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## COMMUNICATION

## Conversion of $\text{NO}_x^{1-}$ ( $x = 2, 3$ ) to NO using an oxygen-deficient polyoxovanadate-alkoxide cluster

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**We report the activation of nitrogen-containing oxyanions using an oxygen-deficient polyoxovanadate-alkoxide cluster. Reduction of  $\text{NO}_2^{1-}$  and  $\text{NO}_3^{1-}$  results in near-quantitative oxygen atom transfer to the coordinatively unsaturated  $\text{V}^{\text{III}}$  ion, and selective formation of NO. These results provide insight into possible mechanisms of oxyanion reduction by polyoxometalates.**

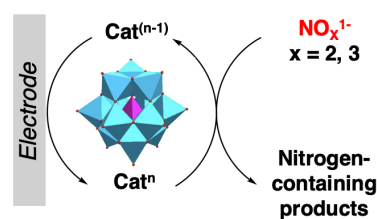
The conversion of nitrogen-containing oxyanions (e.g.  $\text{NO}_2^{1-}$  and  $\text{NO}_3^{1-}$ ) to nitric oxide (NO) are important processes in the denitrification phase of the nitrogen cycle.<sup>1</sup> In nature, the reduction of these environmental contaminants is mediated by metalloenzymes (reductases) that catalyse the one and two-electron reduction of nitrite ( $\text{NO}_2^{1-}$ ) and nitrate ( $\text{NO}_3^{1-}$ ), respectively. Similarly, homo- and heterogeneous metal-oxide architectures have been shown to mediate these chemical transformations.<sup>2</sup> However, despite extensive understanding of the mechanism of  $\text{NO}_x^{1-}$  activation with bio-relevant systems, little is known about the pathways by which metal-oxide clusters mediate the deoxygenation of these substrates.

A particularly active class of compounds for the electrochemical reduction of  $\text{NO}_2^{1-}$  and  $\text{NO}_3^{1-}$  are polyoxometalates (POMs; Figure 1).<sup>3</sup> Indeed, the reactivity of reduced variants of these assemblies with nitrogen-containing oxyanions (in particular,  $\text{NO}_2^{1-}$ ), is so ubiquitous, that researchers often include the electrochemical response of new POM architectures in the presence of these substrates to assess the general reactivity of their systems.<sup>3-7</sup> However, from the perspective of a coordination chemist, it is not inherently obvious how the oxide-terminated surfaces of these clusters might mediate the deoxygenation reactions invoked for POMs. The oxide terminated surfaces of these clusters composed of coordinatively saturated transition metal ions leave little opportunities for inner-sphere reductive processes. To date,

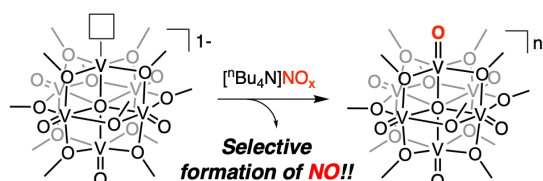
few reports have attempted to investigate the mechanism by which the reduction of  $\text{NO}_x^{1-}$  occurs in these systems, with exceptions relegated to heterometal-functionalized polyoxoanions, where substrate reduction occurs at the coordinatively unsaturated transition metal dopant.<sup>5, 6, 8, 9</sup>

In considering pathways by which this molecular transformation might occur, one can invoke a Mars Van-Krevelen type mechanism, where an oxygen-atom vacancy formed at the surface of a redox-active metal oxide generates an active site for reductive chemistries at the surface of a material.<sup>10</sup> Indeed, the feasibility of this reaction as a step in  $\text{NO}_x^{1-}$  reduction by polyoxoanions is bolstered by independent studies from Launay<sup>11</sup> and Pope<sup>12</sup>. These studies cite the conversion of terminal oxido ligands at a face of a polyoxotungstate Keggin ion ( $[\text{XW}_{12}\text{O}_{40}]^{n-}$ ) to datively bound

