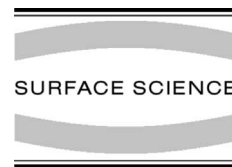




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Electronic properties of the VO₂(0 1 1) surface: density functional cluster calculations

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Abstract

This paper reviews electronic properties of the VO₂(0 1 1) surface. In particular it discusses the nature of surface V–O bonding. In addition, the electronic states of the structurally different surface oxygen sites are described and correlated with their catalytic properties. The calculations are performed by means of the ab initio DFT method. The vanadium dioxide surface is modeled using clusters of different sizes. Results of the study confirm the bonding in vanadium dioxide as a mixture of ionic and covalent character. Further, nucleophilic properties of structurally non-equivalent surface oxygen sites are found to increase with their coordination number. It is shown that in order to describe 5- and 6- fold vanadium centers correctly clusters containing two physical layers are required as models. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vanadium oxide; Density functional calculations; Catalysis

1. Introduction

Vanadium oxide (IV) exhibits four different polymorphic structures that are based on an oxygen bcc lattice with vanadium on the octahedral sites and oxygen octahedra being more or less regular. There are: the VO₂(R), which has rutile structure and is considered as the most stable, the monoclinic VO₂(M) that can be described as a slightly distorted rutile structure, the VO₂(A), which has a tetragonal structure, and the VO₂(B) with a monoclinic structure, very near to the V₆O₁₃

structure. These four polymorphs can be separated into two groups depending on the mutual orientation of the four axes of the oxygen octahedra. In rutile and monoclinic structures the oxygen octahedra are aligned along two perpendicular directions whereas in A and B structures they are aligned mainly along one direction. Moreover, for the last two polymorphs to obtain the stoichiometry of VO₂ only 1/6 of the octahedral sites must be filled by vanadium atoms, which means that there are vacancies. To summarize, one can say that although all four polymorphs correspond to the same stoichiometry, their structures and, what follows, their properties are very different [1–3].

Vanadium dioxide undergoes a first order solid phase transition at 68°C. Below this temperature

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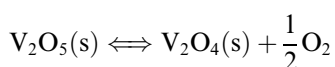
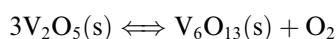
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$\text{VO}_2(\text{M})$ exists whereas above one finds a normal rutile structure. At this temperature the electrical conductivity changes by several orders of magnitude. The transition of A and B polymorphs to the rutile structure is not reversible. The semiconductor-to-metal transformation gives rise to abrupt changes of the physical properties (electrical, magnetic, optical etc. [4]) with a wide range of practical applications. For example, at this transition the transmittance of near infrared radiation is reduced dramatically, creating the possibility of “smart thermochromic windows” [5,6]. Further, changes in resistivity by as large as 10^5 for a single crystal finds an application for creation of critical thermistors and threshold switches [7].

Although vanadium dioxide has been intensively studied with many experimental and theoretical tools there is still no consensus on the extent to which the electron–electron interaction and electron correlation effects are important to understand its physical properties. What is the driving force for the semiconductor–metal phase transition? Is it electron–phonon or electron–electron interaction? There are some indications that this transformation, connected with a small distortion only, results in a metal–metal coupling and, as a consequence, creates a metal–metal bonding along the chains [8–10]. This leads to the suggestion that the electron–phonon interaction is responsible for the vanadium d-band splitting resulting in a fully occupied lower bonding band. Such an idea is supported by first-principles band structure calculations showing that a crystallographic transition would be explained by the formation of charge-density waves accompanied by a lattice distortion and subsequent condensation of phonons [11,12]. Other calculations, however, indicate that a crystallographic distortion is not sufficient to open up a gap and that electron correlation effects probably also play a role in this transition. This leads to the conclusion that although many authors have described the details of the semiconductor–metal phase transition, the nature of the ground state semiconducting phase is still rather uncertain.

Despite its fascinating physical properties vanadium dioxide, like almost any transition metal oxide, is also extremely interesting from the point

of view of catalysis due to a variety of exciting chemical properties arising from the narrow band of d-states and their possible hybridization with ligand orbitals. The phase diagram of vanadium oxides contains a large number of stoichiometric compounds [13]. The main catalytic role is attributed to V_2O_5 , but it is well known that stoichiometric V_2O_5 itself is not useful as a catalyst; it serves always as a basis for working catalysts [14]. Under reaction conditions catalysts prepared from V_2O_5 readily undergo partial reduction that proceeds according to the following processes:



and as the results phases of lower oxides appear which catalytic role is not yet understood.

