Title: Cation synergies affect ammonia adsorption over VO_x and (V,W)O_x dispersed on α -Al₂O₃ (0001) and α -Fe₂O₃ (0001)

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Abstract

The catalytic behavior of oxide-supported metal oxide species depends on the nature of the support and the presence of co-catalysts. We use density functional theory (DFT) to explore the relationship between the structure and chemical behavior of vanadium oxide in light of its industrial use for the selective catalytic reduction of nitric oxide with ammonia (NO-SCR). The relative stabilities of dispersed VO_x monomers, dimers, and long-chain oligomers on two model oxide support surfaces with similar structure but drastically different chemical behavior, α -Al₂O₃ (0001) and α -Fe₂O₃ (0001), are determined. The effect of added tungsten, known to promote NO-SCR, is also investigated on the relatively inert α -Al₂O₃ (0001) support. We find that the adsorption behavior of NH₃, representing the first step of the NO-SCR reaction, depends strongly on the VO_x local structure. Protonation of NH₃ to NH₄⁺ over surface hydroxyls is energetically favorable over VO_x-WO_x dimers and VO_x oligomers, which are stabilized by the reducible α -Fe₂O₃ (0001) support.

Keywords: Nitric oxide reduction; vanadium oxide; oxide support; ammonia adsorption; electronic structure; density functional theory

Graphical abstract

Highlights

- Surface structures were calculated for V atop $\alpha\text{-Al}_2\text{O}_3$ (0001) and $\alpha\text{-Fe}_2\text{O}_3$ (0001).
- Adding W to V creates stronger Brønsted acid sites that convert NH_3 to NH_4^+ .
- $\alpha\text{-Fe}_2\text{O}_3$ (0001) stabilizes oligomeric VO_x species needed for NO-SCR.
- Cation synergies mediated by O ligands explain behavior of NO-SCR catalysts.

1 Introduction

Oxide-supported vanadium oxide (VO_x) is a versatile catalyst for industrial and environmental applications[1, 2], including the selective catalytic reduction of nitric oxide with ammonia (NO-SCR). In this reaction, V plays two synergistic roles[3, 4]. The first step of NO-SCR is the adsorption of NH_3 onto a hydroxylated V acting as a Brønsted acid site. The resulting ammonium cation transfers a proton to a nearby redox V site, “activating” it to bind NO and interact with the ammonium to form N_2 and H_2O [3].

The nature of catalytically active V species depends on their structure and their ligand-mediated interactions with surrounding cations, including the oxide support. VO_x species range from isolated monomers to crystalline species such as V_2O_5 , and in many cases the morphology has consequences for the reactivity. A variety of possible coordination configurations of monomeric VO_x have been proposed under different chemical environments and coordination structures with the oxide support[5-11]. At higher coverages of VO_x , V-O-V bridging bonds form, with subsequent changes in the chemical behavior of V, such as improved reducibility[12, 13]. VO_x on the rutile TiO_2 (110) surface forms complex chains which undergo structural shifts through a reduction-oxidation (redox) cycle[14]. Oligomeric octahedral VO_x at about half-monolayer loading on TiO_2 is highly active[15, 16], and according to the two-site model of NO-SCR, VO_x oligomers are expected to be more active versus isolated VO_x monomers[3].

The catalytic properties of surface species such as VO_x are heavily influenced by the oxide support[17-21]. V cations are more reducible in the presence of other reducible metal cationic species, such as Ti^{4+} ; however, V reducibility decreases as its density increases, since crystalline V_2O_5 does not interact as strongly with the support material[15]. This reducibility from V^{5+} is particularly important to NO-SCR.

The addition of W to VO_x is known to significantly improve NO-SCR activity[22-26]. However, the mechanism of this promotional effect is debated[23-25, 27-31]. W provides Brønsted acid sites to promote NH₃ adsorption[23, 24], but it may serve a structural purpose as well, preventing VO_x from crystallizing into inert forms[25]. Electronic interactions between V and W cations also play a significant role[31, 32]. The influence of cationic W species and the oxide support on VO_x catalysts can be generalized as ligand-mediated cation-cation interactions between V and other species at the catalyst surface.

In this work, we compare the behavior of catalysts supported by different model oxide surfaces. Sapphire (α -Al₂O₃) and hematite (α -Fe₂O₃) have nearly identical structures but drastically different bulk and surface chemistry. Sapphire is a non-reducible ionic insulator, whereas hematite is a reducible semiconductor. The partially covalent character of Fe—O bonds and the available electron configurations of the high-spin 3d⁵ Fe³⁺ cations result in a rich variety of surface chemical phenomena.

Using density functional theory (DFT), we determine the stable coordination environment and electronic structure of sub-monolayer VO_x monomers, dimers, and long-chain oligomers which lie on a cation deficient (0001) surface of sapphire or hematite supports. The relative stabilities of these configurations are assessed, and substantial differences are observed for VO_x supported on sapphire vs. hematite. The effect of WO_x on the stability and chemistry of these structures on sapphire is also investigated. We then assess the role of catalyst structure and composition on the first step of the NO-SCR reaction: the adsorption of NH₃ at a Brønsted acid site and associated proton transfer from the catalyst, yielding NH₄⁺. By calculating the adsorption energy of NH₃ and the associated changes in the atomic and electronic structure of the catalyst upon NH₃

adsorption, we clarify the roles of adsorption site geometry, the V-W interaction, and the effect of the substrate in the initial reaction step.

2 Methods

Plane-wave DFT calculations were performed using the VASP code[33-36]. A projector augmented wave pseudopotential scheme[37] was employed with a 400 eV cutoff energy. Exchange-correlation energies were calculated using the PW91 functional[38], which efficiently gives reasonable results for NH_3 adsorption on surfaces[39].

