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**Interaction between Monomeric Vanadium Oxide Clusters Supported on Titania and Its
Influence on Their Reactivity**

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Abstract

Density functional theory is used to study monomeric vanadium oxide clusters formed by exposing to oxygen a rutile $\text{TiO}_2(110)$ surface on which vanadium atoms have been preadsorbed. Past calculations examined such systems by using one V atom per supercell. This forces all VO_x clusters to be identical and precludes interactions between them. To examine the consequences of this choice, we examine a VO_x and a VO_y cluster in the same supercell. We find that the most stable configuration is obtained when the supercell contains one VO_2 and one VO_3 cluster. The stabilization occurs because of a Lewis acid-base interaction: VO_2 donate electron charge to VO_3 and this lowers the energy substantially. No such interactions were found when the supercell contained VO_x clusters with the same number of oxygen atoms. These finding demonstrate that in some cases it is essential to have two clusters in the supercell and that results obtained with one cluster in supercell can be misleading. We have also studied the reactivity of the clusters with hydrogen, which is considered a descriptor of the ability of the cluster to catalyze the breaking of a C-H bond in an alkane.

1. Introduction

Submonolayers of vanadium oxide supported on another oxide are good catalysts for several partial oxidation reactions and their properties have been examined in several recent review articles.¹⁻³ There is strong evidence that catalytic chemistry of vanadium oxide supported on an oxide is most useful when the VO_x coverage is less or equal to a monolayer.^{1-3, 4, 5-12} The chemistry of such supported VO_x clusters has been examined in a large number of computational studies.¹³⁻²⁶ In this paper we are concerned with monomeric VO_x supported on rutile $\text{TiO}_2(110)$. We have chosen to study a TiO_2 support because VO_x/TiO_2 is an industrially important catalyst,³ its structure can be imaged by STM,⁴⁻¹⁰ and experiments with mass selected clusters have been performed.⁹⁻¹⁰ The quality and the quantity of the information we have for this system is better than for any other support.

The notation VO_x indicates a vanadium oxide cluster formed by adding x oxygen atoms to a vanadium atom adsorbed on TiO_2 . Since the VO_x species considered here are adsorbed on the TiO_2 support, the vanadium atom in the cluster also makes bonds with oxygen atoms from the surface of the support; these oxygen atoms are not included in the symbol VO_x .

In this article we examine a number of systems which are described schematically in Figure 1. Some systems are studied here for the first time and some repeat previous calculations to ensure that they can be compared to the new ones. In this figure the light-blue area represents the support and the dotted vertical lines are the borders of the supercells used in the calculations. We have used two supercells chosen so that one is twice as large as the other. The vertical lines are meant to indicate whether a calculation was performed with the smaller supercell or the larger one. Each panel in the figure shows several periodic replicas of each supercell. The supercells shown schematically in Figure 1a and 1c contain only *one VO_x cluster per supercell*

and such system will be denoted (VO_x) in what follows. These are the systems studied in all previous calculations.¹³⁻²⁶ Because of the periodic boundary conditions, each VO_x cluster in these calculations is identical to its periodic image. In the other systems in the figure (Figure 1b, d-g) each supercell contains *a* VO_x *and a* VO_y *cluster* instead of just one VO_x and they are denoted, in what follows, (VO_x, VO_y); in some calculations $x = y$ and in others $x \neq y$. The ratio of V atoms per Ti atom is the same in all calculations represented in Figure 1, so that their energies can be compared to each other to determine their stability. The stability is decided based on the formation energy (defined in Section 2) of each structure.

It was shown in previous work,²⁷⁻⁴⁶ on a variety of systems, that two species in the same supercell may exchange electrons with each other and that this electron exchange has a strong influence on the binding energy to the surface and on the choice of binding sites. Charge exchange may occur even if the two species consist of the same atoms. For example, if two H atoms are adsorbed on La_2O_3 , one will bind to La to form a hydride and the other to oxygen to form a hydroxyl; the charge transfer from the hydroxyl to the hydride stabilizes this particular structure as compared to both H atoms binding to surface oxygen or both binding to the La atoms.³⁵ These observations have been generalized as propensity rules^{44, 47} that assert that two molecules coadsorbed on an oxide surface bind more strongly to the surface if one of them donates electrons (is a Lewis base) and the other accepts electrons (is a Lewis acid). The tendency to form a Lewis acid-base pair also affects the binding sites: the adsorbates will bind to sites that allow them to exchange electrons. If we apply these rules to the (VO_x, VO_y) system, we expect that for some values of x and y the two-cluster system is stabilized by becoming a Lewis acid-base pair: one cluster donates electron charge to the other. This expectation is the main reason for studying the (VO_x, VO_y) system and for comparing its energy to the energy of

(VO_x) plus the energy of (VO_y). If the two clusters in the large supercell do not interact, these two energies will be equal or very close to each other.

Figure 1 shows a schematic representation of the vanadium oxide systems whose energy was calculated and we will now discuss each panel. In Figure 1a there is one VO₂ cluster per supercell, so all VO₂ clusters are identical; in particular, no charge transfer between them is possible. The system described by Figure 1b was investigated to determine whether two VO₂ clusters *in the same supercell* will exchange electronic charge to lower their energy. We found no charge exchange and the formation energy of the structure in Figure 1b (which is (VO₂,VO₂)) is twice as large than that of (VO₂) (Figure 1a). In other words, the energy per vanadium atom in these two calculations is the same, which means that there is no interaction between two VO₂ clusters located in the same large supercell. The same conclusion is reached from calculations of the formation energies of the systems described by Figures 1c and 1d; the VO₃ clusters that coexist in the same supercell do not exchange charge with each other. So far it appears that using two clusters in the same unit cell provides no benefit: the energy is twice that of a system that has one cluster in the supercell.

The situation is different when one considers systems of the type described by Figure 1e, in which the number of oxygen atoms in the two clusters contained in the same supercell is different. A particular case of this situation is shown in Figure 1f in which VO₂ and VO₃ are present in the same supercell. One would expect that the formation energy E_{lf} of the system in Figure 1f is roughly the same as the formation energy E_{la} of the system in Figure 1a plus the formation energy E_{lc} of the system shown in Figure 1c. The calculations presented here show that this is not the case. Instead, we find that $E_{lf} \ll E_{la} + E_{lc}$.

