

Reactivity of the Oxygen Sites in the V₂O₅/TiO₂ Anatase Catalyst

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We present for the first time a theoretical investigation on the reactivity of the different oxygen sites in a dispersed V₂O₅/TiO₂ slab model. Our model represents anhydrous conditions and contains all the potentially active oxygen sites proposed to date in the literature: vanadyl V=O, bridging V–O–V, interface V–O–Ti, and surface Ti–O–Ti oxygen sites. Geometric features are analyzed in terms of bond distances and site accessibility. Projected density of states diagrams show a decrease of the band gap for the supported system with respect to pure anatase (001). The most energetic levels of the valence band correspond to the oxygen atoms in the V₂O₅ unit, although a further decomposition in terms of mono- and dicoordinated oxygen is not obvious. Atomic hydrogen adsorption on the different sites is tracked. The most exothermic systems are those where H adsorbs on the V₂O₅ oxygen sites due to their higher basicity regarding pure anatase. The heats of adsorption referred to atomic H are V–O–Ti (2.95 eV) > V=O (2.60 eV) > V–O–V (2.17 eV) > Ti–O–Ti (2.07 eV). This means that the most reactive sites are those located at the interface between the V₂O₅ and the TiO₂ unit, while the vanadyl V=O bonds are more stable and would react at a lower extent in hydrogen atomic adsorption. Relaxation makes the adsorption energy decrease: the support relaxes less when hydrogen adsorbs than for the bare V₂O₅/TiO₂ system. H adsorption forms hydroxyl OH bonds by reduction of the vanadium atom, even when the adsorption site is located on the TiO₂ surface sites.

1. Introduction

Metal oxides constitute exciting systems in the fields of science and technology because of their specific properties. Research on metal oxide surfaces is based both on the determination of the basic features ruling their behavior and on the many applications such as catalysis, superconductivity, and gas sensing.^{1–3} The development of metal oxide based surfaces has evolved from the pure-stoichiometric composition to the creation of defects, the metal/oxide interfaces, and finally the oxide/oxide interfaces. Despite the interest generated by these materials, in particular the oxide/oxide interfaces, information is scarce and more studies in the field are needed.

The study of the interaction of atomic and molecular hydrogen with metal oxides is important for several reasons. First, atomic hydrogen and molecular hydrogen serve as probes for the reactivity in a wide range of materials, for both bulk and surfaces.¹ Second, the abstraction of reactant hydrogen is often a key step in many catalytic reactions such as hydrocarbon oxidation^{4,5} and selective catalytic reduction (SCR)^{6,7} in the case of vanadia-based catalysts. Finally, pretreatment of catalysts often consists of exposure to H₂ atmosphere where reduced samples are obtained, or experiments take place in a hydrogen atmosphere.⁸ Reduction of the catalyst is involved in many reactions. It can be associated with H exposure as well as with the presence of oxygen vacancies.

The V₂O₅/TiO₂ anatase catalyst is widely used in industry for the removal of nitrogen oxides NO_x.⁶ This is a determinant process in which the nitrogen oxides are reduced to N₂ and H₂O by means of a reducing agent (usually NH₃ but also CH₄, etc.⁹). The active phase is the V₂O₅ dispersed on anatase TiO₂, which

acts as a support.¹⁰ The extreme efficiency of the catalyst has been attributed to a synergetic effect between the two oxides.¹¹ Despite its importance, the atomic structure of the catalyst and the reactive sites is not well-known. In particular, the coordination of the surface oxygen atoms seems to play a key role in reactivity: mono-, di-, and tricoordinated oxygen atoms behave differently in catalytic conditions, although there is no unanimity in establishing the most reactive one for the SCR process. The effect of the support is also of great importance since it is not always possible to correlate the results from unsupported crystals to those for supported catalysts. Supported materials possess reactive sites at the interface that do not exist in unsupported ones and could be directly involved in the key catalytic steps.

As mentioned above, the nature of the active surface oxygen sites is still uncertain. For pure vanadia, Tepper et al.¹² have conducted HREELS, ARUPS, and XPS experiments to determine the degree of interaction of the V₂O₅(001) surface with molecular and atomic hydrogen (note that in the literature the two surfaces (001) and (010) of V₂O₅ are equivalent). While molecular hydrogen does not interact with the surface, atomic hydrogen induces significant changes in the spectra indicating a strong interaction. According to their results, the most reactive oxygen atom is the bridging one, while terminal and 3-fold coordinated sites are stable with respect to the interaction with atomic hydrogen. Another important feature is that no OH groups were observed in the spectra even after exposure to high doses of atomic hydrogen. The hydroxyl groups would recombine to form water and oxygen vacancies in the surface. Photoemission measures and theoretical cluster studies also reveal the major reactivity of bridging oxygen atoms in the same surface,^{13,14} and in a recent paper by Kolczewski and Hermann the assignment of the experimental NEXAFS peaks on V₂O₅ systems to the different surface oxygen centers is proposed.¹⁵