Atomic relaxations and electronic structure calculations were performed on asymmetric slabs derived from optimized bulk structures. One unit cell of the corundum structure of $\alpha\text{-Al}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ consists of 6 layers of 3 O atoms stacked along the (0001) direction, with 2 cations staggered between each O layer. The O-terminated 1×1 $\alpha\text{-Al}_2\text{O}_3$ (0001) surface supercell used in this work ($a = b = 4.755$ Å, $c = 25.000$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) consists of 19 atoms (four Al_2O_3 formula units, minus one terminal cation) and is shown in **Figure 1**. The $a = b$ lattice parameter agrees well with the experimental value of 4.759 Å[40], and the c supercell lattice parameter was chosen to ensure >10 Å of vacuum space between slab surfaces. The O-terminated side of the slab was decorated with surface species, ligands, and adsorbates. On the opposite side of the slab, the outermost 2 Al cations and 1 oxygen layer (for sapphire) were fixed to calculated bulk values. All other atoms were allowed to relax using a conjugate-gradient[41] or quasi-Newtonian scheme. For hematite, a similar 1×1 supercell[42-44] ($a = b = 5.006$ Å) was employed, with 3 metal cations and 2 oxygen layers fixed; this lattice parameter is slightly contracted from the experimental value of 5.035 Å[40]. Further details on this slab, including densities of states (DOS) calculations, can be found in Ref. [42].

Figure 1: (a) Top $[0001]$ and (b) side $[11\bar{2}0]$ views of the 1×1 O-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) slab used in this work. The “A” and “B” surface cation sites (which are unoccupied in this image) are marked in one 1×1 cell of the periodic slab. In (a), green dotted lines and purple dashed lines join the initial positions of cations in the dimer and oligomer configurations, respectively. The gray rectangle in (b) covers the fixed portion of the slab.

Most calculations reported in this work were performed on 2×1 supercells. $2\times 4\times 1$ k -point meshes[45] were used for structural relaxations, and densities of states were calculated using $4\times 8\times 1$ k -point meshes. For structures with appropriate symmetry, some 1×1 supercell calculations were performed; these employed $4\times 4\times 1$ k -point meshes for structural relaxation and densities of states calculations. For calculations on the hematite slab, spin-polarized calculations were used to accommodate antiferromagnetic ordering of the substrate[46, 47]. Corrections for dipoles along the c direction of our asymmetric slabs[48, 49] were attempted for some test

structures; however, these computationally expensive corrections did not significantly affect relaxed structures, charge densities, or relative supercell energies, and were therefore not used in the calculations reported herein.

Bonding and charge transfer characteristics were measured by Bader charge integration[50, 51], which is sensitive to ionic charge, and bond valence sums (BVS)[52-54], which provide an estimate of the formal valence of cations and anions. BVS were calculated using parameters fit for vanadium[55, 56], tungsten[57], aluminum[58], and iron[58] coordination environments.

3 Results

In Section 3.1, models based upon a non-reducible alumina support are presented for $\frac{1}{2}$ ML VO_x and mixed (V,W) O_x catalysts, followed by analysis of the isostructural VO_x -terminated reducible ferric oxide in Section 3.2.

3.1 Structures on the non-reducible $\alpha\text{-Al}_2\text{O}_3$ (0001) support

3.1.1 The Catalyst: $\frac{1}{2}$ ML VO_x

Vanadium atoms were placed on 2×1 O-terminated sapphire (0001) surface supercells at $\frac{1}{2}$ monolayer equivalent (ML) coverage and allowed to relax. (We define 1 ML as 2 metal cation species per 1×1 surface cell.) Two symmetry-inequivalent surface sites, corresponding to the cation positions if the bulk lattice were extended above the surface O plane, were chosen for catalyst cation placement, as shown in **Figure 1**. Following the literature convention these sites are referred to as the “A” site, which sits above a cation hollow site, and the “B” site, which corresponds to the next bulk-like cation position. Adsorption structures included monomers, where the surface cations occupied the A sites, as well as dimers and oligomers, where selected A and B sites were occupied as shown in **Figure 1(a)**. Four terminal ligand configurations were

tested for all three cation configurations: two O ligands (referred to as $V_1=O$, $V_2=O$); one O and one OH ligand ($V_1=O$, V_2-OH); two OH ligands (V_1-OH , V_2-OH); or no terminal ligands. The latter configuration refers to a “metal terminated” surface similar to that observed for clean α - Al_2O_3 (0001) under ultra-high vacuum conditions[59], but it is unlikely to survive under ambient or catalytic conditions[60] and is included as a reference.

Structural and chemical data for the most stable relaxed structures of 1/2 ML VO_x / O-terminated sapphire (0001) are given in **Table S1** in the Supplementary Information (SI). Relative stabilities are computed as the difference in total energies of relaxed isostoichiometric 2×1 supercells. For each stoichiometry, the monomer case was by far the most stable, with the lowest energy by over 1 eV per 2×1 surface supercell in every case. On all surfaces, the symmetry is mostly preserved: V sits above the surface O layer, forming distorted tetrahedra when a coordinating terminal ligand is available. V-O bond lengths for the case with no terminal ligands and the fully vanadyl terminated surface are comparable to those reported previously for similar structures[60]. Bader charges do not indicate large differences between vanadyl species and hydroxylated V, although they are significantly smaller for cases with no terminal ligands. On the O-terminated sapphire surface, with a nominal surface oxidation state of -3, V^{3+} should be stable; thus, a single terminal hydroxyl group (V-OH) should oxidize this cation to V^{4+} , and a vanadyl group (V=O) would yield V^{5+} . V valence as calculated by the BVS method scales as expected for the coordinate environment, ranging from 3.34 for V with no terminal ligand, 4.10 – 4.33 for singly hydroxylated V, and 4.69 – 4.72 for vanadyl V. Analysis of the underlying Al atoms shows that the topmost substrate Al atom (denoted Al_C) is slightly more oxidized than expected, while the Al_B atom, which sits slightly lower, is partially reduced.

