $^{1-}$; -0.41 V, red) and the products of NO_3^{1-} reduction (stoichiometric, -0.61 V; sub-stoichiometric, -0.59 V) via $[V_6O_6(OCH_3)_{12}]^{1-}$. CV collected in acetonitrile with 0.1 M [nBu_4N][PF₆] as supporting electrolyte.81

are well-established to facilitate the electrocatalytic reduction of these oxyanions,47 it is unclear how these oxide-terminated polyoxoanions bind to the substrate and facilitate the requisite OAT chemistry. In cases where mechanistic insight has been presented, these transformations are commonly mediated by transition metal-substituted polyoxoanions, where substrate activation occurs at the heterometallic centre. 47,125-128

Addition of 1 equiv. of NO₂¹⁻ to complex [V₆O₆(OCH₃)₁₂]¹⁻ resulted in the one-electron reduction of NO₂¹⁻ and OAT to the reduced POV-alkoxide.81 This translated to the release of nitric oxide (NO), and formation of the dianionic POV-alkoxide cluster, $[V_6O_7(OCH_3)_{12}]^{2-}$ (Scheme 3, left). Formation of the fully-oxygenated cluster in its most reduced charge state was confirmed via electronic absorption spectroscopy; the lack of IVCT bands attributed to mixed-valent POV-alkoxides is consistent with the formation of the [V^{IV}₆]²⁻ cluster.⁷³ Confirmation of N-O bond scission was garnered from NO-trapping experiments using cobalt tetraphenylporphyrin (CoTPP). 129-132

We next set out to explore if the oxygen-deficient POValkoxide would be able to mediate the two-electron reduction of NO₃¹⁻. While this transformation is significantly more endergonic than that of nitrite reduction, 133,134 we hypothesized that NO₃¹⁻ activation would follow a similar pathway; following coordination of $\mathrm{NO_3}^{1-}$ to the oxygen deficient POV-alkoxide, two electrons would be transferred to the substrate resulting in N-O bond cleavage (formation of NO_2^{1-}). In this case, the expected reactivity would result in a change in the overall oxidation state distribution of the cluster from $[V^{III}V^{IV}_{5}]^{1-}$ to $[V^{IV}_{5}V^{V}]^{1-}$ (*i.e.*, $[V_{6}O_{7}(OCH_{3})_{12}]^{1-}$). Although addition of [${}^{n}Bu_{4}N$]NO₃ to [$V_{6}O_{6}(OCH_{3})_{12}$]¹⁻ at 21 ${}^{\circ}C$ resulted in only minimal conversion to product, heating the reaction to 70 °C resulted in complete conversion of the oxygen-deficient cluster.

Further analysis of the resulting cluster-containing product by electronic absorption spectroscopy and cyclic voltammetry showed substantial inconsistencies from that which would be expected for the monoanionic POV-alkoxide cluster, $[V_6O_7(OCH_3)_{12}]^{1-}$ (Fig. 11). For example, the absorption spectrum of the crude product contains two IVCT bands located at 392 nm (2594 M⁻¹ cm⁻¹) and 1000 nm (605 M⁻¹ cm⁻¹), consistent with formation of a cluster with a mixed-valent V^{IV/V} oxidation state distribution. However, comparison of the molar absorptivity values between the nitrate reduction product and that of the independently synthesized monoanionic cluster, $[V_6O_7(OCH_3)_{12}]^{1-73}$ revealed that the IVCT intensities

are significantly lower than expected. These results, coupled with an open circuit potential for the product shifted cathodically by 0.2 V (Fig. 11), suggested that complex $[V_6O_7(OCH_3)_{12}]^{1-}$ is not the sole product of this reaction.

