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Stability of V_2O_5 Supported on Titania in the Presence of Water, Bulk Oxygen Vacancies, and Adsorbed Oxygen Atoms

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Abstract

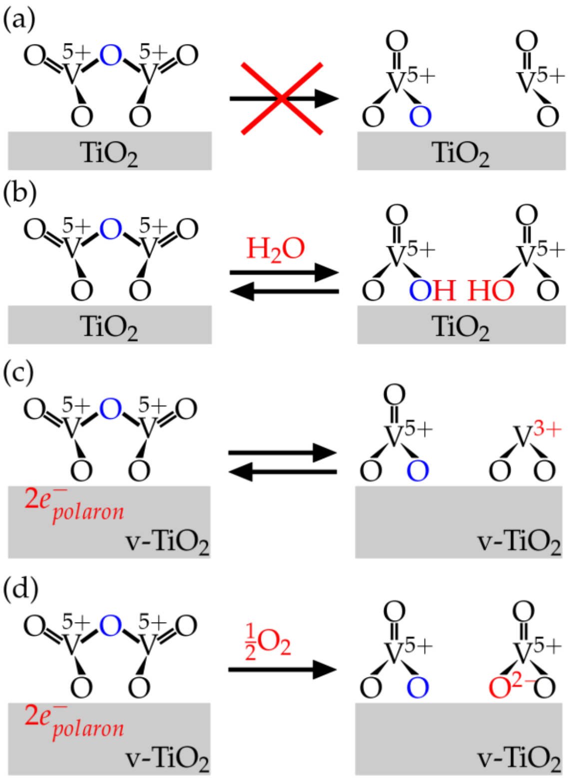
A catalyst consisting of vanadium oxide submonolayers supported on rutile titanium dioxide is used for a variety of reactions. One important question is the difference between the activity of monomeric clusters (having one vanadium atom) and polymeric clusters (having more than one vanadium atom). In the case of oxidative dehydrogenation of alkanes and methanol, the reaction produces water, oxygen vacancies, and hydrogen atoms bound to the surface. For this article we use density functional theory to examine how the presence of these species on the surface affects a V_2O_5 cluster, which we assume to be a representative of a polymeric species. We find that often the presence of other species on the surface can change the composition of the cluster or break it up into two monomeric clusters.

1. Introduction

Vanadium oxide supported on other oxides is an interesting partial oxidation catalyst.[1-3] It is widely accepted that this system is most active if vanadium oxide is a submonolayer, but there is an ongoing debate regarding the nature of the active species. At submonolayer coverage, the vanadium oxide can exist as monomeric or polymeric clusters, depending on the method of preparation and on the reaction condition.[2-4] DFT calculations of total energies suggested that monomeric vanadium oxide clusters, supported on stoichiometric, rutile, $TiO_2(110)$, will bind to each other to form larger clusters.[5-7] The calculations presented here study how the stability of monomeric versus polymeric vanadium oxide clusters depends on the presence of other species on the surface. The species consider are adsorbed H_2O, bulk oxygen vacancies and an adsorbed oxygen atom.

The following notation is used to describe the calculations presented here. (i) $(V_2O_5)/TiO_2$ means that a V_2O_5 cluster is present on the stoichiometric rutile $TiO_2(110)$ surface (Figure 1a). The $\left(VO_3^-,VO_2^+\right)/TiO_2$ notation indicates that two clusters, VO_3^- and VO_2^+, are present on the rutile surface in the same computational supercell (Figure 1b). The dissociation of $(V_2O_5)/TiO_2$ to form $\left(VO_3^-,VO_2^+\right)/TiO_2$ is endoergic. (ii) The notation $(V_2O_5, H_2O)/TiO_2$ represents a system in which a water molecule and a V_2O_5 cluster are coadsorbed on the TiO_2 surface (Figure 2a). The water molecule can react with V_2O_5 to form two VO_3H clusters (Figure 2b); the symbol used for this structure is $(VO_3H, VO_3H)/TiO_2$. (iii) It is well known that unless TiO_2 is carefully prepared, it will have bulk and surface oxygen vacancies. The unpaired electrons formed when an oxygen atom is removed (to make an oxygen vacancy) reduce two Ti ions from the formal charge Ti^{4+} to Ti^{3+}, creating two polarons.[8-14] Oxygen vacancies (or, equivalently, the polarons) are strong Lewis bases (electron donors)[15-16] and vanadium atoms are easily reducible. Therefore, we expect that the presence of an oxygen vacancy, in TiO_2, near the surface (but not in the surface layer), will affect the properties of the V_2O_5 cluster. We use the notation (V_2O_5, $2e^-$)/v-TiO_2 (Figure 3a) to denote a system, where V_2O_5 is bound to a rutile TiO_2(110) surface which has an oxygen vacancy in the bulk (hence the presence of v-TiO_2 in the notation) and two polarons (hence the presence of $2e^-$ in the notation). On the surface that contains a bulk oxygen vacancy, the two electrons will leave the polarons and will "react" with the V_2O_5 cluster to form VO_3^- and VO_2^- (Figure 3b); we use the notation $\left(VO_3^-,VO_2^-\right)/\text{v-TiO}_2$ for this system. (iv) If a reduced TiO_2 surface is exposed to O_2, the oxygen heals surface oxygen vacancies and forms O^{2-} atoms bound to a 5c-Ti atom. The O^{2-} atom gets its negative charge from subsurface defects, which we represent by a bulk oxygen vacancy. The symbol (V_2O_5, O^{2-})/v-TiO_2 denotes this system (Figure 4a). The O^{2-} reacts with V_2O_5 and breaks it into two negatively charged VO_3^- clusters, a state denoted by $(VO_3^-,VO_3^-)/TiO_2$, whose structure is shown in Figure 4b.

The four reactions that break apart the dimeric V_2O_5 cluster are summarized in Scheme 1 and Table 1.



