Atomic-Scale View of VO\textsubscript{X}–WO\textsubscript{X} Coreduction on the \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (0001) Surface

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Supporting Information

ABSTRACT: The catalytic activity of oxide-supported vanadium oxide is improved by the presence of tungsten oxide for the selective catalytic reduction of nitric oxides. We propose a mechanism for V–W synergy through studies of the reduction—oxidation behavior of near-monolayer VO\textsubscript{X} and WOX species grown by atomic layer deposition on the \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (0001) single crystal surface. In situ X-ray standing wave measurements reveal an overlayer of W\textsuperscript{6+} species that is correlated with the substrate lattice as well as a redox-reversible shift from uncorrelated V\textsuperscript{5+} to correlated V\textsuperscript{4+}. X-ray photoelectron spectroscopy and electronic structure calculations show a partial reduction of W\textsuperscript{6+} in the presence of V\textsuperscript{4+}, improving the Brønsted acidity in mixed V–W catalyst systems. This mechanism of V–W synergy suggests that control of W d-states might be used as a design parameter for Brønsted acid sites in multicomponent oxide catalysts.

I. INTRODUCTION

Oxide-supported tungsten oxide provides Brønsted acid sites for a variety of industrially relevant reactions.\(^a–d\) The mechanism of Bronsted acidity is thought to involve a reduction from W\textsuperscript{6+} to a transient state W\textsuperscript{5+} upon exposure to a reductant,\(^e–j\) attributed to the appearance of a d–d transition state near the Fermi energy. However, there is little evidence of low-coverage oxide-supported W\textsuperscript{6+} reducing except at >1 monolayer (ML) catalyst coverage or under severe reducing conditions.\(^k–x\)

Oxide-supported vanadia is promoted by W for the selective catalytic reduction of nitric oxide with ammonia\(^y–z\) and other reactions.\(^13,14\) By itself, oxide-supported V has been proposed to play two roles in this reaction: it provides Brønsted acid sites for NH\textsubscript{3} adsorption, which subsequently activate nearby redox sites for NO adsorption and N–N interaction.\(^15\) The promotional effect of W may be structural, as W forms mixed oxide layers with V and prevents the aggregation of VO\textsubscript{X} species into less reactive nanoparticles.\(^11,12,16\) However, the promotional effect of W may also relate to its Bronsted acidity, and indeed the addition of W to a V-loaded catalyst drastically increases the number of available Bronsted acid sites.\(^9,12,13\)

We investigated the mechanism of V–W synergy by pairing surface- and interface-sensitive X-ray scattering and spectroscopy with electronic structure theory, using the relatively inert \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (0001) single crystal surface as a fixed “stage” upon which to study the fundamental chemistry of the V–W interaction. We find a physical foundation of this chemical synergy that derives from the electronic structure of V–W mixed oxides and is consistent with previous work on this complex solid catalyst.

II. METHODS

Single-side epi-polished \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (0001) wafers from Rubicon Technologies (miscut angle \(\sim\)0.2°) were cleaved into 10 mm \(\times\) 10 mm \(\times\) 1 mm substrates. The substrates were sonicated in acetone and then methanol and finally rinsed in ultrapure (18 M\(\Omega\) cm) DI water before drying under a compressed air jet. Substrates were then annealed in a tube furnace for 4 h at 1200 °C in flowing dry air.\(^17\)

Thin films of vanadia were prepared by atomic layer deposition (ALD) onto the \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} crystals using a viscous flow reactor\(^18\) maintained at 1 Torr under vacuum by flowing 200 sccm N\textsubscript{2}. Crystal surfaces were cleaned in situ at 100 °C by flowing ozone at a rate of 200 sccm for 10 min. Vanadium oxytriisopropoxide (VOTP, Sigma-Aldrich) and Millipore water were then alternately dosed into the reactor.\(^19\) Each dose was separated by purges of N\textsubscript{2} to prevent gas phase reactions.