For this slab in vacuum, formation of the first hydroxyl group by H addition is exothermic (-0.45 eV), while the second hydroxylation is endothermic (0.20 eV), as determined by calculations of the hydrogenation energies $\Delta E_{+\frac{1}{2}H_2}$ (see SI). This suggests that a partially hydroxylated surface would be stable without decomposition into vanadyl- and hydroxyl-rich regions, and the surface is susceptible to hydroxylation in the presence of H₂. The stepwise addition of H to two adjacent and nearly identical V sites enables a simple way to study the interaction between coordinated metal groups at the catalyst surface. As the shifts in Bader charge and BVS indicate (**Table S1**), there is some interaction between the two V sites, despite their separation by over 4.7 Å. In particular, the nature of the hydroxylated V changes significantly in the “mixed termination” state in which it neighbors a vanadyl group instead of another hydroxyl group. The Bader charge of the hydroxylated V increases (2.11 $\rightarrow$ 2.24 *e*), and the BVS of 4.33 suggests that V is relatively oxidized compared to the nominal +4 state.

To characterize this V—V interaction, atom-projected partial densities of states (PDOS) for surface atoms in the cases described above are plotted in **Figure S1** (SI). Two sets of V 3*d* features are observed: a broad V 3*d* – O 2*p* hybridization feature below the Fermi level E_F , and one or more localized *d*-states at or above E_F . Recall that the ground configuration for neutral V is 3*d*³4*s*² and thus V³⁺ would have the nominal *d*²*s*⁰*p*⁰ configuration with E_F falling within the *d*-band. Covalent interactions tend to increase the *s,p,d* occupancy. For structures with the same terminal ligands on each V atom (V₁=O, V₂=O and V₁-OH, V₂-OH), the PDOS of both V sites are degenerate. However, for the mixed-termination case (V₁=O, V₂-OH), the features in the PDOS can be clearly distinguished as belonging to one site or the other. The presence of a nearby vanadyl group narrows the distribution of electronic states on the hydroxylated V, a

possible cause of the increases in Bader charge and BVS. Likewise, some of the vanadyl acceptor d -states above E_F disappear.

The effect of partial reduction to a mixed-termination state can be visualized by subtracting the total charge density of one dispersed V monomer structure from another. The change in charge density through a reduction series from a fully oxidized (vanadyl-only) structure to the mixed-termination structure and finally to a fully hydroxylated structure is shown in **Figure 2**. Analysis of these charge density difference maps shows that when a hydrogen atom is added to the double vanadyl case, there is very little perturbation around the remaining vanadyl group. The hydroxylated V, however, shows significant shifts in the charge density associated with the coordinating oxygen at the surface and around the vanadium atom as compared to the vanadyl case. The addition of a single hydrogen atom per 2×1 surface cell induces significant charge density shifts throughout the near-surface atoms in the lattice, as the O atoms are shifted slightly upward. The next hydrogen addition completely hydroxylates the surface, causing shifts in the surface oxygens and slightly increasing the electron density around the first hydroxylated V atom, in accordance with the results shown in **Table S1**.

Figure 2: Charge difference maps for the reactions of monomer (“A”-site) V species dispersed on the O-terminated α - Al_2O_3 (0001) substrate with the specified terminal ligands: (a) $V_1=O, V_2=O \rightarrow V_1=O, V_2-OH$; (b) $V_1=O, V_2-OH \rightarrow V_1-OH, V_2-OH$; (c) $V_1=O, V_2=O \rightarrow V_1-OH, V_2-OH$. Energies of each reaction are included. Isosurfaces and charge densities in yellow and red indicate increases in charge density, while blue indicates decreases.

3.1.2 NH₃ Adsorption over VO_x

NH₃ adsorption onto a Brønsted acid site is the first step in a NO-SCR reaction cycle[3]. This adsorption event may weaken nearby V=O bonds, reducing the vanadyl species[61] and thereby activating these sites for NO adsorption[3]. We investigate this behavior for different VO_x geometries by simulating the adsorption of an NH₃ molecule onto relaxed half vanadyl / half hydroxyl 0.5 ML VO_x / α -Al₂O₃ surface structures, referred to as O(OH) structures herein.

We note that relaxation of the O(OH) dimer case results in a separation of the vanadia polyhedra, as the V cation initially occupying the A site moves away from the B site cation along the $[\bar{1}\bar{1}20]$ direction. Similarly, the vanadia polyhedra which begin as oligomeric chains relax into dimers, as the A-site V cation moves away from the B site cation along the $[10\bar{1}0]$ direction. In this most stable relaxed configuration, O is displaced from the Al₂O₃ surface in order to bridge the VO_x polyhedra. Meanwhile, the H atom relaxes to a position on a nearby surface O, indicating that hydroxylation of the exposed (and O-defected) Al₂O₃ surface is preferred over reduction of a vanadyl group. Despite these dramatic relaxations, the structures which were initially dimeric and oligomeric were less stable than the initially monomeric structure by 1.92 and 1.78 eV, respectively, per 2×1 supercell.

We consider three cases for NH₃ adsorption, for which relaxed structures are shown in **Figure 3**. For the monomer configuration, the initial structure simulates –OH - - - NH₃ hydrogen bonding, as has been observed for several hydroxylated oxide surfaces[62]. For the structure which began as oligomeric VO_x chains and relaxed to dimers with Al₂O₃ hydroxylation, NH₃ adsorption over the resultant vanadyl group of each VO_x polyhedron is tested; these are denoted as the “dimer-

A” and “dimer-B” adsorption structures, referring to the site over which NH₃ is initially adsorbed.