Scheme 1. Reactions that break up the dimeric V_2O_5 cluster (left) into two monomeric clusters (right). **(a)** The breakup of V_2O_5 into (VO_3^-, VO_2^+)/TiO_2 is energetically unfavorable. **(b)** H_2O facilitates V-O-V bond breaking with formation of (VO_3H, VO_3H)/TiO_2. The energy of (VO_3H, VO_3H)/TiO_2 is comparable to that of a V_2O_5 cluster and a H_2O molecule, both adsorbed on TiO_2. **(c)** A bulk oxygen vacancy (near the surface) stabilizes (VO_3^-, VO_2^-)/v-TiO_2 by reducing the formal charge of the V atom in VO_2^- from 5+ to 3+. **(d)** The reaction of ½O_2 with V_2O_5 adsorbed on a TiO_2 surface having a bulk oxygen vacancy favors V-O-V bond breaking and the formation of (VO_3^-, VO_3^-)/v-TiO_2 by addition of O^{2-} to a V atom.

In the last part of this article we compare the affinity towards hydrogen of the V_2O_5 and the monomeric clusters formed by the reactions outlined in Scheme 1b, 1c and 1d, i.e. (VO_3H,

VO_3H)/TiO_2, (VO_3^-, VO_2^-)/v-TiO_2, and (VO_3^-, VO_3^-)/v-TiO_2 (Table 1 and Figure 5). Hydrogen adsorption energies are investigated because this can be used as a proxy for the initial step of alkane dissociative adsorption.[17-20] We find that the monomeric clusters have a higher affinity for hydrogen than V_2O_5 and therefore speculate that they are more active for alkane dissociation.

2. Computational Details

The vanadium oxide clusters are placed on a p(6×2) TiO_2(110) surface with a thickness of four TiO_2 tri-layers. We consider both a stoichiometric slab and a reduced slab containing a bulk oxygen vacancy in the third tri-layer. The energies of all systems studied here have been calculated by density functional theory (DFT) with the VASP program.[21-24] The exchange-correlation effects are approximated by the PBE functional,[25] with a DFT+U correction of U = 3.5 eV for both Ti and V d-states,[12, 26-28] and a plane-wave basis with a 400-eV energy cutoff. We include one, six, 11, and 12 valence electrons for H, O, V, and Ti atoms, respectively, and describe atomic regions with the PAW method. Reciprocal space is sampled by 2×2 k-points and all calculations are spin polarized. This computational setup is the same as in our previous work[7] and the calculations are directly comparable.

The formal charges of the V atoms are helpful for understanding the stability and reactivity of the different vanadium oxide clusters. We assign a formal charge on a V atom in a vanadium oxide cluster by using both the Bader charge[29-31] and the spin density.[32] The spin density is calculated by integrating the difference between spin-up and spin-down density, over the Bader volume of the atom. The spin-densities on V^{3+}, V^{4+}, and V^{5+} are very close to ±2, ±1, and 0, respectively. This reflects the fact that V^{3+} has two spin-aligned d-electrons, V^{4+} has one d-electron, and V^{5+} has zero d-electrons. The Bader charges for V atoms are rather different from the formal charge: The Bader charge difference between V^{5+} and V^{4+} is ~ 0.2*e*. For this reason, the spin density on V is a better indicator of its formal charge. Values for Bader charges and spin-density differences for the V atoms are included in Table S1 in Supporting Information.

The optimal U value to apply to V d-states is often obtained by optimizing the properties of bulk vanadium oxide compounds.[26] However, the optimal U value is likely to depend on the local surroundings of the V atoms and it is therefore uncertain whether a U value that works well for bulk vanadium oxide can be transferred to the vanadium atom in a small vanadium oxide cluster. For this reason, we have calculated the reaction energies with U values of 2.5 eV, 3.5 eV, and 4.5 eV applied to the V d-states. We report in the text the results obtained with U = 3.5 eV; the results for the other U values are reported in Table S2 in Supporting Information. Reactions for which the formal charges of the V atoms are conserved are not very sensitive to the choice of U value. This is the case for the reactions illustrated in Scheme 1a, b, and d. However, the reaction (V_2O_5, 2e)/v-TiO_2 → (VO_3,VO_2)/v-TiO_2 ((c) in Scheme 1) is very endoergic when U = 2.5 eV and very exoenergetic when U = 4.5 eV. Reactions such as hydrogen adsorption, where one electron is transferred to a vanadium oxide cluster, are also affected by the choice of U. However, the energy difference between H adsorption on two different binding sites is essentially independent on the value of U.

We performed several calculations with the HSE06 functional[33] because it is generally assumed to be more reliable than DFT+U; the HSE results can therefore be used to determine the value of U for vanadium. Due to the high computing-power demands, the HSE06 calculations were performed for the structures obtained with DFT+U (U = 3.5 eV) and only for two reactions in which the formal charge of vanadium changes. The U value of 4 eV, applied to V d-states, gives the best agreement between DFT+U and HSE06; however, a U value of 3.5 eV leads to the same qualitative conclusions. Further details on the HSE06 calculations are presented in Section S3 in Supporting Information.

3. Vanadium oxide on stoichiometric TiO_2(110) surface

3.1. Stoichiometric TiO_2(110) surface. A side view and a top view of a TiO_2(110) surface containing a V_2O_5 cluster are shown in Figure 1a. The TiO_2(110) surface consists of 5c-Ti atoms (colored light gray), in-plane O atoms (dark gray), and O atoms forming the bridging oxygen rows (dark red). The 5c-Ti atoms can form bonds with the O atoms in the vanadium oxide clusters; the bridging O atoms can form bonds with the V atoms in the vanadium oxide clusters.