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between the precursors. The dose and purge length was 30 s per step (2 min per ALD cycle). To ensure sufficient VOTP pressure in the vapor phase, the vessel containing the VOTP was heated to 45 °C. To prevent condensation, the line leading from the VOTP vessel to the reactor was heated to 100 °C.

For W deposition, substrates were loaded into an ALD reactor at 200 °C, which was pumped to 1 Torr and subsequently purged with ultrahigh purity (UHP) N₂ for 20 min at 400 sccm. The sample surface was subsequently exposed to Si₂H₆ and WF₆ with N₂ purges after each exposure for 30–100 s. Details for ALD on the three samples described in this work are given in Table 1. For sample VW, the W-deposited substrate was oxidized at 350 °C in flowing O₂ before being transported to a separate reactor for V ALD.

Catalyst coverage was measured by X-ray fluorescence (XRF) and comparison to calibrated Ba and As ion-implanted standards. X-ray photoelectron (XP) spectra were taken on a Thermo Scientific ESCALAB 250Xi instrument with a monochromated Al Kα beam (hν = 1.49 keV) and a pass energy of 20 eV. Despite the charge compensation via an electron beam and low-energy Ar⁺ beam, lateral differential charging effects resulted in tails in the low binding energy region of each peak in the XP spectrum. XPS peaks were therefore modeled using two Gaussian–Lorentzian peaks: one for the primary peak and a second to model the tail. These models were first fit for the fully oxidized peak, and the same ratio of peak maximum intensities, widths, and energy offsets was used to fit for multiple chemical states in the reduced condition.

The nanoscale surface morphology of the samples was recorded under ambient conditions using a Bruker ICON atomic force microscope (AFM) operated in tapping mode using Si cantilever tips. AFM artifacts were removed through image flattening as well as low-pass and/or Fourier filtering as implemented in Bruker NanoScope software.

XSW measurements at the α-Al₂O₃ (006) Bragg reflection were carried out at the 5-ID-C and 33-ID-D undulator beamlines at the Advanced Photon Source at Argonne National Laboratory. The incident X-ray beam energy was 13.00 keV for samples MW and VW and 7.00 keV for sample MV. Further details about the experiment and setup are described in the Supporting Information.

Slab-model DFT calculations were carried out using the VASP code with a plane-wave basis set with 400 eV cutoff energy. Exchange-correlation energies were obtained by the generalized gradient approximation (GGA) implemented in PW91 functionals using a projector augmented wave (PAW) method. k-point meshes were generated by the method of Monkhorst and Pack. The GGA approach provides sufficient accuracy for calculation of ground state charge distributions and relative surface energies. The clean 20-atom α-Al₂O₃ (0001) supercell used for all calculations is described in the Supporting Information.
III. RESULTS AND DISCUSSION

A. Experimental. Three different near-monolayer (near-ML) catalyst coverages (detailed in Table 1) were deposited atop α-Al2O3 (0001) single crystals. For the α-Al2O3 (0001) single crystal surface, we define 1 ML as the coverage with all bulk-like surface cation positions filled (10.1 atoms nm$^{-2}$). The clean α-Al2O3 (0001) crystal surfaces had <2 Å average root-mean-squared roughness, with ∼50–100 nm wide terraces separated by single- or few-step edges, as shown by atomic force microscopy (AFM) in Figure 1a. After ALD and subsequent redox cycling (described below), sample MW (Figure 1b) forms a very conformal film, while sample MV (Figure 1c) forms nanoparticles on the surface. These particles are believed to form through sintering during the first oxidation but do not appear to change in size or distribution after subsequent exposures to oxidizing or reducing environments. Analysis of AFM images reveal that the particles cover about 15% of the surface, and their volume fraction corresponds to the expected volume of ∼1 ML V2O5. The mixed V−W film (Figure 1d) shows a different morphology than either the V- or W-only samples, with two types of surface features: wide islands, about 1–2 nm high, and larger particles, up to 20 nm high (topographic heights in Figure 1c,d are truncated for clarity).