As reported in **Table S2** (SI), the monomer case is again the most stable, with a >2 eV advantage over the co-stable dimer configurations. The monomer case also has the largest NH₃ adsorption energy (-1.34 eV), as NH₃ abstracts a proton from the hydroxyl group, becoming an NH₄⁺ ion which weakly interacts with the terminal O of both V-O tetrahedra. Bader analysis shows that the NH₄ structure has a total positive charge of 0.81, confirming the assignment as an ammonium cation. The bond length between each V and the terminal O atom (1.66 Å, 1.69 Å) is intermediate between that of the vanadyl (1.61 Å) and hydroxylated (1.78 Å) V-O bonds for the monomer case prior to NH₃ adsorption. While the original vanadyl site remains at V⁵⁺ (with a BVS calculated valence of 4.62 with NH₃ adsorbed vs. 4.69 without), the originally hydroxylated site is substantially oxidized (valence of 4.53 with NH₃ vs. 4.33 without).

For the dimer-A and dimer-B cases, there is no obvious Brønsted-like site associated with V, so the molecule is adsorbed to the terminal O atom of each V. With no nearby H to remove, NH₃ remains roughly neutral (with a Bader charge of -0.10 *e*) and interacts with the V atoms at the center of the V-O tetrahedra in a Lewis acid-like manner, with an NH₃ adsorption energy of only -0.81 eV. If only the V-O coordination is considered in the BVS, V appears to be in a +4 state in both Lewis acid-like configurations; however, the contribution from N is substantial (0.35 – 0.39 *e*). The local structures and NH₃ adsorption energies at Brønsted and Lewis acid sites are similar to those reported for the V₂O₅ (001) surface[63].

Figure 3: Side $[11\bar{2}0]$ (left) and top $[0001]$ (right) views of relaxed structures of NH₃-adsorbed O(OH) cases of 0.5 ML VO_x atop the O-terminated *a*-Al₂O₃ (0001) substrate. (a) Monomer; (b) dimer-A; (c) dimer-B. V atoms and coordination polyhedra are shown in green; O, red; and Al, light blue. The light gray-blue spheres represent N, and the light blue polyhedra represent the N-H coordination for NH₃ and NH₄⁺ species. N—V interactions are identified by purple dotted lines.

Because the most stable ammonia-free dimer structures feature dissociated terminal hydroxyl groups, these cases were re-evaluated by moving the H onto either the terminal or bridging O sites on the relaxed oligomer example and placing the NH₃ above, as in the monomer case.

However, these structures were all substantially less stable than those discussed above and were not considered for further analysis.

Figure S2 (SI) shows the effect of NH₃ adsorption on the V and O PDOS. In the monomer case, NH₃ adsorption results in the conversion of a hydroxyl group attached to cation V₂ into a vanadyl group, whereas in the dimer-B case, NH₃ interacts in a Lewis acid-like manner with the V₂ cation. Interestingly, the PDOS of the V associated with the hydroxyl group on the monomer

structure is less affected than the vanadyl V, possibly due to the change in local symmetry and lengthening of the vanadyl bond. In the dimer case, the unoccupied $3d$ states of the Lewis acidic V atom shift towards E_F , whereas the PDOS for the other V atom shifts further above E_F . There is also stronger hybridization between NH_3 states and the V $3d - \text{O } 2p$ band as compared to the monomer case.

3.1.3 The Bimetallic Catalyst: $\frac{1}{2}$ ML Mixed (V,W) O_x

To investigate the catalytic synergy between vanadia and tungsten oxides, one of the V atoms in each cation configuration was substituted with W. The catalyst coverage of each (V,W) O_x case is therefore $\frac{1}{4}$ ML W and $\frac{1}{4}$ ML V atop the O-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) surface. The terminal ligand configurations include (W=O, V=O), (W=O, V-OH), (W-(OH) $_2$, V=O), and (W-O(OH), V=O), or no additional coordinating ligands. Ligand configurations were chosen to tune the nominal oxidation state of W to the same as that of V or one standard charge greater. Monomer, dimer, and oligomer configurations were initialized and relaxed, and structural and chemical details of the monomer structures are given in **Table S3** (SI).

The mixed V-W monomer configurations are not as strongly favored as for the V-only monomer configurations, with dimer and oligomer configurations only 0.77 – 1.61 eV higher in energy per 2×1 surface cell in the ligand-terminated cases. The valence of V is affected by its nearest cation neighbor (V vs. W), which can be understood by considering the competition for charge donation. In the monomer case with no terminating ligands, for example, V is reduced further by about 0.2 e in the presence of W vs. V. Even though the monomers are separated, a neighboring W atom, with a valence of 4.10, donates roughly one more electron to the system than V, which has a valence of 3.34 in the V-only case. This depletes the available states for V to donate to the substrate, leaving V more reduced.

The W-(OH)₂, V=O structure can be thought of as the result of H₂O dissociative adsorption onto a tungstyl site, leading to a potential Brønsted acid site. This behavior is strongly favored (-0.60 eV per water molecule). By comparing the V=O, W=O and V=O, W-(OH)₂ cases, we see that the oxidation state of V is not strongly affected by the dissociative adsorption of H₂O over tungsten, whereas W is somewhat reduced in the process, with substantial drops in both its valence and Bader charge.

This observation demands a more detailed comparison of the valences of V and W across these cases, which are summarized in **Table 1**. The valence scales as expected for V, whereas the W valence does not agree as closely with expectations. The W Bader charge follows a similar pattern as its BVS valence, although the differences in Bader charges are much smaller. This trend results from shorter W-O_{substrate} bonds for the tetrahedrally coordinated W=O species, whereas the five-fold coordinated W has a much longer average bond length. Even in the W-O(OH) case with one tungstyl group, the small valence contributions from the extended W-O_{substrate} bonds offset the contribution of the close W=O bond, reducing the BVS.

