DFT Study of Hg Oxidation across Vanadia-Titania SCR Catalyst under Flue Gas Conditions

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ABSTRACT: The density functional theory was used to analyze the thermodynamic stability and reactivity of the vanadia-titania catalyst below monolayer regime with the purpose of having a good representation of a commercial SCR catalyst (V_2O_5(<2 wt %)-TiO_2). The objective of this paper is to understand the reactivity of this catalyst in Hg oxidation. The SCR catalyst is modeled as a tetrahedrally coordinated divanadate unit supported on a 3-layer TiO_2(001) slab to represent a catalyst with low vanadia loadings. Under flue gas conditions, the interaction of water with this surface has been studied as a function of pressure and temperature using ab initio thermodynamic calculations, showing that water coverage is temperature-dependent. Adsorbed water acts as a Lewis base, donating electrons to the TiO_2(001) surface support, which increases the negative charge and reactivity of the oxygen atoms of the vanadia dimer. The reactivity of the vanadia dimer toward Hg oxidation is analyzed through the adsorption energies of Hg, HgCl, HCl, and H_2O. Surfaces with high water coverage showed higher reactivity toward HgCl, which has the highest adsorption energy, followed by HCl. The adsorption energies of Hg suggest a negligible interaction with the vanadia dimer. Lateral interactions between neighboring adsorbed flue gas components on the vanadia dimer were studied, suggesting that having H_2O or HgCl adsorbed on a neighboring oxygen atom increases the adsorption energies of Hg and HCl respectively. Temperature, pressure, and entropic effects were taken into account to study the reactivity of these surface interactions under flue gas conditions. Based on these results, it is proposed that the oxidation of Hg to HgCl_2 follows a Langmuir–Hinshelwood mechanism, represented as a cycle where HgCl and HCl interact without poisoning the surface. The proposed steps during the formation of HgCl_2 are the adsorption and dissociation of HCl, adsorption of HgCl, formation of HgCl_2, and its desorption from the surface.

INTRODUCTION

The U.S. Environmental Protection Agency (EPA) proposed the Mercury and Air Toxics Standards (MATS) in December 2011, which require U.S. natural gas and coal-fired power plants to install air pollution control devices to prevent 91% of the Hg present in flue gas from being released. Raising atmospheric levels of gaseous Hg have caused public concern because Hg has been shown to have negative neurological effects, affecting memory, attention, language, and visual skills. In the U.S., 40% of the total coal-fired generating capacity is generated in power plants equipped with selective catalytic reduction (SCR) units that regulate NO_x emissions with the cobenefit of Hg control by oxidizing elemental mercury (Hg^0) to Hg^++. Oxidized Hg is highly soluble in aqueous solutions, making its removal by conventional wet flue gas desulfurization processes possible. A widely employed material in commercial SCR units is titania-supported vanadium and tungsten oxides, that is, V_2O_5-WO_3/TiO_2. The active vanadia phase, V_2O_5, is responsible for NO_2 reduction and can also catalyze Hg^0 oxidation and the undesired SO_2 to SO_3 oxidation reaction. The catalyst’s V_2O_5 content is limited to less than a full monolayer (<2 wt %) not only to avoid SO_3 formation, but also because high loadings of V_2O_5 decrease the temperature at which the TiO_2 anatase-to-rutile phase transformation takes place. This phase transformation leads to a decrease in the surface area and the catalyst’s activity.

Although mercury oxidation in the binary V_2O_5-TiO_2 system has been investigated experimentally, the detailed mechanism of this reaction is still unknown. The presence of HCl in the flue gas plays an essential role in the mercury oxidation, but there is disagreement regarding the specific interactions between Hg, HCl, and the catalyst surface. Senior and Linjewile suggest that adsorbed Hg interacts with gas-phase HCl by an Eley–Rideal mechanism, while Niksa and Fujiiwara suggest a Langmuir–Hinshelwood mechanism in which Hg adsorbs and then reacts with HCl that has previously been adsorbed onto the V_2O_5 surface. The kinetics governing the interaction of HCl and Hg with the surface of V_2O_5 have yet to be reported.

With respect to the TiO_2 support material, the predominant anatase (101) surface is the most stable, however, the (001) surface is also exposed in the anatase powder that is used in the SCR catalyst.
commercial catalysts. This surface has been chosen for most of the theoretical work on modeling vanadia-based catalysts because of the similar geometries between the support and the active phase.\textsuperscript{18–26} Although it is well-known that the clean (001) surface of TiO\textsubscript{2} undergoes a (1 × 4) reconstruction in a wide temperature range (up to 850 °C) and under a variety of experimental conditions\textsuperscript{27–36} to decrease surface energy, water interactions with unreconstructed (001) surfaces have similar surface stabilizing effects. A study by Gong et al.\textsuperscript{37} showed that the surface energy of TiO\textsubscript{2}(001) decreases from 0.98 J/m\textsuperscript{2} for the clean surface to 0.53 and 0.33 J/m\textsuperscript{2} for dissociated water coverages of 1/3 and 1/2 monolayers (ML), respectively. The presence of unsaturated Ti atoms on the (001) surface may act as adsorption sites for H\textsubscript{2}O through Ti–O bonding, while under-coordinated O atoms provide sites for O\textsuperscript{2−} adsorption as function of coverage. They showed that, for low water coverage, water tends to dissociate on the (001) surface, yielding a reconstructed surface with attached hydroxyl groups. However, when supported vanadia systems were studied by Vittadini et al.,\textsuperscript{20} the unit cell used was small, causing vanadia dimers to cover almost the entire surface, which is not a reasonable representation of the low loading associated with SCR systems. Even for loadings higher than a theoretical V\textsubscript{2}O\textsubscript{5} monolayer, only a small fraction (≈10%) of the TiO\textsubscript{2} surface is covered by “towers” (i.e., vertical-growth) of polycrystalline V\textsubscript{2}O\textsubscript{5}.\textsuperscript{33} In addition, their surfaces contain few free surface Ti atoms, which likely exist in real systems leading to possible interactions with the water vapor present in the flue gas.