The fact that E_{lf} is much lower than the “sum of the parts” is consistent with the rules proposed in previous work,^{43-44, 47} which state that coadsorbed molecules will lower their energy if one of them can function as a Lewis base (electron donor) and the other as a Lewis acid (electron acceptor). In the case of (VO_2, VO_3) shown in Figure 1f, the electron charge on VO_2 is less than the electron charge on the VO_2 structure in (VO_2, VO_2) . The electron charge missing from VO_2 is located mostly on VO_3 (which is more negative in (VO_2, VO_3) than in (VO_3, VO_3)). This is why we use for the system shown in Figure 1f the notation (VO_3^-, VO_2^+) . A similar situation is shown in Figure 1g, where the two clusters have the same stoichiometry as in Figure 1f (they both have three oxygen atoms per vanadium) but have different geometry (the two clusters are isomers). One structure, which we denote $OV(O_2)$, contains a peroxide group and the other is a VO_3 cluster. Our calculations show that $OV(O_2)$ is a Lewis base and VO_3 is a Lewis acid. The energy of formation of this pair is comparable to that of (VO_3^-, VO_2^+) . The essential difference between the systems in Figure 1f and 1g, which are the systems having the highest stability (the clusters have the highest binding energy to the oxide), and all other systems studied here is that they form an acid-base pair.

Figure 1: A schematic description of the systems studied here. The light-blue strip represents the TiO_2 support. VO_x signifies a vanadium oxide cluster consisting of a vanadium atom and x oxygen atoms acquired from gaseous oxygen (not from the oxygen of the support). The vertical bars indicate the size of the supercells: We use a small supercell containing one VO_x cluster and a supercell twice as large containing both a VO_x and a VO_y cluster. The figures show the periodic replicas of the cells. For example in (a) the supercell contained one VO_2 cluster while in (b) it contained two. The clusters in (a) cannot exchange electrons; the ones in (b) could exchange electrons but did not. The blue arrows and the plus and minus signs on the clusters in (f) and (g) indicate that charge transfer took place and show which cluster gained electron charge and which lost it. The absence of such arrows indicates an absence of electron transfer between clusters.

What are the consequences of these findings? In previous work the energies and the vibrational frequencies of the VO_2 and VO_3 clusters described by Figure 1a and 1c were calculated and used to estimate the free energies of the two systems. The thermodynamic equilibrium conditions were then used to calculate the coverage of VO_2 and VO_3 when the TiO_2 surface having V atoms adsorbed on it is in thermodynamic equilibrium with gaseous oxygen, at a given temperature and partial pressure. This, in turn, was used to propose the redox couple for oxidation reactions catalyzed by supported vanadium clusters: VO_3 was the oxidant and VO_2 the reduced species. An implicit assumption in these calculations was that the binding energy of VO_2 to the surface is not affected by the presence of VO_3 and vice-versa. In this article we show that this assumption, which was made because of the need to use a small supercell which could accommodate only one cluster, is not correct.

Our calculations imply that if one prepares VO_x by oxidizing vanadium atoms adsorbed on the surface of the stoichiometric support, the result is likely to be a mixture of VO_2 and VO_3 , or a mixture of $\text{OV}(\text{O}_2)$ and VO_3 . They also imply that if mass-selected VO_2 clusters are deposited on stoichiometric rutile $\text{TiO}_2(110)$ and then exposed to oxygen, the result would be a mixture of VO_2 and VO_3 or $\text{OV}(\text{O}_2)$ and VO_3 and not a surface covered exclusively with VO_3 . The fact that not all VO_2 clusters will be oxidized to VO_3 is not a kinetic effect (due to a short exposure time to oxygen) but a thermodynamic limitation.

In the last part of this article, we consider adsorption of $\frac{1}{2}\text{H}_2$ in order to assess the reactivity of the clusters shown in Figure 1. The main observation is that the stable clusters, $(\text{VO}_3^-, \text{VO}_2^+)$ and $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$, are significantly less reactive toward hydrogen adsorption than $(\text{VO}_3, \text{VO}_3)$.

2. Computational details

The large rutile $\text{TiO}_2(110)$ supercell is a $p(6\times 2)$ surface slab with four stoichiometric TiO_2 layers. All atoms in the four layers are allowed to relax; in particular, we do not force the geometry of the bottom layer to be that of the bulk oxide. In the supercell two VO_x clusters are placed on the surface so that the V atoms are separated by 11 Å. Density functional theory (DFT) calculations have been performed with the VASP program.⁴⁸⁻⁵¹ Exchange-correlation effects are approximated by the PBE functional.⁵² The DFT+U correction is applied to both the metal ions in the support and in the clusters, following the approach of references.⁵³⁻⁵⁴ While it is agreed that GGA+U gives more reliable results than GGA, there isn't yet agreement regarding the best values for U. We use $U = 3.5$ eV on Ti and on V d-states based on the suggestions made in the literature.^{41, 55-57} While the value of U for TiO_2 has been tested and accepted as reasonable, less is known about the U for the V atom in a VO_x cluster. For bulk V_2O_5 Watson used⁵⁶ $U = 4$ eV and Ceder recommended an U between 3 and 3.3 eV. Henkelman²⁶ used $U = 4.5$ eV for V when studying vanadium oxide clusters supported on TiO_2 . The present paper reports and analyzes results obtained using $U = 3.5$ eV for V. We have also performed calculations with $U = 2.5$ eV and $U = 4.5$ eV and found that while the energies of formation depend on U (Table S4 in Supporting Information), the observation that $(\text{VO}_3, \text{VO}_2)$ is more stable than either $(\text{VO}_2, \text{VO}_2)$ or $(\text{VO}_3, \text{VO}_3)$ is not affected by the U value. We note that the use of smaller U values on Ti and V leads to results, where polaron formation (electron localization) is less likely to occur. This may explain the finding that the charge on the VO_2 cluster supported on anatase⁵⁸ is different from the ones reported here. This study used $U = 2.3$ eV for Ti, and 2.0 eV for V.

The calculations are performed with the projector augmented wave method (PAW), a plane wave basis set with an energy cutoff of 400 eV is used, and one, 6, 11, and 12 valence

electrons are included for H, O, V, and Ti, respectively. Reciprocal space is sampled by 2×2 k-points for the large supercell. In the small supercell, the surface is spanned by a parallelogram that gives both the same coverage and pattern of vanadium oxide clusters as the large supercell when repeated. Here, reciprocal space is sampled by 2×4 k-points. All calculations are spin polarized.

The formal charges of the V atoms are important for understanding the electron transfer between clusters. We calculate them by two methods. One is the Bader charge⁵⁹⁻⁶¹ on the vanadium atoms and the other is the spin-density difference in the Bader volume³⁸ of the vanadium atoms. The latter method is much more sensitive than the Bader charge method: the difference between the spin-density difference on V^{4+} and that on V^{5+} is close to 1, while the difference in the Bader charge on V atoms with different formal charge is 0.2 electrons. We find that while a formal charge assignment based on Bader charge is less convincing, it is always consistent with that based on spin-density difference. Bader charges and spin-density differences for the V atoms are included in Table S1 in Supporting Information.

To determine the relative stability of various systems we use the formation energies defined below. In the case when there are two clusters in a supercell the formation energy of a specific system is the energy of the reaction eq 1.