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Ozkan et al.¹⁶ have studied the reducibility of V_2O_5 samples with H_2 and NH_3 by TPD and spectroscopic catalyst characterization, finding that ammonia is more effective in the reduction of the substrate. Reduction takes place at the surfaces to a major extent; only after high dosages of hydrogen is the bulk fully reduced. Reduction of the unsupported catalysts has also been associated with the interaction of the reducing agent with terminal oxygen atoms (vanadyl $V=O$ groups). Upon reaction, vacancies are formed in the surface that are replenished by gas-phase oxygen or lattice oxygen diffusion as for V_2O_5/TiO_2 SCR catalysts. They associate the vanadyl sites with the NH_3 adsorption and subsequent oxidation, and the bridging oxygen with the NO reduction in the SCR reaction. MSINDO cluster¹⁷ and density functional theory (DFT) periodic¹⁸ calculations on the hydrogen adsorption on the unsupported (010) V_2O_5 surface conclude that terminal oxygen atoms of the vanadyl groups present the highest activity toward hydrogen adsorption; i.e., the adsorption energy on such sites is the most exothermic. Even the 3-fold coordinated oxygen atoms in the $V_2O_5(010)$ surface have been proposed to be responsible for the catalytic activity of V_2O_5 .¹⁹ Periodic semiempirical Hartree–Fock calculations indicate that, upon creation of an oxygen vacancy in the perfect $V_2O_5(001)$ surface, the most stable system corresponds to the uptake of the 3-fold coordination oxygen. This result is confirmed by IR studies on the oxidation of DMSO catalyzed by V_2O_5 carried out in the same work. A cluster model consisting of a V_2O_7 unit supported on the (100) anatase surface has been recently proposed by Jug and co-workers²⁰ together with a reaction mechanism for the SCR process.²¹

Despite the research conducted on hydrogen interaction with V_2O_5 , it is not possible to correlate the results obtained from unsupported crystals with those obtained for supported catalysts. Besselman et al.²² conclude from temperature programmed reduction (TPR) experiments that supported vanadia/titania samples are easier to reduce than unsupported V_2O_5 . Topsøe et al.²³ also find that the $V-OH$ and $V=O$ bands disappear while $Ti-OH$ bands appear in H_2 atmosphere. The vanadia species would agglomerate upon reduction and disperse upon oxidizing conditions in a reversible process. More recent spectroscopic experiments carried out by Bulushev et al.⁸ also report the disappearance of the $V=O$ signals and the formation of new hydroxyl groups probably associated with titania; however, they did not study the region characteristic for the polymeric species because of a strong adsorbance by the titania support. They conclude that “the nature of hydroxyl groups associated with supported vanadia species and the structure of reduced vanadia species need further clarification”. Wachs and co-workers have probed the redox properties of the vanadia-supported catalysts with TPR in a hydrogen environment.^{24,25} They conclude that the specific support does have an effect on the redox properties of surface vanadia species for the SCR process. In situ Raman spectra in SCR conditions show that the terminal $V=O$ bond is perturbed by the reduction but the attribution of such bonds to the rate-determining step during SCR is doubtful; instead, the bridging $V-O$ –support bond could be responsible for it. This is supported by ^{18}O exchange experiments showing that the time required for exchanging the terminal $V=^{18}O$ to $V=^{16}O$ during the SCR is extremely long and it can be considered as too stable to react. The implication of the $V-O$ –support bond comes from the correlation of the catalytic activity with the electropositivity of the metal of the support ($ZrO_2 > TiO_2 \gg Al_2O_3 > SiO_2$). Went et al.²⁶ recorded the Raman spectra for vanadia-supported catalysts exposed to water and ethanol and found that the $V=O$ band shifted to lower energies but the band associated with

polymeric species (bridging oxygens) did not change, indicating that the vanadyl bond would be the only active site involved in such adsorption processes. For titania-supported samples, the adsorbates would coordinate to the oxygen sites but would not induce any hydrolysis of the $V-O$ –support bond which is strong.

The present paper aims at studying the reactivity of the different oxygen sites in a V_2O_5 supported on anatase TiO_2 model by means of periodic DFT calculations for the first time. To track the reactivity of the different oxygen sites, we have first analyzed the geometric features of the model and the electronic structure. This will permit us to determine the energetic levels of the different oxygen sites. Next, we have investigated the adsorption of H on a V_2O_5/TiO_2 anatase slab. We consider not only the oxygen sites in the active phase V_2O_5 but also those present in the support TiO_2 and in the interface between them. Surface relaxation playing an important role in the stabilization of intermediates will be the object of special attention. We hope to provide important information on the active sites of V_2O_5/TiO_2 involved in the catalytic reactions.

2. Methods and Models

The VASP code has been used for all calculations.^{27,28} The GGA PW91 functional^{29,30} combined with plane waves under 400 eV are employed. The Vanderbilt ultrasoft pseudopotentials^{31,32} represent the core electrons. The integrations in the Brillouin zone are performed on a $5 \times 5 \times 1$ grid. The conjugate gradient algorithm is used for the geometry optimization. As the program performs calculations in three dimensions, a vacuum space must be left to avoid interaction between slabs; in all our calculations a vacuum of at least 7 Å is present between two successive layers. This methodology has shown to be appropriate to the study of transition metal oxides.^{33–35}

The adsorption energy is calculated with the formula

$$E_{\text{ads}} = E_{\text{H}} + E_{\text{slab}} - E_{\text{H+slab}}$$

where positive values indicate an exothermic process. The reference for $(1/2)H_2 \rightarrow H$ is 2.29 eV. The H atom has been calculated in a $10 \times 10 \times 10 \text{ Å}^3$ unit cell. No correction for basis set superposition error is necessary since plane waves are used. Polarized calculations with $N_{\alpha} - N_{\beta} = 1$ are employed for the H adsorption (one H per unit cell).