Optimal V\textsubscript{2}O\textsubscript{5} loadings fall within the low coverage regime (i.e., <2 wt %), in which the disperse vanadia species are present as isolated monomeric and polymeric vanadium oxide units.\textsuperscript{34–36} Studies of V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} anatase) using X-ray absorption spectroscopy (EXAFS/XANES)\textsuperscript{37,38} indicate that, for low surface coverage, the vanadia oxide layer is characterized by isolated vanadium oxide species with the vanadium atoms having 4-fold coordination. Two different approaches have been used to model coverages of vanadia below monolayer loadings. Using a cluster-based approach the effects of the V\textsubscript{2}O\textsubscript{5} cluster size and support on the reactivity of the cluster have been previously examined;\textsuperscript{18,20,26,39,40} however, investigations employing cluster models are challenged by border effects and limited ability to investigate coverage effects. To avoid these limitations, other computational studies\textsuperscript{22–24} have modeled this system using a periodic approach consisting of monomeric and dimeric vanadia species supported on TiO\textsubscript{2}. These studies have focused on the stability of the vanadia species and the reactivity of the surface oxygen atoms toward NO\textsubscript{2} reduction. Typical temperatures for NO\textsubscript{2} reduction across the SCR unit range from 500 to 700 K.\textsuperscript{4,9,41} However, Granite et al.\textsuperscript{42} suggested that, for Hg oxidation, the relevant SCR temperatures are 333, 410, and 449 K, because lower temperatures favor Hg\textsuperscript{2+} adsorption,\textsuperscript{43} which may be one step in the Hg oxidation mechanism.

In the current work, the role of the support (TiO\textsubscript{2}(001)) and the active phase, vanadia oxide, toward Hg oxidation is investigated. Several TiO\textsubscript{2}(001) supported submonolayer vanadia systems were tested to select a starting point for this study. The thermodynamic stability of different surfaces is investigated for temperatures ranging between 100 and 800 K, which serves as an absolute upper limit for the SCR conditions. Because the focus of this work is on flue gas conditions in which water vapor is present in significant amounts (≈10 wt%), water interactions are investigated using the unreconstructed 4 × 2 (15.18 × 7.59 Å\textsuperscript{2}) TiO\textsubscript{2}(001) surface, with an adequate number of sites for water to interact with both the vanadia dimer and the TiO\textsubscript{2} support. The thermodynamic stability of different hydroxylated surfaces is studied under flue gas conditions using ab initio thermodynamic calculations. The change in the stability of the vanadia dimer with the degree of hydroxylation/hydration is also investigated through the analysis of the formation energies and the projected density of states (PDOS) of the most stable hydroxylated surfaces. Bader charge analysis is used to determine the surface charge distribution to infer the chemical reactivity by comparing the adsorption energies of the species likely playing a primary role in Hg oxidation (e.g., Hg, HCl, and HgCl). Finally, the effect of temperature and pressure on the adsorption energies of these gas-phase species is analyzed to understand the chemical nature of the SCR surface under flue gas conditions using ab initio thermodynamics. The results of this study may be used to determine the optimal conditions for Hg oxidation and provide insight into the mechanism associated with Hg oxidation across SCR catalysts.

\section*{Computational Methodology}

\subsection*{Density Functional Theory}

Plane-wave DFT calculations were performed using the Vienna ab initio simulation package (VASP)\textsuperscript{44} using the Perdew–Burke–Enzerhof (PBE) generalized-gradient approximation (GGA).\textsuperscript{45} For the TiO\textsubscript{2} bulk calculations, a projector augmented wave (PAW)\textsuperscript{46} pseudopotential was used with an optimized energy cutoff of 500 eV. The number of k-points for the Brillouin zone integration was chosen according to a Monkhorst-Pack\textsuperscript{47} of 6 × 6 × 6 with a convergence criterion of 10\textsuperscript{−4} eV. The optimized lattice parameters for bulk TiO\textsubscript{2} (a = 3.80, b = 3.80, c = 9.55) are in reasonable agreement with experimental measurements\textsuperscript{48} (a = 3.79, b = 3.78, c = 9.52) and previous DFT calculations (a = 3.83, b = 3.83, c = 9.62).\textsuperscript{25}

The TiO\textsubscript{2} (001) surface was simulated using a 4 × 2 (15.18 × 7.59 Å\textsuperscript{2}) unit cell, without symmetry, and the inclusion of a dipole correction. The unit cell used in the current work is larger than those of previous studies\textsuperscript{20,22} to investigate the effect of coverage in the water adsorption mode. The slabs were separated by a vacuum space of 15 Å to prevent interaction between periodic images and to cancel any dipole moment potentially created by them. A 2 × 4 × 1 k-mesh was used. The slab thickness optimization was established based upon two convergence criteria: convergence in the change of interlayer distances of the TiO\textsubscript{2}(001) slab with respect to the bulk TiO\textsubscript{2}, and convergence of the adsorption energies of small atoms or molecules (i.e., H\textsubscript{2}, CO, NO) for slabs with increasing number of layers. These two criteria were satisfied using a 3-layer-slab, which is used in the subsequent calculations. The way in which the atomic layers are defined in the current work is shown in Figure 9 in Appendix A, along with a full description and calculations regarding the slab thickness optimization.

The lattice parameters from the bulk V\textsubscript{2}O\textsubscript{5} system obtained in our previous study is used as a reference for the vanadia...
species. The optimized lattice parameters (a = 11.53, b = 3.58, c = 4.76) are in reasonable agreement with experimental measurements (a = 11.51, b = 3.56, c = 4.37) and previous DFT calculations (a = 11.65, b = 3.57, c = 4.66). Unlike a and b, their unit vector c differs more from the experimental value because we did not account for the existing van der Waals-based interlayer interaction in our DFT calculation. Gas phase molecules (H2O, HgCl, HCl, Hg) have been calculated as isolated molecules in a 20 × 20 × 20 (Å³) periodic box.

**Ab Initio Thermodynamic Calculations.** Using a procedure similar to that of our previous work, ab initio thermodynamic calculations were carried out to predict the relative thermodynamic stability and composition of different terminated V2O5−TiO2(001) surfaces in contact with a flue gas environment as a function of temperature and pressure. The composition of the flue gas was set to H2O (10 wt %), HCl (4 ppm), O2 (5 wt %), and Hg (40 ppb). Mercury chloride, HgCl, is likely an intermediate species whose concentration has not been measured experimentally; however, to solve the surface free energy equation, defined below, it is necessary to define a value for its concentration. The extent of mercury oxidation across the SCR unit analyzed at different scales varies between 20 and 60%, depending on the operating conditions. Therefore, assuming that approximately 20% of the Hg present in the flue gas oxidizes to HgCl2 creating HgCl as an intermediate, a HgCl concentration of 1 ppb was chosen. This is a valid approximation because the value that enters in the surface free energy equation is the logarithm of the partial pressure of the gas species so the effect in the final surface free energy results is negligible.