The notation (VO_x, VO_y) indicates that there are two clusters in the supercell and one is VO_x and the other is VO_y . In all cases the clusters are spatially separated and are distinct from V_2O_{x+y} . The energy of this reaction defines the energy of formation of (VO_x, VO_y) . The reaction (eq 1) was chosen so that the systems we plan to compare have the same number of atoms and their energy is always referenced to the left-hand side of eq 1. The energy of formation contains the

energy of the species 2V. Because 2V appears in every reaction studied here, the energy of 2V is irrelevant when two formation energies are compared (which is what we do here). The energy of 2V in the present calculations is the energy to remove two V atoms from vanadium metal. These formation energies (i.e. the energies of the reaction eq 1) for different values of x and y, are used to estimate the formation free energies. These allow us to determine which of the systems shown in Figure 1 is most stable.

For the systems using the smaller supercell we calculate the energy of the reaction eq 2.

The notation (VO_x) indicates that the supercell contains only one VO_x cluster. In the calculations using the smaller supercell, it is not possible to examine the interaction between clusters because they are periodically repeated and therefore are forced to be identical from one supercell to another. Previous calculations on the $(\text{VO}_x)/\text{TiO}_2(110)$ system have all used this type of calculation (one cluster per supercell).

3. Structure, formation energy, and density of states of $(\text{VO}_x, \text{VO}_y)$

In this section we examine the structures, the formation energies, and the projected density of states (PDOS) of various pairs of vanadium oxide clusters: $(\text{VO}_2, \text{VO}_2)$, $(\text{VO}_3, \text{VO}_3)$, $(\text{VO}_3^-, \text{VO}_2^+)$, and $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$. The unit cell in these calculations is twice as large as the one used to calculate the properties of (VO_2) and (VO_3) . The surface concentration of the vanadium oxide clusters is the same in the two kinds of calculations.

3.1. Structure of the $\text{TiO}_2(110)$ surface. Before we examine the vanadium oxide clusters, we remind the reader of some of the prominent features of the $\text{TiO}_2(110)$ surface.⁶² Figure 2a shows

the surface of the $\text{TiO}_2(110)$ surface with two VO_2 clusters on it, viewed from the side and from above. We discuss here only the $\text{TiO}_2(110)$ surface as seen in this figure. The red spheres represent the oxygen atoms in the bridging-oxygen row. Each bridging oxygen is bonded to two Ti atoms which are six-fold coordinated, are located below the bridging oxygens, and are unavailable for bonding with adsorbates. The dark gray spheres represent the in-plane oxygen atoms. The light gray spheres, located between the in-plane oxygen atoms, are the five-coordinated titanium ($5c\text{-Ti}$) atoms.

3.2. Properties of $(\text{VO}_2, \text{VO}_2)$. The structure of the $(\text{VO}_2, \text{VO}_2)$ system, shown schematically in Figure 1b, is shown in detail in Figure 2a. Two VO_2 clusters are present in the supercell. The vanadium atoms are magenta and the two oxygen atoms that each vanadium atom acquired from the gas phase (when the system was prepared) are yellow. Each “yellow oxygen atom” is bonded to vanadium and to a $5c\text{-Ti}$ atom. The structure is consistent with the STM images of mass-selected VO_2 clusters obtained by Price *et al.*¹⁰ There is no vanadyl group in this structure (the vanadyl is a V=O group in which the oxygen is double bonded and single coordinated to a V atom). This conclusion can be tested, in principle, by Raman spectroscopy.

The formation energy of $(\text{VO}_2, \text{VO}_2)$ is -13.05 eV (the formation energies for all systems studied here are given in Table 1). This is equal to the energy of formation of two VO_2 clusters in (VO_2) (which is shown schematically in Figure 1a). Because the supercell used for $(\text{VO}_2, \text{VO}_2)$ is twice as large as the one used for (VO_2) , the vanadium concentration in the two systems is the same. The fact that the formation energy of $(\text{VO}_2, \text{VO}_2)$ is equal to twice the formation energy of (VO_2) indicates that *there is no interaction and no charge transfer* between the two VO_2 clusters present in the same supercell. This means that, for this particular example, there is

nothing to gain by doubling the supercell and the previous calculations using the scheme in Figure 1a are as accurate as the ones using the scheme in Figure 1b. However, this is not going to be the case when one studies reactions, where charge transfer between clusters occurs.

The Bader charge and the spin-density difference (Table S1 in Supporting Information) of the vanadium atoms marked α and β in Figure 2a indicate that they have a formal charge of (4+), which matches the formal charge of 2- for the O atoms in the cluster. The projected density of states (PDOS) for (VO₂, VO₂) shows that two electrons (one on each vanadium atom) reside in orbitals whose energy is at the top of the valence band (Figure 2b). These are the two electrons that make the vanadium atoms have formal charge 4+ (instead of the more common 5+). They also suggest that VO₂ is likely to be an electron donor (Lewis base) if it is paired up with an adsorbate that can be an electron acceptor.

In this article we use PDOS for a qualitative examination of the difference between the HOMOs and the LUMOs of various systems. The energy of these orbitals is referenced with respect to the energy of the Ti 3s core states.

Figure 2: The structure of the $(\text{VO}_x, \text{VO}_y)$ clusters: first column side view, second column top view, third column the density of states. For each figure E_f is the formation energy of the clusters defined by eq 1. (a) The structure of $(\text{VO}_2, \text{VO}_2)$. (b) The projected density of states (PDOS) of $(\text{VO}_2, \text{VO}_2)$. (c) The structure of $(\text{VO}_3, \text{VO}_3)$. (d) The PDOS of $(\text{VO}_3, \text{VO}_3)$. (e) The

structure of $(\text{VO}_3^-, \text{VO}_2^+)$. (f) The PDOS of $(\text{VO}_3^-, \text{VO}_2^+)$. (g) The structure of $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$. (h) The PDOS of $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$. The formal charges of the V atoms (obtained from Bader charge and spin-density difference analysis and shown in Table S1) are indicated by V^{4+} or V^{5+} . V atoms are marked α and β and O atoms in (c) and (g) are marked ν , τ and γ , δ to identify states localized on these atoms in the PDOS plots. The PDOS is plotted around the Fermi level (ϵ_F), and the plots are aligned by matching the position of Ti 3s core states (0 eV).