**Polyoxometalates: Well-precedented electrocatalysts for  $\text{NO}_x^{1-}$  reduction**



**This work: Insights into possible mechanisms by which metal-oxide clusters mediate  $\text{NO}_x^{1-}$  reduction**



**Figure 1.** Polyoxometalate clusters are well-established electrocatalysts for the reduction of  $\text{NO}_x^{1-}$ , however little is known about the mechanism by which these oxide-terminated surfaces mediate this transformation. Here, we present a surface-approach for probing possible reactive sites in these metal-oxide architectures.

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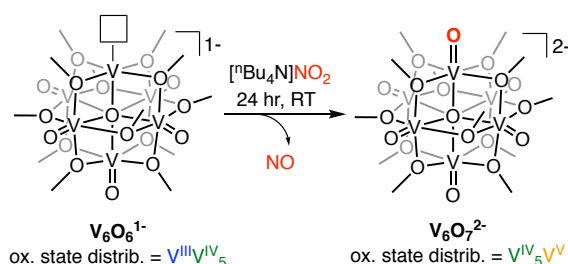
Electronic Supplementary Information (ESI) available: <sup>1</sup>H NMR and infrared spectra of  $\text{V}_6\text{O}_6^{1-}$  and  $[\text{^nBu}_4\text{N}]\text{NO}_2$  or  $[\text{^nBu}_4\text{N}]\text{NO}_3$ , CoTPP control experiments, <sup>1</sup>H NMR and electronic absorption spectra of *in situ* nitrite and nitrate reduction with CoTPP, electronic absorption spectra and CV of  $\text{V}_6\text{O}_7^{1-}$  via independent synthesis, <sup>1</sup>H NMR, electronic absorption, and CV spectra of substoichiometric nitrate reduction with  $\text{V}_6\text{O}_6^{1-}$ . See DOI: 10.1039/x0xx00000x

aqua moieties under reducing conditions at low pH. The reactivity of the W(IV)-aqua moieties, generated by the  $6e^-/6H^+$  surface activation of the cluster, in organic solvent have demonstrated that these reduced entities are active toward oxygen atom transfer reactions (e.g. OAsR<sub>3</sub>, OSR<sub>2</sub>, ONPh).<sup>13</sup> However, the stoichiometric reactivity of these reduced assemblies with nitrogen-containing oxyanions has not been studied.

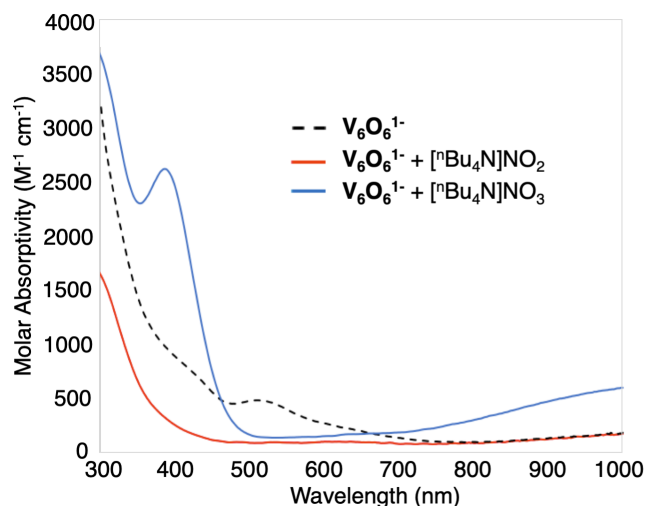
Our laboratory has developed synthetic strategies for the isolation of oxygen-deficient, organofunctionalized polyoxovanadate assemblies.<sup>14</sup> The polyoxovanadate-alkoxide (POV-alkoxide) clusters have many features similar to that of plenary POM motifs, however these complexes feature bridging alkoxide ligands that increase their solubility in organic solvents, providing handles for *in situ* analysis of reaction mixtures. Furthermore, reactivity in these systems is constrained to the terminal oxido moieties of the assembly.<sup>15</sup>,<sup>16</sup> Our ability to generate and handle a cluster with a single oxygen atom vacancy at its surface prompted interest in understanding whether these reduced terminal positions in POMs might be active for the reduction of NO<sub>x</sub><sup>1-</sup>.