The ab initio thermodynamic methodology has been explained in detail in previous studies, so only the steps and explanations relevant to the current work are presented. As suggested by Rogal and Reuter, when discussing the stability of phases that result from adsorbing different species simultaneously on a given surface, it is possible to refer to the cost of creating a surface with respect to the clean surface. In this way, the stability of different surfaces is evaluated based on the Gibbs free energy of adsorption, which for a semi-infinite slab with the surface in equilibrium with a gas-phase reservoir (e.g., H2O, HCl, Hg, HgCl) at a given temperature T and pressure p is defined as

\[
\Delta G^{ad}(T, p) = \frac{1}{A} \left[ G_{\text{system}} - G_{\text{clean}} - \sum N_i \mu_i \right]
\]

where \( G_{\text{system}} \) is the Gibbs free energy of the surface covered with any adsorbates, \( G_{\text{clean}} \) is the Gibbs free energy of the corresponding clean surface, \( N_i \) is the number of gas phase species, and \( \mu_i \) is the chemical potential of these gas phase species (\( \mu_{\text{H}_2\text{O}}, \mu_{\text{HCl}}, \mu_{\text{HgCl}}, \mu_{\text{Hg}} \)). The Gibbs free energy terms in eq 1 are defined as \( G = E_{\text{total}} + E_{\text{vib}} + E_{\text{conf}} + pV \). Previous DFT studies consider that, for any \( p < 100 \text{ atm} \) and any \( T < 1000 \text{ K} \), the contributions from pressure (pV) and configurational free energy (\( E_{\text{conf}} \)) may be neglected. Rogal and Reuter also suggested that vibrational free energies of the solid bulk and surface cancel each other so that only the vibrational contribution from the adsorbed species requires consideration. In the current system, the differences in the vibrations associated with the vanadia dimers in \( G_{\text{system}} \) and \( G_{\text{clean}} \) differ less than 10 meV/Å² for any \( T < 1000 \text{ K} \), falling within the accuracy of the DFT predictions, and they were therefore not included in the surface free energy calculations. However, as reported by Sum et al., the vibrational contributions of adsorbed hydroxyl and water functional groups to the surface free energy is not negligible and it needs to be included. In the current study, the vibrational free energies of the adsorbed hydroxyl and water groups are calculated using the harmonic oscillator approximation presented in Figure 10 in Appendix B.

The chemical potential of the system components are temperature- and pressure-dependent, as can be seen from eq 2.

\[
\mu(T, p) = E_{\text{tot}}^{\text{DFT}} + E_{\text{vib}}^{\text{DFT}} + \mu(T, p^0) + k_BT \ln \left( \frac{P}{P^0} \right)
\]

where \( \mu(T, p^0) \) can be obtained from the NIST-JANAF thermophysical tables at standard pressure \( p^0 = 1 \text{ atm} \). The free energy arises from the zero-point vibrations and \( E_{\text{vib}}^{\text{DFT}} \) is the total energy. This relationship only holds for a surface in equilibrium with a gas-phase environment. Therefore, it is necessary to establish physical limits to confirm these gas-phase conditions. The upper limit for the chemical potential of water vapor is \( \mu_{\text{H}_2\text{O}} = -0.91 \text{ eV} \), which corresponds to the critical point of water, and the flue gas conditions of interest are within this limit. The final equation to calculate the Gibbs free energy of adsorption as a function of pressure and temperature is

\[
\Delta G^{ad}(T, p) = \frac{1}{A} \left[ E_{\text{total}} - E_{\text{clean}} + \Delta E_{\text{vib}}^{\text{tot}} - N_{\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}} - N_{\text{HCl}} \mu_{\text{HCl}} - N_{\text{HgCl}} \mu_{\text{HgCl}} - N_{\text{Hg}} \mu_{\text{Hg}} \right]
\]

### RESULTS

**Modeling TiO2(001)-Supported Vanadia Oxide Species.** Vanadia species are present on the surface as monomeric and polymeric structures in the low loading regime (i.e., <2 wt %). The advantage of using dimeric species is the possibility of modeling the active sites that participate in the catalytic activity, that is, vanadyl \( (\text{V} = \text{O}(1)) \) and bridging \( (\text{V} = \text{O}(2)-\text{V}) \), as shown in Figure 1. To represent vanadia species below monolayer coverage, dimeric vanadia species were chosen, similar to Vittadini et al. to model the simplest polyvanadate structure with two adjacent metal sites in tetra-coordinated-O environments. Due to the reconstruction of the \( \text{TiO}_2(001) \) surface, the support in Vittadini's vanadia dimer system follows the so-called "ad-molecule" (ADM) model, which requires a (1 × 4) unit cell. However, a larger and more computational expensive unit cell would be required to model the interaction of water molecules with both the support and the isolated vanadia dimer, which is the purpose of the current study. To be able to use a small unit cell but still account for the surface reconstruction, Vittadini et al. approximated the energy of the ADM model by adding the reconstruction energy to the energy of a (1 × 1)- unreconstructed-(2 × 2)TiO2(001) slab. Following this procedure, the isolated vanadia dimer supported on a (4 × 2)- unreconstructed-TiO2(001) surface was modeled, adding the reconstruction energy during the stability analysis. The reconstruction energy is calculated as the difference between the surface energies of (1 × 1)- unreconstructed and (1 × 4)-reconstructed TiO2(001) slabs, which are 0.124 and 0.098 eV/Å², respectively.

The stability analysis allows us to establish the starting vanadia–titania structure. Three possible dimeric structures are shown in Figure 1, differing only in the orientation of the V–
O(2)–V bond and the missing surface oxygen atoms. Of these three systems, structure A is chosen as the structure used in the subsequent calculations due to its lowest formation energy and the smallest change in the interlayer distance with respect to structure B and C. A full description of the formation energy calculations and the change in the interlayer distances for these three structures are presented in the Appendix C.

**Interaction with H$_2$O.** The interaction with H$_2$O is done in the (4 × 2)-unreconstructed (15.18 × 7.59 Å$^2$), which has four unique Ti atoms that water may interact with molecularly (MoI), dissociatively (Dis), or via some combination (Mix). As was indicated by Vittadini et al.,$^{21}$ at low water coverage dissociation is favored because it decreases the surface energy of the system due to surface reconstruction.$^{31}$ This surface reconstruction upon water dissociation is shown in Figure 2.

