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Adsorption of molecular and atomic hydrogen on vacuum-cleaved $V_2O_5(0\,0\,1)$

B. Tepper [a], B. Richter [a], A.-C. Dupuis [a], H. Kuhlenbeck [a,*], C. Hucho [b], P. Schilbe [c], M.A. bin Yarmo [d], H.-J. Freund [a]

[a] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abteilung Chemische Physik, Faradayweg 4-6, 14195 Berlin, Germany*
[b] *Paul-Drude-Institut, Hausvogteiplatz 5-7, 10117 Berlin, Germany*
[c] *Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany*
[d] *Faculty of Science and Technology, School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia*

Abstract

The $(0\,0\,1)$ surface of a vacuum-cleaved V_2O_5 single crystal has been studied using high-resolution electron energy loss spectroscopy (HREELS), UV-photoelectron spectroscopy angular resolved photoemission spectra (ARUPS) and X-ray photoelectron spectroscopy (XPS). Special emphasis was put onto the interaction with molecular and atomic hydrogen and the existence of hydroxyl groups on the surface. Dosage of atomic hydrogen induces reduction of the $V_2O_5(0\,0\,1)$ surface as is obvious from the evolution of intensity near to the Fermi edge in the photoelectron spectra. Even after strong reduction no indications of OH groups could be observed in the spectra. Detailed inspection of the ARUPS and HREELS data and comparison with theory leads to the conclusion that the hydrogen induced defects on the surface are most likely missing bridging oxygen atoms whereas the terminal oxygen atoms of the vanadyl groups appear to be stable with respect to removal by atomic hydrogen. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Divanadium pentoxide V_2O_5 is a widely used industrial catalyst for a variety of chemical reactions. Oxidation of hydrocarbons and sulfur dioxide are examples. The catalytic behavior of V_2O_5 in most oxidation reactions has been discussed based on the reduction–oxidation mechanism proposed by Mars and van Krevelen, in which lattice oxygen is abstracted by the reactant gas molecule during catalytic reaction, and the catalyst is reoxidized by O_2 [1]. It is often assumed that especially vanadyl oxygen atoms take part in this process [2]. The chemical structure of the catalyst surface under reaction conditions is still under debate, but it is generally accepted that, depending on the respective reaction and the

* Corresponding author. Tel.: +49-30-8413-4222; fax: +49-30-8413-4307.
E-mail address: kuhlenbeck@fhi-berlin.mpg.de (H. Kuhlenbeck).

reaction conditions, lower oxidation states of vanadium are present at the catalyst surface and play an active role in the catalytic process [2–5]. In this work we present a detailed HREELS, UPS and XPS study on the interaction of vacuum-cleaved $V_2O_5(0\,0\,1)$ with atomic and molecular hydrogen addressing questions regarding formation of surface hydroxyl groups and hydrogen induced defect formation. For the latter topic the question, which type of oxygen atom is removed by interaction with hydrogen was in the center of interest.

Several theoretical studies on V_2O_5 (electronic structure, defects, adsorption) have been published by the group of Hermann. For an overview of the work of this group and other theoretical studies see Ref. [6] and references therein.

Due to the limited availability of V_2O_5 single crystals and since it is not yet possible to prepare well ordered V_2O_5 thin films there are only few adsorption studies on well defined single crystal surfaces (see for instance Refs. [4,7]). In other studies microcrystalline material was investigated assuming that most of the adsorbate molecules bind to $(0\,0\,1)$ surfaces of the crystallites (see for instance Refs. [8,9]).

2. Experimental

HREEL spectra were taken with a Delta 0.5 HREELS spectrometer built by VSI GmbH. The spectra presented in this paper were recorded in specular geometry ($\alpha_i = \alpha_r = 65°$) with a primary energy of 7.5 eV and an energy resolution of 2.1 meV (17 cm^{-1}) for spectra of a clean surface. After reduction of the surface by atomic hydrogen the FWHM of the elastic peak increased to values of up to 6.7 meV for strongly reduced surfaces.

The photoelectron data were taken using a VSW ARIES spectrometer with an electron analyzer rotatable in two orthogonal planes for angular resolved electron detection. A helium discharge lamp served as a source for UV radiation. The data presented here have been taken with He(II) light (40.8 eV) incident at 45° with respect to the surface normal and the analyzer was set to detect electrons emitted normal to the surface. The pass energy of the analyzer was set to 15 eV which

corresponds to a resolution of about 200 meV. Since V_2O_5 represents an insulating material which does not exhibit clearly visible intensity near to the Fermi edge a reference spectrum of the metallic sample holder was taken to determine the high energy cutoff of the spectra, needed for energy calibration.