Table 1. Comparison of V and W valence calculated by bond valence summation for stable monomer structures in 0.5 ML V and 0.25 ML V, 0.25 ML W cases described in **Tables S1** and **S3** in the SI. The “expected” oxidation state is calculated as the opposite sign of the sum of the formal charge of the coordinating environment, including O²⁻, (OH)⁻, and a surface site with a combined oxidation state of -3 on the O-terminated α -Al₂O₃ (0001) surface.

Terminal coordination	Expected oxidation state	V valence		W valence
		V only	Mixed V,W	
No terminal ligands	+3	3.34	3.15	4.10
-OH	+4	4.10, 4.11, 4.33	3.83	--
=O	+5	4.69, 4.72	4.60, 4.68, 4.72	5.62
-(OH) ₂	+5	--	--	5.18
-(O,OH)	+6	--	--	5.33

3.1.4 NH₃ Adsorption over (V,W)O_x

The adsorption of NH₃ onto hydroxyl groups in the W coordination polyhedron, expected to be the Brønsted acid site of interest for NO-SCR, was tested for selected low-energy monomer and dimer cases with V=O, W-(OH)₂ or V=O, W-O(OH) terminal ligand coordination environments, referred to as O(OH)₂ and O₂(OH), respectively. Results for relaxed stable configurations are given in **Table S4** (SI) and **Figure 4**. In the O(OH)₂ structures, the most stable adsorption site of NH₃ was determined for the different hydroxyl sites available. Note that the “dimer” structure was initialized as an oligomer structure prior to NH₃ adsorption, but the V cation migrated significantly from the B-site during relaxation, breaking the oligomer chain. In the monomer case, NH₃ weakly adsorbs (-0.56 eV), relaxing to a geometry with hydrogen bonds forming between N and a surface hydroxyl H (1.6 Å) and between an ammonia H and a hydroxyl O (2.1 Å). The dimer case is remarkably close behind in stability (0.48 eV) from the monomer structure due to its strong NH₃ adsorption energy (-1.69 eV), a consequence of the formation of NH₄⁺ by abstraction of a proton from a W-OH group. The interaction distances between the three ammonium H atoms nearest to the surface and the nearby tungstyl or vanadyl oxygen atoms are 1.6 – 1.8 Å, with the shortest being for the W=O - - - H interaction. However, this only causes subtle changes in the valence of the cations, a slight oxidation of W and reduction of V.

Despite the differences in structure between the O₂(OH)-terminated cases, the ammonia adsorption energy is the same (-0.51 eV). The coordination structure and valences of V and W barely change with the addition of ammonia, since NH₃ interacts weakly with these W surface sites, forming a 1.6 Å H - - - N hydrogen bond with the hydroxyl group. This is in stark contrast to the V-only cases on sapphire, where the NH₃ either removes the hydroxyl H to become NH₄⁺ ($E_{\text{NH}_3\text{-ads}} = -1.34$ eV) or coordinates with the metal cation ($E_{\text{NH}_3\text{-ads}} = -0.81$ eV).

Figure 4: Side $[11\bar{2}0]$ (left) and top $[0001]$ (right) views of relaxed structures of NH_3 -adsorbed mixed V,W-terminated cases on the O-terminated $\alpha\text{-Al}_2\text{O}_3$ (0001) substrate with (a,b) $\text{O}(\text{OH})_2$ and (c,d) $\text{O}_2(\text{OH})$ terminal ligand stoichiometry. (a,c) Monomer; (b,d) dimer. V and W atoms and coordination polyhedra are shown in green and blue, respectively; O, red; and Al, light blue. The light gray-blue spheres represent N, and the light blue polyhedra represent the N-H coordination for NH_3 and NH_4^+ species. The shortest H-bond interactions are identified by purple dotted lines.

The $\text{O}(\text{OH})_2$ cases exemplify how local cation configuration and structure influence chemical behavior, namely between N - - - H hydrogen bonding and H abstraction to NH_4^+ . **Figure 5(a,b)** shows the effect of NH_3 adsorption on these two structures via charge density difference maps. In the monomer case, charge difference maps reveal small perturbations in the ligand environment around V and W, although most of the changes are localized on the W hydroxyls. In

the PDOS (**Fig. 5(c,d)**), there is a subtle rearrangement of the sharp V and W *d*-states just above E_F . Prior to NH_3 adsorption, the greatest proportion of W states sit directly above E_F , with the V states slightly higher; however, upon adsorption, the order reverses. There is also an NH_3 state present at about 4 eV below E_F , hybridized with the cation *d* – O 2*p* band. The effects of NH_3 adsorption are more drastic on the dimer structure. Prior to adsorption, W and V share a narrow band just above E_F . When NH_3 adsorbs and abstracts a proton from a tungsten hydroxyl group, the W states above E_F vanish, and the V features split. Although the V valence does not change significantly, the change in its charge density could be attributed to a lengthening of the vanadyl bond from 1.60 to 1.69 Å as O interacts with the ammonium ion.

Figure 5: (a,b) Charge density difference maps for NH₃ adsorption onto the (a) monomer and (b) dimer O(OH)₂ structures of mixed V,W-terminated O-terminated α -Al₂O₃ (0001). Isosurfaces are drawn at the same charge density values in both cases. Blue regions indicate increased charge density upon NH₃ adsorption, while yellow regions indicate decreased charge density. (c,d) NH_n PDOS and W, V, and ligand and bridging O difference PDOS for the relaxed structure of NH₃ adsorbed on the (c) monomer and (d) dimer O(OH)₂ structures. Difference PDOS indicate the change in PDOS after NH₃ adsorption and subsequent relaxation relative to the Fermi level E_F . For clarity, NH_n PDOS are truncated, and the O 2p contribution has been scaled by a factor of 1/3.