In a previous work we studied different models for the vanadia/titania catalyst on the (100) and (001) anatase surfaces. Although the most stable anatase plane is the (101),³⁶ the (100) and (001) ones are found in the commercial catalyst particules.³⁷ In this work we showed that the most stable arrangement for a V_2O_5/TiO_2 anatase model was that of a linear V_2O_5 cluster on a (001) plane anatase slab. The formation of such a model from the independent parts is exothermic by 5.19 eV in a 2×2 unit cell³⁵ and 6.43 eV for a 2×3 unit cell, with the V_2O_5 linear unit lying on one face in the [110] direction so as to maximize interaction with the support. The 2×2 unit cell ($7.57 \times 7.57 \text{ Å}$) is used in the present work, since a compromise between dispersion and computational effort has to be reached: a smaller unit cell would favor overlapping between V_2O_5 units and dispersion would not be correctly described, while a larger unit cell would severely increase the calculation requirements. The coverage in this situation, one V_2O_5 cluster on a 2×2 TiO_2 unit cell, simulates less than a full monolayer and reflects the dispersion of the V_2O_5 units, essential for the catalytic activity. The anatase slab consists of three stoichiometric layers as shown in Figure 1. The V_2O_5 unit is then dispersed on the support and

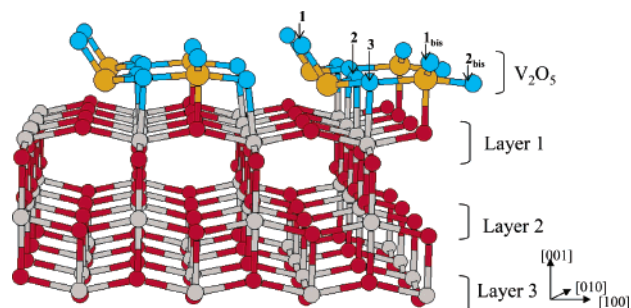


Figure 1. Side view of the $\text{V}_2\text{O}_5/\text{TiO}_2$ slab model. The V_2O_5 unit lies in the [110] direction of the anatase structure. The oxygen sites in this unit are labeled: sites 1 and 1bis correspond to terminal vanadyl $\text{V}=\text{O}$ bonds; 2 and 2bis are interface $\text{V}-\text{O}-\text{Ti}$ sites (in the gas-phase cluster they were also terminal); 3 is the bridging $\text{V}-\text{O}-\text{V}$ site. Three layers are used for representing the (001) anatase slab.

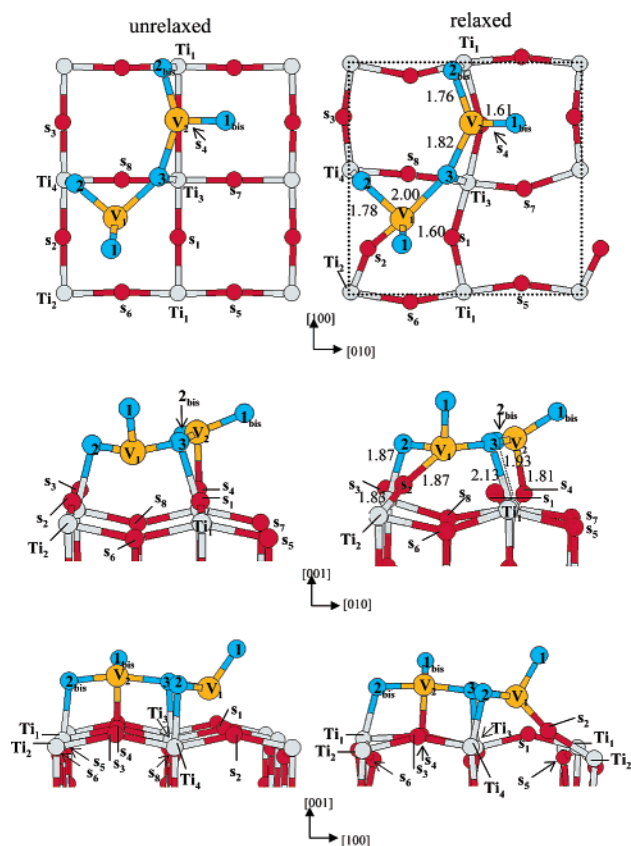


Figure 2. Unrelaxed (left) and relaxed (right) unit cells for the $\text{V}_2\text{O}_5/\text{TiO}_2$ slab model. The top figures are top views and the middle and bottom figures are side views. The labeling of the sites is noted in the text. Distances are in angstroms. Note the important arrangement in the surface TiO_2 sites to adapt to the V_2O_5 unit. This arrangement does not take place for the bare (001) anatase surface. As a result of the interaction between vanadia and titania, V—O—Ti sites (sites 2, 2bis, and s2) and are exposed and available for reactivity.

exhibits three different oxygen sites: terminal ($\text{V}=\text{O}$), bridging between two vanadium atoms ($\text{V}-\text{O}-\text{V}$), and bridging between V and surface Ti ($\text{V}-\text{O}-\text{Ti}$); the latter corresponds to the interaction of a gas-phase cluster terminal oxygen with the surface. The surface also exhibits oxygen sites ($\text{Ti}-\text{O}-\text{Ti}$). All of them are shown in Figure 2 and are presented in more detail in the next section.

Relaxation has been taken into account at three steps: first, only the V_2O_5 unit; second, including the first surface layer; third, two outermost surface layers. The local environment and the role of the support can thus be explored.