Water originally adsorbs on the Ti$^{4+}$ atom, with one of the H atoms interacting with a neighboring O(2) atom, leading to the stretching and finally cleavage of the Ti$^{4+}$–O(2) bond. This action produces two hydroxylated Ti atoms, that is, HO–Ti$^{4+}$ and H–O(2)–Ti$^{4+}$. Because the adsorption and dissociation of one water molecule leads to the hydroxylation of two Ti atoms, this coverage is considered as θ = 0.5. The different configurations for water adsorption/dissociation for each of the coverages tested are summarized in Table 1. The atoms that participate in the water adsorption/dissociation are indicated in Figure 3, where examples of dissociative and molecular water adsorption are also illustrated.

The thermodynamic stability of the different hydroxylated and hydrated surfaces was calculated using eq 3 as a function of temperature, yielding a straight line for each surface. The surface associated with the lowest-lying line corresponds to the most stable structure under the given flue gas conditions. For simplicity, only the structures with the lowest Gibbs free energies of adsorption are shown in Figure 4, while all the others are presented in Figure 11 in the Appendix D.

In Figure 4, the different stable regions are separated by red-dashed vertical lines at 100, 150, 240, and 390 K. The most stable surface in each region is illustrated in Figure 5 where the evolution of surface hydroxylation/hydroxilation with temperature can be seen. The first region corresponds to temperatures below 100 K, where, due to the high water vapor concentration in the flue gas and the low temperature, water molecules interact with all Ti and V−O(2) atoms on the surface. As the temperature increases, water desorbs from the vanadia dimer. This indicates that water interacts more strongly with the undercoordinated Ti atoms of the support than with the vanadia dimer. This result differs from the prediction of Calatayud and Minot,$^{24}$ who suggested that V$_2$O$_5$ units are hydroxylated before the TiO$_2$(001) support based on their investigation of H interactions with the supported system. Between 150 and 240 K, water molecules begin desorbing from the support, leaving room for water dissociation to take place. For this reason, the most stable structure in this region is Mix-1, in which both molecular and dissociative water molecules coexist on the surface. As the water coverage decreases, the dissociative adsorption mode becomes more stable, in agreement with previous theoretical$^{21}$ and experimental$^{65}$ studies. Above 390 K, water completely desorbs from the surface, leading to the clean surface, A.

Comparing the results of the current work with previous studies is difficult due to the differences in model systems and theoretical approaches used in the various studies. Vittadini et al.$^{21}$ studied the interaction of water with the unreconstructed (1 × 1)-TiO$_2$(001) surface obtaining adsorption energies of −1.44 eV for the dissociative case and −0.81 eV for the molecular case, for a water coverage of 1/2 ML. For the same coverage conditions in the current system, adsorption energies of −1.24 eV for the dissociative case and −0.84 eV for the molecular case were obtained. The difference in the adsorption energies may be due to the presence of the vanadia dimer, which was shown to change the geometry of the support. Also, lateral interactions between water molecules and the vanadia dimer may affect water adsorption. The interaction of water with the surface may be further studied through the analysis of density of states, DOS, which is shown in Figure 12 in the Appendix D.

The surface reactivity of the most stable hydroxylated surfaces for T > 150 K (Mix-1, Dis-3 and A) are analyzed by Bader charge analysis to determine the charge distribution during the dehydroxylation process. An attempt to correlate the atomic charge of the surface atoms of the vanadia dimer with their reactivity toward the gas species likely playing a role in Hg oxidation, for example, Hg, HCl, and HgCl$_2$ was made as a first step in understanding the reaction mechanism.

**Bader Charge Analysis.** In this work, the Bader charge analysis is used to determine the electronic changes associated with the dehydration process. The atomic charges for the
different surface atoms (labeled in Figure 6 for clarity) of the Mix-1, Dis-3, and A surfaces are summarized in Table 2.

Table 2. Summary of Atomic Charge of the Oxygen Atoms of the Vanadia Dimer as a Function of Hydroxylation/Hydration

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<tr>
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<tbody>
<tr>
<td>O(1)–V</td>
<td>–0.66</td>
<td>–0.62</td>
<td>–0.59</td>
</tr>
<tr>
<td>O(2)</td>
<td>–0.88</td>
<td>–0.90</td>
<td>–0.88</td>
</tr>
<tr>
<td>O(2)*–V</td>
<td>–0.89</td>
<td>–0.88</td>
<td>–0.88</td>
</tr>
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</table>
negative. This effect is most significant for the O(1) atoms, that is, the first row of Table 2. This increase in the charge transfer between the hydroxylated support and vanadia dimer may yield a stronger dimer—support interaction. This increase in the stability of the vanadia dimer as a function of water adsorption was verified through the analysis of the formation energies and the PDOS of the different hydroxylated/hydrated surfaces, and it is shown in Table 7 and Figure 13 in Appendix F.

In the next section, these changes in the electronic structure of the three most stable surfaces for $T > 100$ K (Mix-1, Dis-3, and A) are linked with the change in reactivity of the vanadia dimer by analyzing the interaction with gas species Hg, HCl, and HgCl.

**Reactive Sites: Adsorption Energies of Hg, HgCl, and HCl.** Elucidating the mechanism of Hg oxidation requires analyzing the adsorption energies of Hg, HgCl, and HCl species, which are likely involved in the oxidation mechanism. Because the ab initio thermodynamic results suggest that the degree of hydroxylation/hydration of the surface changes with temperature within the working conditions of the SCR unit, we examine the interaction of Hg, HgCl, and HCl with the most stable surface under those conditions, that is, Mix-1 (150–240 K), Dis-3 (240–390 K), and A (>390 K), which are shown in Figure 5. The adsorption energies of Hg, HgCl, and HCl at different adsorption sites are summarized in Table 3. The adsorption sites chosen in this work are the surface oxygen atoms of the vanadia dimer are labeled in Figure 6.

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<tbody>
<tr>
<td>O(1)–Hg</td>
<td>−0.039</td>
<td>−0.006</td>
<td>0.947</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>−0.028</td>
<td>−0.005</td>
<td>0.941</td>
<td></td>
</tr>
<tr>
<td>O(1)–HgCl</td>
<td>−0.744</td>
<td>−0.776</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>O(2)–HgCl</td>
<td>−0.223</td>
<td>−0.234</td>
<td>0.675</td>
<td></td>
</tr>
<tr>
<td>O(1)–HCl</td>
<td>−0.303</td>
<td>−0.146</td>
<td>0.792</td>
<td></td>
</tr>
<tr>
<td>O(2)–HCl</td>
<td>−0.093</td>
<td>−0.071</td>
<td>0.885</td>
<td></td>
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<tr>
<td>O(1)–Cl/</td>
<td>1.626</td>
<td>1.664</td>
<td>2.546</td>
<td></td>
</tr>
<tr>
<td>O(1)–H</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td></td>
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<tr>
<td>O(2)–Cl/</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td></td>
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<tr>
<td>O(1)–H</td>
<td>ND</td>
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“The cases in which HCl dissociative adsorption does not occur are indicated by “ND”, which stands for “no dissociation”.