Given that NO₂¹⁻ reduction occurs at room temperature, we hypothesized that the nitrogen-containing byproduct of nitrate reduction, NO21-, could be competing with the two-electron reduction of NO₃¹⁻; following deoxygenation of NO₃¹⁻, unreacted starting material ([V₆O₆(OCH₃)₁₂]¹⁻) would preferentially reduce the in situ generated NO21-, resulting in the formation of the dianionic POV-alkoxide cluster, [V₆O₇ $(OCH_3)_{12}$]²⁻. To test this hypothesis, a substicchiometric amount of ["Bu₄N]NO₃ (0.5 equiv.) was added to [V₆O₆ $(OCH_3)_{12}$]¹⁻. Analysis of the resulting product by ¹H NMR revealed that although only half of the required substrate was added, complete conversion of the oxygen-deficient cluster was observed (Scheme 3). Further analysis of the cluster-containing products in the substiochiometric reaction, via cyclic voltammetry, confirm that the same ratio of POV-alkoxide clusters are formed regardless of NO₂¹⁻ equivalence (Fig. 11).

To analyse both the effect of changing the surface structure and oxidation state distribution of the Lindqvist cluster, we opted to investigate the reactivity of the redox-series of monovacant POV-ethoxide clusters, $[V_6O_6(OC_2H_5)_{12}]^n$ (n = 1-, 0, 1+) with NO_x^{1-} (x = 2, 3).82 Spectroscopic investigations of the POV-ethoxides have revealed that the sitedifferentiated vanadium(III) centre retains its oxidation state across all three charge states of the cluster, 78,80,135 providing a method for analysing the influence of the oxidation state of remote vanadyl ions (i.e., cluster redox potential) on N-O bond scission. Furthermore, alteration of the bridging alkoxide chain length, from methoxide to ethoxide, presents the opportunity to concurrently analyse the effect of changing the steric accessibility of the active VIII ion on reaction rate (Fig. 12).

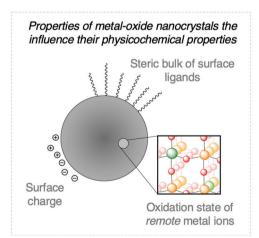
Table 3 Comparative reaction times and temperatures for NO_x^{1-} (x = 2, 3) reduction via $[V_6O_6(OCH_3)_{12}]^{1-}$ and the redox-series of POV-ethoxide clusters. Table is reprinted, in part, with permission from E. M. M. Brittney, et al., Inorg. Chem. (DOI: 10.1021/acs.inorgchem.0c02052). Copyright 2020 American Chemical Society

	Complex	Ox. state distrib.	${ m NO_2}^{1-}$ reduction conditions	NO ₃ ¹⁻ reduction conditions
1 2 3 4	$\begin{array}{l} \left[V_6O_6(OCH_3)_{12}\right]^{1-} \\ \left[V_6O_6(OC_2H_5)_{12}\right]^{1-} \\ \left[V_6O_6(OC_2H_5)_{12}\right]^{0} \\ \left[V_6O_6(OC_2H_5)_{12}\right]^{1+} \end{array}$	$\begin{array}{c} V^{III}V^{IV}{}_{5} \\ V^{III}V^{IV}{}_{5} \\ V^{III}V^{IV}{}_{4}V^{V} \\ V^{III}V^{IV}{}_{3}V^{V}{}_{2} \end{array}$	24 h, 21 °C 30 min, 21 °C 5 min, 21 °C 15 min, 21 °C	24 h, 70 °C 24 h, 50 °C 1.5 h, 50 °C 96 h, 50 °C

Collectively, these investigations revealed that NO_r¹⁻ reduction is influenced by three factors. As expected, both the ligand identity (i.e., Table 3, entry 1 vs. 2) and oxidation state distribution of neighbouring vanadyl moieties (i.e., Table 3, entry 2-4) significantly influence the rate of NO_x¹⁻ activation, with OAT reaction times ranging from 5 minutes to 96 hours. Furthermore, our investigations revealed that ion-pairing interactions, in particular, repulsive substrate-cluster interactions, hinder the rate of OAT for both nitrite and nitrate reduction (Table 3, entry 2 vs. entries 3, 4). We anticipate that similar consequences might be observed in the analogous reduction chemistries with heterogenous systems. These factors reveal design strategies that could improve the OAT reactivity of metal oxides, ultimately resulting in the synthesis of new, efficient heterogeneous catalysts for the activation of oxyanions.