TABLE 1: Atomic Displacements (in Å) of the Oxygen Atoms in the Support TiO₂ Surface, with Respect to the Ideal Bulk-Terminated Slab (See Numbering in Figure 2)^a

	relaxation step I			relaxation step II		
	[010]	[100]	[001]	[010]	[100]	[001]
O s1	-0.445	0.007	0.137	-0.463	-0.001	0.152
O s2	0.576	-0.344	0.354	0.589	-0.354	0.369
O s3	0.469	-0.083	-0.054	0.483	-0.086	-0.051
O s4	-0.237	0.146	0.041	-0.238	0.164	0.045
O s5	-0.033	0.303	0.116	-0.043	0.302	0.123
O s6	0.029	-0.291	0.007	0.037	-0.319	0.003
O s7	0.026	-0.275	0.149	0.040	-0.313	0.184
O s8	-0.015	0.176	0.059	-0.037	0.164	0.070
Ti ₁	-0.074	0.068	0.142	-0.077	0.068	0.177
Ti ₂	-0.033	0.024	-0.031	-0.028	0.038	-0.052
Ti ₃	0.013	-0.100	0.018	0.046	-0.110	0.020
Ti ₄	-0.032	0.304	0.147	-0.034	0.315	0.195

^a Only the values for the first layer are reported; the second layer presents displacements smaller than 0.06 Å.

3. Results and Discussion

The Surface. *Surface Structure.* We have shown in a previous work³⁴ that the interaction of a V_2O_5 unit over the anatase (001) surface leads to a rearrangement of the surface atoms that does not take place for the bare surface. Such reconstruction is thermodynamically favorable and leads to the most stable model for the V_2O_5 /anatase system. Table 1 shows the atomic displacements of the atoms in layers 1 and 2 with respect to the ideal positions. Step I involves relaxation of the surface layer 1 together with the V_2O_5 unit; step II involves relaxation of layers 1 and 2 together with the adsorbate. The unrelaxed and relaxed systems are also shown in Figure 2.

Relaxation is important for the atoms in the first layer of the support. The highest displacements are on the order of 0.60 Å and are associated with the surface 2-fold coordinated oxygen atoms s1–s4, involving [010], [100], and [001] directions. Titanium atoms only move in the [100] and [001] directions with atomic displacements ranging between 0.10 and 0.32 Å. The second layer, released in step II, presents atomic displacements smaller than 0.06 Å. The energetic gain upon relaxation of one and two surface layers is 2.18 and 0.18 eV, respectively. We conclude that relaxation of the first support layer is crucial in geometric and energetic terms while relaxation of the second one seems to affect them only to a minor extent.

As we are concerned about the reactivity of oxygen atoms in the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst, let us describe the different sites present in our model (see Figure 2): (i) two terminal oxygen atoms of the V_2O_5 unit (vanadyl $\text{V}=\text{O}$ sites, 1 and 1bis); (ii) two terminal oxygen atoms of the V_2O_5 unit in interaction with the surface titanium atoms ($\text{V}-\text{O}-\text{Ti}$ sites, 2 and 2bis); (iii) one bridging oxygen atom in the V_2O_5 unit, bonded to two vanadium atoms ($\text{V}-\text{O}-\text{V}$, site 3); (iv) four surface oxygen $\text{O}_{2\text{C}}$ atoms, with three in principle available for reactivity with V_2O_5 ($\text{Ti}-\text{O}-\text{Ti}$ sites s1, s2, and s3), and one bonded directly to a vanadium atom (s4); (v) four surface oxygen $\text{O}_{3\text{C}}$ atoms (s5–s8).

Our model thus contains the different oxygen sites proposed in the literature as reactive in pure V_2O_5 (terminal and bridging atoms), as well as oxygen sites in the interface (V–O–Ti sites) and surface sites. Table 2 presents the selected bond lengths between the oxygen atom sites and their closest neighbors. The terminal vanadyl bonds $\text{V}=\text{O}$ (sites 1 and 1bis) present short distances around 1.60 Å. They are not fully coordinated, but the stability of the vanadyl bond is well-known. Some authors state that it must be too stable to react,²⁵ although some others attribute reactivity to these sites.^{17,18,26} The bridging oxygen