To deepen our mechanistic understanding of the role of oxygen atom vacancies at the surface of POMs in the reduction of nitrogen-containing oxyanions, we opted to probe the reactivity of the previously reported, oxygen-deficient cluster, [tBu<sub>4</sub>N][V<sub>6</sub>O<sub>6</sub>(OCH<sub>3</sub>)<sub>12</sub>] (V<sub>6</sub>O<sub>6</sub><sup>1-</sup>), with NO<sub>2</sub><sup>1-</sup>.<sup>14</sup> We hypothesized that the one-electron reduction of NO<sub>2</sub><sup>1-</sup> by the vanadium-oxide cluster would afford cleavage of an N-O bond, resulting in oxygen atom transfer from nitrite to the reduced POV-alkoxide. This would lead to the release of NO, and formation of the dianionic, fully-oxygenated species, [V<sub>6</sub>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>]<sup>2-</sup> (V<sub>6</sub>O<sub>7</sub><sup>2-</sup>). Addition of one equivalent of tetrabutylammonium nitrite ([tBu<sub>4</sub>N][NO<sub>2</sub>]) in tetrahydrofuran (THF) resulted in a gradual colour change from brown/red to blue over the course of 24 hr, consistent with cluster oxidation (Scheme 1). Analysis of the reaction mixture by <sup>1</sup>H NMR spectroscopy revealed formation of a fully-oxygenated POV-alkoxide cluster, as indicated by a single resonance located at ~24 ppm (Figure S1).

**Scheme 1.** Reduction of NO<sub>2</sub><sup>1-</sup> with V<sub>6</sub>O<sub>6</sub><sup>1-</sup>.



Assignment of the charge-state of a POV-alkoxide is not possible by <sup>1</sup>H NMR spectroscopy alone, given the similarities in spectra of clusters across a range of oxidation states. To verify the formation of V<sub>6</sub>O<sub>7</sub><sup>2-</sup> following reaction of V<sub>6</sub>O<sub>6</sub><sup>1-</sup> with NO<sub>2</sub><sup>1-</sup>, characterization of the product was carried out via electronic absorption and infrared spectroscopies. These two analytical techniques have been reported to inform on the



**Figure 2.** Electronic absorption spectra of complex V<sub>6</sub>O<sub>6</sub><sup>1-</sup> (black) and the reactions of V<sub>6</sub>O<sub>6</sub><sup>1-</sup> with NO<sub>2</sub><sup>1-</sup> (red) and NO<sub>3</sub><sup>1-</sup> (blue). See supporting information for detailed analysis (Figure S2).