From the results shown in Table 3, two factors will be analyzed that affect the adsorption energy: the nature of the gas species and the degree of hydroxylation/hydration of the surface. The adsorption energies are correlated with the results of the Bader charge analysis for increased understanding of the changes that take place in the electronic structure upon hydroxylation.

**Nature of the Gas Species.** A comparison of the adsorption energies among the three species indicates that HgCl has the highest affinity for the surface. The two HgCl orientations tested differ by which atom, Hg or Cl, was interacting directly with the surface. The configuration in which the chlorine atom is singly coordinated, that is, Cl—Hg-surface, was energetically favored. The HCl interaction was also studied by placing H and Cl atoms on both the O(1) atoms of the vanadia dimer, the optimized configurations for the H and Cl atoms are placed closer on the surface, that is, Cl interacting with the chlorine atom is singly coordinated, that is, Cl—Hg-surface, was energetically favored. The HCl interaction was also studied by placing H and Cl atoms on both the O(1) atoms of the vanadia dimer, the optimized configuration in which the Cl atom moves away from the surface, interacting directly with the H atom in a molecular mode, so dissociation does not take place (labeled as “ND” in Table 3).

**Degree of Hydroxylation.** From left to right in each row of Table 3, it can be seen that the adsorption energies decrease, some of them even becoming thermodynamically unfavorable, as the degree of hydroxylation decreases. The strongest adsorption energies take place on the Mix-1 surface, which has the highest degree of hydroxylation of the three surfaces. This may be due to the increased concentration of negatively charged O atoms on the Mix-1 surface. However, negative charge is not the only factor influencing the strength of adsorption since the O(2) atom is more negative than the O(1) atom in all of the surfaces yet does not necessarily indicate higher reactivity. Steric effects associated with the more constrained location of the bridging O(2) atom may also be responsible for the smaller adsorption energies for this atom.

Up to this point, only the adsorption of single species (Hg, HgCl, or HCl) on different oxygen atoms of the supported vanadia dimer have been of focus. To account for lateral interactions, simultaneous adsorption of multiple flue gas species on the oxygen atoms of the supported vanadia dimer was carried out on the three most stable hydroxylated surfaces (Mix-1, Dis-3, and A). From the adsorption study of single components, it was shown that O(1) was the most reactive oxygen atom in the vanadia dimer. The study of simultaneous adsorption will be limited to the adsorption of different combinations of Hg, HCl, HgCl, and H₂O on the two O(1) sites of the vanadia dimer. The adsorption energies are calculated using eqs 4 and 5 and the energies are summarized in Table 4.

$$E_{ad} = E_{Hg−X} − (E_X + E_{Hg}^{gases})$$ (4)
Table 4. Change in the Adsorption Energy of Either Hg or HCl Adsorbed on the O(1) Oxygen Atom Due to Lateral Interactions of a Coadsorbed Gas Species X (X = H₂O, HCl, Hg, and HgCl) on the Neighboring O(1) Oxygen Atom

<table>
<thead>
<tr>
<th>Hg-X</th>
<th>Mix-1</th>
<th>Dis-3</th>
<th>A</th>
<th>HCl-X</th>
<th>Mix-1</th>
<th>Dis-3</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>empty</td>
<td>−0.039</td>
<td>−0.006</td>
<td>0.921</td>
<td>empty</td>
<td>−0.203</td>
<td>−0.146</td>
<td>0.729</td>
</tr>
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<td>−0.002</td>
<td>0.000</td>
<td>Hg</td>
<td>−0.166</td>
<td>−0.144</td>
<td>−0.123</td>
</tr>
<tr>
<td>H₂O</td>
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<td>−0.022</td>
<td>−0.057</td>
<td>H₂O</td>
<td>−0.252</td>
<td>−0.097</td>
<td>−0.085</td>
</tr>
<tr>
<td>HgCl</td>
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<td>−0.014</td>
<td>−0.009</td>
<td>HgCl</td>
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<td>−0.233</td>
<td>−0.223</td>
</tr>
<tr>
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<td>−0.004</td>
<td>0.457</td>
<td>HCl</td>
<td>−0.173</td>
<td>−0.124</td>
<td>0.360</td>
</tr>
</tbody>
</table>

\[ E_{\text{ad}} = E_{\text{HCl-X}} - (E_X + E_{\text{HCl}}) \]  

where \( E_{\text{Hg-X}} \) and \( E_{\text{HCl-X}} \) are the energies of the surface (Mix-1, Dis-3, or A) with either Hg or HCl adsorbed onto one of the O(1) atoms and X adsorbed on the other O(1) atom (X = HCl, Hg, H₂O, or HgCl), \( E_X \) is the energy of the surface, with X adsorbed on one O(1) atom, and \( E_{\text{Hg}} \) and \( E_{\text{HCl}} \) are the energies of the Hg and HCl in gas.

In general, changes in the adsorption energies smaller than 0.01 eV/atom may be considered negligible because they are within the calculation error of VASP. From Table 4 it is possible to see that lateral interactions due to a neighboring adsorbate increases the adsorption energies of both Hg and HCl on the water free surface (surface A), independently of the nature of the second adsorbate. Water adsorbed on a neighboring O(1) atom increases the adsorption energies of Hg and HCl on surfaces Mix-1 and A, but decreases the energy for surface Dis-3. Having HCl, HgCl, or a second Hg atom adsorbed on a neighboring O(1) atom either slightly decreases or has a negligible effect on the adsorption energies of Hg. As for the adsorption of HCl, Hg has a negligible effect on the hydroxylated supported system while it increases the HCl adsorption energy in the case of the water free surface. The strongest effect on HCl adsorption is due to a neighboring adsorbed HgCl compound, which increases the HCl adsorption energy suggesting a strong cooperative effect. The effect of temperature and pressure on the adsorption energies of both single and multiple adsorbate interactions are studied in the next section, and those results are then used to propose a mechanism for the Hg oxidation.