3.2 Structures on the reducible α -Fe₂O₃ (0001) support

3.2.1 The Catalyst: $\frac{1}{2}$ ML VO_x

Results for selected ligand coordinations of monomeric V on the O-terminated α -Fe₂O₃ (0001) surface are shown in **Table S5** (SI). All monomer structures were significantly more stable than dimer or oligomer structures, and their cations remain at A-site positions. Bond lengths and V Bader charges are in good agreement with values reported previously for vanadyl groups on hematite[44]. Compared to V on sapphire, the vanadyl V=O bond length is about the same, and the V-O_{substrate} bonds are slightly longer for hematite, resulting in a somewhat less positive valence. The V-OH bond lengths are also similar, but the hydroxylated V has much shorter V-O_{substrate} bonds on hematite. This yields a valence almost indistinguishable from that of the vanadyl V: in both cases the BVS values are closer to those expected for V⁵⁺. Another notable difference is observed in the reduction chemistry: the hydrogenation energies $\Delta E_{+\frac{1}{2}H_2}$ are much more exothermic than on sapphire, with the first reduction step slightly more exothermic than the second (-1.20 eV and -0.88 eV for hematite vs. -0.45 eV and 0.20 eV for sapphire). This suggests that in the presence of hydrogen, the surface vanadyl ligands would be more reactive. However, the consequence of hydrogenation is not V reduction, but in fact a slight reduction of the near-surface Fe³⁺ cations. As observed for near-surface Al cations on sapphire, the Fe_C cations closest to the surface are more oxidized (by about 0.2 *e*) than their Fe_B counterparts sitting slightly lower in the near-surface cation layer.

PDOS of the surface atoms in these three monomer configurations are shown in **Figure S3** (SI). For all PDOS calculations on hematite surfaces, an on-site +*U* correction of 2 eV was applied to the Fe 3*d* electrons to account for strong *d*-electron localization[64]. The V *d*-states below and

above E_F are not significantly different between the fully hydroxylated surface and the mixed hydroxyl-vanadyl case. The appearance of the vanadyl d -states is also similar between the purely vanadyl-terminated surface and the mixed case, although the Fermi level shifts from the middle of the bandgap to the bottom of the V d -band above E_F .

Figure 6 shows the change in charge density upon sequential addition of hydrogen atoms onto a vanadyl-terminated surface. When adding a hydrogen atom to half of the vanadyl groups, there is a significant distortion of electron density as the cation and its coordination environment shifts in space. These effects reach well beyond the first coordination shell; significant movements of the near-surface Fe cations are observed. The coordination environment around the remaining vanadyl is mostly unaffected. When the second half of the vanadyl groups are hydroxylated, similar charge density perturbations occur around the new hydroxyl group as in the first hydroxylation, with further inward shifts of the subsurface Fe cations. In contrast to our results for sapphire, the charge density associated with sub-surface oxygen atoms is not significantly affected.

Figure 6: Charge difference maps for the reactions of monomer (“A”-site) V species dispersed on the O-terminated $\alpha\text{-Fe}_2\text{O}_3$ (0001) substrate with the specified terminal ligands: (a) $V_1=O, V_2=O \rightarrow V_1=O, V_2-OH$; (b) $V_1=O, V_2-OH \rightarrow V_1-OH, V_2-OH$; (c) $V_1=O, V_2=O \rightarrow V_1-OH, V_2-OH$. Energies of each reaction are included. Isosurfaces and charge densities in yellow and red indicate increases in charge density, while blue indicates decreases.

3.2.2 NH₃ Adsorption over VO_x

The stable monomer, dimer, and oligomer configurations with V-O(OH) termination were investigated for NH₃ adsorption onto the hydroxyl. Results are detailed in **Table S6** (SI), and the relaxed structures are shown in **Figure 7**. In the monomer and dimer cases, there is practically no interaction between NH₃ and the surface. However, for the oligomer case, there is a strong interaction ($E_{\text{NH}_3-\text{ads}} = -1.62$ eV) as the hydroxyl proton is removed, yielding NH₄⁺ species which sit between oligomer rows. These ammonium cations interact with the remaining vanadyl groups, with H - - O distances of 1.7 – 2.0 Å. The strongest interaction is with the substrate as a 1.6 Å hydrogen bond is formed with a surface O atom. The effect of NH₃ adsorption on the electronic states of the oligomer surface is shown in **Figure S4**. On the clean oligomer surface, the spin-up states of the upper V *d*-band are somewhat filled, more so for the hydroxylated V than the vanadyl-terminated V. Upon ammonia adsorption, the total occupied fraction of the V *d*-bands decreases by more than half. The ammonium ion contributes very little to the electronic structure near E_F .

Figure 7: Side $[11\bar{2}0]$ (left) and top $[0001]$ (right) views of relaxed structures of NH_3 adsorbed on (a) monomer, (b) dimer, and (c) oligomer O(OH)-terminated configurations of 0.5 ML VO_x on the O-terminated $\alpha\text{-Fe}_2\text{O}_3$ (0001) substrate.

4 Discussion

4.1 V-W synergy

The effect of W on sapphire-supported V was investigated by replacing half the adsorbed V with W for a nominal coverage of 0.25 ML of each. This mixed-metal surface partially stabilizes the dimer and oligomer structures vs. for 0.5 ML V alone. While the dimer and oligomer structures never reach lower energies than those for the monomers in this work, it is possible that W could stabilize catalytically active (oxyhydr)oxide oligomers on real catalyst supports with more complex surface morphologies.