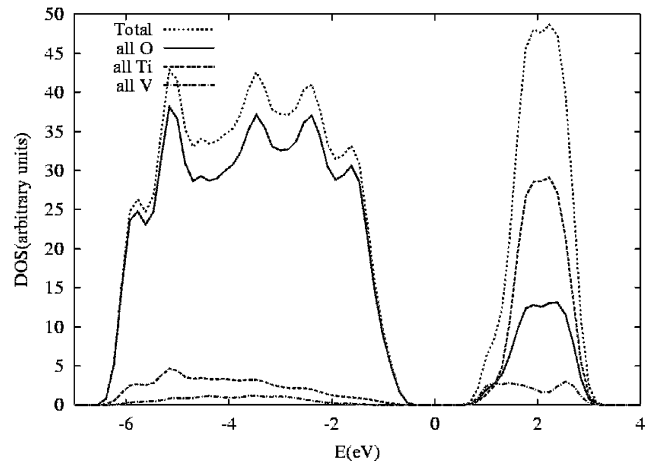
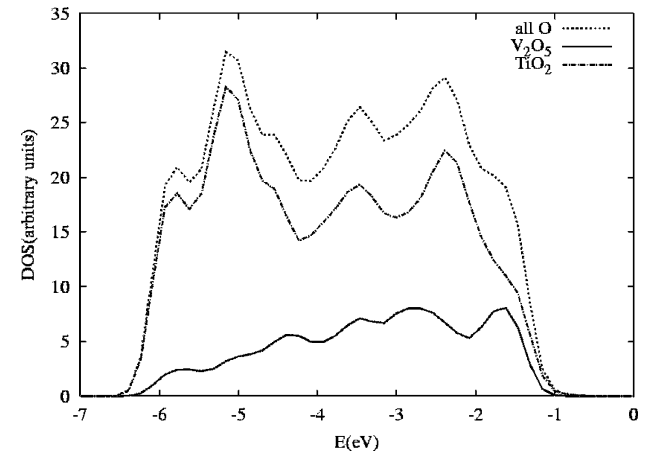
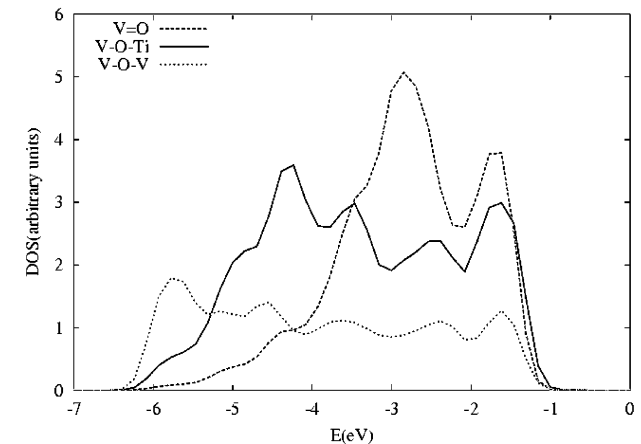
TABLE 2: Selected Distances (in Å) for the Most Representative Bonds in the V_2O_5/TiO_2 Slab Model, with Pure V_2O_5 (001) Surface,³⁸ Gas-Phase V_2O_5 Cluster,^{39,40} and Anatase(001) Distances³⁵ Reported for Comparison

site	bond	distance	comparison to available data
1	O_1-V_1	1.600	1.58 Å $V=O$ in pure V_2O_5 (001) 1.58–1.62 Å $V=O$ in gas-phase V_2O_5 clusters
1bis	$O_{1bis}-V_2$	1.611	1.58 Å $V=O$ in pure V_2O_5 (001) 1.58–1.62 Å $V=O$ in gas-phase V_2O_5 clusters
2	O_2-V_1	1.776	1.77–2.02 Å $V-O-V$ in pure V_2O_5 (001) 1.74–1.85 Å $V-O-V$ in gas-phase V_2O_5 clusters
	O_2-Ti_4	1.873	1.95 Å $Ti-O_{apical}$ in relaxed bare anatase (001)
2bis	$O_{2bis}-V_2$	1.760	1.77–2.02 Å $V-O-V$ in pure V_2O_5 (001) 1.74–1.85 Å $V-O-V$ in gas-phase V_2O_5 clusters
	$O_{2bis}-Ti$	1.928	1.95 Å $Ti-O_{apical}$ in relaxed bare anatase (001)
3	O_3-V_1	2.002	1.77–2.02 Å $V-O-V$ in pure V_2O_5 (001) 1.74–1.85 Å $V-O-V$ in gas-phase V_2O_5 clusters
	O_3-V_2	1.824	1.77–2.02 Å $V-O-V$ in pure V_2O_5 (001) 1.74–1.85 Å $V-O-V$ in gas-phase V_2O_5 clusters
	O_3-Ti_3	2.128	1.95 Å $Ti-O_{apical}$ in relaxed bare anatase (001)
s1	$O-Ti_3$	1.935	1.78–2.18 Å $Ti-O_{2C}-Ti$ in relaxed bare anatase (001)
	$O-Ti_4$	1.906	1.78–2.18 Å $Ti-O_{2C}-Ti$ in relaxed bare anatase (001)
	$O-V_1$	2.134	1.77–2.02 Å $V-O-V$ in pure V_2O_5 (001) 1.74–1.85 Å $V-O-V$ in gas-phase V_2O_5 clusters
s2	$O-Ti_2$	1.868	1.78–2.18 Å $Ti-O_{2C}-Ti$ in relaxed bare anatase (001)
	$O-V_1$	1.829	1.77–2.02 Å $V-O-V$ in pure V_2O_5 (001) 1.74–1.85 Å $V-O-V$ in gas-phase V_2O_5 clusters
s3	$O-Ti_4$	1.774	1.78–2.18 Å $Ti-O_{2C}-Ti$ in relaxed bare anatase (001)
	$O-Ti_2$	1.852	1.78–2.18 Å $Ti-O_{2C}-Ti$ in relaxed bare anatase (001)
s4	$O-Ti$	1.815	1.95 Å $Ti-O_{apical}$ in relaxed bare anatase (001)