Ex situ X-ray photoelectron spectroscopy (XPS) shows nearly clean surfaces with traces of Na, K, and adventitious C. The presence of residual Si from W ALD cannot be ruled out, since trace Si 2s and 2p peaks might be overwhelmed by Al loss features from the substrate. Detailed scans of the O 1s−V 2p and W 4f spectra were conducted after exposures to oxidizing (OX, 350 °C in O2) and reducing (RD, 400 °C in 5% H2 bal N2) conditions in a quartz tube furnace with a gas flow rate of 200 sccm. After each reaction step, the samples were cooled to room temperature in flowing gas and were subsequently transported in air to the XPS system, with air exposures limited to a few minutes. XPS results for the O 1s, V 2p, and W 4f peaks are shown in Figure 2. Fitted binding energies of V and W XPS peaks, along with the fractional composition of different chemical states of V and W, are given in Table 2. Binding energies are calibrated to the adventitious C 1s peak at 284.8 eV.

The oxidation state of V can be determined by measuring the binding energy (BE) of the V 2p XP doublet. However, on an insulating oxide substrate such as sapphire, O 1s is a convenient

Table 2. Fitted O 1s−V 2p3/2 Binding Energy Differences (in eV) and Fitted W 4f7/2 Binding Energies (and Fractions Thereof) for Samples after Oxidation (OX) and Reduction (RD)$^a$

<table>
<thead>
<tr>
<th></th>
<th>MV</th>
<th>VW</th>
<th></th>
<th>MW</th>
</tr>
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<tbody>
<tr>
<td>W OX</td>
<td>35.77 (100%)</td>
<td>35.72 (100%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RD</td>
<td>35.93 (39%)</td>
<td>35.82 (100%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V OX</td>
<td>13.13 (100%)</td>
<td>13.27 (100%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RD</td>
<td>13.13 (63%)</td>
<td>13.32 (72%)</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>14.6 (37%)</td>
<td>14.54 (28%)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$W 4f7/2 binding energies are calibrated to the C 1s peak.
internal standard, so we consider the binding energy difference (BED) between the V 2p\textsubscript{3/2} and O 1s peaks. Reported O 1s−V 2p\textsubscript{3/2} BEDs for V\textsuperscript{5+}, V\textsuperscript{4+}, and V\textsuperscript{3+} are 12.8−12.9, 13.8−14.35, and 14.6−14.84 eV, respectively, from the O 1s peak at 530.1 eV in bulk vanadium oxides\textsuperscript{29,30} and on less strongly ionic oxide substrates.\textsuperscript{31−35} For the films studied herein, which are only a few angstroms thick, the bulk sapphire O 1s signal, with a BE of 531.6 eV, may dominate the O 1s spectrum.\textsuperscript{36} The O 1s−V 2p\textsubscript{3/2} BEDs may therefore be somewhat larger than the values for bulk vanadium oxide. For V XPS, the V 2p\textsubscript{3/2} and V 2p\textsubscript{1/2} peaks do not necessarily have the same width and symmetry, and overlap between the O 1s and V 2p\textsubscript{1/2} states further complicates fitting.\textsuperscript{37,38} Thus, for V binding energy determination, only the V 2p\textsubscript{3/2} peak was fit. The V 2p\textsubscript{1/2} contribution was modeled in the full O 1s−V 2p spectrum by a broad Gaussian−Lorentzian peak. Because of sample charging effects, the O 1s peak cannot be analyzed in detail.

After oxidation, the O 1s−V 2p\textsubscript{3/2} BEDs are 13.1−13.3 eV, which is slightly larger than the expected value of 12.8−12.9 eV for V\textsuperscript{5+} in bulk V\textsubscript{2}O\textsubscript{5}. Considering that the Al\textsubscript{2}O\textsubscript{3} O 1s peak is at a somewhat higher binding energy than that of vanadium oxides, these signals are assigned to V\textsuperscript{5+}. In the reduced state, two-state fits reveal a significant fraction of V with a lower binding energy, centered at a BED value of 14.5−14.6 eV. Assuming the same BED shift from the expected bulk VO\textsubscript{X} values for V\textsuperscript{5+} (about 0.3−0.4 eV), we assign the reduced fraction to V\textsuperscript{4+}.