Table 1: Summary of reactions

Reaction	Scheme in Figure 1	Figure number	Reaction energy	Formal charge of V atoms in the reaction product
Formation of $2(\text{VO}_x)$				
$3\text{O}_2 + 2\text{V} + \text{TiO}_2(110) \rightarrow 2(\text{VO}_2)/\text{TiO}_2(110) + \text{O}_2$	(a)		-13.05 eV	4+
$3\text{O}_2 + 2\text{V} + \text{TiO}_2(110) \rightarrow 2(\text{VO}_3)/\text{TiO}_2(110)$	(c)		-14.12 eV	5+
Formation of $(\text{VO}_x, \text{VO}_y)$				
$3\text{O}_2 + 2\text{V} + \text{TiO}_2(110) \rightarrow (\text{VO}_2, \text{VO}_2)/\text{TiO}_2(110) + \text{O}_2$	(b)	Figure 2a	-13.05 eV	(4+, 4+)
$3\text{O}_2 + 2\text{V} + \text{TiO}_2(110) \rightarrow$	(d)	Figure 2c	-14.12 eV	(5+, 5+)

(VO ₃ , VO ₃)/TiO ₂ (110)				
3O ₂ + 2V + TiO ₂ (110) → (VO ₃ ⁻ , VO ₂ ⁺)/TiO ₂ (110) + ½O ₂	(f)	Figure 2e	-14.90 eV	(5+, 5+)
3O ₂ + 2V + TiO ₂ (110) → (VO ₃ ⁻ , OV(O ₂) ⁺)/TiO ₂ (110)	(g)	Figure 2g	-15.12 eV	(5+, 5+)
Adsorption of ½H₂ on (VO_x)				
½H ₂ + (VO ₂)/TiO ₂ (110) → (VO ₂ H)/TiO ₂ (110)			-1.17 eV	3+
½H ₂ + (VO ₃)/TiO ₂ (110) → (VO ₃ H)/TiO ₂ (110)			-2.56 eV	5+
Adsorption of ½H₂ on (VO_x, VO_y)				
½H ₂ + (VO ₂ , VO ₂)/TiO ₂ (110) → (VO ₂ H, VO ₂)/TiO ₂ (110)		Figure 4a	-1.17 eV	(3+, 4+)
½H ₂ + (VO ₃ , VO ₃)/TiO ₂ (110) → (VO ₃ , VO ₃ H)/TiO ₂ (110)		Figure 4c	-2.56 eV	(5+, 5+)
½H ₂ + (VO ₃ ⁻ , VO ₂ ⁺)/TiO ₂ (110) → (VO ₃ H, VO ₂)/TiO ₂ (110)		Figure 4e	-1.26 eV	(5+, 4+)
½H ₂ + (VO ₃ ⁻ , OV(O ₂) ⁺)/TiO ₂ (110) → (VO ₃ , VO ₃ H)/TiO ₂ (110)		Figure 4g	-1.56 eV	(5+, 5+)

3.3. *Properties of (VO₃,VO₃).* The structure of (VO₃,VO₃) is shown in Figure 2c and schematically in Figure 1d. The V atoms are magenta, the oxygen atoms bound to V and originating from the gas (when the cluster was prepared by oxidizing adsorbed V) are yellow. The vanadium atom makes “bonds” with the three oxygen atoms from the gas and with two bridging oxygen atoms from the surface. The vanadium atom and the five oxygens to which it is bonded form a square pyramid, which is a common binding motif in vanadium-oxygen compounds including bulk V₂O₅.⁶³ One of the oxygen atoms in the VO₃ cluster (the one sticking up) belongs to a vanadyl (V=O). This is easily identified because the oxygen-vanadium bond is shorter and contributes a higher frequency mode to the vibrational spectrum of the cluster (see the calculated vibrational frequencies in Table S2 in Supporting Information). The other two oxygen atoms in the cluster bridge the V atom with the 5c-Ti atoms. The formation energy of (VO₃, VO₃) is -14.12 eV, which is lower than the energy of formation of (VO₂, VO₂). This is consistent with the known preference of vanadium atoms to have a square pyramid coordination, which is achieved in (VO₃, VO₃).

The formation energy of (VO₃,VO₃) is twice the formation energy of (VO₃), which indicates that there is no difference between a calculation using the scheme shown in Figure 1c and the one shown in Figure 1d: the energy per vanadium cluster is the same. The VO₃ clusters in the large supercell (which contains two VO₃ clusters) have a chance to exchange charge but they do not exchange charge. The vanadium atoms in them have identical Bader charges and the spin-density difference on them is very small (within the error of calculation it is equal to zero (Table S1)). Based on this, we assign a formal charge of 5+ to each vanadium atom.

It is interesting to consider what happens in going from (VO₂, VO₂) to (VO₃, VO₃) by adding one oxygen atom to each VO₂ cluster. When this is done, vanadium shifts from V⁴⁺ to

V^{5+} , but this provides the added O atom with only one electron instead of two. The support cannot provide the needed electron and therefore there is an electron deficit in the cluster, which suggests that this cluster is a Lewis acid. This is also suggested by the PDOS in Figure 2d which shows the presence of two orbitals above and near the Fermi level.²⁶ They are localized on the two oxygen atoms (ν and τ on one cluster and γ and δ on the other, in Figure 2c). These empty orbitals are likely electron acceptors, which again suggest that this cluster is a Lewis acid. Crudely one could think of VO_3 as having too much oxygen or equivalently, as having an electron deficit as far as the oxygen atoms are concerned.

3.4. *Properties of (VO_3^-, VO_2^+) .* The structure of a system containing a VO_2 cluster and a VO_3 cluster in the same supercell is shown in Figure 2e and was shown schematically in Figure 1f. We use the notation (VO_3^-, VO_2^+) for this system to emphasize the fact that the VO_2 cluster donates an electron to VO_3 and therefore the coadsorption of these two clusters benefits from an energy lowering due to an acid-base interaction. This charge transfer takes place “spontaneously”: we did nothing to force the clusters into this state other than optimize their geometry. Because of the charge transfer, both V atoms have 5+ formal charges. If VO_2 and VO_3 did not interact, the energy would be half of that of (VO_2, VO_2) plus half that of (VO_3, VO_3) . Using the energies given in Figure 2, this would be $(-13.05 \text{ eV} - 14.12 \text{ eV})/2 = -13.58 \text{ eV}$. The calculated energy of (VO_3^-, VO_2^+) is -14.90 eV and therefore the charge exchange between the clusters lowers the energy by $14.90 \text{ eV} - 13.58 \text{ eV} = 1.32 \text{ eV}$. It is therefore energetically more favorable to have (VO_3^-, VO_2^+) than to have either (VO_2, VO_2) or (VO_3, VO_3) . If Figure 2e is compared to Figure 2a, one observes that VO_2^+ in (VO_3^-, VO_2^+) has a vanadyl oxygen while all oxygen atoms in (VO_2, VO_2) make bonds with the 5c-Ti atoms and there is no vanadyl. This

structural modification when VO_2 changes to VO_2^+ is consistent with the fact that the vanadium atom is V^{5+} in VO_2^+ and V^{4+} in VO_2 .