Conclusions and outlook

In summary, over the past four years we have investigated Lindqvist POV-alkoxide clusters as atomically-precise analogues of vanadium oxide materials, with particular interest in studying defect formation in RMOs. Driven by our ultimate goal



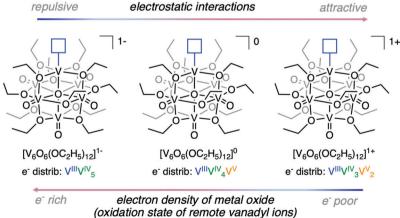


Fig. 12 Physicochemical properties that influence the reactivity of metal oxides, including chemical composition of surface ligands, surface charge, and the oxidation state of remote metal ions surrounding the catalytically active metal centre (left). Key: red, O; green, V.; orange, remote vanadyl ions. Structure-function investigations reveal the role these properties play in dictating the rate of oxyanion reduction at the surface of oxygen-deficient POV-alkoxide clusters. Figure is reprinted, in part, with permission from B. E. Petel, et al., Inorg. Chem., (DOI: 10.1021/acs.inorgchem.0c02052). Copyright 2020 American Chemical Society.

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of gaining a molecular-level insight into the structural and electronic perturbations of metal oxide supports during catalysis (i.e., the MvK mechanism; vacancy formation, substrate adsorption, substrate activation, product desorption), we began by developing new methods for the post-synthetic removal of oxygen-atoms from terminal vanadyl ions within the cluster core. Indeed, addition of reductants (e.g., V(Mes)3(thf) or PR3) or acid to the fully-oxygenated vanadium oxide clusters resulted in the generation of a redox-series of oxygen-deficient POV-alkoxide clusters that feature up to two coordinatively unsaturated vanadium ions. Rigorous electronic characterization of the mono- and di-vacant clusters revealed that oxygenatom removal results in the formation of VIII moieties as sitedifferentiated ions that are decoupled from the remaining Robin and Day Class II delocalized cluster core. In addition, structural characterization, via SCXRD, revealed that O-atom removal results in significant lattice distortions; the reduced vanadium ion(s) is pulled toward the centre of the cluster, resulting in a ~ 0.2 Å truncation of the V-O_c bond.

We have also analysed the reactivity of the reduced POValkoxides by investigating transformations relevant to the reduction of chemical pollutants and other oxygenated substrates. While not described herein, we have also demonstrated that the oxygen-deficient POV-alkoxides can mediate the deoxygenation of organic substrates, such as the conversion of styrene oxide to styrene. In all cases, substrate reduction and OAT results in restoration of an oxygen atom to the sitedifferentiated VIII ion. Analysis of reaction parameters that influence substrate reduction revealed that OAT is influenced by the sterics of the alkoxide ligands surrounding the active VIII ion, substrate-cluster electrostatic interactions, and cluster charge state or redox potential. Collectively, these investigations have revealed that polyoxometalates can serve not only as structural and electronic models for reduced RMOs but also provide a method for modelling heterogenous OAT processes that invoke the MvK mechanism.