charge-state of the metal-oxide cluster, as both contain diagnostic features that are sensitive to the oxidation state distribution of vanadyl moieties across the hexavanadate core.<sup>15-17</sup> The electronic absorption spectrum of the product is largely featureless, with a weak absorption at 622 nm (108 M<sup>-1</sup> cm<sup>-1</sup>), which is attributed to a spin-forbidden d<sub>xy</sub>-d<sub>x<sup>2</sup>-y<sup>2</sup></sub> transition for V<sup>IV</sup> ions within the Lindqvist cluster (Figure 2).<sup>17</sup> Notably, the lack of intervalence charge transfer (IVCT) bands associated with mixed-valent (V<sup>IV</sup>/V<sup>V</sup>) variants of the POV-alkoxide cluster ([V<sup>IV</sup><sub>6-x</sub>V<sup>V</sup><sub>x</sub>(OCH<sub>3</sub>)<sub>12</sub>)<sup>n</sup> (n = -1, 0, +1) suggests that the product possesses an iso-valent oxidation state distribution of vanadyl moieties, consistent with the electronic structure of V<sub>6</sub>O<sub>7</sub><sup>2-</sup> ([V<sup>IV</sup>]<sub>6</sub>).<sup>17</sup> The infrared spectrum of the product contains two absorption bands located at 937 cm<sup>-1</sup> (V=O<sub>t</sub>; O<sub>t</sub>= terminal oxo) and 1059 cm<sup>-1</sup> (O<sub>b</sub>-CH<sub>3</sub>; O<sub>b</sub>= bridging oxo) (Figure S3). These energies are consistent with those reported for V<sub>6</sub>O<sub>7</sub><sup>2-</sup>.<sup>16</sup>

To evaluate the non-cluster containing products of the reaction of NO<sub>2</sub><sup>1-</sup> with V<sub>6</sub>O<sub>6</sub><sup>1-</sup>, we turned our attention to detection of nitric oxide (NO). We opted to use cobalt(II) tetraphenylporphyrin (CoTPP) given its well-established affinity for NO.<sup>18, 19</sup> After conducting a series of control experiments (via electronic absorption spectroscopy, Figure S4) to confirm no reactivity between CoTPP and substrate or the parent and reduced clusters, we devised an *in situ* experiment where the NO scavenger complex was added directly to the reaction mixture. Similar to the results observed in the absence of CoTPP, complete consumption of the oxygen-deficient cluster was noted, along with formation of the NO-ligated CoTPP complex (confirmed by <sup>1</sup>H NMR, Figures S5-S6).<sup>20</sup> Further analysis of the reaction mixture by electronic absorption spectroscopy revealed the expected bathochromic shift of the absorption feature diagnostic for NO-CoTPP.<sup>21-23</sup> Collectively, these data confirm formation of NO following reduction of nitrite by V<sub>6</sub>O<sub>6</sub><sup>1-</sup> (Figure S7).

NO<sub>2</sub><sup>1-</sup> activation mediated by metal complexes generally requires photolysis,<sup>24, 25</sup> protonation,<sup>26</sup> or the addition of other additives (e.g. PR<sub>3</sub>, SR<sub>2</sub>)<sup>27-29</sup> to facilitate N-O bond scission. Thus, the reactivity of the oxygen-deficient POV-alkoxide with

this substrate is surprising. An exception was recently reported by Schelter and coworkers: addition of  $\text{NO}_2^-$  to a pentavalent uranium complex ( $\text{U}^{\text{V}}\text{Cl}_2(\text{N}(\text{SiMe}_3)_2)_3$ ) results in oxygen atom transfer (OAT) from  $\text{NO}_2^-$  to the actinide centre.<sup>30</sup> Initial coordination of the substrate to the reduced uranium ion through its oxygen atom was supported by DFT calculations. Subsequent cleavage of the N-O bond of the oxyanion is facilitated by single electron transfer from uranium to the substrate, resulting in the release of NO and the formation of a new, one-electron oxidized uranium species with a terminal oxido ligand ( $\text{U}^{\text{VI}}\text{OCl}(\text{N}(\text{SiMe}_3)_2)_3$ ). We invoke similar reactivity for our oxygen-deficient polyoxoanion. Addition of  $\text{NO}_2^-$  results in the cleavage of the N-O bond, release of NO, and formation of a one-electron oxidized cluster with a new  $\text{V}^{\text{IV}}=\text{O}$  bond at its surface (replacing the site-differentiated  $\text{V}^{\text{III}}$  centre).