3.2. Unassisted V_2O_5 breakup into monomers. We first consider vanadium oxide clusters on the stoichiometric TiO_2(110) surface without any other adsorbed molecules. The dimeric

$(V_2O_5)/TiO_2$ cluster is shown in Figure 1a where it has the structure proposed by Henkelman and co-workers.[5] The two V atoms are colored pink and the five O atoms that are not part of the TiO_2 surface are colored yellow. This color scheme is used in all figures. To understand the color code, imagine that the V_2O_5 cluster was formed by adsorbing two V atoms on the surface and then exposing the surface to oxygen. The five yellow oxygen atoms are the ones acquired by vanadium atoms from the gas during oxidation. Each V atom uses a "yellow oxygen atom" to bind to a 5c-Ti atom and form a V-O-Ti group. An additional yellow oxygen atom binds the two V atoms to each other to form a V-O-V group. The remaining two oxygen atoms form two vanadyl groups in which the oxygen forms a double bond with the vanadium atom. Both V atoms in V_2O_5 are tetrahedrally coordinated, which is a coordination often found in vanadium-oxygen compounds.[34-35] Bader charge and spin-density analysis indicate that the formal charges are 5+ for each V atom and 2– for each O atom.

Monomeric vanadium oxide clusters have been predicted to exist as pairs of spatially separated VO_3^- and VO_2^+ clusters, if $TiO_2(110)$ has no oxygen vacancy and the system is in thermal equilibrium with a pure oxygen atmosphere, at temperatures above 200 K.[7] Figure 1b shows the structure of the TiO_2 surface having adsorbed a pair (VO_3^-, VO_2^+) of monomers. We use the notation $(VO_3^-, VO_2^+)/TiO_2$ because the VO_2 cluster donates an electron to the VO_3 cluster. This electron transfer allows both V atoms to have a formal charge of 5+ and all oxygen atoms to have a formal charge of 2–. The $(VO_3^-, VO_2^+)/TiO_2$ configuration also forms one additional V-O-Ti bond compared to the $(V_2O_5)/TiO_2$ cluster. We found that the $(VO_3^-$,

VO_2^+)/TiO_2 clusters are +0.92 eV less stable than the dimeric (V_2O_5)/TiO_2 cluster (Table 1). Therefore, V_2O_5 clusters will not dissociate into monomeric clusters on the stoichiometric TiO_2(110) surface. We speculate that the vanadium oxide clusters supported on defectless, clean (i.e. no other adsorbates) TiO_2 will form polymeric structures if the system is prepared at temperatures at which the clusters have some mobility. The diffusion barrier for monomeric vanadium oxide clusters on ceria is around 2 eV,[36] so it is likely that monomeric vanadium oxide clusters are kinetically stable up to high temperatures.

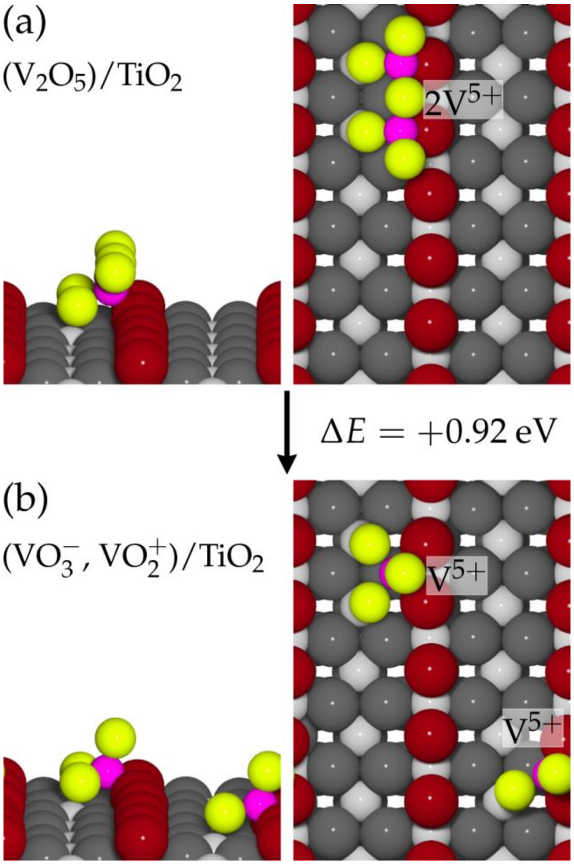


Figure 1. (a) Structure of the (V_2O_5)/TiO_2 cluster. **(b)** Dissociation of (V_2O_5)/TiO_2 into (VO_3^-, VO_2^+)/TiO_2, which is the most stable monomeric vanadium oxide configuration on

stoichiometric $TiO_2(110)$, in oxygen atmosphere and above 200 K. The dissociation is energetically unfavorable. All V atoms have 5+ formal charge.

Table 1. Reactions that break the V_2O_5 cluster into two monomers and reaction between vanadium oxide clusters and hydrogen

Reaction	**Figure**	**Δ*E***
Stoichiometric $TiO_2(110)$ surface		
$(V_2O_5)/TiO_2 \rightarrow (VO_3^-, VO_2^+)/TiO_2$	1	+0.92 eV
$(V_2O_5, H_2O)/TiO_2 \rightarrow (VO_3H, VO_3H)/TiO_2$	2	+0.09 eV
Reduced $TiO_2(110)$ surface (v-TiO_2)		
$(V_2O_5, 2e^-)/\text{v-}TiO_2 \rightarrow (VO_3^-, VO_2^-)/\text{v-}TiO_2$	3	–0.09 eV
$(V_2O_5, O^{2-})/\text{v-}TiO_2 \rightarrow (VO_3^-, VO_3^-)/\text{v-}TiO_2$	4	–0.58 eV
Reactions with hydrogen		
$\frac{1}{2}H_2 + (V_2O_5)/TiO_2 \rightarrow V_2O_5H/TiO_2$	5a	–0.87 eV
$\frac{1}{2}H_2 + (VO_3H, VO_3H)/TiO_2 \rightarrow (VO_3H_2, VO_3H)/TiO_2$	5b	–1.16 eV
$\frac{1}{2}H_2 + (VO_3^-, VO_2^-)/\text{v-}TiO_2 \rightarrow (VO_3H^-, VO_2^-)/\text{ v-}TiO_2$	5c	–1.01 eV
$\frac{1}{2}H_2 + (VO_3^-, VO_3^-)/\text{v-}TiO_2 \rightarrow (VO_3H^-, VO_3^-)/\text{ v-}TiO_2$		–1.02 eV

3.3. V_2O_5 breakup by exposure to H_2O. Water is often produced by in many reactions catalyzed by VO_x submonolayers supported on TiO_2, such as the partial oxidation of hydrocarbons or methanol or by the reduction of NO_x by ammonia.[37] Therefore, water will be adsorbed on the surface and water vapor will be present in the gas. We investigate here the effect of water on the $(V_2O_5)/TiO_2$ surface.