The PDOS for $(\text{VO}_3^-, \text{VO}_2^+)$ is shown in Figure 2f. $(\text{VO}_3^-, \text{VO}_2^+)$ does not have a localized electron on the vanadium in VO_2^+ (unlike what is observed for $(\text{VO}_2, \text{VO}_2)$), and it does not have an empty state on the VO_3^- (unlike what is observed for $(\text{VO}_3, \text{VO}_3)$). This is because an electron has moved from VO_2 to fill an empty state in VO_3 .

3.5. Properties of $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$. This system is shown schematically in Figure 1g and in detail in Figure 2g. The notation $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ is used because we find that the VO_3 cluster gains electronic charge spontaneously (i.e. we did nothing to cause charge exchange, except vary the geometry to find the minimum energy). $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ has the same number of atoms as $(\text{VO}_3, \text{VO}_3)$, but two oxygen atoms (marked ν , τ in Figure 2g) form a peroxide group which explains why the notation $\text{OV}(\text{O}_2)^+$ is used (the O_2 is a peroxide whose formal charge is O_2^{2-}). We call this a ‘peroxide’ because the O-O bond length is 1.46 Å, which is very close to the O-O bond length in HOOH (which is 1.453 Å),⁶⁴ and the frequency of a vibrational mode whose amplitude consists mainly of a stretch of the O-O bond is 889 cm^{-1} , which is close to the O-O stretch mode in HOOH (which is 878 cm^{-1}).⁶⁵ Vanadium oxide clusters that are structurally similar to the $\text{OV}(\text{O}_2)^+$ cluster (clusters containing both a peroxide group and a vanadyl O atom) have been proposed in connection with VO_3 clusters supported on alumina and silica.⁶⁶⁻⁶⁷ The presence of a peroxide group was detected by Molinary and Wachs for VO_x supported on silica at temperature below 225 K.⁶⁸ The low thermal stability of the peroxide is consistent with thermodynamic calculations presented later in this article. The V atoms in both clusters have a formal charge of 5+. The $\text{OV}(\text{O}_2)^+$ cluster needs four of the five electrons that the vanadium

atom can supply (to form one O^{2-} and one O_2^{2-}). The remaining electron is transferred to the VO_3 cluster, similar to what we observed for the (VO_3^-, VO_2^+) system. The $(VO_3^-, OV(O_2)^+)$ configuration has a formation energy of -15.12 eV and is therefore the most stable configuration considered in Figure 2, as far as the formation energy is concerned. The PDOS of $(VO_3^-, OV(O_2)^+)$ is shown in Figure 2h and is similar to the PDOS of (VO_3^-, VO_2^+) : there are no states in the band gap.

Formation energies for (VO_2, VO_2) , (VO_3, VO_3) , (VO_3^-, VO_2^+) , and $(VO_3^-, OV(O_2)^+)$ have been calculated with different U values applied to the V d-states (Supporting Information). The formation energies are affected by the choice of U , but the charge transfer is unaffected in (VO_3^-, VO_2^+) and $(VO_3^-, OV(O_2)^+)$ and they remain significantly more stable than (VO_2, VO_2) and (VO_3, VO_3) at U values between 2.5 eV and 4.5 eV.

3.6. Thermodynamic equilibrium between (VO_3^-, VO_2^+) and $(VO_3^-, OV(O_2)^+)$. We imagine that vanadium oxide clusters are prepared by depositing V atoms on the stoichiometric $TiO_2(110)$ surface, exposing them to oxygen at a given pressure and temperature, and allowing the system to reach thermodynamic equilibrium. We can then use a combination of thermodynamics and statistical mechanics to determine which clusters will be present on the surface. This is particularly important because the calculated formation energies for (VO_3^-, VO_2^+) and $(VO_3^-, OV(O_2)^+)$ are so close to each other (the energy difference is -0.22 eV) that it is not safe to decide which clusters are formed based on energy alone. Given that energy disfavors strongly all systems except (VO_3^-, VO_2^+) and $(VO_3^-, OV(O_2)^+)$, we only study the equilibrium composition for the reaction eq 3.

For this purpose we have calculated the vibrational spectrum of the systems in question, where the Hessian matrix is obtained by a finite difference approximation and only the vanadium atoms and the oxygen atoms bounded to vanadium are allowed to vibrate. The vibrational frequencies are given in Table S2 in Supporting Information. To calculate the configuration entropy we use the ideal lattice-gas model for the clusters: the ratio between the two cluster concentrations (surface coverages) is given by eq 4.

$$\theta(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)/\theta(\text{VO}_3^-, \text{VO}_2^+) = \exp(-\Delta G^\circ/kT) \quad (4)$$

ΔG° is the standard free energy of the reaction

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

and ΔH° is the reaction enthalpy

$$\Delta H^\circ = U[(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)] - U[(\text{VO}_3^-, \text{VO}_2^+)] - \frac{1}{2}U[\text{O}_2(\text{g})] - \frac{1}{2}p\Delta V[\text{O}_2(\text{g})] \quad (6)$$

The internal energies (U) of the clusters are calculated from the DFT formation energies plus the contributions from the vibrations of the clusters. The internal energy of O_2 is taken from the NIST tables (<http://kinetics.nist.gov/janaf/>). The reaction entropy ΔS° includes the entropy of $\frac{1}{2}\text{O}_2(\text{g})$ (from NIST tables) and the vibrational entropies of the clusters. A few numerical results based on this methodology are shown in Table S3 in Supplementary Information.

We find that when the partial pressure of O_2 is 1 atm the surface is covered with $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ at temperatures below ~200 K. Above this temperature, the coverage switches to mostly $(\text{VO}_3^-, \text{VO}_2^+)$. Therefore, the system having higher energy becomes more stable due to the entropy. Lower O_2 partial pressure will favor $(\text{VO}_3^-, \text{VO}_2^+) + \frac{1}{2}\text{O}_2$ even further. These

considerations suggest that (VO_3^- , VO_2^+) will be mostly present under reaction conditions that use temperatures higher than 200 K.

4. Can Ti^{4+} act as a Lewis acid to counteract the effect of VO_3 ?

It is well known that Ti atoms in TiO_2 act as Lewis acids when a Lewis base is adsorbed on the surface. For example, adsorbing hydrogen transfers one electron to form a polaron⁶⁹⁻⁷¹ in which Ti has formal charge Ti^{3+} and the oxygen atoms surrounding the reduced titanium atom are slightly distorted from the position they had when Ti had formal charge 4+. The formation of an oxygen vacancy results in the formation of two polarons, since two unpaired electrons are created by the removal of one oxygen atom.^{41, 71-72} When VO_2 is coadsorbed with VO_3 , one would like to test whether it is possible that VO_2 donates an electron to Ti to form a polaron, rather than donate an electron to VO_3 . These are both acid-base processes and the question can be phrased as follows: which is a stronger acid, Ti^{4+} or VO_3 ?