**Ab Initio Thermodynamics for Hg, HgCl, and HCl Terminated Surfaces.** Adsorption energies presented in Tables 3 and 4 have been calculated with DFT values obtained at 0 K and therefore they are not indicative of the change in adsorption energies with temperature. Ab initio thermodynamic calculations were carried out to include the effect of the temperature and pressure on the adsorption energies of Hg, HgCl, HCl, H₂O, and their combinations. In this way, the entropic effects are being taken into account, which become important at high temperatures. More than 30 surfaces were tested, but for simplicity, only the most stable surfaces are presented in this section. The most stable surfaces correspond to those where stable gas species interact with the O(1) atoms, as was shown in Table 4, in which both Hg and H₂O and HgCl and HCl were simultaneously adsorbed on O(1) sites. The changes in the Gibbs free energy of adsorption of these surfaces as a function of temperature are shown in Figure 7.

Figure 7 shows the decrease in the adsorption energies of Hg, HgCl, HCl, H₂O and their combinations with increasing temperature. At higher temperatures, the entropy loss during adsorption overcomes the adsorption energy, breaking the surface–adsorbate bond. At low temperatures, the surfaces with both HgCl and HCl adsorbed (magenta lines) on the three hydroxylated surfaces are the most energetically favored, while Hg interactions (green lines) have the lowest adsorption energies. The adsorption energy lines of the individual Hg, HgCl and HCl adsorbed on the surfaces Mix-1 and Dis-3 cross between 220 and 250 K, which may be due to the transition between Mix-1 and Dis-3 surfaces at 240 K, as shown in Figure 4.

These ab initio results indicate that, in the limit of thermodynamic equilibrium, the adsorption of Hg, HCl, HgCl, and their combinations are not energetically favored for \( T > 300 \) K, suggesting that poisoning of our surface catalyst under flue gas conditions is not expected. The Sabatier principle indicates that the ideal catalyst lies in a region of trade-off between weakly adsorbing reactant species and easily desorbing products to avoid the poisoning of the active sites. The same reasoning was employed by Jones et al.\(^\text{21}\) to select suitable catalysts for the steam reforming reaction. These thermodynamic results may be used as a basis to begin kinetic modeling in order to completely understand the reactivity of the current system toward Hg oxidation. Investigation of the relatively stable surface species provides an indication of the likely intermediates playing a role in the Hg oxidation pathway. Based on the adsorption energies shown in Tables 3 and 4 and the results in Figure 7, it can be seen that HCl and HgCl adsorb stronger than Hg, and that HgCl has a cooperative effect on the HCl adsorption, such that these two species may interact simultaneously on the surface. Based on these results, the mechanism of Hg oxidation through the formation of HgCl₂ is proposed in Figure 8.

The proposed oxidation mechanism represents a cycle where HgCl and HCl interacts without poisoning the surface, since the original catalyst is the first and last step of the reaction. The proposed Hg oxidation mechanism may involve the following
steps: the adsorption of HCl (steps 1 and 5) and adsorption of HgCl (step 2) on the surface, following a Langmuir–Hinshelwood mechanism. The dissociation of adsorbed HCl (steps 3) occurs due to the stretching of the H−Cl bond that takes place during the interaction of the Cl atom with the Hg atom from HgCl to form HgCl₂ (steps 3 and 4). Three products are formed and desorbed from the surface in this cycle, HgCl (step 7), HgCl₂ (step 4), and H₂O (step 8). Due to the weak Hg adsorption energies, it is proposed that HgCl is formed following an Eley–Rideal mechanism where gas phase Hg interacts with adsorbed HCl. An oxygen vacancy may be created (step 8) during water desorption, but it is likely that it is replenished due to the presence of oxygen in flue gas.

The previously proposed Hg oxidation mechanism involving an Eley–Rideal mechanism, where Hg adsorbs on the surface followed by an interaction with gas phase HCl, should not be ignored. An analysis of the activation barriers associated with each step of both mechanisms is necessary in order to discard one of them. A Langmuir–Hinshelwood mechanism is proposed due to the stronger HCl and HgCl interaction with the surface, and the higher concentration of HCl in the gas phase compared to Hg. Future work will focus on building the kinetic model, where a wider range of possible reactions paths will be considered, so it may be possible to establish rate-determining steps and activation energies involved in Hg oxidation, which could validate the proposed mechanism.

■ CONCLUSIONS

With the purpose of having a good representation of a commercial SCR catalyst (V₂O₅ (<2 wt %)−TiO₂) whose vanadia content falls below the monolayer regime, the active phase was modeled as a vanadia dimer supported on a 3-layer TiO₂(001) slab. This model allows us to study the active sites that participate in the catalytic activity: vanadyl oxygen (V=O(1)) and bridging O (V−O(2)−V). The significant concentration of water vapor present in the flue gas (∼10%) and the stabilization effect that water has on the TiO₂(001) surface led us to study the thermodynamic stability of different hydrated and hydroxylated surfaces as a function of pressure and temperature. In agreement with previous experimental and theoretical work, it was shown that water interacts in a molecular or in a dissociative fashion depending on the water coverage, which is temperature dependent. A dehydration process takes places with increasing temperatures leading to a water free surface above 390 K.

The reactivity of the vanadia dimer is analyzed through the adsorption energies of Hg, HgCl, HCl, H₂O, and their combinations, which are likely involved in the Hg oxidation mechanism. These adsorption energies are correlated with the results of the Bader charge analysis and PDOS of the vanadia dimer for increased understanding of the changes in the electronic structure upon dehydration. In the first part of the reactivity analysis, temperature and pressure effects are not taken into account to understand the individual effect of hydroxylation on the adsorption energies, calculated at 0 K. It was observed that adsorbed water acts a Lewis base, donating electrons to the support, which increases the negative charge on the oxygen atoms of the vanadia dimer. This increase in charge leads to higher reactivity toward HgCl, which has the highest adsorption energy, followed by HCl. The adsorption energies of Hg suggest a weak interaction with the vanadia dimer only on surfaces with high water coverage.

In the second part of the reactivity analysis, ab initio thermodynamic calculations were carried out to take into account the effect of temperature and entropy loss on the adsorption energies of Hg, HgCl, HCl, H₂O and their combinations. Adsorption energies of these species decrease with increasing temperatures, becoming energetically unfavorable at T > 300 K. A mechanism to explain Hg oxidation has been proposed based on the adsorption energies calculated at 300 K. This mechanism may involve the adsorption of HCl and HgCl, following a Langmuir–Hinshelwood mechanism. The
oxidation of Hg to HgCl₂ is represented as a cycle, where HgCl and HCl interact without poisoning the surface, since the original catalyst is the first and last step of the reaction. Some of the steps during the formation of HgCl₂ may include adsorption and dissociation of HCl, adsorption of HgCl, formation of HgCl₂, and its desorption from the surface.