Water adsorbs[38] molecularly on a clean, stoichiometric $TiO_2(110)$ surface and binds to a 5c-Ti atom. The adsorption energy is –0.86 eV (this is the energy of $H_2O(g) + TiO_2(110) \rightarrow H_2O/TiO_2(110)$). When a V_2O_5 cluster is present on the surface, water will adsorb on an adjacent 5c-Ti atom (Figure 2a) and the adsorption energy is –0.98 eV. The presence of the V_2O_5 cluster increases slightly the adsorption energy of water (on 5c-Ti, away from the cluster). The reaction $(H_2O, V_2O_5)/TiO_2 \rightarrow (VO_3H, VO_3H)$ (see Figure 2b) is uphill by 0.09 eV. Within the accuracy of DFT, the structures $(H_2O, V_2O_5)/TiO_2$ and $(VO_3H, VO_3H)/TiO_2$ are equally likely to be present on the surface. Seven additional product configurations were investigated, including four where the atoms form a dimeric cluster. Here we discuss the structure having the lowest energy; the others are presented in Figure S2 in Supporting Information.

In the two VO_3H clusters, the V atoms have the square pyramidal configuration that is present in bulk V_2O_5.[39] Two of the four oxygen atoms in the pyramid are from the bridging oxygen row of the $TiO_2(110)$ surface; the other two are “yellow oxygen atoms”, which form Ti-O-V bridges; the hydrogen atom is bound to one of the yellow oxygens at the basis of the pyramid (Figure 2b). A study by Hofmann *et al*.[40] has shown that water molecules give similar stabilization of monomeric vanadium oxide clusters compared to dimeric clusters when supported on ZrO_2. Bader charge analysis of the configurations in Figure 2 indicates that the formal charges are 5+ for the V atoms and 2– for the O atoms before and after the reaction between $(V_2O_5)/TiO_2$ and the water molecule, i.e. no oxidation or reduction of the vanadium atom takes place in this reaction. Experiments[41] also found that the 5+ formal charge of V atoms is preserved when V_2O_5 reacts with water.

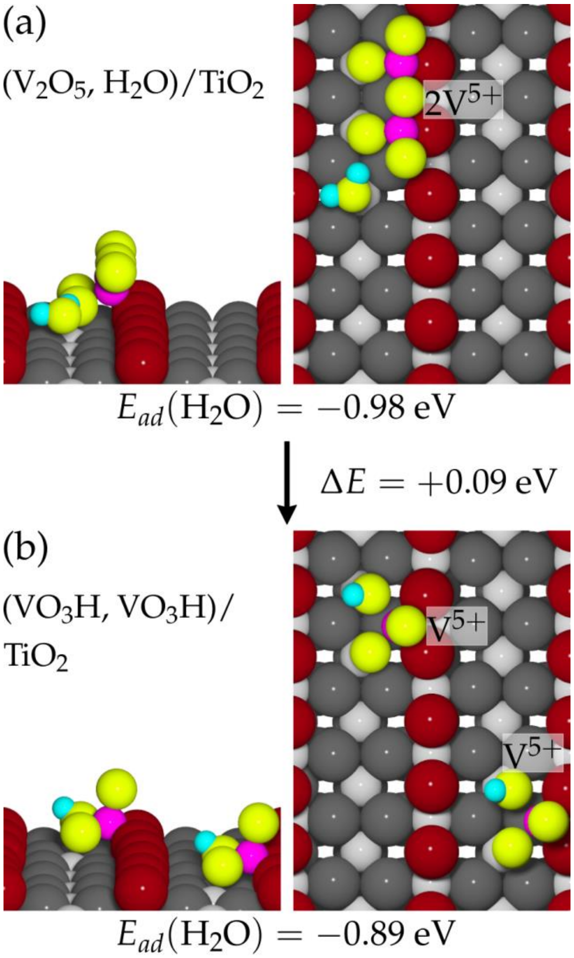


Figure 2. Atomic configuration and adsorption energy of **(a)** molecular H_2O adsorbed adjacent to the $(V_2O_5)/TiO_2$ cluster and **(b)** the $(VO_3H, VO_3H)/TiO_2$ clusters formed by the reaction of V_2O_5 with water. The V atoms have 5+ formal charges before and after the reaction with water.

The calculations involving the water molecule are relevant to investigations under ultra-high vacuum conditions. At high water partial pressures, a water film may form on the TiO_2(110) support.[42] Such conditions are significantly different from what we model here, and the properties of the vanadium oxide clusters might resemble the properties of vanadium oxide in aqueous medium.[43]

4. Vanadium oxide on the reduced v-TiO_2(110) surface

4.1. The reduced v-TiO_2(110) surface. Rutile TiO_2 has a tendency to form oxygen vacancies that act as Lewis bases.[15-16, 44-45] Here we examine the effect of an O vacancy present in the third layer of the TiO_2 slab. We do this because the supported V_2O_5 clusters are most often prepared by oxidation of vanadium precursors and we assume that after the preparation there are few oxygen vacancies in the surface layer but there may be some in the bulk. Indeed, a defect-free (110) surface with a reduced subsurface region has been prepared by exposing reduced rutile TiO_2 to water and oxygen at room temperature.[45] The removal of an oxygen atom, to form a vacancy, leaves behind two “unpaired electrons” that were involved in forming Ti-O bonds. Each electron migrates[8, 12, 14, 46] to a Ti ion, reducing its formal charge from Ti^{4+} to Ti^{3+}.