The question is also interesting for kinetics. We propose that if electrically neutral, mass-selected VO_2 and VO_3 are coadsorbed, it is energetically favorable to form (VO_3^- , VO_2^+). However, to form this charged pair from neutral VO_2 and VO_3 , the electron needs to travel from VO_2 to VO_3 . This will happen if VO_2 changes into a polaron and VO_2^+ , followed by the diffusion of the polaron to reach a VO_3 cluster and form VO_3^- . This process would be very slow if the conversion of VO_2 to VO_2^+ and a polaron is energetically unfavorable.

These considerations prompted us to do calculations with a single VO_2 cluster in the large supercell and investigate the energy of the process (VO_2 , Ti^{4+}) $\rightarrow$ (VO_2^+ , Ti^{3+}). The left-hand-side symbol indicates that the VO_2 cluster is neutral and all Ti atoms have the formal charge 4+,

and the right-hand-side symbol indicates that one Ti atom is Ti^{3+} and the cluster is positively charged. We can force the system to make a polaron by using a procedure described previously.^{41, 71, 73} The calculations find that the transition $(\text{VO}_2, \text{Ti}^{4+}) \rightarrow (\text{VO}_2^+, \text{Ti}^{3+})$ is endoergic and requires an energy input of 0.76 eV. Figure 3 shows the structure of VO_2 before (Figure 3a) and after (Figure 3b) polaron formation. The position of the polaron is shown by a green sphere. After the electron transfer takes place, the VO_2 cluster changes structure: one oxygen atom that bridged V with a 5c-Ti, prior to polaron formation and cluster ionization afterwards forms a vanadyl group. The formal charge of the V atom changes from 4+ to 5+. The energy of this process will depend on the position of the polaron⁴¹ and we have not investigated all possible positions. The fact that the process is uphill signifies that the $\text{VO}_2\text{-Ti}^{4+}$ pair is a weak acid-base pair. As we have pointed out, if VO_2 and VO_3 coexist in the supercell, the charge transfer $(\text{VO}_2, \text{VO}_3) \rightarrow (\text{VO}_2^+, \text{VO}_3^-)$ lowers the energy substantially, which indicates that the two clusters form a strong acid-base pair. We conclude that VO_3 is a much stronger acid than Ti^{4+} .

These findings suggest that if a strong base is adsorbed on a site of the TiO_2 surface, in the $(\text{VO}_2, \text{VO}_3)$ system, it is likely that the base will donate electrons to VO_3 and that VO_2 will stay neutral. Therefore, we anticipate that strong bases, such as H, CH_3 , oxygen vacancies, and alkali metals, will affect strongly the $(\text{VO}_2, \text{VO}_3)$ system, will charge VO_3 negatively, and will prevent VO_2 from donating an electron.

Figure 3: Side view and top view of (a) (VO₂, Ti⁴⁺) and (b) (VO₂⁺, Ti³⁺) where an electron has been transferred to a 5c-Ti reducing it to (3+). The electron transfer has an energy cost of +0.76 eV and causes a structural rearrangement of the VO₂⁺ cluster.

5. Reactivity of (VO_x, VO_y) clusters: reaction with a hydrogen atom

It is fairly common to use the binding energy of a hydrogen atom to an oxygen atom of the oxide surface, as a descriptor of the ability of an oxide to break the C-H bond; the stronger the bond of H with the oxide, the lower the activation energy for the dissociative adsorption of methane. This rule, for the reaction of methane with small oxide clusters, seems to have been proposed by Sauer in a chapter of a book edited by Morokuma and Musaev⁷⁴ and in later papers.⁷⁵⁻⁷⁶ Later, we made the same suggestion⁷⁷ based on the fact that the reaction path of methane on oxide surfaces shows that the early, abrupt rise in the energy along the reaction path is due to the abstraction of the hydrogen.

In this section we describe the results of our calculations of the adsorption energy of a H atom to the clusters studied here. The hydrogen atom could bind to the TiO₂ support or to a vanadium oxide cluster. We find that for all system considered here, hydrogen binds to an oxygen atom of the vanadium cluster.

5.1. *Reaction between (VO₂, VO₂) and ½H₂.* We consider first ½H₂ adsorption on (VO₂, VO₂) and have calculated that the energy of reaction eq 7 is –1.17 eV. The negative sign indicates that the energy of the final state is lower than that of the initial state (the hydrogenation of the cluster is exoergic).

The structure of (VO₂H, VO₂) is shown in Figure 4a. The hydrogen atom is cyan. Forming the H-O bond does not cause a substantial distortion of the cluster. H is an electron donor and its electron is donated to the V atom in VO₂H to give it the formal charge 3+.

The PDOS for (VO₂H, VO₂) is shown in Figure 4b. By comparing Figure 4b and Figure 2b (which gives the PDOS for the system prior to ½H₂ adsorption), we see that the addition of the H atom creates an additional filled orbital localized on the V³⁺ atom in the VO₂H cluster. The presence of this new state does not markedly change the orbital energy of the electron that was already localized on the V atom prior to ½H₂ adsorption. The two electrons localized on V³⁺, in the VO₂H cluster, have the same spin orientation (formally the state is a triplet) in accordance with Hund's rule. The energy of the electronic configuration in which the spins of these two electrons have opposite direction (a singlet) is higher by 0.46 eV than that of the triplet (Figure S3 in Supporting Information). The occupied orbital, located on the vanadium atom in the VO₂ cluster (cyan in Figure 2b), has not been affected by the fact that a H atom has bonded to

the other VO₂ cluster to form VO₂H. This suggests, again, that the two VO₂ clusters located in the same supercell do not communicate with each other.

We compare now the energy of reaction eq 7 with the energy of the reaction in which a hydrogen atom is adsorbed on VO₂ in a small supercell (the system shown schematically in Figure 1a). The energy of the reaction

is −1.17 eV, which is equal to that of reaction eq 7 (see also Table 1). We conclude that (VO₂) and (VO₂, VO₂) have the same structural and chemical properties. Therefore using a larger supercell, with two VO₂ clusters in it, is not necessary for this particular system.

Figure 4: (a) $\frac{1}{2}\text{H}_2$ adsorption on $(\text{VO}_2, \text{VO}_2)$ to form $(\text{VO}_2\text{H}, \text{VO}_2)$ and (b) the projected DOS for $(\text{VO}_2\text{H}, \text{VO}_2)$. (c) $\frac{1}{2}\text{H}_2$ adsorption on $(\text{VO}_3, \text{VO}_3)$ to form $(\text{VO}_3, \text{VO}_3\text{H})$ and (d) the projected DOS for $(\text{VO}_3, \text{VO}_3\text{H})$. (e) $\frac{1}{2}\text{H}_2$ adsorption on $(\text{VO}_3^-, \text{VO}_2^+)$ to form $(\text{VO}_3\text{H}, \text{VO}_2)$ and (d) the projected DOS for $(\text{VO}_3\text{H}, \text{VO}_2)$. (g) $\frac{1}{2}\text{H}_2$ adsorption on $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ to form $(\text{VO}_3, \text{VO}_3\text{H})$ and (d) the projected DOS for $(\text{VO}_3, \text{VO}_3\text{H})$ (identical to (d)). The formal charges of the V atoms (obtained from Bader analysis) are indicated by the symbols V^{3+} , V^{4+} or V^{5+} . V atoms are marked α and β and O atoms in (c) and (g) are marked ν , τ and γ , δ to identify states localized on these atoms in the PDOS plots. The PDOS is plotted around the Fermi level (ϵ_F), and the plots are aligned by matching the position of Ti 3s core states (0 eV).