Because the active vanadia phase, V₂O₅, is responsible for NO₃ reduction and the undesired SO₂ to SO₃ oxidation reaction, the impact of other flue gas components, such as sulfur dioxide (SO₂), sulfur trioxide (SO₃), nitrogen monoxide (NO), and nitrogen dioxide (NO₂), on mercury oxidation across the SCR unit will also be examined in future work. These results from DFT may aid in the design of improved catalysts for mercury oxidation while simultaneously maintaining optimal performance for NO₃ reduction.

**APPENDIX**

**Appendix A: Modeling the TiO₂(001) Support**

The TiO₂(001) surface has been studied previously, and is shown in Figure 9. It is composed of five-coordinated Ti atoms bonded to two O atoms along the (001) direction and to three O atoms in the (010) direction. In the TiO₂ bulk structure, the bond distances between the Ti and O atoms from the upper and lower layer, in the (001) direction, are identical (i.e., in bulk, the atomic distance, Ti²−O₁, equals the atomic distance, Ti−O₃*, as shown in Figure 9). However, in the case of the slab calculations, the atomic distances are different since the 1st layer (i.e., bottom layer) is fixed to the bulk parameters, while the surface is unconstrained. For this reason, the interlayer distance is defined as the average distance between Ti²−O₃ and Ti²−O₃*, where x is defined as the layer number counted from the bottom of the slab. The way in which the atomic layers are defined in the current work is shown in Figure 9.

In general, larger models are preferred for representing real systems, but the computational cost increases with size. To balance computational time and accuracy, the optimal slab thickness was established based upon two convergence criteria: convergence in the change of interlayer distances of the TiO₂(001) slab with respect to the bulk and convergence of the adsorption energies of small atoms or molecules (i.e., H, CO, NO).

The change in the interlayer distances with respect to the optimized TiO₂ bulk structure as the system is allowed to relax was compared for slabs with increasing number of layers. Accuracy is reached when the inner layer distance does not change with respect to the bulk configuration. The inner-layer spacings of the bulk, 3-layer, 4-layer, and 5-layer slabs, and percent difference were calculated and negligible changes (<1.5%) were obtained for all cases considered. Similar changes in the bond distances were obtained by Calatayud and Minot, who also modeled the TiO₂(001) surface as a 3-layer slab with a fixed bottom layer.

The other parameter validated during the slab optimization is the change in the adsorption energies of small atoms or molecules (i.e., H, CO, NO) with increasing number of layers. The convergence criterion for adsorption energies is reached if the change of the adsorption energy with respect to the 5-layer slab is within 0.01 eV/atom. The adsorption energies are calculated using eq 6:

\[ E_{\text{ad}} = E_{\text{system}} - (E_{\text{gas-phase}} + E_{\text{clean}}) \]

where \( E_{\text{system}} \), \( E_{\text{gas-phase}} \), and \( E_{\text{clean}} \) are the calculated energies of the surface after adsorption of X atom/molecule, the energy of X in the gas phase and the energy of the clean surface prior to adsorption, respectively. As is shown in Table 5, convergence in the adsorption energies for CO and NO is achieved using a 3-layer slab with the bottom layer fixed to the bulk parameters. Although convergence in the adsorption energy of H is not reached until the use of a 4-layer slab, the lower computational cost and negligible changes in the inner-layer spacing collectively justify the use of the 3-layer slab.

**Appendix B: Vibrational Contributions of the Surface Hydroxyl and Water Groups**

The vibrational frequency contribution sourced from the adsorbed hydroxyl and water functional groups, \( \Delta F_{\text{Vib-ad}} \), was calculated to understand its contribution to the total Gibbs free energy. In the current study the vibrational free energies of the adsorbed hydroxyl and water groups are calculated using the harmonic oscillator approximation as:

\[ F_{\text{HOOH}} = \sum_{\nu} \left( \frac{\hbar \omega_{\nu}}{2} + k_{\nu} T \ln(1 - e^{-\hbar \omega_{\nu}/k_{\nu} T}) \right) \]

in which the sum is over the vibrational modes, \( \omega_{\nu} \), of each of the N adsorbed atoms. The vibrational contribution of each surface is shown in Figure 10 and was calculated by diagonalizing the complete dynamic matrix while leaving the substrate fixed. The line colors represent a different number of water molecules, molecularly and dissociatively adsorbed. It can be seen that the vibrational contribution increases with increasing number of water molecules interacting with the surface. At temperatures below 600 K, the mechanism by which water is adsorbed does not significantly influence the vibrational contribution, although dissociated water molecules provide a smaller contribution than molecularly absorbed water molecules at temperatures above 600 K.

**Appendix C: Modeling TiO₂(001)-Supported Vanadia Oxide Species**

Three possible dimeric structures are shown in Figure 1, differing only in the orientation of the V−O(2)−V bond and...
the missing surface oxygen atoms. Both structures A and C have a V–O(2)–V bond lying in the (100) direction, but they differ in their missing surface oxygen atom. Structure A is missing the O atoms indicated with black arrows in Figure 1, while structure C is missing the O atoms indicated with grey arrows. In the case of structure B, the V–O(2)–V bond follows the (010) direction with the missing O atoms corresponding to those indicated by black arrows.

Following the procedure used by Vittadini et al., the relative stability of each vanadia structure was analyzed based on the formation energies, using the (1 × 4)-reconstructed TiO2(001) and V2O5 bulk, E_{vVO2})\text{form} phase as references. The energy of the former is obtained by adding the reconstruction energy, E_{recon} to the energy of the (1 × 1)-unreconstructed (4 × 2) TiO2(001) slab, E_{uncon}. The formation energy, E_{form}, is defined as

\[ E_{\text{form}} = E_{\text{uncon}} - [E_{\text{vVO2})\text{form}} + E_{\text{TiO2}} + E_{\text{recon}}] \] (8)

The formation energies are −0.33, 0.75, and 3.49 eV for structures A, B, and C, respectively. Structure A is the most stable dimer configuration, and it is equivalent to structure D1, the most stable dimer structure in Vittadini et al. They suggested that the structural similarity between D1 and the (1 × 4)-reconstructed TiO2(001) explains the higher stability of D1 surface. The interaction of the vanadia dimer with the support leads to a geometry distortion of the later. The changes in the inner layer distances measured with respect the 3-layer-unreconstructed TiO2(001) slab are shown in Table 6.