The NO-SCR reaction begins with the adsorption of NH_3 onto a Brønsted acid site, forming an NH_4^+ cation and thereby “activating” a nearby redox site[3]. Previously reported calculations of VO_x clusters with hydroxyl or adsorbed water ligands show that NH_3 adsorbs over an oligomeric $\text{V}^{5+}\text{-OH}$ Brønsted acid site with subsequent abstraction of a proton and conversion to NH_4^+ , with an NH_3 adsorption energy of -110 to -135 kJ/mol (-1.14 to -1.40 eV), depending on the oligomer structure[65-67]. However, NH_3 adsorbed on $\text{V}^{5+}=\text{O}$ species or other oligomer structures assumes a hydrogen-bonding configuration, with a weaker NH_3 adsorption energy of -50 to -72 kJ/mol (-0.52 to -0.75 eV)[65]. Sun *et al.*[24] calculated NH_3 adsorption energies of only -15.85 kcal/mol (-0.69 eV) and -17.12 kcal/mol (-0.74 eV) over Brønsted sites on $\text{V}_2\text{O}_9\text{H}_8$ and VWO_9H_7 clusters, respectively. However, the discrepancy between these results and earlier work on a nearly identical $\text{V}_2\text{O}_9\text{H}_8$ cluster[67], which gave a Brønsted-like NH_3 adsorption energy of -28.65 kcal/mol (-1.24 eV), was not explained.

In accordance with most of the reviewed literature, our work on VO_x dispersed on sapphire shows two regimes of NH_3 adsorption over V-centered Brønsted and Lewis acid sites, with NH_3

adsorption energies of -1.17 – -1.34 eV and -0.81 eV, respectively. The structures showing Brønsted acidity were V monomers, whereas dimers consisting of corner-sharing distorted tetrahedra showed Lewis acidity. In the mixed V-W structures, however, Lewis-like interactions between the metals and NH_3 were not observed. Different H-bonded structures ($\text{OH}-\text{N}$, $\text{O}-\text{H}$) occurred with NH_3 adsorption energies in the range of -0.51 – -0.76 eV. Brønsted-like adsorption was observed for a V-W dimer configuration with the two cation coordination polyhedra sharing an edge. The NH_3 adsorption energy for this case, -1.69 eV, shows that NH_3 interacts much more strongly with the mixed W-V structures than with V alone.

We note that in the cases in which the ammonium cation is formed, there are no NH_4^+ states near the Fermi level (either above or below E_F). The lack of filled donor states or unfilled acceptor states near E_F suggests that the ammonium cation is very stable and may not be reactive in the geometries studied. However, this does not exclude the possibility that perturbations to the electronic structure of the surrounding cations and ligands may “activate” the catalyst for NO adsorption. Interactions with additional NH_3 beyond the first adsorption event may also be important. For example, NH_3 forms complexes with adsorbed NH_4^+ [68] and Cu cations[69] in Cu-incorporated zeolite catalysts, and this additional NH_3 may play structural or chemical roles through the NO-SCR cycle. Calculations of further NO or NH_3 adsorption and analysis of the subsequent structural and electronic perturbations would clarify the ultimate effect of surface structure and stoichiometry on the NO-SCR activity of oxide-supported V and V-W catalysts.

4.2 Substrate effects

Analysis of the coordination environments of V on the O-terminated (0001) surfaces of hematite and sapphire shows that the dimer and oligomer structures are less likely to disperse into monomers on hematite. X-ray scattering and spectroscopy measurements of 0.5 ML V on

hematite (0001) have indeed suggested a minority fraction of polymerized VO_x along with majority $\text{V}_A=\text{O}$ monomers under realistic conditions[70]. Rudimentary assumptions about substrate-induced strain suggest that the dimers and chains might be more likely to “stretch apart” on the hematite surface as the lateral lattice parameter of the hematite cell ($a = 5.01 \text{ \AA}$) is 5.3% larger than that of sapphire ($a = 4.76 \text{ \AA}$). However, the stabilization of VO_x dimers and oligomers may be attributed to the chemical “flexibility” of hematite due to the reducibility of Fe^{3+} cations and the greater degree of covalency in Fe-O interactions.

The effect of the substrate on catalytic behavior is highly dependent on the bonds between the catalyst metal and the oxygen atoms in the oxide substrate[17]. While the BVS of all cations on the hematite substrate are slightly underpredicted versus their nominal +3 oxidation state, the differences in coordination-dependent BVS between the sapphire- and hematite-supported cases can be ascribed to the degree of charge transfer between the substrate atoms and the charge available to the metal atoms adsorbed on the surface. We therefore use the Bader charges on the oxygen atoms in the V coordination environment (summarized in **Table 2**) as a measure of charge localization on the ligands. For the terminal oxygen atoms (O_t), constituting the vanadyl or hydroxyl oxygens, there is very little dependence on the substrate. However, a large difference is observed for the substrate oxygens (O_s) which coordinate with V and the substrate ($\text{V-O}_s\text{-M}_s$, $\text{M}_s = \text{Al}$ or Fe). In sapphire, the Bader partition of each coordinating substrate oxygen atom contains about 0.4 more electrons per atom than for hematite; that is, fewer O states are available to receive charge from surface species such as V. On hematite, however, V can donate charge to available O states, resulting in a more cationic oxidation state.

Table 2: Bader charges on O atoms in the V-O coordination environment for 0.5 ML V monomers. The first value in each cell is that for V supported on sapphire, followed that for hematite. Values corresponding to vanadyl groups are shown in normal text; hydroxyl, *italic*; and V-O-M_S “surface” bridging oxygens, **bold**.