5.2. *Reaction between $(\text{VO}_3, \text{VO}_3)$ and $\frac{1}{2}\text{H}_2$.* Figure 4c shows the structure of $(\text{VO}_3, \text{VO}_3\text{H})$, which is formed by the reaction between $\frac{1}{2}\text{H}_2$ and $(\text{VO}_3, \text{VO}_3)$ (eq 9).

As in the case of (VO_2H , VO_2), the adsorption of H causes no large structural change in the cluster. However, the density of states changes substantially (Figure 4d), as compared to that of (VO_3 , VO_3). H donates an electron and as a result, one of the LUMOs seen in Figure 2d disappears. This happens without forming a localized HOMO; the electron donated by H is spread among the oxygen atoms. This is clearly displayed when we compare the PDOS in Figure 4d to the one in Figure 2d. In the absence of H, the system has an additional empty orbital localized on oxygen and this orbital disappears when H is adsorbed. Furthermore, the orbital that disappeared was localized on the oxygen atoms in the cluster that has bonded the H atom. It is very curious that this electron is not used by the system to reduce the vanadium atom: both V atoms have formal charge 5+, as they had before H adsorption. This happens because there is “too much oxygen” in the VO_3 cluster and there are not enough electrons to “satisfy the needs” of these oxygen atoms.

The energy of the reaction eq 9 is -2.56 eV. This is much larger than the energy produced when H binds to (VO_2 , VO_2), which is consistent with the Lewis acid-base rules. (VO_3 , VO_3) has a deficit of electrons and it is therefore a Lewis acid which will react strongly with H (which is a Lewis base). The fact that the electron provided by H went to the oxygen atoms rather than to V^{5+} indicates that the group of oxygens in VO_3 is a stronger acid than V.

As shown in Table 1 the energy for binding one H atom to (VO_3) is the same as the energy for binding one H atom to (VO_3 , VO_3). There is no interaction between the two VO_3 clusters in the supercell and there is no need to have a larger supercell in calculations in which there are only VO_3 clusters on the surface.

5.3. *Reaction between $(\text{VO}_3^-, \text{VO}_2^+)$ and $\frac{1}{2}\text{H}_2$.* We examine now the adsorption of H on the $(\text{VO}_3^-, \text{VO}_2^+)$ system. The lowest energy structure is obtained when H binds to VO_3 to form $(\text{VO}_3\text{H}, \text{VO}_2)$ (Figure 4e). Both clusters are now essentially neutral. H provides an electron and its presence causes a substantial rearrangement of the charge distribution in the system. The additional electron ends up converting VO_2^+ to VO_2 , the vanadium atom in the VO_2 cluster is reduced from V^{5+} to V^{4+} , and the VO_2 cluster adopts the flat geometric configuration that does not contain a vanadyl group. H forms a bond with VO_3 to produce VO_3H , whose structure is shown in Figure 4e.

The PDOS shows that H adsorption creates a new occupied orbital at the top of the valence band and localized on the VO_2 cluster (Figure 4f).

The $\frac{1}{2}\text{H}_2$ adsorption energy on $(\text{VO}_3^-, \text{VO}_2^+)$ to form $(\text{VO}_3\text{H}, \text{VO}_2)$ is -1.26 eV. The $(\text{VO}_3^-, \text{VO}_2^+)$ system is therefore only slightly more reactive (-0.1 eV) than $(\text{VO}_2, \text{VO}_2)$ for hydrogen adsorption, even though it has one more O atom and the V atom changes formal charge from $5+$ to $4+$ instead of from $4+$ to $3+$.

5.4. *Reaction between $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ and $\frac{1}{2}\text{H}_2$.* Hydrogen adsorption on $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ leads to the same final state as hydrogen adsorption on $(\text{VO}_3, \text{VO}_3)$, namely $(\text{VO}_3, \text{VO}_3\text{H})$ (Figure 4g). The energy of this hydrogenation reaction is different: it is -1.56 eV. The binding of the H atom breaks the O-O bond in the peroxide group in the $\text{OV}(\text{O}_2)^+$ cluster. This formally requires two electrons, but only one electron is supplied by the H atom and an empty orbital appears on the VO_3 cluster just above the Fermi level (Figure 4h). After H adsorption both clusters are neutral.

The results of the formation reactions (eq 1) and the hydrogenation reactions are summarized by the diagram shown in Figure 5. To compare the reactions, we have defined the reaction energies to have a common reference, namely $3\text{O}_2(\text{g}) + \frac{1}{2}\text{H}_2(\text{g}) + 2\text{V} + \text{TiO}_2(110)$. The horizontal bars at the left side of the figure correspond to the formation energies reported in Figure 2; the bars on the right side are the energies of the systems after hydrogenation. Figure 5 shows that the more stable clusters, i.e. $(\text{VO}_3^-, \text{VO}_2^+)$ and $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$, have lower reactivity towards $\frac{1}{2}\text{H}_2$ adsorption than does $(\text{VO}_3, \text{VO}_3)$. The $(\text{VO}_3^-, \text{VO}_2^+)$ system is 1.3 eV less reactive and the $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ system is 1.0 eV less reactive towards hydrogen adsorption than $(\text{VO}_3, \text{VO}_3)$. The figure also shows that the clusters with more oxygen, i.e. $(\text{VO}_3, \text{VO}_3)$ and $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$, are stabilized more than the other clusters when they form $(\text{VO}_3, \text{VO}_3\text{H})$. This is another indication that the presence of additional bases on the surface, such as H atoms, will strongly influence the thermodynamics of the supported vanadium oxide clusters.

Figure 5: The horizontal bars on the left side of the graph represent the formation energies of various systems containing a VO_x and a VO_y cluster per unit cell. The bars on the right side of

the graph show energies of the systems after hydrogenation. All energies are referenced to a common state, namely $3\text{O}_2(\text{g}) + \frac{1}{2}\text{H}_2(\text{g}) + 2\text{V} + \text{TiO}_2(110)$. For example, the topmost line at the left gives the energy of the reaction $3\text{O}_2(\text{g}) + \frac{1}{2}\text{H}_2(\text{g}) + 2\text{V} + \text{TiO}_2(110) \rightarrow (\text{VO}_2, \text{VO}_2) + \text{O}_2(\text{g}) + \frac{1}{2}\text{H}_2(\text{g})$.