Looking forward, the ability to further expand Lindqvist POV-alkoxide clusters as atomically-precise models for metal oxides is promising, given the recently developed syntheses of heterometal-functionalized POV-alkoxide $[V_{6-x}O_{7-x}(OCH_3)_{12}(MX')_x]$ (x = 1, MX' = FeOTf, ¹³⁶ FeCl, ¹³⁷ GaCl, ¹³⁷ Ti(OCH₃), ¹³⁸ Hr(OCH₃), ¹³⁸ Zr(OCH₃); x = 2, MX' = Ti(OCH₃)). ¹³⁹ These multimetallic clusters can serve as structural and electronic models for cationically doped transition metal oxides which are commonly used as catalysts in industrially relevant transformations.¹⁵ Indeed, it is well established that the chemical and photochemical behavior of a metal oxide can be modified by introducing heterometallic dopants. Ideally, analyzing vacancy generation on $[V_{6-x}O_{7-x}(OCH_3)_{12}(MX')_x]$ will provide atomistic insight into the consequences of dopant addition on the MvK reactivity of metal oxides. In particular, we are interested in investigating the relative ability to mediate V=O bond cleavage on the heterometallic systems, the location of the resulting unsaturated vanadyl ion (i.e., cis- vs. trans- to the heterometal), as well as the influence of the heterometal on substrate deoxygenation. Ultimately, insights from this work will reveal important design considerations for the generation of ternary metal oxides as heterogeneous catalysts for small molecule activation and chemical valorization.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- 1 *Metal Oxides: Chemistry and Applications*, ed. J. L. G. Fierro, Taylor & Francis Group, Boca Raton, Fl, 2006.
- 2 A. Ruiz Puigdollers, P. Schlexer, S. Tosoni and G. Pacchioni, ACS Catal., 2017, 7, 6493–6513.
- 3 J. C. Vedrine, Metal Oxides in Heterogeneous Catalysis, Elsevier, Saint Louis, United States, 2018.
- 4 C. Yuan, H. B. Wu, Y. Xie and X. W. Lou, Angew. Chem., Int. Ed., 2014, 53, 1488–1504.
- 5 X. Yu, T. J. Marks and A. Facchetti, *Nat. Mater.*, 2016, **15**, 383–396. 6 X. Xia, Y. Zhang, D. Chao, C. Guan, Y. Zhang, L. Li, X. Ge,
- I. M. Bacho, J. Tu and H. J. Fan, Nanoscale, 2014, 6, 5008-5048.
- 7 J. C. Védrine, Catalysts, 2017, 7, 341-366.
- 8 T. N. Pham, T. Sooknoi, S. P. Crossley and D. E. Resasco, ACS Catal., 2013, 3, 2456–2473.
- 9 M. Hara, K. Nakajima and K. Kamata, Sci. Technol. Adv. Mater., 2015, 16, 034903.
- 10 P. Schwach, X. Pan and X. Bao, Chem. Rev., 2017, 117, 8497-8520.
- 11 H. Chen, C. E. Nanayakkara and V. H. Grassian, *Chem. Rev.*, 2012, 112, 5919–5948.
- 12 X. Jiang, X. Nie, X. Guo, C. Song and J. G. Chen, Chem. Rev., 2020, 120, 7984–8034.
- 13 S. Dang, H. Yang, P. Gao, H. Wang, X. Li, W. Wei and Y. Sun, *Catal. Today*, 2019, 330, 61–75.
- 14 R.-P. Ye, J. Ding, W. Gong, M. D. Argyle, Q. Zhong, Y. Wang, C. K. Russell, Z. Xu, A. G. Russell, Q. Li, M. Fan and Y.-G. Yao, *Nat. Commun.*, 2019, **10**, 5698.
- 15 E. W. McFarland and H. Metiu, Chem. Rev., 2013, 113, 4391-4427.
- 16 J. A. H. Dumesic and G. W. Boudart, Handbook of Heterogeneous Catalysis, ed. H. K. G. Ertl, F. Schüth and J. Weitkamp, 2008.
- 17 J. Jia, C. Qian, Y. Dong, Y. F. Li, H. Wang, M. Ghoussoub, K. T. Butler, A. Walsh and G. A. Ozin, *Chem. Soc. Rev.*, 2017, 46, 4631–4644.
- 18 P. L. Gai-Boyes, Catal. Rev., 1992, 34, 1-54.
- 19 P. Mars and D. W. van Krevelen, Chem. Eng. Sci., 1954, 3, 41-59.
- C. Doornkamp and V. Ponec, J. Mol. Catal. A: Chem., 2000, 162, 19–32.
- 21 P. Schlexer, D. Widmann, R. J. Behm and G. Pacchioni, ACS Catal., 2018, 8, 6513–6525.