However, in many experimental papers it has been shown that the changes in the chemical state of V_2O_5 affect considerably its catalytic properties in hydrocarbon oxidation. According to the literature [15–17], VO_2 seems to be the active species when supported on the titania. Such catalysts are applied in partial oxidation of several hydrocarbons and in selective reduction of nitric oxide. It is also believed that, for *o*-xylene oxidation, the presence of V(IV) surface sites modifies the reactivity of titania, enhancing it considerably as compared to pure TiO_2 . Therefore, it is clear that a study of VO_2 as well as other vanadium oxide compounds might provide additional valuable information on the catalytic behavior of V_2O_5 .

To answer the question about special catalytic properties of vanadia-based catalysts one can use the concept of coordinative unsaturation, one of the most important concepts in the reactivity of oxide surfaces. It assumes the existence of surface sites where the coordination of metal and oxygen is less than optimal. Two factors are important: first, the unsaturated ions are able to act as acidic or basic adsorption sites and, second, they are bonded to the lattice less strongly than coordinatively saturated ones, so that they may be more easily removed, for instance, in oxidation processes. Therefore, the key properties of V–O surfaces for catalytic purposes are the coordination

environment, oxidation state, and redox properties of surface centers. Since geometric and electronic structure are consistently linked to each other, the geometric rearrangement at the surface will alter the electronic structure of the surface and vice versa. Each of the above mentioned parameters can be varied, if not specified by experiment. The main objective of theoretical considerations is to supply information about the role of various centers in the oxidation process, i.e. to provide molecular level insights into the physico-chemical processes that occur on a catalyst surface under reaction conditions.

Experimental papers suggest two surfaces of vanadium dioxide, the (1 1 0) and (0 1 1), as interesting and main cleavage planes. In this paper we focus our attention only on the (0 1 1) plane of monoclinic VO₂ which corresponds directly to the most stable low-index face, the (1 1 0) plane of rutile [18]. The heteroepitaxial growth of VO₂ on the (1 1 0) surface of rutile [19] has been observed experimentally in studies of the catalytic activity of V–O systems [20].

In the present work we report systematic studies on the effect of cluster size performed in order to define a correct model of the surface. In addition, we give an electronic description of the surface and discuss the relation between types of bonding and catalytic properties.

2. Computational details

Below 68°C vanadium dioxide crystallizes in a compact system with monoclinic structure and lattice constants: $a = 5.743 \text{ \AA}$, $b = 4.517 \text{ \AA}$, and $c = 5.375 \text{ \AA}$ [21–26]. Its crystal unit cell is twice as large as in tetragonal symmetry and contains 12 atoms, 4 V and 8 O (see Fig. 1). The VO₆ octahedron is distorted, yielding three distances in the range 1.76–1.87 Å and three in 2.01–2.05 Å with angles varying between 78° and 99°. The adjacent VO₆ units are connected by edges or corners (see Fig. 2). As a result the oxygen centers share three octahedra each becoming 3-fold coordinated with respect to their vanadium neighbors. The (0 1 1) surface can be described by alternating rows of two quasi-rectangular O planes (A, A') and one

VO plane (B, with atoms density twice as large as that in the O planes) in a stacking sequence ...BAA'BAA'B... This allows three different ideal surface terminations, BAA', ...AA'B, and ...A'BA where the latter (see Fig. 2) is expected to be the energetically lowest in analogy with the surface structure of the rutile type TiO₂ [27]. This leads to 5- and 6-fold coordinated vanadium centers, V(5) and V(6), as well as to 2- and 3-fold coordinated oxygen centers, O(2) and O(3), at the ideal bulk terminated VO₂(0 1 1) surface as indicated in Fig. 1. The (0 1 1) surface is built from two types of alternating linear chains, one created from octahedra and the second one from square pyramids appearing due to truncation where neighboring octahedra are joined by edges, whereas neighboring square pyramids are joined by corners. As a consequence the surface is characterized by rows of oxygen atoms sticking out of the surface and O–V–O valleys. A cut along the (0 1 1) surface reduces the coordination number of some vanadium centers (from 6 to 5) and oxygen centers (from 3 to 2) which may lead to their different activity in chemisorption and catalysis.