XPS core-level spectra were recorded with light from the U49/1-PGM monochromator at the BESSY II synchrotron radiation source in Berlin. The photon energy was set to 625 eV and the energy scale was calibrated relative to the energy of the $Au\,4f_{7/2}$ core level obtained by taking a spectrum of a gold foil mounted at the back of the sample holder. The photon beam was incident at 55° relative to the sample surface normal and electrons were recorded in normal emission.

Atomic hydrogen was generated with a AS-H35 hydrogen atom doser provided by Physikalisches Büro Steinmüller GmbH, Austria. It is based on a concept published by Bischler and Bertel [10]. The atomic hydrogen doses given in the following are the doses of molecular hydrogen admitted to the atomic hydrogen source. Since the degree of dissociation is about 80% and the sample was positioned directly in front of the doser the given values may be considered approximately correct.

V_2O_5 single crystals are not commonly available; only a few groups in the world prepare them. Part of the V_2O_5 single crystals used for our studies was grown at the University of Augsburg by the group of S. Horn using the chemical transport method (for details see Ref. [11]) and another part was grown at the Paul-Drude-Institut in Berlin by zone melting [12] as part of a cooperation within the Sonderforschungsbereich 546 of the Deutsche Forschungsgemeinschaft. The crystals made by zone melting usually exhibited the better quality: it was easier to cleave them and the cleavage planes were always homogeneous which was not the case for the samples grown by chemical transport.

Typical sizes of the V_2O_5 single crystals were 10 mm along [0 1 0], 3 mm along [1 0 0] and 2 mm along [0 0 1]. They were cleaved in situ with a blade giving high quality $(0\,0\,1)$ oriented surfaces.

All spectra presented in this work have been recorded at room temperature.

3. Results and discussion

3.1. The structure of V_2O_5

The lattice of divanadium pentoxide (V_2O_5) is orthorhombic with lattice parameters $a = 11.519$ Å, $b = 3.564$ Å and $c = 4.373$ Å [13]. The structure consists of layers characterized by periodic arrangements of edge and corner sharing VO_5 pyramids sticking out at both sides of the layer. As shown in Fig. 1 there are three inequivalent types of oxygen atoms: terminal vanadyl oxygen atoms O(1) coordinated to one vanadium atom and bridging oxygen atoms O(2) and O(3) coordinated to two and three vanadium atoms, respectively. The interaction between the V_2O_5 layers is small. Therefore the crystals cleave easily along the [0 0 1] plane.

Fig. 2 exhibits a LEED pattern of V_2O_5(0 0 1). The surface is very sensitive to the LEED beam; significant degradation is obvious after a few seconds. Therefore it was not possible to obtain a background-free image. The ratio of the lengths of the two reciprocal lattice vectors b^* and a^* is about 3.2 as expected for a non-reconstructed surface.

3.2. HREELS results

V_2O_5 exhibits 39 optical phonon modes. Symmetry considerations [14] show that 15 modes are infrared active, 21 modes are Raman active and 3
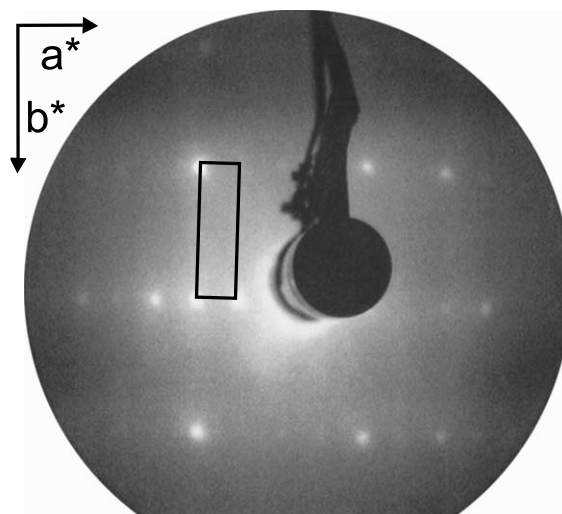

Fig. 2. LEED pattern of a freshly UHV-cleaved V_2O_5(0 0 1) surface: $E = 154$ eV.