$V-O-V$ presents bond distances of 1.824 and 2.002 Å to the nearest vanadium atoms. We note, however, that this oxygen atom is bound to the support in our model and is therefore 3-fold coordinated. Its reactivity should be decreased. Two of the initially gas phase terminal oxygen atoms interact now with the anatase support, sites $V-O-Ti$ 2 and 2bis, exhibiting bond lengths $O-V$ 1.77 Å and $O-Ti$ 1.90 Å. Such bond distances are characteristic of bridging bonds, and these atoms cannot be considered terminal but bridging and are supposed to be reactive. The bond lengths found for the pure V_2O_5 (001) surface are $V=O$ 1.58 Å, $V-O-V$ 1.77–2.02 Å, and $V-O$ 2.79 Å (the latter corresponds to weak bonds between the layers).³⁸ The bond lengths for gas-phase clusters are $V=O$ 1.58–1.62 Å and $V-O-V$ 1.74–1.85 Å.^{39,40} The perfect bare anatase (001) presents a $Ti-O_{apical}$ distance of 1.97 Å, whereas the relaxed (001) anatase structure exhibits $Ti-O_{apical}$ 1.94 Å and two different $Ti-O_{2C}$ distances: 1.78 and 2.18 Å.³⁵

Electronic Structure. The total density of states (DOS) and projected DOS of the fully relaxed V_2O_5/TiO_2 system in the region near the Fermi level are shown in Figure 3. The total DOS corresponds to a semiconductor structure with a band gap of approximately 1.10 eV. The experimental band gap for pure V_2O_5 is 2.3 eV,⁴¹ and for anatase it is 3.2 eV.⁴² The valence band (VB) is about 6 eV wide and is mainly composed of oxygen p orbitals. The conduction band (CB) presents a major contribution of metallic centers: titanium states are centered in the middle of the band and vanadium states in the borders. The lower part of the CB is then composed of vanadium states and accounts for the smaller band gap with respect to pure anatase. We will focus on the VB and on the V_2O_5 oxygen atoms. Two projections of the DOS are used to discuss the role of each component: first (Figure 4), we project on the oxygen atoms coming from V_2O_5 and anatase units; next (Figure 5) we decompose into the different oxygen site contributions inside V_2O_5 , i.e., terminal, bridging, and $V-O-Ti$ sites.

The projection on the O atoms coming from the support spreads between -1 and -6.5 eV and presents several peaks in the middle VB region. The oxygen atoms coming from the

**Figure 3.** Total and O-, Ti-, and V-projected density of states for the V_2O_5/TiO_2 slab model. The valence band is mainly composed of oxygen sites; the conduction band is mainly composed of metal states.**Figure 4.** O-Projected density of states in the valence band region. Decomposition into total oxygen contribution, oxygen in V_2O_5 , and oxygen in TiO_2 . The peak at -1.6 eV is mainly due to the V_2O_5 oxygen atoms.**Figure 5.** O-Projected density of states in the valence band region. Decomposition into the different oxygen atoms of the V_2O_5 unit. $V=O$ represents terminal oxygen (sites 1 and 1bis), $V-O-Ti$ the oxygen atoms bonded to the support (sites 2 and 2bis), and $V-O-V$ the bridging oxygen (site 3). The region close to the band gap presents contributions from all three types of atoms.

V_2O_5 mainly contribute to the upper part of the DOS (peak at -1.6 eV) although they spread from -1 to -6 eV. This implies that the most reactive O atoms are provided by V_2O_5 . This is another reason for finding a smaller band gap: the upper part

TABLE 3: Adsorption Energy (in eV) for H Interaction with the V₂O₅/TiO₂ Slab Model, OH Distances (in Å), and OH Orientations^a

site	I	II	III	OH distance	OH orientation
1	2.60	2.35	2.37	0.975	toward O1, [010] direction
1bis	2.84	2.60	2.60	0.974	toward O1
2	3.19	2.96	2.95	0.973	[100] direction
2bis	3.21	2.81	2.81	1.005	toward O1
3	2.35	2.14	2.17	0.980	[001] direction
s1	2.25	2.03	2.03	0.983	toward s3
s2	4.06 ^b	2.61	2.58	0.977	toward O3
s3	2.60	2.51	2.52	1.008	toward 1bis

^a Note that only values higher than 2.29 eV can be considered exothermic. Three degrees of relaxation have been considered including the V₂O₅ unit (I), one anatase layer (II), and two anatase layers (III).

^b A reorganization leading to a polymer in the [100] direction takes place.

of the VB is higher and the lowest part of the CB is lower than that for pure anatase.

Regarding the decomposition of the oxygen present in V₂O₅ (Figure 4), the contribution of terminal V=O, bridging V—O—Ti, and V—O—V oxygen is reported. They are centered in the upper, middle, and lower regions of the VB, respectively. The vanadyl V=O states are concentrated between −1 and −4 eV and exhibit two main peaks at −1.6 and −2.8 eV. The contribution of the V—O—Ti atoms spreads between −1 and −5 eV and shows several peaks: −1.6, −2.4, −3.5, and −4.2 eV. The bridging V—O—V atom presents states all along the VB and a main peak at −5.8 with others at higher energies, among them one at −1.6 eV. Note that all the oxygen sites in the V₂O₅ unit present a peak near −1.6 eV in the region closer to the gap. This means that they all possess almost the same energetic levels. A finer analysis of the DOS does not allow determining which one among the three sites is the most reactive in terms of electronic levels.

In conclusion, the regions associated with reactivity (upper region of the VB and the lower of the CB) are composed of states coming from the V₂O₅ unit. Projections of the DOS on the different oxygen sites of V₂O₅ show similar contributions to the upper region of the VB; it is not possible from our analysis to assign a marked reactivity to any of them.