The (0 1 1) VO₂ surface is modeled by clusters of different size and geometry cut off from the unrelaxed surface [21–26]. Clusters are constructed by successive addition of neighboring shells starting from the VO₅ square pyramid to describe 5-fold coordinated vanadium or VO₆ octahedra to describe 6-fold coordinated vanadium. All bond lengths are fixed to bulk experimental values and hydrogen atoms are used to saturate the free valencies at peripheral oxygen atoms. For all atoms in the clusters formal oxidation states following from VO₂ stoichiometry are assumed and the neutrality of the clusters is obtained by saturating hydrogen atoms. Since many chemical properties of clusters show a strong dependence on cluster size a sequence of model clusters of systematically increasing size is studied in an attempt to achieve cluster size convergence (see Fig. 3 for one-layer clusters and Fig. 4 for two-layer clusters). To model the different adsorption sites on the (0 1 1)VO₂ surface two different series of clusters are used, the first one to model 5-fold vanadium consists of V₃O₁₁H₁₀, V₇O₂₃H₂₀, V₁₃O₃₇H₂₂ clusters. The second series of clusters describes 6-fold

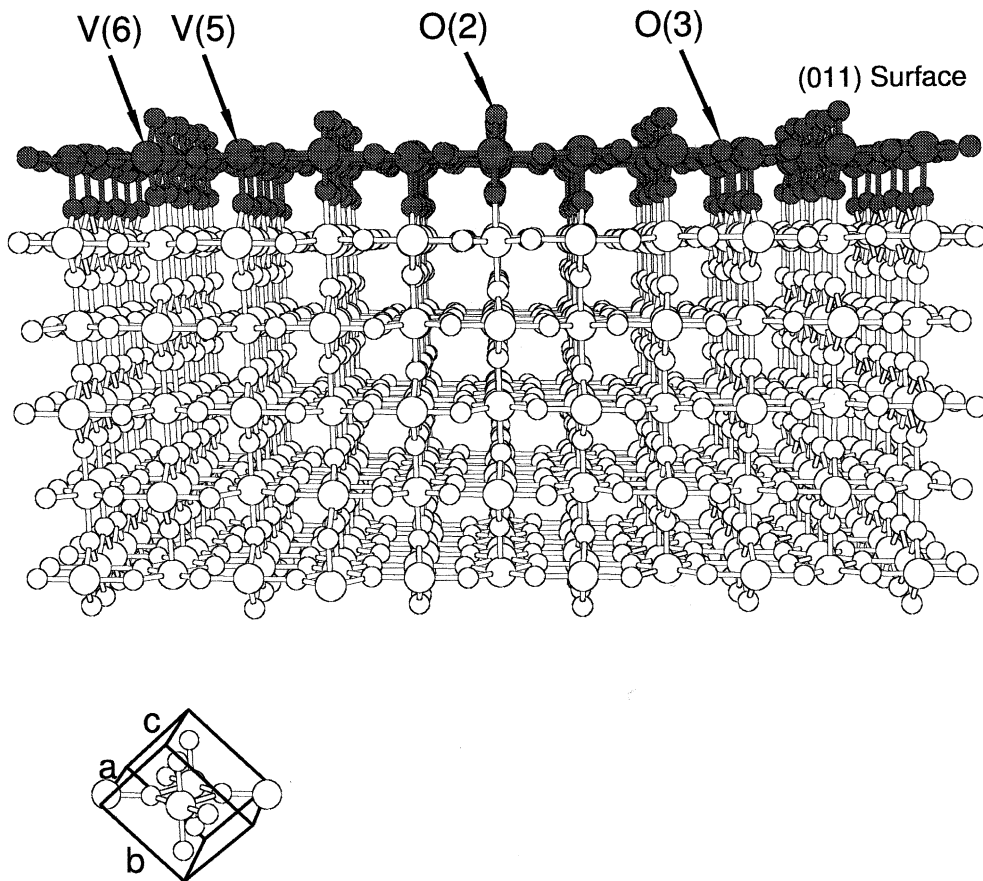


Fig. 1. Crystal section of monoclinic VO_2 with netplane stacking along the (011) direction. All atoms of the $\text{VO}_2(011)$ surface layer (crystal layer) are emphasized by darker shaded balls. Vanadium (oxygen) centers are shown as large (small) balls. Inequivalent vanadium, 5- and 6-fold coordinated and oxygen centers, doubly coordinated O(2) and triply coordinated O(3), are marked accordingly. The monoclinic elementary cell is added at the bottom.

coordinated vanadium and is built of $\text{V}_3\text{O}_{14}\text{H}_{16}$, $\text{V}_7\text{O}_{24}\text{H}_{20}$, $\text{V}_{13}\text{O}_{40}\text{H}_{28}$ clusters. In order to study the effect of the second surface layer on the electronic structure of the (011) surface the $\text{V}_{11}\text{O}_{34}\text{H}_{24}$, $\text{V}_{11}\text{O}_{30}\text{H}_{16}$, and $\text{V}_{17}\text{O}_{42}\text{H}_{16}$ (built of V_7O_{16} and $\text{V}_{10}\text{O}_{26}$ clusters from the first and second layer) clusters are used. The largest cluster possesses not only the correct nearby neighbors for both 5- and 6-fold coordinated vanadium but also has 16 dangling bonds that are saturated by hydrogen forming OH groups. In addition it forms a model that is the same for both penta- and hexa-coordinated vanadium (see Fig. 4).