The group consisting of the reduced Ti and the oxygen atoms surrounding it (which shift their position when Ti is reduced) is frequently called a polaron. The chemical properties of the reduced TiO_2 surface depend on the positions of these polarons, but we do not investigate this dependence here because of the very large number of possible polaron pair positions. All the results reported here were obtained with the polarons located near the vacancy in the configuration[41] proposed in a previous study.

The binding energy of the V_2O_5 cluster to the reduced TiO_2 is larger than the binding energy to the stoichiometric one by 0.11 eV. The presence of the vacancy stabilizes the V_2O_5 cluster.

4.2. V_2O_5 breakup aided by electrons from a bulk O vacancy. We use the notation (V_2O_5, $2e^-$)/v-TiO_2 for the V_2O_5 cluster on the reduced TiO_2 slab, to indicate the presence of two polarons in TiO_2 (Figure 3a). It is possible that the oxygen vacancy will supply electrons to the vanadium atoms in V_2O_5 and we envision three possibilities: None of the vanadium atoms in V_2O_5 is reduced by the electrons supplied by the vacancy; one or both vanadium atoms in V_2O_5 is/are reduced and the cluster does not break up; the cluster takes the electrons and breaks up into two monomers. To find a structure in which one electron migrates onto the V_2O_5 cluster, we force the oxygen atoms to move slightly away from vanadium and then optimize the geometry and find a local energy minimum.[12, 46] In this local minimum one of the vanadium atoms has the formal charge 4+. When DFT+U is used, the energy of the local minimum is higher than the energy of (V_2O_5, $2e^-$)/v-TiO_2 by 0.11 eV; the state in which the formal charge on one V is 4+

is less stable than the state in which both vanadium atoms have the formal charge 5+. However, when we use HSE06, the state with one V^{4+} is more stable than (V_2O_5, $2e^-$)/v-TiO_2 by -0.01 eV. Since these energy differences are within the DFT error, we conclude that both species (V_2O_5 with V^{5+} and two polarons, or V_2O_5 with V^{4+} and one polaron) are likely to be present on the surface at the temperatures at which this supported vanadium oxide catalyst is used.

The density of states (DOS) of the (V_2O_5, $2e^-$) /v-TiO_2 system (two polarons and a neutral V_2O_5) has two localized orbitals in the band gap (Figure 3b), which correspond to the two polarons. There are no states in the gap related to the V_2O_5 cluster.

In Figure 3c, the V_2O_5 cluster has been broken into a VO_2 cluster and a VO_3 cluster (this is schematically represented in Scheme 1c). The Bader charge analysis indicates that both clusters have become negatively charged and therefore we use the notation (VO_3^-, VO_2^-)/v-TiO_2 to represent them. The (VO_3^-, VO_2^-)/ v-TiO_2 configuration is more stable by -0.09 eV than (V_2O_5, $2e^-$)/v-TiO_2 (Table 1). A HSE06 calculation finds that (VO_3^-, VO_2^-)/v-TiO_2 is more stable by -0.33 eV. The Bader charge analysis indicates that the V atom in VO_2^- (marked β in Figure 3c) has a formal charge of 3+, which matches with formal charges of 2– on O atoms in VO_2^-. The oxygen atoms in the VO_2^- cluster are both bonded to the 5c-Ti atoms and the cluster does not contain a vanadyl. The projected DOS for (VO_3^-, VO_2^-)/v-TiO_2 (Figure 3d) shows that the two excess electrons (originating from the polarons) are localized on the V atom in VO_2^- (marked β in Figure 3c). These electrons are responsible for reducing the formal charge of the V atom from 5+ to 3+.