The formal oxidation state of W can be determined by analyzing the W 4f doublet: the W 4f\textsubscript{7/2} BEs for W\textsuperscript{6+}, W\textsuperscript{5+}, and W\textsuperscript{4+} are 35.5−35.6, 34.5−34.7, and 33.1−33.3 eV, respectively.\textsuperscript{7,8,39,40} No significant change is observed in the W 4f spectrum for sample MW, as shown in Figure S2a. However, the RD W 4f spectrum for sample VW, shown in Figure 2d, is best fit as two doublets offset by 0.45 eV from each other. The

Figure 3. α-Al\textsubscript{2}O\textsubscript{3} (006) XSW fluorescence yield fits and a typical fitted reflectivity curve for (a, c) W and (b, d) V on samples (a) MW, (b) MV, and (c, d) VW. The chemical condition corresponding to each data set is indicated.
separation between the higher-BE doublet (corresponding to \( W^{6+} \)) and the lower-BE doublet is much smaller than the expected 0.8–1.1 eV shift from \( W^{6+} \) to \( W^{5+} \). In each case, there is little change in the O 1s spectrum (Figure S2b).

The X-ray standing wave (XSW) technique was used to probe the interface structure of V and W on \( \alpha-Al_2O_3 \) (0001) under oxidizing and reducing environments as described below. For a narrow angular range near an \( H = hkl \) Bragg condition of a nearly perfect crystal, the Bragg reflectivity is nearly unity, and interference between the incident and reflected X-ray beams forms an XSW. As the angle between the incident X-ray beam and the crystal is increased through the reflection condition, the phase \( \phi_H \) of the outgoing X-ray plane wave shifts by \( \pi \), corresponding to a shift of the XSW toward the crystal surface by 1/2 the crystal plane spacing \( d_{hkl} \). By simultaneously monitoring the X-ray Bragg reactivity \( R_H(\theta) \) from a single crystal and normalized XRF yield \( Y_H(\theta) \) of a selected surface species (i.e., V or W) as the angle \( \theta \) between the crystal and the incident beam is changed, the coherent fraction \( f_H \) and position \( P_H \) of that selected surface species with respect to the \( H = hkl \) diffraction planes of the substrate may be determined from the equation

\[
Y_H = 1 + R_H + 2\sqrt{R_H^2 - \cos(\phi_H - 2\pi P_H)}
\]

\( P_H \) ranges from 0 to 1, corresponding to the relative position within one \( d \)-spacing (\( d_{hkl} \)). The statistically averaged position of surface atoms may therefore be measured with very high precision. \( f_H \) also ranges from 0 to 1, with 1 corresponding to complete coherency with the substrate lattice and 0 corresponding to either a “random” distribution relative to the substrate primitive unit cell or a special case such as two equally occupied positions separated by \( 1/d_{hkl} \).

XSW measurements were performed after treatments at 350 °C for 30 min in 200 sccm flowing \( O_2 \) (OX), 400 °C for 30 min in 200 sccm flowing 3% \( H_2 \) balloon He (RD), and reoxidizing at the same conditions as OX (OX2). The reaction gas was kept flowing through the sample chamber at room temperature during in situ XSW measurements. XSW data from the \( \alpha-Al_2O_3 \) (006) reflection are compiled in Figure 3, including measurements for the “as deposited” (AD) cases prior to redox treatments. The shifts in the symmetry of the V Ka fluorescence yield relative to the reflectivity curve indicate changes in the fraction of V occupying sites that are correlated with the substrate lattice. Conversely, the absence of such shifts in W L\( \beta_1 \) XRF yields indicate no significant changes in the position of W relative to the substrate lattice.