The electronic properties of the (011) VO_2 surface are calculated within the DFT framework

[28–33] using a DFT-LCGTO program package.¹ This approach is widely used to probe heterogeneous catalytic systems that contain transition metal atoms, which are expected to possess large correlation effects due to the d-electrons. For the exchange and correlation within DFT we restricted ourselves to the local-density approximation (DFT-LDA) with the Vosko–Wilk–Nusair (VWN) parameterization [34]. This approximation has been shown to be successful in describing the structural ground-state properties of solids [35]

¹ A modified version of the deMon package developed by A. St.-Amant and D.R. Salahub (University of Montreal) with extensions by L.G. Pettersson and H. Hermann is used here.

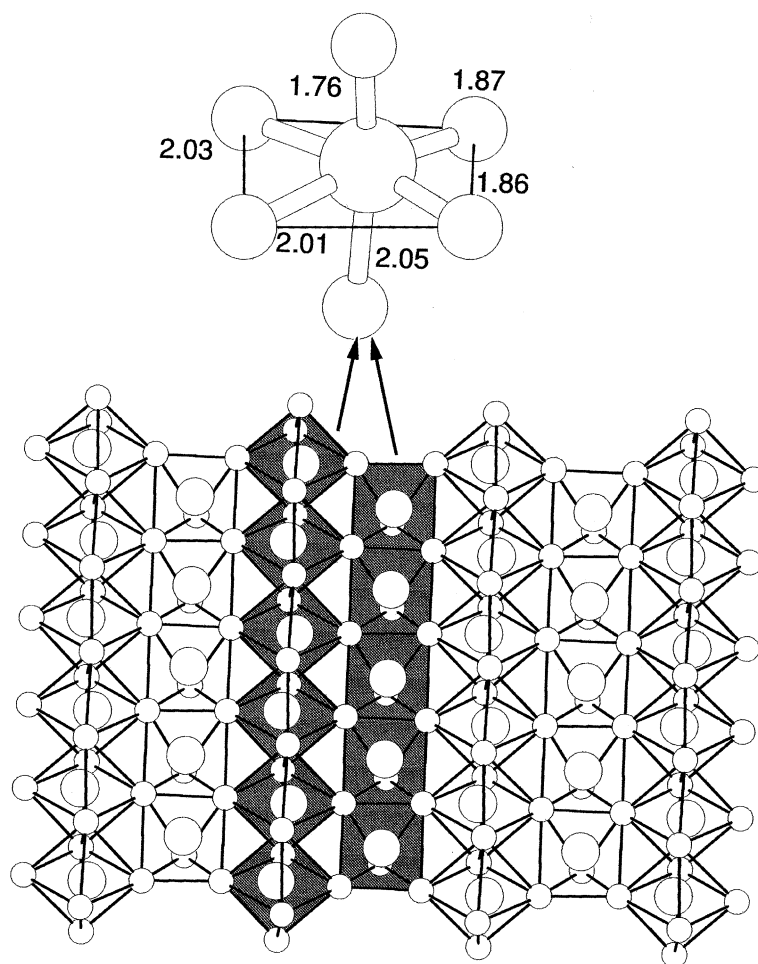


Fig. 2. A perspective view of the (011)VO₂ surface together with the VO₆ building unit. Two sets of chains formed by different linkages of the VO₆ building units are shown.

and in addition, it was verified as reasonable for the description of VO₂ [12]. Kohn–Sham orbitals are represented by linear combinations of atomic orbitals using extended basis sets of contracted Gaussian-type orbitals (CGTO) of double zeta quality with polarization functions for transition metals [36,37]. The fitting of the charge density is done analytically, whereas for V_{xc} we use a grid of 32 radial shells per atom with 45, 35 and 32 angular points for V, O, and H, respectively.

Traditional quantum mechanical tools such as Mulliken population analysis [38–41] and Mayer bond orders [42,43] are applied to examine interatomic binding at the surface. In addition, total

density of states (DOS) as well as partial atom projected density of states (PDOS) are evaluated. Although basis set effects preclude the use of Mulliken populations as an absolute indicator of atomic charges and bond orders as a measure of bond stability, the relative trends in both quantities that describe the nature of the bonding are usually reliable. Moreover, these simple qualitative considerations are very useful for understanding general trends in the measured observables. One should add that the results of Mulliken population analysis differ from the formal valence charges because, by definition, each bond is classified as at least partly covalent.