- 22 M. A. Henderson, W. S. Epling, C. L. Perkins, C. H. F. Peden and U. Diebold, J. Phys. Chem. B, 1999, 103, 5328-5337.
- 23 A. R. Almeida, J. A. Moulijn and G. Mul, J. Phys. Chem. C, 2011, 115, 1330-1338.
- 24 N. Kumari, M. A. Haider, M. Agarwal, N. Sinha and S. Basu, J. Phys. Chem. C, 2016, 120, 16626-16635.
- 25 C. E. Senseman and O. A. Nelson, Ind. Eng. Chem., 1923, 15,
- 26 W. i. K. Schreiber, Grenzflachen-Katalyse, Leipzig, 1933.
- 27 C. R. D. J. M. Weiss and R. M. Burns, Ind. Eng. Chem., 1923, 15, 005.
- 28 E. B. Maxted, J. Soc. Chem. Ind., 1928, 47, 101.
- 29 P. H. Calderbank, Ind. Chem., 1952, 201.
- 30 C. Doornkamp, M. Clement and V. Ponec, Appl. Catal., A, 1999, 188,
- 31 A. V. Mironenko and D. G. Vlachos, J. Am. Chem. Soc., 2016, 138, 8104-8113.
- 32 L. J. Lauhon and W. Ho, Rev. Sci. Instrum., 2001, 72, 216-223.
- 33 C. Bai, Scanning Tunneling Microscopy and Its Application, Shenghai Scientific & Technical Publishers, China, 2nd, Revised Edition edn,
- 34 R. V. Lapshin, Meas. Sci. Technol., 2007, 18, 907-927.
- 35 F. Marinello, M. Balcon, P. Schiavuta, S. Carmignato and E. Savio, Meas. Sci. Technol., 2011, 22, 1-9.
- 36 U. Diebold, Surf. Sci. Rep., 2003, 48, 53-229.
- 37 F. Gołek, P. Mazur, Z. Ryszka and S. Zuber, Appl. Surf. Sci., 2014, 304, 11-19.
- 38 M. Ek, Q. M. Ramasse, L. Arnarson, P. Georg Moses and S. Helveg, Nat. Commun., 2017, 8, 1-9.
- 39 K. Hermann, M. Witko, R. Druzinic and R. Tokarz, Appl. Phys. A: Mater. Sci. Process., 2001, 72, 429-442.
- 40 A. Michalak, M. Witko and K. Hermann, Surf. Sci., 1997, 375, 385-394.
- 41 K. Hermann, M. Witko and R. Druzinic, Faraday Discuss., 1999, 114, 53-66.
- 42 M. T. Pope and A. Muller, Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications, Berlin, 2001.
- 43 N. I. Gumerova and A. Rompel, Nat. Rev. Chem., 2018, 2, 0112.
- 44 X. Lopez, J. J. Carbó, C. Bo and J. M. Poblet, Chem. Soc. Rev., 2012, **41**, 7537–7571.
- 45 P. Gouzerh and A. Proust, Chem. Rev., 1998, 98, 77-112.
- 46 T. Ueda, ChemElectroChem, 2018, 5, 823-838.
- 47 M. Sadakane and E. Steckhan, Chem. Rev., 1998, 98, 219-238.
- 48 J.-J. Ye and C.-D. Wu, Dalton Trans., 2016, 45, 10101–10112.
- 49 D. C. C. Soumyajit Roy and T. N. Parac-Vogt, Editorial: Polyoxometalates in Catalysis, Biology, Energy and Materials Science, 2019.
- 50 D.-L. Long, R. Tsunashima and L. Cronin, Angew. Chem., Int. Ed., 2010, 49, 1736-1758.
- 51 F. F. Bamoharram, Synth. React. Inorg., Met.-Org., Nano-Met. Chem., 2011, 41, 893-922.
- 52 J. T. Rhule, C. L. Hill, D. A. Judd and R. F. Schinazi, Chem. Rev., 1998, 98, 327-358.
- 53 T. Yamase, in Biomedical Inorganic Polymers: Bioactivity and Applications of Natural and Synthetic Polymeric Inorganic Molecules, ed. W. E. G. Müller, X. Wang and H. C. Schröder, Springer Berlin Heidelberg, Berlin, Heidelberg, 2013, pp. 65-116.
- 54 M. Genovese and K. Lian, Curr. Opin. Solid State Mater. Sci., 2015, **19**, 126–137.
- 55 H. D. Pratt, N. S. Hudak, X. Fang and T. M. Anderson, J. Power Sources, 2013, 236, 259-264.
- 56 H. D. Pratt, W. R. Pratt, X. Fang, N. S. Hudak and T. M. Anderson, Electrochim. Acta, 2014, 138, 210-214.
- L. E. VanGelder, T. R. Cook and E. M. Matson, Comments Inorg. Chem., 2019, 39, 51-89.
- 58 M. Samaniyan, M. Mirzaei, R. Khajavian, H. Eshtiagh-Hosseini and C. Streb, ACS Catal., 2019, 9, 10174–10191.
- 59 A. M. Khenkin, L. Weiner, Y. Wang and R. Neumann, J. Am. Chem. Soc., 2001, 123, 8531-8542,
- 60 A. M. Khenkin and R. Neumann, Angew. Chem., Int. Ed., 2000, 39, 4088-4090.
- 61 I. Efremenko and R. Neumann, J. Am. Chem. Soc., 2012, 134, 20669-20680.
- 62 A. M. Khenkin, G. Leitus and R. Neumann, J. Am. Chem. Soc., 2010, 132, 11446-11448.