The XSW-derived coherent fractions and positions \( f_{006}, P_{006} \) are given in Table 3, where the averages of OX and OX2 results are shown as “oxidized” and the RD results are shown as “reduced”. Coherent positions are reported relative to the average bulk Al cation position as a fraction of the \( \alpha-Al_2O_3 \) (006) \( d \)-spacing of 2.166 Å; for reference, \( P_{006} \) of bulk Al and O atoms are \( \pm 0.0115 \) and 0.5, respectively. For values of \( f \) below 0.1, systematic errors make the value of \( P \) less reliable; some results for \( P \) have been omitted accordingly.

### B. Computational

**Density functional theory (DFT) calculations.** Density functional theory (DFT) calculations were performed for 1/2 ML W, 1/2 ML V, and 1/2 ML V atop 1/2 ML W on a monoclinic Al-terminated \( \alpha-Al_2O_3 \) (0001) surface supercell (lattice parameters: \( a = b = 4.784 \text{ Å}, c = 25 \text{ Å} \)) shown in Figure S3 of the Supporting Information. Surface cations were terminated with three O atoms per surface unit cell and were allowed to relax with different initial surface cation arrangements. Reduction by \( H_2 \) was modeled as a stoichiometric series of 0, 1, 2, or 3 H atoms atop the O-terminated surfaces. The relative stabilities of these models were determined by surface energy analysis as shown in Figure 4a. Relative surface energies were calculated by subtracting the contribution of each H atom (one-half the total energy of an \( H_2 \) molecule) from the total energy of each relaxed supercell and then referencing these values to the lowest energy structure for each cation stoichiometry. By comparing relative surface energies for incremental addition of H to the O-terminated surfaces for each cation stoichiometry, stable structures under reducing conditions are proposed; these are shown in Figure 4b–d. W alone on the sapphire surface is by far the most stable when fully O-terminated with no additional adsorbed H. For V alone, the case with 1 dissociatively adsorbed \( H_2 \) molecule per surface cell is most stable. For the VW stoichiometry, both 1 and 1.5 \( H_2 \) molecules per surface cell are roughly costable. However, the doubly H-terminated structure is more consistent with XSW and spectroscopic data, as discussed below.

Table 3. XSW-Derived Coherent Fractions (\( f \)) and Coherent Positions (\( P \)) for the (006) Crystal Reflection of \( \alpha-Al_2O_3 \), with Error Values on the Last Reported Digit Given in Parentheses, and Simulated XSW Results for \( P_{006} \) Derived from DFT Calculations of the Reduced-State Structures

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<tr>
<th></th>
<th>MV</th>
<th>MW</th>
<th>VW</th>
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<tbody>
<tr>
<td>reduced</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( f_{006} ) (V)</td>
<td>0.23(3)</td>
<td>0.21(3)</td>
<td></td>
</tr>
<tr>
<td>( P_{006} ) (V)</td>
<td>0.11(2)</td>
<td>0.23(1)</td>
<td></td>
</tr>
<tr>
<td>oxidized</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( f_{006} ) (V)</td>
<td>0.10(5)</td>
<td>0.09(3)</td>
<td></td>
</tr>
<tr>
<td>( P_{006} ) (V)</td>
<td>0.11(1)</td>
<td>0.09(3)</td>
<td></td>
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<tr>
<td>DFT (reduced)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( P_{006} ) (V)</td>
<td>0.125</td>
<td>0.278</td>
<td></td>
</tr>
<tr>
<td>( P_{006} ) (W)</td>
<td>0.202</td>
<td>0.186</td>
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Structural and chemical details of the structures shown in Figure 4 are given in Table 4. Calculated cation positions \( P_{006} \) from each structure (provided in Table 3) can be compared directly with XSW-measured coherent positions. The calculations match very well with the experimental values for MW and the reduced cases of MV and VW, aside from an overstretching of V into the vacuum for the mixed V–W calculation. Cation charges calculated by the method of Bader are roughly one-half of the expected formal charge, indicating a mixed covalent-ionic character. Bond valence sums (BVS) give a theoretical estimate of the cation valence and were calculated using parameters for V–O\(^{5+} \) and W–O\(^{5+} \) coordination environments. BVS show values close to those expected for W\(^{6+} \) and V\(^{4+} \) in the W- and V-only cases, respectively. In the mixed V–W case, V is oxidized by 0.10 \( e^- \) versus the V-only case, whereas W undergoes a significant reduction of 0.33 \( e^- \) from the W-only case.