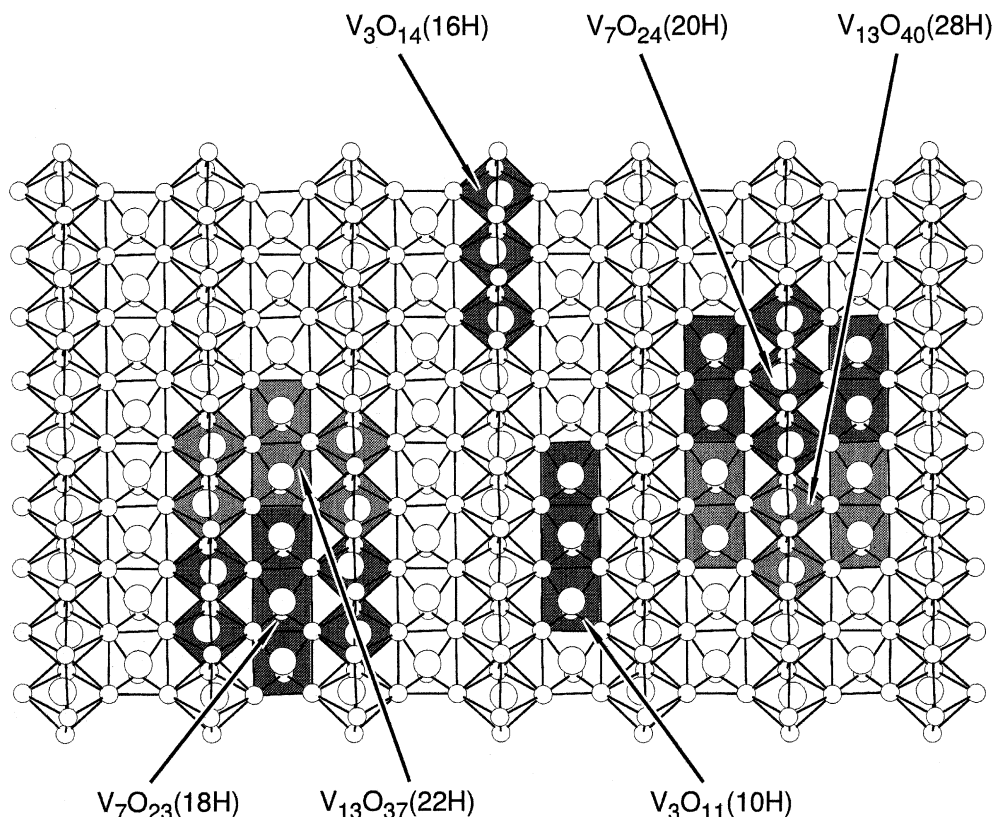


Fig. 3. The $\text{VO}_2(011)$ surface. Substrate clusters ($\text{V}_3\text{O}_{11}\text{H}_{10}$, $\text{V}_7\text{O}_{23}\text{H}_{18}$, $\text{V}_{13}\text{O}_{37}\text{H}_{22}$ describing 5-fold coordinated vanadium, V(5), and $\text{V}_3\text{O}_{14}\text{H}_{16}$, $\text{V}_7\text{O}_{24}\text{H}_{20}$, $\text{V}_{13}\text{O}_{40}\text{H}_{28}$ modeling 6-fold coordinated vanadium, V(6)) used in this study are indicated. Vanadium (oxygen) centers are shown as large (small) balls.

The geometries of all calculated VO_2 clusters are kept fixed in the ideal configuration of the VO_2 crystal. Such an assumption, where neither relaxation nor reconstruction is taken into account, can serve as a first step in calculating the electronic structure of surfaces. In addition, it serves as a reference for comparing with experimental data and for understanding the physical origin of possible modifications in electronic or atomic structure of the surface.

3. Results and discussion

Tables 1 and 2 list electronic structure parameters (atomic charges and bond orders) for two series of clusters describing 5- and 6-fold

coordinated vanadium, respectively. For 5-fold coordinated vanadium the $\text{V}_3\text{O}_{11}\text{H}_{10}$, $\text{V}_7\text{O}_{23}\text{H}_{18}$, $\text{V}_{13}\text{O}_{37}\text{H}_{22}$ clusters modeling one layer and $\text{V}_{11}\text{O}_{34}\text{H}_{24}$, $\text{V}_{17}\text{O}_{42}\text{H}_{16}$ clusters modeling two layers are considered. In the case of six-coordinated vanadium a set of $\text{V}_3\text{O}_{14}\text{H}_{16}$, $\text{V}_7\text{O}_{24}\text{H}_{20}$, $\text{V}_{13}\text{O}_{40}\text{H}_{28}$ one-layer clusters and the two-layer $\text{V}_{11}\text{O}_{30}\text{H}_{16}$, and $\text{V}_{17}\text{O}_{42}\text{H}_{16}$ clusters are discussed. All electronic parameters correspond to the ground state of each of the clusters found by minimizing its total energy. They are reported for atoms close to the centers of the clusters.