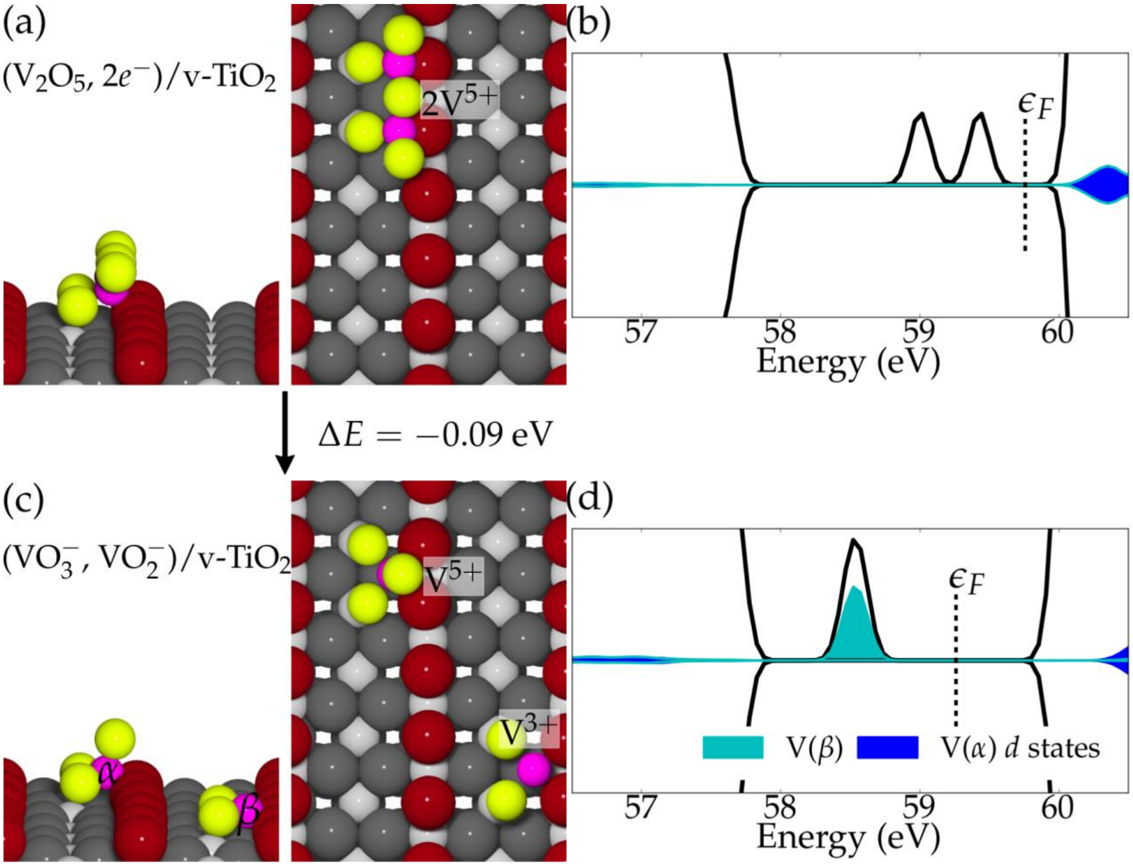


Figure 3. **(a)** The structure of the $(V_2O_5, 2e^-)$/v-TiO_2 cluster. The TiO_2 support is reduced (contains one bulk O vacancy per supercell) and two polarons are present near the vacancy. **(b)** The projected density of states (PDOS), near the Fermi level (ϵ_F), for the $(V_2O_5, 2e^-)$/v-TiO_2 system. The two orbitals in the band gap are occupied by the electrons forming the polarons. The V_2O_5 cluster does not contribute states in the band gap. **(c)** The structure of (VO_3^-, VO_2^-)/v-TiO_2. This configuration is more stable by -0.09 eV than $(V_2O_5, 2e^-)$/v-TiO_2. The V atom in VO_2^- has been reduced from V^{5+} to V^{3+}. **(d)** PDOS for the (VO_3^-, VO_2^-)/v-TiO_2 system. The two excess electrons are situated in two degenerate orbitals whose energy is in the band gap and which are localized on the V atom in VO_2^- (marked β in c).

The two DOS plots are aligned by matching the position of Ti 3s core states (which are taken to have an energy of 0 eV).

In this section, we have included a bulk oxygen vacancy to supply the two excess electrons ($2e^-$). However, we suspect that any electron donor can play the same role; this could be Ti interstitials,[45-48] hydrogen in the bulk or on the surface, or higher-valence dopants.[16] To affect the vanadium oxide cluster the electron donor must be stable at the temperatures and conditions of interest. This is why we consider a bulk oxygen vacancy and not a surface oxygen vacancy; surface oxygen vacancies react with O_2 or water molecules at low temperatures and are annihilated,[49-50] while bulk oxygen vacancies are kinetically stable due to high diffusion barriers.[51]

4.3. V_2O_5 breakup when an O atom is present on the v-TiO_2 surface. If a reduced TiO_2 surface is exposed to gaseous O_2, the oxygen adsorbs on the vacancy and dissociates: one O atom heals the vacancy and the other is adsorbed on the 5c-Ti.[45, 52-53] In this way, it is also possible to form adsorbed oxygen atoms on the surface of (V_2O_5, $2e^-$)/v-TiO_2. We examine here the adsorption of ½O_2(g) on (V_2O_5, $2e^-$)/v-TiO_2 to form a state in which O is bound to a 5c-Ti, far from the V_2O_5 cluster (Figure 4a). The energy of the reaction ½O_2(g) + (V_2O_5, $2e^-$)/v-TiO_2 → (O^{2-}, V_2O_5)/v-TiO_2 is –1.51 eV. The energy gain of this reaction is large because O is a strong Lewis acid and the two polarons located under the surface layer are Lewis bases.

As a result, the O atom annihilates the two polarons, and two Ti^{3+} are converted to Ti^{4+}, a process that has been discussed previously[54] for TiO_2 in the absence of V_2O_5. The large exothermicity of the reaction is consistent with the general rule[15-16, 55-57] that acid-base interactions on an oxide surface substantially lower the energy two coadsorbed molecules. The adsorption of O on the 5c-Ti has very little effect on the V_2O_5 cluster: they coexist but do not interact. The next question is whether the adsorbed oxygen atom will react with the V_2O_5 cluster. One could imagine that the system might make a $V_2O_6^{2-}$ cluster, but we find that the preferred path is the reaction $(V_2O_5, O^{2-})/v\text{-}TiO_2 \rightarrow (VO_3^-, VO_3^-)/v\text{-}TiO_2$, whose energy is –0.58 eV (Table 1 and Figure 4b). This prediction could be verified since the breakup of the cluster should be observable by STM.[58-60] The $V_2O_6^{2-}$ clusters whose energy we have examined as possible products are presented in Figure S3 in Supporting Information.