Hydrogen Adsorption. We have selected the following adsorption sites on the V₂O₅/TiO₂ system (see Figure 2):

On the V₂O₅ unit are two terminal oxygen atoms (V=O sites 1 and 1bis), two terminal oxygens in interaction with Ti (V—O—Ti sites 2 and 2bis), and the bridging oxygen V—O—V (site 3).

On the surface are three dicoordinated atoms (s1, s2, and s3). We have not considered neither the O_{2C} interacting with V (site s4) nor the surface O_{3C} (3-fold oxygen atoms should be by far less reactive than the 2-fold ones).

Table 3 shows the adsorption energy for the different sites. OH bonds orient to maximize interactions.

The main feature is that all surface sites present close adsorption energy values. Note that the reported values are referred to atomic H; only those values higher than 2.29 eV (the reference for (1/2)H₂) can be considered exothermic. The most favorable sites are those involving the V₂O₅ unit, while the sites on the surface always present lower values. This means that the reactive sites of the catalyst are directly related to the V₂O₅ presence, this structure being more reducible than pure anatase.

The most thermodynamically favorable adsorption site is the bridging oxygen between the V₂O₅ unit and the TiO₂ surface (V—O—Ti site 2, 2.95 eV). The best adsorption energy on a

terminal V=O bond is 2.60 eV. This seems to confirm the higher reactivity of the interface oxygen sites as proposed by Wachs and co-workers^{24,25} despite the undercoordination of V=O. Indeed, the V—O—support bonds are very strong²⁶ and could explain the enhanced activity of supported systems. In dispersed materials, these sites are accessible on the catalyst surface but they recombine to form V—O—V bonds as the V₂O₅ content increases. They are the most basic sites of the surface. We look for a geometric reason for the reactivity: they present in the catalyst model O—V distances slightly longer than the bridging O in bulk V₂O₅, and O—Ti distances shorter than the apical O—Ti bond in anatase (001), becoming more reactive than the reference systems. They are also accessible on the catalyst surface. We note that sites 2, 2bis, and s2 show a similar geometric environment (Table 2; V—O—Ti bonds are for site 2 1.776 and 1.873 Å; for 2bis, 1.760 and 1.928 Å; and for s2, 1.829 and 1.868 Å) and present similar adsorption energies. It is, however, rather difficult to perform a finer analysis to explain the order in adsorption energy for these three sites. We note that H bonding is especially important for 2bis according to the OH distance.

Regarding the bridging oxygen atom V—O—V (site 3), the heat of H adsorption is small. This is due to the fact that, as mentioned above, this atom interacts with the substrate and is indeed 3-fold coordinated and not bridging.

Relaxation decreases the strength of adsorption. Relaxed systems show less adsorption energy than unrelaxed ones. Relaxation of the first surface layer is very important in terms of geometry and also energy. The second layer is not so important. Yin et al. and Homann et al. also note the effect of relaxation in a negative increase of E_{ads} . For the O1, O2, and O3 sites on pure V₂O₅(010), Yin et al.¹⁸ report values of 2.70 > 2.61 > 2.57 eV, respectively (periodic DFT calculations); Homann et al.¹⁷ report about 2.6 > 2.1 > 1.8 eV, respectively (cluster MSINDO calculations). A finer analysis of the relaxation effect shows no severe changes in the trends when increasing the degrees of freedom. At step I, where only the V₂O₅ unit is free to relax, the most important feature is the artificial evolution of the site s2 to a polymer in the [100] direction, caused by the limited degrees of freedom. Sites 2 and 2bis show the most exothermic values followed by sites 1bis, 1, s3, 3, and s1. However, relaxation of the first support layer clearly stabilizes site 2 with respect to site 2bis. Sites s2, 1bis, and s3 show almost the same E_{ads} values. After relaxation of the second layer of the support, there are no qualitative changes in the trends: sites 2 and 2bis are the most favorable followed by 1bis, s2, and s3. The least favorable are sites 3 and s1.

V₂O₅/TiO₂ vs TiO₂. The most exothermic value for the H adsorption on the bare anatase (001) surface is 2.20 eV as H⁺/H[−] and 1.56 eV as H⁺/O_{2C}.³⁵ In the presence of V₂O₅, the sites on the surface show $E_{\text{ads}} = 2.58$ eV as H⁺/O_{2C}. The apparent gain in E_{ads} is due to the higher basicity of the O sites in the presence of V₂O₅. The most favorable adsorption mode (H on the V—O—Ti sites of the supported V₂O₅/TiO₂ model, 2.95 eV) explains the higher reducibility of vanadia with respect to pure titania.

It is clear from our results that the OH groups are more stable on the vanadia unit than on titania in the V₂O₅/TiO₂ model. This is in agreement with the experimental results by Topsøe et al.,²³ where mixed catalysts would expose preferentially V—OH groups rather than Ti—OH, achieving a complete coverage of the titania surface.