All vanadium atoms are characterized by positive whereas all oxygen atoms by negative charges, the values being different from the formal valence oxidation states. This due to two factors, the bonds character as well as to Mulliken analysis

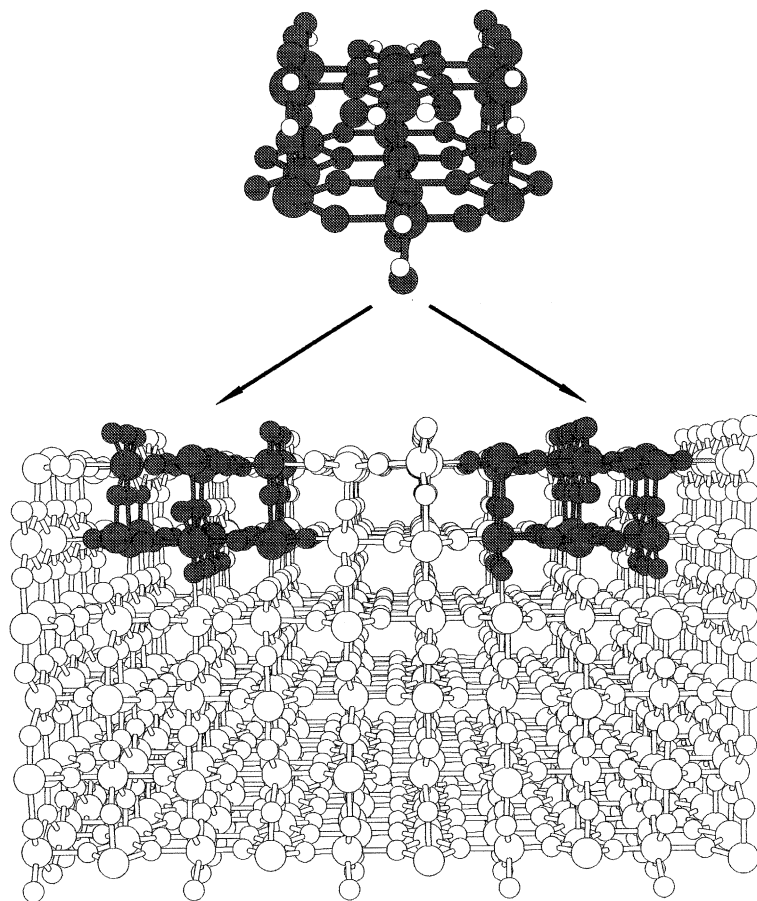


Fig. 4. A perspective view of the largest two-layer cluster $V_{17}O_{42}H_{16}$ (built of V_7O_{16} and $V_{10}O_{26}$ clusters from the first and second layer). In addition the way of cutting this cluster out of the bulk is shown. Vanadium (oxygen) centers are shown as large (small) balls.

where, by definition, each bond is classified as at least partly covalent. The atomic charges allow us to identify vanadium atoms as Lewis acid centers whereas oxygen atoms as Lewis centers of basic character. For vanadium centers the atomic charges increase slightly with the size of the surface model (in the range of 1 to 1.5/1.6, see Tables 1 and 2) and stabilize (converge) for two-layer clusters (negligible difference between $V_{11}O_{34}H_{24}$ and $V_{17}O_{42}H_{16}$ clusters, see Table 1, and between $V_{11}O_{30}H_{16}$ and $V_{17}O_{42}H_{16}$ clusters, see Table 2). The metal centers yield charges of about +1.5 for V(5) and of +1.24 for V(6) for the one-layer clusters, and of +1.5 for V(5) and of +1.6 for V(6) for the largest two-layer cluster. This indicates that

convergence in the calculated quantities is achieved with respect to the number of layers, rather than the number of nearest neighbors. Therefore one can conclude that one-layer models cannot be used to describe accurately surface vanadium centers, especially hexacoordinated vanadium. This is due to the fact that the VO_2 crystal is rather compact. Therefore, the differences in V–O bond distances are only $\sim 0.3 \text{ \AA}$ and the influence of the bulk becomes important.