Atom-projected partial densities of states (PDOS) for the surface species of these models are shown in Figure 5; densities of states for the complete slab are shown in Figure S4 of the Supporting Information. PDOS analysis reveals that, as expected, the fully oxidized and very stable W\(^{6+} \) surface (Figure 5a) has a broad valence band corresponding to covalent O 2p–W 5d interactions. The partially hydroxylated V\(^{4+} \) structure (Figure 5b) also shows a broad valence band, with a hydroxyl...
feature at its deep end. However, sharp V d-states (hybridized with the O 2p orbitals of the surface ligands) are present at and just above the Fermi energy $E_F$. Combining these cation terminations, the reduced V$^{4+}$/W$^{6+}$ case (Figure 5c,d) shows d-states around $E_F$ for both W and V. As shown in the band-projected charge density map for the d-states near $E_F$ (Figure 5d), the cations are separated by 3.31 Å, and therefore these features are not due to cation orbital overlap. No vacant states further above $E_F$ appeared in our calculations.

IV. DISCUSSION

In the oxidized condition, XPS shows that V and W are fully oxidized (V$^{5+}$, W$^{6+}$). Upon treatment in a dilute H$_2$ atmosphere, 37% of V$^{5+}$ on sample MV and 28% of V$^{5+}$ on sample VW reduce to V$^{4+}$. W 4f XP spectra reveal no W

reduction for sample MW, which is corroborated by DFT calculations that show a sharp increase in surface energy upon H addition to fully O-terminated W/α-Al$_2$O$_3$ (0001) (see Figure 4a). However, sample VW shows a shift of the W 4f doublet toward lower binding energy. Since the shift is too small to correspond to a reduction to W$^{5+}$, this subtle charge screening effect suggests a collective partial reduction of 60% of the W$^{6+}$ to W$^{5−δ}$.

Table 4. Local Cation Coordination Environment, Bader Charges ($q_B$), and Bond Valence Sums (BVS) for Low-Energy Structures atop the Al-Terminated α-Al$_2$O$_3$ (0001) Surface Supercell, Denoted as S$^a$

<table>
<thead>
<tr>
<th></th>
<th>S−W−O$_3$</th>
<th>S−W−O$_3$−O−O(OH)$_2$</th>
<th>S−V−O(OH)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>W−O coord (Å)</td>
<td>1.78, 1.78, 1.78, 2.10, 2.17</td>
<td>1.81, 1.82, 1.83, 2.10, 2.17</td>
<td>2.10, 2.10</td>
</tr>
<tr>
<td>$q_B$ (W) (e)</td>
<td>2.89</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>BVS(W) (e)</td>
<td>5.71</td>
<td>5.38</td>
<td></td>
</tr>
<tr>
<td>V−O coord (Å)</td>
<td>1.60, 1.79, 1.80, 2.25, 2.39</td>
<td>2.30, 2.39</td>
<td>1.97, 1.99, 2.16</td>
</tr>
<tr>
<td>$q_B$ (V) (e)</td>
<td>2.16</td>
<td>2.12</td>
<td></td>
</tr>
<tr>
<td>BVS(V) (e)</td>
<td>4.34</td>
<td>4.24</td>
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</table>

$q_B$ and BVS values are given in units of elementary charge e.

Figure 5. Atom-resolved partial densities of states (PDOS) relative to the Fermi energy $E_F$ for surface atoms of relaxed structures of (a) $1/2$ ML W$^{6+}$, (b) $1/2$ ML V$^{4+}$, and (c) $1/2$ ML V$^{4+}$/ $1/2$ ML W$^{6+}$ on Al-terminated α-Al$_2$O$_3$ (0001). Contributions from the terminal O layer are included in (a−c) as well as the O layer between V and W in (c). (d) Band-projected charge density map corresponding to the partially filled d-band near $E_F$ in (c). Charge density is shown as a slice parallel to the (1120) plane through the cation cores. Al atoms shown in sky blue; O, red; H, beige; W, blue; and V, green.