Structure A has the smallest interlayer change, with 0.26 Å in the (001) direction, respectively. The small change in the support seems to be responsible for the higher stability of structure A, which is the structure used in subsequent calculations.

**Appendix D: All Molecularly and Dissociatively Adsorbed Water Configurations Tested**

The thermodynamic stability of all hydroxylated and hydrated surfaces tested is shown in Figure 11. The water coverage and the adsorption sites occupied by water for each surface is summarized in Table 1 in the paper. The Gibbs free energy of adsorption was calculated using eq 3 as a function of temperature, yielding a straight line for each surface. The surface associated with the lowest-lying line corresponds to the most stable structure under the given flue gas conditions.

At lower temperatures, the lines representing surface with high water coverage (green, blue, and yellow lines that represent 5, 4, and 3 adsorbed water molecules) have more negative Gibbs free energy. However, as the temperature increases, the relative stability is shifted to those surfaces with less adsorbed water (red and black lines that represent 2 and 1 adsorbed water molecules). Surface Mol-7 (grey line with circles) and surface Mol-2 (black line with squares) represent a water molecule interacting with the vanadia dimer and a Ti atom of the support. The relative position of these lines, with Mol-2 lying at lower Gibbs adsorption energy, indicates that water rather interacts with the support than with the vanadia dimer.

**Appendix E: PDOS Hydroxylated Surfaces**

Figure 12a shows the projected density of states, PDOS, of all oxygen and hydrogen atoms of structures Mol-5 and Dis-3, which represent molecularly and dissociative water adsorption, respectively, for full coverage, that is, θ = 1. Figures 12b and 12c focus on the contribution to the valence band of the individual oxygen and hydrogen atoms involved in the water adsorption modes. Figure 12a shows the relative position of the oxygen and hydrogen peaks for both types of water adsorption, which may be used to compare their relative stabilities. The peaks generated during molecular adsorption of water are located at lower energies, which suggests a higher stability. These results complement the ab initio predictions that indicate higher

![Figure 10. Vibrational contribution of surface hydrogen groups (−H, H2O, and −OH) to the surface free energy of different hydroxylated and hydrated (vanadia-TiO2) surfaces.](image)

![Figure 11. All molecularly and dissociatively adsorbed water configurations tested. The color scheme is the same as in Figure 10 and it is linked to the number of adsorbed water molecules. Green = five water molecules, blue = four water molecules, yellow = three water molecules, red = two water molecules, and black = one water molecule.](image)

<table>
<thead>
<tr>
<th>structure</th>
<th>ΔE_{mol} (%)</th>
<th>ΔE_{vdw} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.26</td>
<td>1.62</td>
</tr>
<tr>
<td>B</td>
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<td>1.98</td>
</tr>
<tr>
<td>C</td>
<td>0.37</td>
<td>3.16</td>
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</table>
stability for molecular water adsorbed surfaces for the case of high-water coverage. The PDOS of oxygen and hydrogen atoms during water dissociation are represented in Figure 12b, which shows two overlapping O and H peaks at −7 and −5.5 eV, which correspond to the O–H interaction between the two hydroxylated Ti atoms generated during the dissociation of one molecule of water. As described in Figure 2, one of the −OH groups comes from the dissociation of water on a surface Ti atom (labeled as O−OH) and another coming from the breaking of the Ti−O(2) bond during the interaction of the surface O(2) atom coordinate with the −H atom (labeled as Os−H). The lower energy peak, that is, −7 eV, has a larger contribution from the H−Os interaction (grey line), while the −5.5 eV peak has a larger contribution due to the O−H interaction of the hydroxyl group (black line). The PDOS of the oxygen and hydrogen atoms during molecular water adsorption are represented in Figure 12c, which shows a strong peak at −8.7 eV, which is composed mostly by the O−H interaction in the adsorbed water molecule (labeled as O−H₂O). The presence of a second peak at −5.5 eV is due to the H−O interaction between neighboring adsorbed water molecules. The tilted position of the adsorbed water molecule towards the surface also creates a weak interaction between the H atom and a surface oxygen atom, subsequently leading to a small contribution to both peaks (labeled as Os−H).

Appendix F: Dimer Stability as a Function of Water Adsorption: Formation Energies and PDOS

In the Bader charge analysis section, it was suggested that the increase in the charge transfer between the hydroxylated support and vanadia dimer may yield a stronger dimer-support interaction. The relative stability of the vanadia dimer as a function of water adsorption is evaluated by comparing the formation energies of vanadia species on different hydroxylated/hydrated surfaces. The formation energies, \( E_{\text{form}} \), which are summarized in Table 7, were calculated in a similar way as in the TiO₂ slab optimization section, but modifying the formation equation to add the energy of an isolated water molecule as

\[
E_{\text{form}} = E_{\text{uncon}}^{\text{hydr}} - [E_{\text{vVO}_2} + E_{\text{TiO}_2} + E_{\text{recon}} + E_{\text{H}_2\text{O}}] \tag{9}
\]

Larger formation energies are obtained with increasing number of adsorbed water, which may be correlated to a higher stability of the vanadia dimer. This stronger bond between the dimer and support may be the result of a larger charge transfer from the adsorbed water to the surface. The increase in the stability of the vanadia dimer is also seen in Figure 13, which presents the change in the PDOS of O(1) and V atoms with the degree of hydroxylation. The contribution to the conduction band of oxygen species is due to the O(2p) density of states. Only the PDOS of the O(1) atom are shown because O(1) is the oxygen atom from the vanadia dimer with the greatest change in charge during the dehydration process.

Figure 13 shows a slight shift in both the conduction and valence bands to lower energies with increasing number of adsorbed water molecules. This shift to lower energies supports the idea of increasing stability of the vanadia dimer through charge donation from the adsorbed water to the support.

Table 7. Formation Energies as a Function of Hydroxylation/Hydration

<table>
<thead>
<tr>
<th>surface</th>
<th>#H₂O</th>
<th>( E_{\text{form}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol-5</td>
<td>4</td>
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</tr>
<tr>
<td>Mix-1</td>
<td>3</td>
<td>−2.18</td>
</tr>
<tr>
<td>Dis-3</td>
<td>2</td>
<td>−1.65</td>
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<tr>
<td>A</td>
<td>0</td>
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</tbody>
</table>
Background information on the research community and the historical context of the field.

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