Adsorption Mechanism. Regarding the adsorption mechanism, H adsorbs on an oxygen site and an electron transfer takes

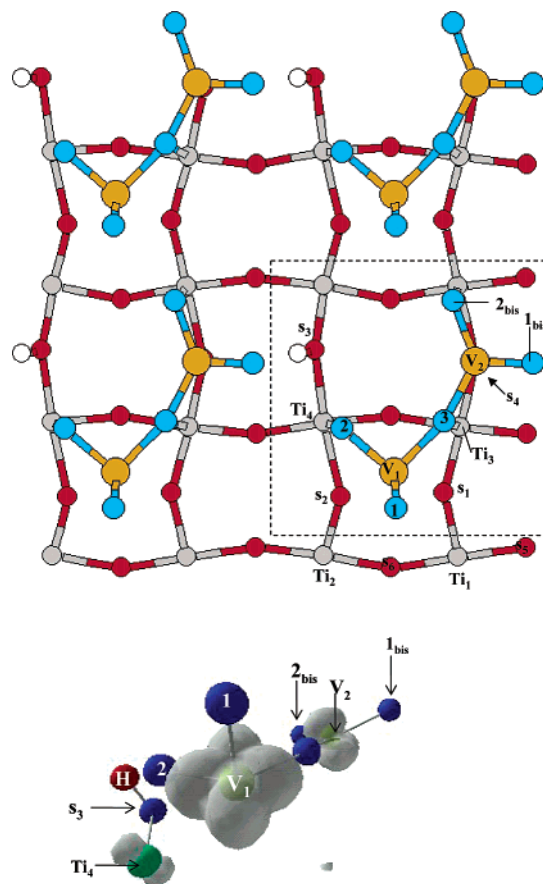


Figure 6. Adsorption of H on surface site s_3 . Top: a top view of the optimized model. Only the uppermost atoms are shown for clarity. Bottom: spin density isosurface for the same system (side view). The spin density is localized on the V_1 atom despite the adsorption of H on a surface Ti—O—Ti site.

place from the hydrogen to the vanadium site through the oxygen atom. The charge on the vanadium centers, calculated within the atomic sphere method, passes from $+4.6e$ before reduction to $+4.0e$ after reduction for all the systems studied; this confirms the formal reduction of V^{5+} to V^{4+} .

It could be expected to have the spin density equally distributed between the two vanadium atoms: charge values seem to indicate that. However, we found from our approach that spin density is concentrated on one vanadium center (magnetization values are on the order of $0.45e$ for one vanadium atom and $0.20e$ for the other in all systems). Figure 6 displays the spin density isosurface of the site s_3 which is concentrated on one vanadium atom. Note that on the pure titania, upon atomic hydrogen adsorption at the same level of calculation, the spin density was equally distributed on all the titanium atoms of the surface. For the V_2O_5/TiO_2 system, even when the adsorption sites considered are those on the titania surface (Ti—O—Ti) bonds, the spin density is always located on the vanadium atom. A finer analysis should be done to further understand the location of the extra electron upon reduction.

4. Conclusions

We have investigated the reactivity of a supported V_2O_5/TiO_2 catalyst model by means of periodic DFT calculations for the first time. It corresponds to anhydrous conditions and models dispersion of dimeric V_2O_5 species on the substrate. Our model contains all the sites proposed in the literature as being potentially reactive: terminal $V=O$ sites, bridging $V-O-V$

sites, interface $V-O-Ti$ sites, and surface $Ti-O-Ti$ sites. The main results are summarized below.

1. V_2O_5 interacting with anatase (001) 2×2 lying in the $[110]$ direction has been chosen as the catalyst model. This model presents the following exposed oxygen sites: $V=O$, $V-O-V$, $V-O-Ti$, and $Ti-O-Ti$.

2. Relaxation of the outermost titania layer involves atomic displacements of 0.60 \AA in the $[010]$, $[100]$, and $[001]$ directions for the oxygen atoms, and of 0.30 \AA in the $[100]$ and $[001]$ directions for the titanium atoms. Relaxation of the second titania layer involves atomic movements of less than 0.06 \AA . The energetic gain upon relaxation of one and two surface layers is 2.18 and 0.18 eV , respectively. We conclude that relaxation of the first support layer is crucial in geometric and energetic terms while the second one seems to affect them only to a minor extent.

3. An analysis of the total and projected DOS shows that the most reactive regions are associated with the vanadia unit: the upper region of the valence band is composed of V_2O_5 oxygen states and the lower part of the conduction band is composed of vanadium states. This could account for the decrease in the band gap value with respect to pure anatase. It is not possible to identify the most reactive oxygen on the V_2O_5 unit from our analysis since $V=O$, $V-O-V$, and $V-O-Ti$ contribute almost equally to the upper part of the valence band.

4. Upon atomic hydrogen adsorption the $V-O-Ti$ sites present the higher adsorption energies (2.95 eV). Note that only E_{ads} values higher than 2.29 eV can be considered as exothermic. This is consistent with the enhanced activity of supported catalyst with respect to unsupported ones, and is in agreement with experimental results. The order of hydrogen adsorption energy on the different oxygen sites is $V-O-Ti > V=O > V-O-V > Ti-O-Ti$. The $V-O-V$ is indeed in our model a 3-fold coordinated oxygen, not a bridging one.

5. Hydroxyl groups are formed that interact when possible via hydrogen bonds. The adsorption energy values involving the vanadia unit are higher than those for the surface, in agreement with experimental results. In comparison to the pure anatase (001) surface, hydrogen adsorption is more favorable in vanadia-supported systems.

6. Relaxation induces a decrease of E_{ads} . This means that relaxation is more important for the bare V_2O_5/TiO_2 model than for the hydrogenated systems.

7. Regarding the adsorption mechanism, hydrogen transfers an electron to the substrate that reduces the vanadium atom, even when considering adsorption on an anatase surface site. This corresponds to the higher reducibility of vanadium compared to titanium atoms.

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