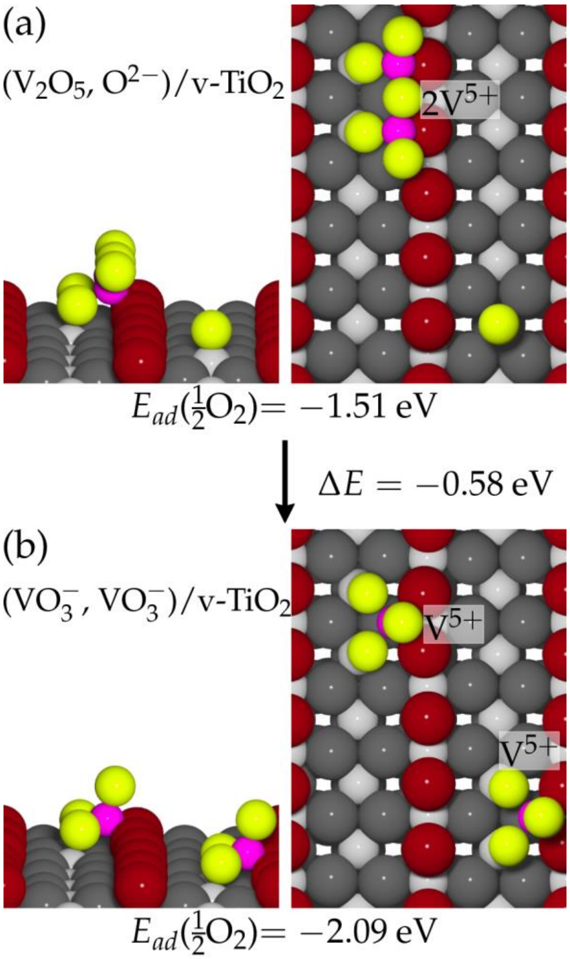


Figure 4. (a) The atomic configuration after the reaction $(V_2O_5, 2e^-)/\text{v-}TiO_2 + ½O_2(g) \rightarrow (V_2O_5, O^{2-})/\text{v-}TiO_2$. The oxygen atom binds to a 5c-Ti and V_2O_5 is hardly affected. The two polarons initially present lose their electrons, which are transferred to O^{2-}. The reaction energy (E_{ad}(½O_2)) is –1.51 eV. **(b)** The chemisorbed O^{2-} reacts with V_2O_5 and breaks it up. The energy of the reaction $(V_2O_5, O^{2-})/\text{v-}TiO_2 \rightarrow (VO_3^-, VO_3^-)/\text{v-}TiO_2$ is –0.58 eV.

5. Hydrogen adsorption

Hydrogen binding to an oxide surface is a descriptor of the ability of the surface to dissociate an alkane.[17-20] This rule has been proposed because in many calculations the methane dissociation takes place through a disconcerted (i.e. as opposed to concerted) mechanism: as the methane molecule approaches the surface, the C-H bond stretches, an OH bond is formed, and after that CH_3 finds a binding site or goes into the gas phase. When one compares CH_4 dissociation on different oxides, their ability to dissociate methane differs mainly through their ability to form the O-H bond. This is why the strength of that bond is a rough proxy for the ability of an oxide to dissociate methane. This observation is useful if one intends to do a rapid screening for methane dissociation because one can ignore oxides that do not bind H strongly. It is for this reason that we examine the energy of the reaction of hydrogen with $(V_2O_5)/TiO_2$, with $(VO_3H$, with $VO_3H)/TiO_2$, with $(VO_3^-, VO_2^-)/\text{v-}TiO_2$, and with $(VO_3^-, VO_3^-)/\text{v-}TiO_2$.

The energy of the reaction $\frac{1}{2}H_2 + (V_2O_5)/TiO_2 \rightarrow (V_2O_5H)/TiO_2$ is –0.87 eV. The structure of the product is shown in Figure 5a. The hydrogen binds to one of the vanadyls in V_2O_5 to form a hydroxyl, in agreement with the findings of Henkelman and co-workers.[5] The formal charge on the V atom to which the OH is bonded is reduced to 4+ (Figure 5a).

Next, we consider $\frac{1}{2}H_2$ adsorption on $(VO_3H, VO_3H)/TiO_2$, a structure that would be present on the surface if V_2O_5/TiO_2 were exposed to water prior to being exposed to hydrogen. Water exposure is unavoidable, in many applications, because the partial oxidation reactions catalyzed by V_2O_5/TiO_2 produce water. The energy of the reaction $\frac{1}{2}H_2 + (VO_3H, VO_3H)/TiO_2 \rightarrow (VO_3H_2, VO_3H)/TiO_2$ is –1.16 eV. The structure of the final state is shown in Figure 5b, where the H atom added to the $(VO_3H, VO_3H)/TiO_2$ cluster is colored green. The V atom in the VO_3H_2 cluster is reduced to a formal charge of 4+.

The energy of the reaction ½H_2 + (VO_3^-, VO_2^-)/v-TiO_2 → (VO_3H^-, VO_2^-) is –1.01 eV. The structure of the product (VO_3H^-, VO_2^-)/v-TiO_2 is shown in Figure 5c. In that product, the vanadium atom in VO_3H^- has the formal charge 4+, while the vanadium atom in VO_2^- still has the formal charge 3+. The (VO_3^-, VO_3^-)/v-TiO_2 has the same hydrogen affinity (–1.02 eV) as (VO_3^-, VO_2^-)/v-TiO_2. This indicates that hydrogen adsorption on VO_3^- is not affected by the neighboring cluster.

The calculated ½H_2 adsorption energies suggest that monomeric vanadium oxide clusters are more reactive than the dimeric (V_2O_5)/TiO_2 cluster. The energy differences are not large, but it may be possible to pick conditions that favor either dimeric clusters or monomeric clusters and use this as a way to modify the catalytic activity of supported vanadium oxide.