Following the successful reduction of  $\text{NO}_2^-$ , we set out to explore the activation of the more thermodynamically challenging substrate for deoxygenation,  $\text{NO}_3^-$ . Molybdenum-containing nitrate reductases catalyse the reduction of  $\text{NO}_3^-$  through a mechanism in which an oxygen atom is transferred from the oxyanion to a molybdenum(IV) centre.<sup>31, 32</sup> This results in the formation of  $\text{NO}_2^-$ , with concurrent two-electron oxidation of the metal centre to form a  $\text{Mo}(\text{VI})=\text{O}$  moiety. Drawing inspiration from enzymatic reduction of  $\text{NO}_3^-$ , we opted to explore the reactivity of our reduced POV-alkoxide cluster with this substrate. We hypothesized that  $\text{NO}_3^-$  activation would follow a similar pathway to that of the native enzyme, in that N-O bond cleavage would result in OAT to the site differentiated  $\text{V}^{\text{III}}$  centre, changing the overall oxidation state distribution of the cluster from  $[\text{V}^{\text{III}}\text{V}^{\text{IV}}_5]^{1-}$  to  $[\text{V}^{\text{IV}}_5\text{V}^{\text{V}}]^{1-}$ . Similar OAT mechanisms for  $\text{NO}_3^-$  reduction have been reported for d-<sup>33, 34</sup> and f-block<sup>35, 36</sup> metal complexes.

Addition of an equivalent of tetrabutylammonium nitrate ( $[\text{nBu}_4\text{N}]\text{NO}_3$ ) to  $\text{V}_6\text{O}_6^{1-}$  in THF at room temperature afforded minimal conversion to the oxidized POV-alkoxide (Figure S8). However, heating of this reaction mixture to 70 °C afforded a gradual colour change from brown/red to green over the course of 24 hr. Analysis of the crude reaction mixture by  $^1\text{H}$  NMR spectroscopy revealed formation of a fully-oxygenated POV-alkoxide (Figure S9).

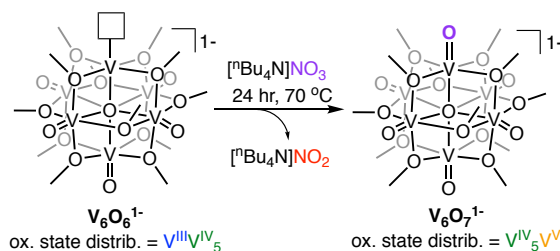
Characterization of the cluster-containing product of the reaction of  $\text{V}_6\text{O}_6^{1-}$  and  $[\text{nBu}_4\text{N}]\text{NO}_3$  by IR spectroscopy revealed two strong absorption bands corresponding to  $\nu(\text{V}=\text{O}_i)$  and  $\nu(\text{O}_b-\text{CH}_3)$ , located at 953 and 1043  $\text{cm}^{-1}$ , respectively (Figure S10). These infrared absorptions are substantially shifted from that of  $\text{V}_6\text{O}_7^{2-}$  (937, 1055  $\text{cm}^{-1}$ ), however closely resemble values reported for the *monoanionic* POV-alkoxide,  $[\text{nBu}_4\text{N}][\text{V}_6\text{O}_7(\text{OCH}_3)_{12}]$  ( $\text{V}_6\text{O}_7^{1-}$ ;  $\nu(\text{V}=\text{O}_i)$ : 953  $\text{cm}^{-1}$ ,  $\nu(\text{O}_b-\text{CH}_3)$ : 1047  $\text{cm}^{-1}$ ).<sup>14, 16</sup> To further discern the charge-state of the product of the reaction of  $\text{NO}_3^-$  and  $\text{V}_6\text{O}_6^{1-}$ , electronic absorbance spectroscopy was employed (Figure 2). The spectrum of the crude product contains two IVCT bands located at 392 nm ( $2594 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 1000 nm ( $605 \text{ M}^{-1} \text{ cm}^{-1}$ ). The presence of these absorbances are consistent with formation of a cluster with a mixed-valent  $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$  charge-state. However, further analysis revealed lower values of molar absorptivity for these features as compared to those reported