Figure 4. (a) Surface energies with convex hull lines for different amounts of H adsorbed onto fully O-terminated $1/2$ ML V, $1/2$ ML W, and $1/2$ ML V / $1/2$ ML W (VW) structures. Surface energies are calculated relative to the lowest-energy structure for each cation stoichiometry. (b−d) (1120) views of selected stable DFT-relaxed surface models for (b) $1/2$ ML W, (c) $1/2$ ML V, and (d) $1/2$ ML V / $1/2$ ML W atop Al-terminated α-Al$_2$O$_3$ (0001). Al atoms shown in sky blue; O, red; H, beige; W, blue; and V, green.
XSW results show a clear difference between the behavior of W and V on the $\alpha$-Al$_2$O$_3$ (0001) surface. For samples MW and VW, there is no significant change in the position of correlated W between the OX and RD states and no effect of codeposited V. In the OX state for samples MV and VW, the V coherent fraction ($f_{000} \sim 0.1$) is too small to accurately measure any coherent position of V. Upon reduction, the coherent fraction of V increases substantially. The amount of correlated V in the RD state is similar to the fraction determined by XPS to reduce to V$^{4+}$, suggesting a partial transition from uncorrelated V$^{5+}$ to correlated V$^{4+}$. We have observed similar phenomena for >1 ML VO$_x$ on $\alpha$-TiO$_2$ (110), which undergoes a redox-reversible structural transition from uncorrelated V$_2$O$_5$ to VO$_2$ which is epitaxial (correlated) to the rutile substrate lattice. As the coherent fraction of sample MV (corresponding to $\sim$0.2 ML V) exceeds the areal fraction of the interface between the nanoparticles and the surface (15%), we conclude that reduction causes V$^{4+}$ to spread out over the sapphire surface, perhaps as dispersed species or as regions of an ultrathin (oxyhydr)oxide film that cannot be detected by AFM in ambient conditions.

The coherent position of reduced V is significantly different on the V-only MV sample versus the codeposited VW sample, indicating that the geometry of coherent V is modified by WO$\delta$. The DFT-calculated coherent position of V (0.278) in the mixed V–W case is substantially further from the surface than the XSW-measured value (0.23). The measured value lies between the calculated positions for the mixed V–W structure and the V-only case (0.125) and could therefore be interpreted as a superposition of two coherent populations of V. A surface with 33% and 67% of the coherent V in the calculated V/$\alpha$-Al$_2$O$_3$ (0001) and V/W/$\alpha$-Al$_2$O$_3$ (0001) structures, respectively, would be measured as a $P_{000}(V)$ value of 0.23. The measured coherent fraction would be 90% of the actual sum of the two coherent populations of V. The corresponding actual fractions of coherent V would be about 0.08 (0.07 ML) of the V/$\alpha$-Al$_2$O$_3$ structure and 0.16 (0.14 ML) of the V/W/$\alpha$-Al$_2$O$_3$ structure. Aside from these small losses in the coherent fraction due to multiple coherent populations, the noncorrelated fraction of W and V is structurally “invisible” to the XSW measurement and exists in an incoherent phase, likely in the nanoparticles on the surface.