5.5. Relation to experiments. It would be difficult to test by experiments the predictions made here because the present calculations were performed on stoichiometric TiO_2 surfaces. The $\text{TiO}_2(110)$ surfaces prepared in ultra-high vacuum are known to have oxygen vacancies. We have hinted in this article that vacancies, which are strong Lewis bases, are likely to affect the acid-base chemistry of the cluster pairs. In principle one could attempt to prepare vacancy-free surfaces by exposure to oxygen at appropriate temperature. However this process is difficult to control. (1) When exposed to oxygen, the vacancies bind one oxygen atom and form another oxygen adatom on the 5c-Ti. This adatom is very reactive and a strong acid and therefore it is likely to affect the chemistry of the surface. The vacancies in the second layer may or may not be annihilated by exposure to oxygen. If they are present they will affect the acid-base chemistry. (2) TiO_2 contains interstitial Ti atoms,⁷⁸ which are strong electron donors and which migrate to the surface when the oxide is exposed to oxygen when attempting to remove oxygen vacancies from the surface. All in all, a stoichiometric surface without vacancies in the second or third layer will be very difficult to prepare and its preparation would be difficult to confirm with certainty.

Assuming that somehow a stoichiometric TiO_2 sample has been prepared, we predict that if V atoms are deposited on the surface and oxidized, the surface will consist of VO_2 and VO_3 in roughly equal numbers. This prediction can be tested by STM. We also predict that if mass-

selected VO_2 clusters are deposited on a stoichiometric TiO_2 surface and then are exposed to oxygen, only about half of the clusters will be converted to VO_3 .

In this paper we have only considered the stability of monomeric vanadium oxide clusters, but at sufficiently high temperature the clusters may become mobile and form bigger clusters.^{6, 26} Calculations show that V_2O_5 is more stable than $(\text{VO}_3^-, \text{VO}_2^+)$. Therefore, experiments with isolated clusters need to be conducted under conditions that ensure that their mobility along the surface is low.

6. Summary

Prior computational work on the properties of supported VO_x clusters has used one vanadium atom per supercell. The periodic boundary conditions force all clusters to be identical: in particular, this means that they cannot interact with each other by charge exchange. The main goal of the present study has been to show that in some cases the acid-base interaction between clusters can be important and that in these cases one must use a supercell that contains two clusters. To demonstrate this we performed two kinds of calculations. In one kind each supercell contained one VO_x cluster, with x being either 2 or 3. In another kind, the supercell size was doubled and contained two monomeric clusters, VO_x and VO_y , with the pairs $\{x,y\}$ having one of the values $\{2,2\}$, $\{3,3\}$, or $\{2,3\}$. The sizes of the two kinds of supercells were selected so that in all calculations the concentration of V atoms on the surface was the same. The two clusters contained in the large supercell were placed as far as possible from each other to eliminate interactions due to the strain induced in the support by the clusters. We found that for $(\text{VO}_2, \text{VO}_2)$ and $(\text{VO}_3, \text{VO}_3)$, there is essentially no difference between the predictions of the calculations performed with one VO_x in a small supercell and the predictions of calculations in

which two VO_x are located in a supercell that was twice as large. This means that there is no acid-base interaction between the clusters in $(\text{VO}_2, \text{VO}_2)$ and $(\text{VO}_3, \text{VO}_3)$. The situation is dramatically different when the large supercell contains a VO_2 and a VO_3 cluster. In this case we found that VO_2 donates an electron to VO_3 and this acid-base interaction stabilizes the system so that its energy of formation is much lower (more negative) than the binding energy of VO_3 alone plus the binding energy of VO_2 alone. A similar acid-base interaction was found in $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$.

Thermodynamic calculations predicted that if a stoichiometric TiO_2 surface, on which isolated V atoms were adsorbed, is exposed to oxygen at pressure of 1 atm and temperature above 200 K, the surface will be covered with VO_2^+ and VO_3^- in roughly equal amounts.

We have also studied the energetics of the reaction of hydrogenation as a test of the reactivity of the clusters. We have found that hydrogen prefers to bind to the vanadium clusters (not to the TiO_2 support). An interesting finding is that the $(\text{VO}_3, \text{VO}_3)$ surface leads to the same hydrogenated state as $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ in spite of the fact that $(\text{VO}_3, \text{VO}_3)$ has much higher energy than $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$. If the Brønsted-Evans-Polanyi relation is valid, then the activation energy of $(\text{VO}_3, \text{VO}_3) + \frac{1}{2}\text{H}_2 \rightarrow (\text{VO}_3, \text{VO}_3\text{H})$ will be smaller than that of $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+) + \frac{1}{2}\text{H}_2 \rightarrow (\text{VO}_3, \text{VO}_3\text{H})$. The rate of a reaction is the rate constant multiplied with the probability that the initial state is present in the system. In the case of $(\text{VO}_3, \text{VO}_3) + \frac{1}{2}\text{H}_2 \rightarrow (\text{VO}_3, \text{VO}_3\text{H})$, the probability that $(\text{VO}_3, \text{VO}_3)$ is present is low, but the rate constant is likely to be higher than in the hydrogenation of $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$. It follows that, in general, one cannot assume *a priori* that the products are always formed from the reactants that have the lowest energy. While this conclusion is speculative, it warns that when studying reaction mechanisms one should consider the reactivity of some of the higher-energy configurations of the reactants.

We emphasize that we are not speaking of electronically excited states but of various isomers of the reactants in the electronic ground state.

We know that the Ti^{4+} ions in the TiO_2 support are acid and worried that they may compete with VO_3 for the electron donated by VO_2 . We found that this is not the case: VO_3 is a much stronger acid than Ti^{4+} .

This paper has investigated only the interaction between two vanadium oxide clusters supported on $\text{TiO}_2(110)$. Given the large number of examples of the strong effect of the acid-base interaction, it is reasonable to expect that this effect exist on other oxide supports.

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Supporting Information

Tables showing (i) the Bader charges and Bader spin-density differences for the V atoms, (ii) calculated vibrational frequencies for the vanadium oxide clusters, (iii) selected thermodynamic data used to compare the relative abundance of $(\text{VO}_3^-, \text{VO}_2^+)$ and $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$, and (iv) formation energies of $(\text{VO}_2, \text{VO}_2)$, $(\text{VO}_3, \text{VO}_3)$, $(\text{VO}_3^-, \text{VO}_2^+)$ and $(\text{VO}_3^-, \text{OV}(\text{O}_2)^+)$ calculated with different U values applied to the V d-states; figures showing structural motifs that were found less stable than the ones presented in the text.

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