for  $\text{V}_6\text{O}_7^{1-}$  (392 nm ( $3583 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 1000 nm ( $814 \text{ M}^{-1} \text{ cm}^{-1}$ ); Figure S11).<sup>14</sup> This discrepancy suggests that the product of  $\text{V}_6\text{O}_6^{1-}$  and  $[\text{nBu}_4\text{N}]\text{NO}_3$  might in fact be a mixture of clusters with varying oxidation state distributions (namely complexes  $\text{V}_6\text{O}_7^{1-}$  and  $\text{V}_6\text{O}_7^{2-}$ ). Electrochemical analysis of the crude reaction mixture in acetonitrile revealed four quasi-reversible events, consistent with complete oxygen atom transfer from the substrate to the reduced scaffold (Figure S12).<sup>16</sup> However, the open circuit potential (OCP) measurement of the sample revealed zero current at -0.61 V (vs.  $\text{Fc}^{0/+}$ ) which is cathodically shifted from the OCP value for complex  $\text{V}_6\text{O}_7^{1-}$  (-0.41 V vs.  $\text{Fc}^{0/+}$ ). This shift provides further support for the formation of multiple charge states of the cluster-containing product upon  $\text{NO}_3^-$  reduction.

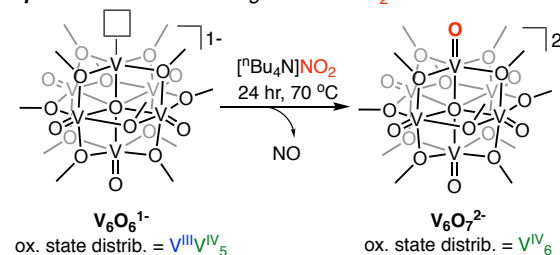
Given that  $\text{NO}_2^-$  reduction with  $\text{V}_6\text{O}_6^{1-}$  occurs at room temperature, we posed that the observed mixture of  $\text{V}_6\text{O}_7^{1-}$  and  $\text{V}_6\text{O}_7^{2-}$  obtained from the activation of  $\text{NO}_3^-$  might be a result of competitive reactions between the oxygen-deficient POV-alkoxide cluster and both nitrogen oxides ( $\text{NO}_2^-$  being formed in solution following the two electron reduction of  $\text{NO}_3^-$ ). To assess whether the cluster was competent for the *complete* reduction of  $\text{NO}_3^-$  to NO, a substoichiometric amount of  $[\text{nBu}_4\text{N}]\text{NO}_3$  was added to  $\text{V}_6\text{O}_6^{1-}$  (Scheme 2). Analysis by  $^1\text{H}$  NMR spectroscopy revealed complete consumption of the oxygen deficient POV-alkoxide, despite addition of only one half of an equivalent of substrate (Figure S13). These results suggest that formation of  $\text{NO}_2^-$  in solution upon the reduction of  $\text{NO}_3^-$  is immediately followed by a reaction of this by-product with unreacted starting material ( $\text{V}_6\text{O}_6^{1-}$ ). The OCP of the product (-0.59 V vs.  $\text{Fc}^{0/+}$ ) compares favourably with the above result, confirming that a mixture of cluster-containing products are formed regardless of the number of equivalents of  $[\text{nBu}_4\text{N}]\text{NO}_3$  added to  $\text{V}_6\text{O}_6^{1-}$  (Figure S14). Finally, examination of the electronic absorption spectra of the *in situ* reaction of substrate, cluster, and CoTPP revealed formation of half an equivalent of NO (Figure S15).<sup>21</sup>

Scheme 2. Reduction of  $\text{NO}_3^-$  with  $\text{V}_6\text{O}_6^{1-}$ .