Oxygen centers are negatively charged and their nucleophilic character slightly increases with the coordination number. Triply coordinated oxygen centers O(3) have negative charges of about -0.7 , while doubly coordinated centers carry charges of

Table 1

The electronic structure (atomic charges and bond orders) for clusters modeling pentacoordinated vanadium V(5) at the (0 1 1)VO₂ surface

Atoms	One-layer cluster			Two-layer cluster	
	V ₃ O ₁₁ H ₁₀	V ₇ O ₂₃ H ₁₈	V ₁₃ O ₃₇ H ₂₂	V ₁₁ O ₃₄ H ₂₄	V ₁₇ O ₄₂ H ₁₆
Charges					
V5	0.97	1.48	1.52	1.43	1.49
O2	-0.55	-0.51	-0.51	-0.51	-0.50
O2'	-0.52	-0.50	-0.50	-0.49	-0.49
O3	-	-0.70	-0.71	-0.69	-0.71
O3'	-	-0.68	-0.69	-0.67	-0.68
Bond lengths (Å)					
Bond orders					
V ^{2.03} O ^{2.01} V	0.85/0.90	0.99/0.97	0.97/0.98	0.99/1.00	0.98/1.05
V ^{1.86} O ^{1.87} V	0.94/0.93	1.07/0.95	1.06/0.97	1.11/0.96	1.09/1.02
V ^{2.03} O ^{2.01} V V 1.76	-	0.35/0.47 0.99	0.41/0.42 0.98	0.34/0.46 1.04	0.34/0.45 1.06
V ^{1.86} O ^{1.87} V V 2.05	-	0.59/0.72 0.62	0.65/0.68 0.65	0.61/0.71 0.61	0.65/0.61 0.66
HOMO (eV)	-4.74	-5.31	-5.34	-5.92	-5.51

approximately -0.5. This means that a higher coordination number for O atoms favors the accumulation of electron charge at these centers and indicates larger ionic contributions to the V-O(3) bond in comparison with V-O(2) bonding. This may be of a particular importance in view of the reactivity of the different surface sites with respect to chemical reactions proceeding at the surface. Here, two factors should be considered, the nucleophilicity of the oxygen centers as well as strength of their bonds with respect to the surface. The increased charge at the triply coordinated oxygen sites may hint at their increased local reactivity with respect to nucleophilic attacks.

The systematic analysis of clusters of different size yields electronic properties that are converged for the V₁₇O₄₂H₁₆ cluster. Since this two-layer cluster represents both V(5) and V(6) surface sites cluster (when viewed from the top and the bottom) we limit our further discussion to this cluster only. The actual charges of vanadium [+1.5, +1.6] and oxygen [-0.5, -0.7] atoms are far from the formal charges +4 and -2 assigned, to V and O in

vanadium dioxides of VO₂ stoichiometry. This means that the calculations indicate an interatomic binding at the (0 1 1)VO₂ surface which is determined by both ionic and covalent contributions, with some distinction between doubly and triply coordinated surface oxygens. The covalent contributions to the bonds can be discussed using bond order concepts. The doubly coordinated oxygen atoms are bonded to the neighboring vanadium atoms by two single bonds. The difference (0.14–0.17 Å) in V-O(2) and V-O(2') bond distances projects only slightly into bond orders (difference about 0.1). Triply coordinated oxygen O are bonded to their vanadium atoms by one single and two very weak bonds. Here, however, the difference in bond distances is clearly visible in the bond order values. The O(3), coordinated to vanadium by two long and one shorter distance, is bonded to vanadium by two very weak and one almost single bond. The three bond orders for the other triply coordinated oxygen, O(3'), linked to its neighboring vanadium by two bonds of about 1.8 Å and one of about 2 Å distance, are about

Table 2

The electronic structure (atomic charges and bond orders) for clusters modeling hexacoordinated vanadium V(6) at the (011)VO₂ surface

Atoms	One-layer cluster			Two-layer cluster	
	V ₃ O ₁₄ H ₁₆	V ₇ O ₂₄ H ₂₀	V ₁₃ O ₄₀ H ₂₈	V ₁₁ O ₃₀ H ₁₆	V ₁₇ O ₄₂ H ₁₆
Charges					
V6	0.98	1.19	1.24	1.53	1.57
O2	−0.55	−0.52	−0.49	−0.46	−0.46
O2′	−0.53	−0.50	−0.48	−0.45	−0.45
O3	–	−0.68	−0.73	−0.67	−0.71
O3′	–	−0.67	−0.72	−0.65	−0.68
Bond lengths (Å)					
Bond orders					
V ^{2.03} O ^{2.01} V	0.91/0.92	0.83/1.11	0.89/0.97	0.94/0.98	0.95/0.99
V ^{1.86} O ^{1.87} V	0.96/0.96	1.06/0.89	0.99/0.98	1.09/0.93	1.04/0.99
V ^{2.03} O ^{2.01} V V ^{1.76}	–	0.55/0.62 0.71	0.57/0.53 0.70	0.62/0.67 0.61	0.55/0.65 0.70
V ^{1.86} O ^{1.87} V V ^{2.05}	–	0.81/0.81 0.30	0.75/0.75 0.34	0.83/0.87 0.27	0.69/0.91 0.33
HOMO (eV)	−3.63	−3.57	−4.63	−5.58	−5.51

half single bonds. Taking the sum of bond orders as a measure of surface oxygen stability, the surface oxygen sites may be ordered as O(3) < O(3′) < O(2) < O(2′), although the differences in values are quite small. The respective values indicate the mobility of surface oxygen centers to be similar with a slight preference for the triply coordinated oxygen sites.