- 63 R. Neumann and A. M. Khenkin, Chem. Commun., 2006, 2529-2538.
- 64 A. M. Khenkin and R. Neumann, J. Am. Chem. Soc., 2008, 130, 14474-14476.
- 65 H. Goldberg, I. Kaminker, D. Goldfarb and R. Neumann, Inorg. Chem., 2009, 48, 7947-7952.
- 66 B. B. Sarma, R. Carmieli, A. Collauto, I. Efremenko, J. M. L. Martin and R. Neumann, ACS Catal., 2016, 6, 6403-6407.
- 67 B. B. Sarma, I. Efremenko and R. Neumann, J. Am. Chem. Soc., 2015, 137, 5916-5922.
- 68 T. Minato, K. Suzuki, K. Yamaguchi and N. Mizuno, Chem. Eur. J., 2017, 23, 14213-14220.
- 69 K. Piepgrass and M. T. Pope, J. Am. Chem. Soc., 1987, 109,
- 70 K. Piepgrass and M. T. Pope, J. Am. Chem. Soc., 1989, 111, 753-754.
- 71 C. D. Johann Spandl, I. Brüdgam and H. Hartl, Angew. Chem., Int. Ed., 2003, 42, 1163-1166.
- 72 C. Daniel and H. Hartl, J. Am. Chem. Soc., 2005, 127, 13978-13987.
- 73 C. Daniel and H. Hartl, J. Am. Chem. Soc., 2009, 131, 5101-5114.
- 74 S. Surnev, M. G. Ramsey and F. P. Netzer, Prog. Surf. Sci., 2003, 73,
- 75 A. Walsh and K. T. Butler, Acc. Chem. Res., 2014, 47, 364-372.
- 76 L. E. VanGelder, A. M. Kosswattaarachchi, P. L. Forrestel, T. R. Cook and E. M. Matson, Chem. Sci., 2018, 9, 1692-1699.
- 77 B. E. Petel, W. W. Brennessel and E. M. Matson, J. Am. Chem. Soc., 2018, 140, 8424-8428.
- 78 B. E. Petel, R. L. Meyer, W. W. Brennessel and E. M. Matson, Chem. Sci., 2019, 10, 8035-8045.
- 79 B. E. Petel, A. A. Fertig, M. L. Maiola, W. W. Brennessel and E. M. Matson, Inorg. Chem., 2019, 58, 10462-10471.
- 80 E. Schreiber, B. E. Petel and E. M. Matson, J. Am. Chem. Soc., 2020, 142, 9915-9919.
- 81 B. E. Petel and E. M. Matson, Chem. Commun., 2020, 56, 555-558.
- 82 E. M. M. Brittney and E. Petel, Inorg. Chem., 2020, DOI: 10.1021/ acs.inorgchem.0c02052.
- 83 A. L. Odom, C. C. Cummins and J. D. Protasiewicz, J. Am. Chem. Soc., 1995, 117, 6613-6614.