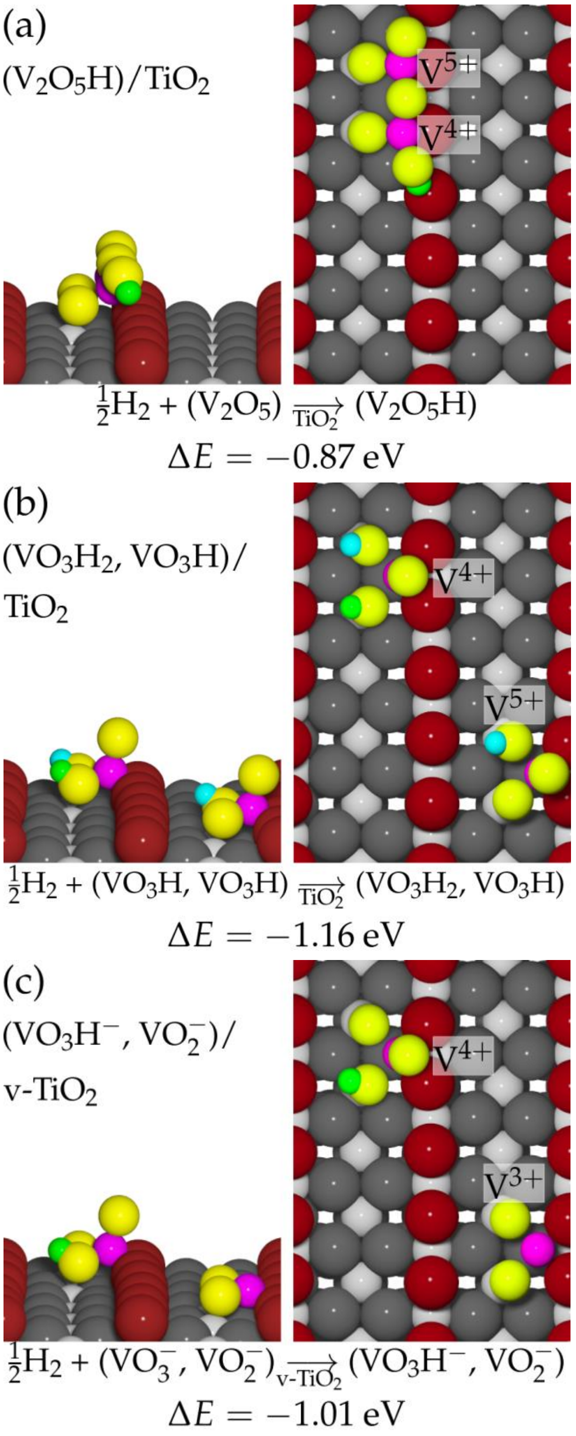


Figure 5. **(a)** Structure of the product of the reaction ½H_2 + $(V_2O_5)/TiO_2$→ $(V_2O_5H)/TiO_2$. The reaction energy is –0.87 eV. **(b)** Structure of the product of the reaction ½H_2 + $(VO_3H, VO_3H)/TiO_2$ → $(VO_3H_2, VO_3H)/TiO_2$. The reaction energy is –1.16 eV. **(c)** Structure of the

product of the reaction ½H_2 + (VO_3^-, VO_2^-)/v-TiO_2 → (VO_3H^-, VO_2^-)/v-TiO_2. The reaction energy is –1.01 eV. The formal charges on the vanadium atoms in the products are indicated in the figure.

6. Summary

Supported vanadia submonolayers are used as catalysts for a variety of reactions. One of the questions raised by that research is whether the clusters having a single vanadium atom (monomers) are more (or less) active than those consisting of many vanadium atoms (polymers). Due to limitations in computational power, it is not possible to perform calculations involving "polymers" with more than two vanadium atoms. Here we assume that a V_2O_5 cluster is representative of a polymeric species and investigate how it is affected by the presence of other molecules on the surface; in particular, we investigate the effect of water, oxygen, hydrogen, and oxygen vacancies in the TiO_2 support. The present calculations show that V_2O_5 adsorbed on a clean, defectless rutile TiO_2(110) surface is stable: it would cost 0.92 eV to break it up into adsorbed VO_2^+ and VO_3^-, even though this break-up is benefits from a Lewis acid-base interaction between the two fragments. V_2O_5 reacts with water and breaks up to form two VO_3H clusters, but the reaction energy is slightly uphill (+0.09 eV). At the temperatures of interest to catalysis such clusters will be present on the surface. TiO_2 is known to have oxygen vacancies and these are strong electron donors. If a vacancy is present in the "subsurface" (second or third layer), it will cause the dissociation of V_2O_5 into VO_3^- and VO_2^- and the energy of this reaction is slightly downhill (–0.09 eV). If oxygen vacancies are present on the TiO_2 surface, they will react with O_2 and generate single O atoms bound to the 5c-Ti row. Such atoms will take two electrons from bulk oxygen vacancies to form an O^{2-} species. The O^{2-} will react with V_2O_5 to form two VO_3^-. The energy of this reaction is –0.58 eV.

These findings are relevant to the oxidative dehydrogenation reactions performed on supported vanadium oxide catalysts such as methanol oxidation to formaldehyde, and ethane or propane oxidative dehydrogenation to the corresponding alkenes. While the VO_x/TiO_2 catalysts for these processes are not as good as the commercial ones, they are scientifically interesting. These reactions involve a reductant (e.g. propane, or ethane, or methanol) and an oxidant (O_2). The reaction mechanism is that proposed by Mars-van Krevelen: the reductant takes oxygen from the oxide surface and creates oxygen vacancies, and the gaseous oxygen in the gaseous feed heals them. Under steady state conditions, oxygen vacancies, hydroxyls, and adsorbed oxygen atoms are all present on the surface. The present calculations indicate that these species will affect the vanadium oxide clusters; in particular, the clusters are broken apart into a variety of monomers as listed in Table 1.

In principle, the species predicted here could be observed in experiments that deposit mass-selected clusters on TiO_2 in ultra-high vacuum and detects them by STM.

Supporting Information. Table of Bader charges and spin-density differences for the V atoms in the vanadium oxide clusters; Reaction energies calculated with different U values applied to the V d-states and two reaction energies calculated with HSE06; Figures showing structural motifs that were found to be less stable than the ones presented in the text.

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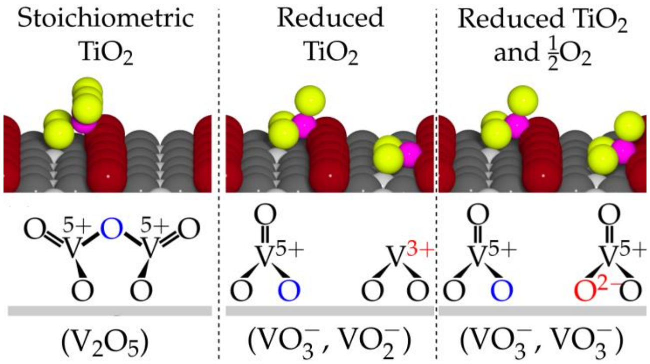
TOC Graphic


Stoichiometric TiO2
Reduced TiO2
Reduced TiO2 and ½O2
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O O
O V 5+ O O
V 3+ O O
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O V 5+ O2− O
(V2O5)
(VO3−, VO2−)
(VO3−, VO3−)