Additional information on the electronic properties of the VO₂(011) surface may be obtained from total (DOS) and atom projected densities of states (PDOS) of the model clusters. The investigation of the partial contributions to the total density of states can also be used to identify and monitor (in the experiment) differently coordinated oxygens. The dense energetic distribution of the Kohn–Sham valence levels in the present V₁₇O₄₂ cluster allows both DOS and PDOS definitions by Gaussian broadening of the cluster levels (FWHM) where in the present calculations a broadening of 0.4 eV (full width at half maximum) is used. Fig. 5 shows DOS and PDOS curves for the energy region between −16.0 and −3.0 eV which covers the

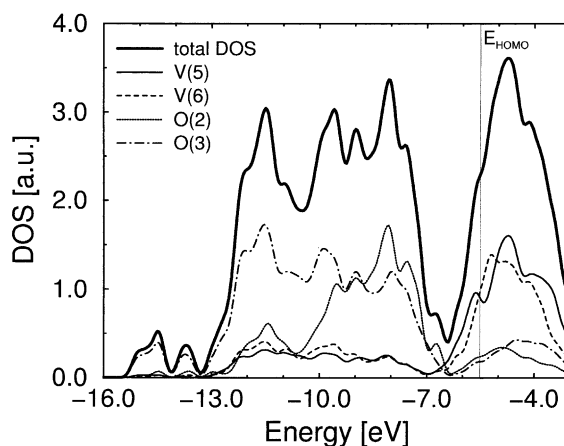


Fig. 5. Total (DOS) and atom projected (PDOS) curves for the V₁₇O₄₂H₁₆ cluster. In the plots a Gaussian broadening of 0.4 eV is applied and the HOMO energy is marked by a thin vertical line.

valence energy region up to and slightly above the highest occupied level (HOMO). The DOS of the unoccupied levels remains finite above the HOMO

reflecting the metallic character of the monoclinic $\text{VO}_2(011)$ surface. The small Peierls gap of 0.6 eV found in the experiment [44], cannot be reproduced by the calculation. This is mainly due to limitations of density functional theory discussed elsewhere [12]. In the valence energy region between -13.0 and -7.0 eV the DOS is dominated by O 2p contributions due to 2- and 3-fold coordinated surface oxygens O(2,3). Here the PDOS of the 2-fold coordinated species is peaked at -8.0 and -11.5 eV while that of O(3) is distributed over the whole energy range. This different behavior suggests different local bonding and may be used to distinguish between the two oxygen species in experiments that probe the DOS such as photoemission [45]. Fig. 5 shows further that the DOS of the energy range starting at -6.5 eV, i.e. 1 eV below the HOMO level, and extending above is characterized by contributions stemming from 5- and 6-fold coordinated surface vanadium V(5,6). While there is a small 0.4 eV shift between the two PDOS curves near the HOMO level further discrimination between the two V species seems very difficult.

4. Conclusions

The $(011)\text{VO}_2$ surface is characterized by V–O bonds of mixed ionic and covalent character. Charges for vanadium and oxygen ions are smaller than expected from their formal valence charges. Oxygen ionicity scales with the coordination numbers of the corresponding oxygen sites. The character and energetic distribution of the highest valence orbitals indicates a metallic character for the monoclinic $\text{VO}_2(011)$ surface. The valence region of the density of states is attributed to the vanadium; however, two differently coordinated surface vanadium sites, V(5) and V(6), are difficult to distinguish. Surface oxygen species are bound quite strongly to the surface and due to the difference in O(2) and O(3) electron states can be used to monitor these sites during the catalytic reaction.

The $(011)\text{VO}_2$ surface exhibits both metallic and oxygen unsaturated centers and, as a consequence, similar activity towards a potential adsorbate for

both cationic and anionic surface centers. This may explain the low sensitivity to any surface reaction. Therefore, it is not interesting as a catalyst, which is fully confirmed by the experimental observation [46]. However, it can serve as a source to provide the necessary electrons for reoxidation of the surface V–O based catalysts, as is suggested by experiment [14].

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