- 84 N. E. Brese and M. O'Keeffe, Acta Crystallogr., Sect. B: Struct. Sci., 1991, 47, 192-197.
- 85 I. D. Brown and K. K. Wu, Acta Crystallogr., Sect. B: Struct. Sci., 1976, 32, 1957-1959.
- 86 W. Liu and H. H. Thorp, Inorg. Chem., 1993, 32, 4102-4105.
- 87 R. H. Holm, Chem. Rev., 1987, 87, 1401-1449.
- 88 S. B. Yu and R. H. Holm, Inorg. Chem., 1989, 28, 4385-4391.
- 89 R. R. Conry and J. M. Mayer, Inorg. Chem., 1990, 29, 4862-4867.
- 90 J. Paudel, A. Pokhrel, M. L. Kirk and F. Li, Inorg. Chem., 2019, 58, 2054-2068.
- 91 M. Castiñeira Reis, M. Marín-Luna, C. Silva López and O. N. Faza, Inorg. Chem., 2017, 56, 10570-10575.
- 92 T. Saito, T. Sunaga, N. Sakai, Y. Nakamura, S. Yamamoto, D. Iriuchijima and K. Yoza, Inorg. Chem., 2005, 44, 4427–4432.
- 93 K. Oya, H. Seino, M. Akiizumi and Y. Mizobe, Organometallics, 2011, 30, 2939-2946.
- 94 J. S. Kanady, J. L. Mendoza-Cortes, E. Y. Tsui, R. J. Nielsen, W. A. Goddard and T. Agapie, J. Am. Chem. Soc., 2013, 135, 1073-1082.
- 95 R. F. Hudson, Structure and mechanism in organophosphorus chemistry, Academic, New York, 1965, vol. 6, pp. 68-70.
- 96 H. K. Wang, Acta Chem. Scand., 1965, 19, 879–882.
- 97 J. Gangopadhyay, S. Sengupta, S. Bhattacharyya, I. Chakraborty and A. Chakravorty, Inorg. Chem., 2002, 41, 2616-2622.
- 98 P. Basu, B. W. Kail and C. G. Young, Inorg. Chem., 2010, 49, 4895-4900.
- 99 M. N. Golovin, M. M. Rahman, J. E. Belmonte and W. P. Giering, Organometallics, 1985, 4, 1981-1991.
- 100 C. A. Tolman, Chem. Rev., 1977, 77, 313-348.
- 101 M. S. Reynolds, J. M. Berg and R. H. Holm, Inorg. Chem., 1984, 23, 3057-3062.
- 102 L. E. V. Anjula, M. Kosswattaarachchi, O. Nachtigall, J. P. Hazelnis, W. W. Brennessel, E. M. Matson and T. R. Cook, J. Electrochem. Soc., 2019, 166, A464-A472.
- 103 Y. Chen, Z. Wang, S. Chen, H. Ren, L. Wang, G. Zhang, Y. Lu, J. Jiang, C. Zou and Y. Luo, Nat. Commun., 2018, 9, 818.