	V ₁ -OH, V ₂ -OH	V ₁ =O, V ₂ -OH	V ₁ =O, V ₂ =O
O _t (-V ₁)	<i>-1.45, -1.44</i>	-0.68, -0.68	-0.62, -0.61
O _s (-V ₁)	-1.46, -1.04	-1.50, -1.08	-1.52, -1.06
O _t (-V ₂)	<i>-1.46, -1.44</i>	<i>-1.50, -1.41</i>	-0.62, -0.61
O _s (-V ₂)	-1.47, -1.04	-1.41, -1.03	-1.52, -1.06

There are clear differences in the effect of reduction on vanadium species supported on sapphire vs. hematite. As shown in **Tables S1** and **S5**, the reduction of monomeric V supported on hematite is much more exothermic than on sapphire. However, the hydroxylated V species have shorter V-O bonds on hematite vs. sapphire. This leads to a calculated valence that is much closer to the expected value for V⁵⁺ than V⁴⁺, despite V sitting at the center of a distorted tetrahedron with one hydroxyl group and three oxygens bridging to the support surface. **Figures 2** and **6** show that a reduction event from V=O to V-OH on either surface leads to a shift in the surface oxygen atoms towards V. To compensate for this shift in charge, the sapphire surface requires significant movements of charge through the near-surface lattice, indicated by the significant lobes of charge density shift around deeper oxygen layers in **Figure 2(a)**. On hematite, however, these perturbations are mitigated by shifts in the topmost Fe³⁺ layers. The differences can also be viewed through the near-surface substrate cation coordination environments, given in **Tables S1** and **S5**. Within their coordination environments, the difference between the shortest and longest Al-O bond calculated for near-surface Al atoms among the sapphire-supported V monomer cases are 0.08 for Al_C and 0.19 for Al_B. For hematite-supported V monomers, the ranges in Fe-O bond lengths are 0.16 for Fe_C and 0.25 for Fe_B. Altogether, the

hematite surface is better able to accommodate structural changes caused by exposure to reactive environments such as H_2 . The dissociative adsorption of H_2 over dispersed, monomeric vanadyl groups is therefore more strongly favored over hematite than sapphire by about 1.8 eV per H_2 molecule. The strongly exothermic hydrogenation of VO_x on the reducible hematite surface is comparable with the hydrogenation of VO_x monomers on TiO_2 substrates[21].

The adsorption of NH_3 on the hematite-supported V-O(OH) oligomer is very exothermic (-1.62 eV per NH_3) and results in significant changes to the coordination structure of V as a result. The hydroxylated V gives up its proton to NH_3 , forming an NH_4^+ cation and a somewhat stretched vanadyl group. The other V=O bond stretches towards NH_4^+ as well, from 1.61 to 1.64 Å. The valence of each vanadium cation is very close to that expected for V^{5+} . In contrast, for similar Brønsted-like interactions on sapphire-supported V, the vanadyl groups are extended much further (1.66 – 1.70 Å), resulting in a somewhat lower measured valence. Significant distortions in the surface hematite lattice (as shown in **Figure 7**) might allow the V polyhedra to move into better positions to coordinate, reducing the overall energy of adsorption.

The generalized gradient exchange-correlation approximation (GGA) as employed in the PW91 functionals used here is known to poorly describe localized *d*-electrons in α - Fe_2O_3 , resulting in errors such as an under-predicted bandgap[47]. These errors can be mitigated by the GGA+*U* approach. In previous work, we found that the use of PW91+*U* modifies the relative energy of relaxed WO_x / α - Fe_2O_3 surface structures by up to 0.2 eV / 1×1 supercell, causing uncertainties in the assignment of ground-state structures with energy differences within that margin[42].

However, for the PW91 calculations of VO_x / α - Fe_2O_3 reported herein, relative energies exceed 1.3 eV / 2×1 supercell (Table S5) except for the case of NH_3 adsorption, where the monomer structure is favored vs. the oligomer structure by only 0.68 eV / 2×1 supercell (Table S6). We

find these margins wide enough to justify the use of the far more computationally efficient PW91 scheme for the screening of several structures, resorting to PW91+*U* for final electronic structure calculations.

5 Conclusions

Using density functional theory, several configurations of a dispersed VO_x catalyst were investigated on the (0001) surface of α -Al₂O₃. The local chemical environment surrounding VO_x was then modified, either by the addition of the co-catalyst WO_x or by switching the substrate to α -Fe₂O₃. Dispersed V monomers were found to be the most stable configurations in all cases, although the addition of W or the use of a hematite substrate improved the relative stability of dimer or oligomer structures with bridged catalyst coordination polyhedra. Substrate-dependent differences in the chemical behavior of V were observed, particularly the much stronger dissociative chemisorption of H₂ on hematite vs. sapphire, which can be attributed to the chemical and structural “flexibility” of the reducible hematite substrate. Both the addition of W and the use of a hematite substrate strengthened the adsorption of NH₃ onto Brønsted acid sites, yielding NH₄⁺ and simulating the putative first step in the NO-SCR reaction.

We note that all relative stabilities were calculated for *dispersed* metal oxide species while neglecting the possibility of extended structures such as V₂O₅ nanoparticles. VO_x has been shown to be well dispersed on γ -Al₂O₃ or δ -Al₂O₃ at coverages below about ½ ML, whereas above ½ ML crystalline V₂O₅ appears[12]. However, to calculate the stability of dispersed species relative to crystalline V₂O₅ formation would require large-scale calculations of the complex interface between V₂O₅ and our substrate materials. While such a study is beyond the

scope of this work, the possibility of multi-scale modeling to address the full phase space of VO_x-support interactions is intriguing.

This work covers VO_x and WO_x adsorbed onto clean O-terminated (0001) surfaces of sapphire and hematite; depending on surface preparation and ambient conditions, real substrates might instead be initially terminated by hydroxyl groups[71, 72] or substrate cations[32, 42, 44, 59]. Moreover, the surfaces of real oxide-supported catalysts are far more complex and defect-rich than any single crystal termination such as those studied here. Nevertheless, the use of relatively simple models enables a well-controlled study of the physical underpinnings of catalytic behavior, providing broader insight into cation synergies and support effects in oxide-supported catalysts.

Acknowledgements

M.E.M. was supported by a National Science Foundation Graduate Research Fellowship under Grant DGE-0824162. M.E.M. and D.E.E. were supported in part by the Institute for Catalysis in Energy Processes (U.S. Department of Energy (DOE) under Contract DE-FG02-03ER15457). Computational equipment support was provided by the Initiative for Sustainability and Energy at Northwestern University. Atomic structure and charge density plots were made using VESTA software[73].

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