The agreement between experimental and theoretical results in both structure (validated by XSW) and electronic states (probed by XPS) constitutes a strong argument for the partial reduction of W$^{6+}$. DFT calculations for W/$\alpha$-Al$_2$O$_3$ (0001) in the absence and presence of V reveal that (a) protonation of oxidized V/W/$\alpha$-Al$_2$O$_3$ (0001) is stable, whereas protonation of oxidized W/$\alpha$-Al$_2$O$_3$ (0001) is not, and (b) upon protonation of oxygen ligands in the V coordination environment, negative charge is spontaneously transferred to W. From our PDOS calculations, W d-states appearing near $E_F$ in Figure 5 correspond to those involved in the W($6d-\delta$) model of Bronsted acidity, suggesting that the formation of Bronsted acid sites might be facilitated via coreduction of W with V. Bond valence analysis of the $1/2$ ML V / $1/2$ ML W structure shows a reduction of W by 0.33 $\epsilon$ relative to the fully oxidized $1/2$ ML W$^{6+}$ case, further corroborating this assignment of W($6d-\delta$). The shift in W Bader charge is much smaller than the bond valence shift, suggesting that W reduction is due to the redistribution of covalently shared charge more than ionic charge transfer. While our ground-state DFT models cannot provide a dynamic mechanism for reduction and charge transfer, the degeneracy of V and W states indicates that no perturbation is needed to facilitate charge transfer between the two cations—a “zero-cost transfer” of electronic charge from easily reducible V to less reducible W occurs upon reduction of the catalyst surface.

This work expands upon a detailed survey of model catalyst behavior on several different single crystal oxide support materials. Previously, we found that sub-ML$^7$ and ML$^{16}$ WO$\delta$ supported on rutile $\alpha$-TiO$_2$ (110) (which shares stoichiometry with the anatase used in industry as a support for V–W catalysts) did not reduce from W$^{6+}$ under similar reducing conditions as reported here. However, the addition of V enables the reduction of W$^{6+}$ to W$^{5+}$ and V$^{4+}$ on $\alpha$-TiO$_2$ (110).$^{10}$ Sub-ML W$^{6+}$ has also been shown to reduce to W$^{5+}$ on the Fe$_2$O$_3$ (0001) surface under similar conditions.$^{44,52}$ While $\alpha$-Fe$_2$O$_3$ has nearly the same crystal structure as $\alpha$-Al$_2$O$_3$, it is reducible, has a more complex electronic structure, and is therefore less chemically “inert” overall.

The V–W coreduction reported in the present work occurs in relative chemical isolation on the $\alpha$-Al$_2$O$_3$ (0001) surface, which provides a structural template but is not likely a significant source or sink of electrons or H$^+$; that is, the reduction of W$^{6+}$ can be attributed mostly to the contribution of V. We acknowledge that the morphologies of these well-controlled model catalysts on single crystal surfaces may not resemble real oxide-supported catalyst particles. However, these conditions are necessary to observe the chemical interaction of low-coverage V and W species independent of the high concentration of potentially reactive surface defects present on real catalyst supports.

V. CONCLUSIONS

Structural, spectroscopic, and computational analysis of V and W oxides deposited by ALD onto the $\alpha$-Al$_2$O$_3$ (0001) single crystal surface provides an explanation of the synergy observed in mixed V–W catalysts for reactions such as the selective catalytic reduction of nitric oxides. XSW and XPS reveal a redox-reversible atomic-scale transition from V$^{5+}$ which is uncorrelated to the substrate lattice to an ordered V$^{4+}$ phase. Meanwhile, W$^{6+}$ is shown to partially reduce in the presence of V$^{4+}$, but not when deposited alone on $\alpha$-Al$_2$O$_3$ (0001). DFT-calculated results for surface atomic and electronic structures are verified by comparison with XSW atomic positions and oxidation states derived from XPS.

Taking together results from various single crystal surface geometries and chemistries, we conclude that W$^{6+}$ reduction is facilitated by coreductants such as V$^{5+}$ or Fe$^{3+}$. Electronic structure analysis of these reduced W species suggests that the presence and properties of localized W d-states near the Fermi energy may be a useful parameter for the targeted design of Bronsted acid sites in mixed oxide catalysts, a step forward in the d-band engineering of multicomponent catalysts.$^{53,54}$

ASSOCIATED CONTENT

Supporting Information

XSW experimental details, W 4f spectra from sample MW and O 1s spectra from samples MW and VW, details of the slab model used for DFT calculations, and additional densities of states. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b04802.
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