104 B. Li, L. Xie, Z. Wang, S. Chen, H. Ren, Y. Chen, C. Wang, G. Zhang,

- J. Jiang and C. Zou, Angew. Chem., Int. Ed., 2019, 58, 13711-13716. J. Tucher, L. C. Nye, I. Ivanovic-Burmazovic, A. Notarnicola and C. Streb, Chem. - Eur. J., 2012, 18, 10949-10953.
- 106 Q. Chen, D. P. Goshorn, C. P. Scholes, X. L. Tan and J. Zubieta, I. Am. Chem. Soc., 1992, 114, 4667-4681.
- 107 V. W. Day, W. G. Klemperer and D. J. Maltbie, J. Am. Chem. Soc., 1987, **109**, 2991-3002.
- 108 G. Arana, N. Etxebarria, L. A. Fernandez and J. M. Madariaga,
- J. Solution Chem., 1995, 24, 611-622. 109 N. Etxebarria, L. A. Fernández and J. M. Madariaga, J. Chem. Soc., Dalton Trans., 1994, 3055-3059.
- 110 J. P. Launay, J. Inorg. Nucl. Chem., 1976, 38, 807-816.

Feature Article

- 111 L. P. Kazansky and J. P. Launay, Chem. Phys. Lett., 1977, 51, 242-245.
- 112 Y. Jeannin, J. P. Launay and M. A. S. Sedjadi, Inorg. Chem., 1980, 19, 2933-2935.
- 113 H. Ichida, K. Nagai, Y. Sasaki and M. T. Pope, J. Am. Chem. Soc., 1989, 111, 586-591.
- 114 M. M. Montemore, M. A. van Spronsen, R. J. Madix and C. M. Friend, Chem. Rev., 2018, 118, 2816-2862.
- 115 M. W. Roberts, Chem. Soc. Rev., 1989, 18, 451-475.
- 116 F. Yang, J. Graciani, J. Evans, P. Liu, J. Hrbek, J. F. Sanz and J. A. Rodriguez, J. Am. Chem. Soc., 2011, 133, 3444-3451.
- 117 M. Shelef, K. Otto and H. Gandhi, J. Catal., 1968, 12, 361-375.
- 118 L. Kundakovic and M. Flytzani-Stephanopoulos, J. Catal., 1998, 179, 203-221.
- 119 Y. Moro-Oka, Y. Morikawa and A. Ozaki, J. Catal., 1967, 7, 23-32.
- 120 S. Malkhandi, P. Trinh, A. K. Manohar, K. C. Jayachandrababu, A. Kindler, G. K. Surya Prakash and S. R. Narayanan, J. Electrochem. Soc., 2013, **160**, F943–F952.
- 121 Y. Zhu, X. Liu, S. Jin, H. Chen, W. Lee, M. Liu and Y. Chen, J. Mater. Chem. A, 2019, 7, 5875-5897.
- 122 H. Osgood, S. V. Devaguptapu, H. Xu, J. Cho and G. Wu, Nano Today, 2016, 11, 601-625.

- 123 S. Yan, C. DiMaggio, S. Mohan, M. Kim, S. O. Salley and K. Y. S. Ng, Top. Catal., 2010, 53, 721-736.
- 124 P. J. Denny and M. V. Twigg, in Studies in Surface Science and Catalysis, ed. B. Delmon and G. F. Froment, Elsevier, 1980, pp. 577-599, vol. 6.
- 125 Y. X. Wenliang Sun, H. Liu, J. Kong, S. Jin, G. Xie and J. Deng, Indian J. Chem., Sect. A: Inorg., Phys., Theor. Anal., 1997, 36, 1023-1030.
- 126 W. Sun, F. Yang, H. Liu, J. Kong, S. Jin, G. Xie and J. Deng, J. Electroanal. Chem., 1998, **451**, 49-57.
- 127 W. Sun, S. Zhang, X. Lin, L. Jin, S. Jin, J. Deng and J. Kong, I. Electroanal. Chem., 1999, 469, 63-71.
- 128 S. Dong, X. Xi and M. Tian, J. Electroanal. Chem., 1995, 385, 227-233.
- 129 C. L. Ford, Y. J. Park, E. M. Matson, Z. Gordon and A. R. Fout, Science, 2016, 354, 741.
- 130 G. Cioncoloni, I. Roger, P. S. Wheatley, C. Wilson, R. E. Morris, S. Sproules and M. D. Symes, ACS Catal., 2018, 8, 5070-5084.
- 131 C. M. Moore and N. K. Szymczak, Chem. Sci., 2015, 6, 3373-3377.
- 132 M. Kumar, N. A. Dixon, A. C. Merkle, M. Zeller, N. Lehnert and E. T. Papish, Inorg. Chem., 2012, 51, 7004-7006.
- 133 R. H. Holm and J. P. Donahue, Polyhedron, 1993, 12, 571-589.
- 134 D. D. Wagman, The Nbs Tables of Chemical Thermodynamic Properties: Selected Values for Inorganic and C2 and C2 Organic Substances in Si Units., American Chemical Society and the American Institute of Physics for the National Bureau of Standards, Washington, DC, 1982.
- 135 M. L. Maiola, B. E. Petel, W. W. Brennessel and E. M. Matson, Dalton Trans., 2020, DOI: 10.1039/D0DT01077D.
- 136 F. Li, L. E. VanGelder, W. W. Brennessel and E. M. Matson, Inorg. Chem., 2016, 55, 7332-7334.
- 137 R. L. Meyer, W. W. Brennessel and E. M. Matson, Polyhedron, 2018, **156**, 303-311.
- 138 L. E. VanGelder, W. W. Brennessel and E. M. Matson, Dalton Trans., 2018, 47, 3698-3704.
- 139 L. E. VanGelder, P. L. Forrestel, W. W. Brennessel and E. M. Matson, Chem. Commun., 2018, 54, 6839-6842.