**Step 1: Reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$**



**Step 2: Reduction of *in situ* generated  $\text{NO}_2^-$  to NO**



These results, detailing the activation of  $\text{NO}_2^{1-}$  and  $\text{NO}_3^{1-}$  using oxygen-deficient POV-alkoxide clusters provide insight into a possible mechanism of electrocatalytic  $\text{NO}_x^{1-}$  activation (e.g. formation of an open-coordination site followed by  $\text{NO}_x^{1-}$  reduction at the reduced metal ion). However, it is worth noting that experiments probing the potential electrocatalytic activity of  $\text{V}_6\text{O}_7^{1-}$  toward the reduction of nitrite and nitrate afforded no current response consistent with catalysis. The inactivity of the POV-alkoxide cluster suggests that bridging oxygen atoms found in plenary POM motifs likely play an important role in the reduction of  $\text{NO}_x^{1-}$  (POV-alkoxide clusters have only *terminal* oxygen sites available for small molecule activation).

In this work, we have expanded upon the reactivity of oxygen-deficient POV-alkoxide clusters toward small molecule activation by demonstrating their ability to facilitate  $\text{NO}_x^{1-}$  ( $x = 2, 3$ ) reduction. Through spectroscopic analysis, we have shown that the one-electron reduction of  $\text{NO}_2^{1-}$  results in N-O bond cleavage and formation of a fully oxygenated cluster and nitric oxide. Furthermore, we present the reactivity of the O-deficient cluster with  $\text{NO}_3^{1-}$ , illustrating that these clusters can fully deoxygenate the more “inert” oxyanion, resulting in formation of NO. The additive-free, stoichiometric reactivity of the reduced metal ion embedded within the POV-alkoxide cluster toward N-O bond cleavage and oxygen atom transfer, demonstrates new reactivity for these oxygen-deficient species. These results provide insight into the mechanism by which metal oxides can facilitate molecular transformations of relevance to the activation of oxygenated substrates.

### Conflicts of interest

There are no conflicts to declare.

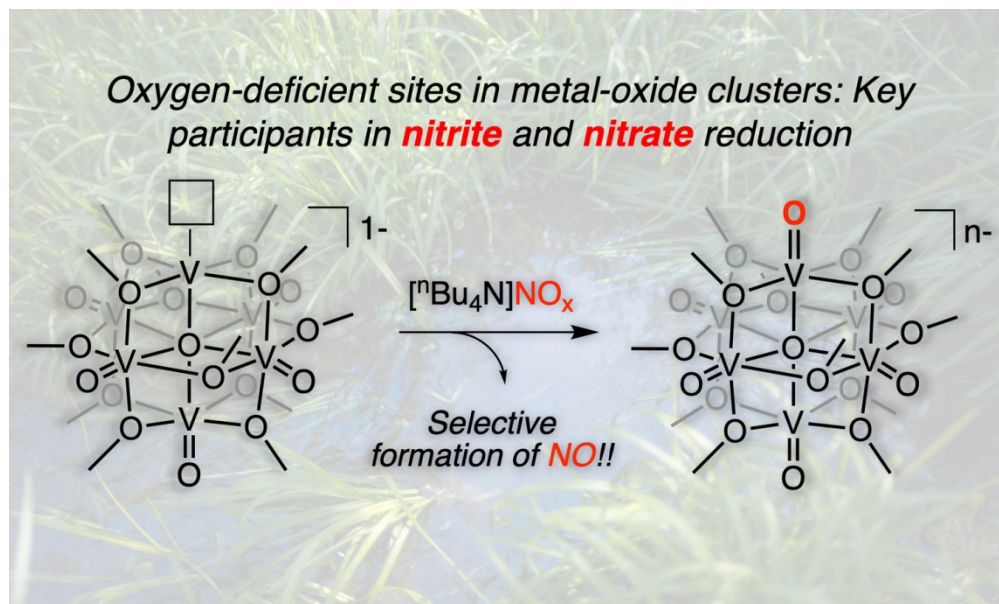
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