modes are inactive. Based on the extension of dielectric theory to anisotropic materials [15], and IR-data of V_2O_5, Poelman et al. [16,17] have generated a computer simulation of a HREEL spectrum which is reproduced in Fig. 3 in comparison with a spectrum of a freshly UHV-cleaved V_2O_5(0 0 1) surface. The experimental spectrum in Fig. 3 exhibits 10 characteristic losses which can be assigned to the three different types of oxygen atoms O(1), O(2) and O(3), respectively [16,17]. Table 1 compares the energies of the phonon losses
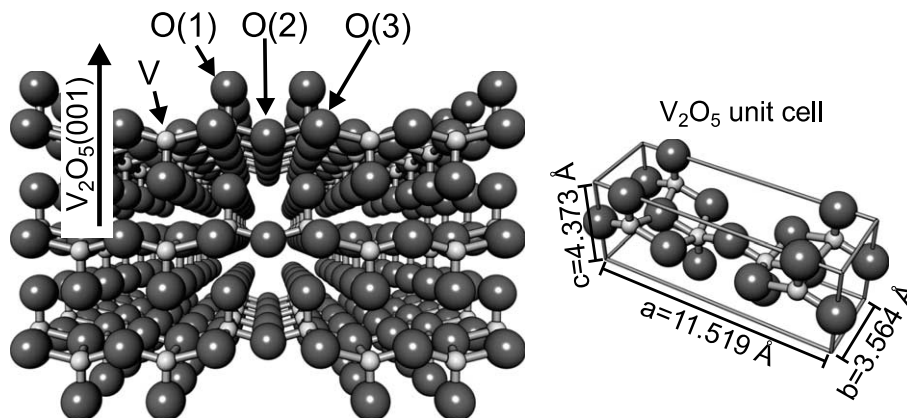

Fig. 1. Crystal structure of V_2O_5. The different types of oxygen atoms [O(1), O(2) and O(3)] are labeled.
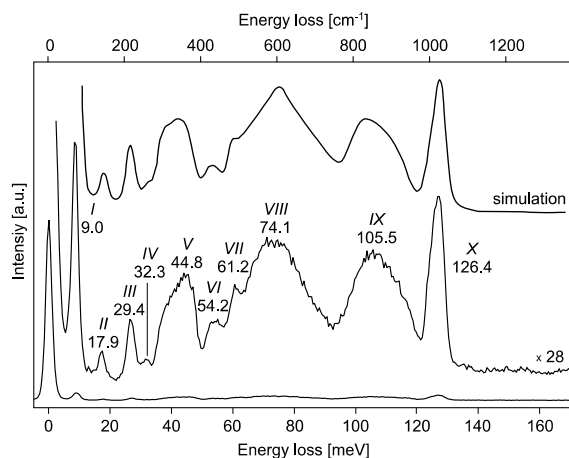
Fig. 3. Comparison of a HREEL spectrum of a freshly UHV-cleaved $V_2O_5(0\,0\,1)$ surface and a computer simulation (reproduced from Ref. [17]). The positions of the experimentally determined energy losses are indicated and the assignments are given in Table 1: $E = 7.5$ eV, FWHM = 2.1 meV, $\alpha_i = \alpha_r = 65°$, $T = 300$ K.

Fig. 4. Experimental HREEL spectra of $V_2O_5(0\,0\,1)$ after adsorption of increasing doses of molecular hydrogen: $E = 7.5$ eV, FWHM = 2.1 meV, $\alpha_i = \alpha_r = 65°$, $T = 300$ K.

Table 1
Experimental single loss energies, calculated energies [17] and assignments according to Poelman et al. [16] for the IR active phonon modes of V_2O_5

Peak no.	Calculated energy (meV)	Experimental energy (meV)	Assignment
I	9.0	8.9–9.5	Chain translation ∥ c
II	17.9	17.7	Chain translation ∥ a
III	29.4	26.3–27.9	V–O(1) deformation ∥ b
IV	32.3	32.4–32.9	V–O(3) deformation ∥ c
V	44.8	37.6–48.4	V–O(1) deformation ∥ a
VI	54.2	51.0–72.7	V–O(3) stretch + deformation ∥ a
VII	61.2	58.7–60.8	V–O(2) deformation ∥ c
VIII	74.1	62.8–104.5	V–O(3) stretch ∥ b
IX	105.5	95.2–118.9	V–O(2) stretch ∥ a
X	126.4	121–128.7	V–O(1) stretch ∥ c

in the experimental spectrum with the calculated ones [16,17]. It is obvious from this table and Fig. 3 that the agreement between theory and experiment is nearly perfect.

An important reaction step in the catalytic oxidation of hydrocarbons is the abstraction of
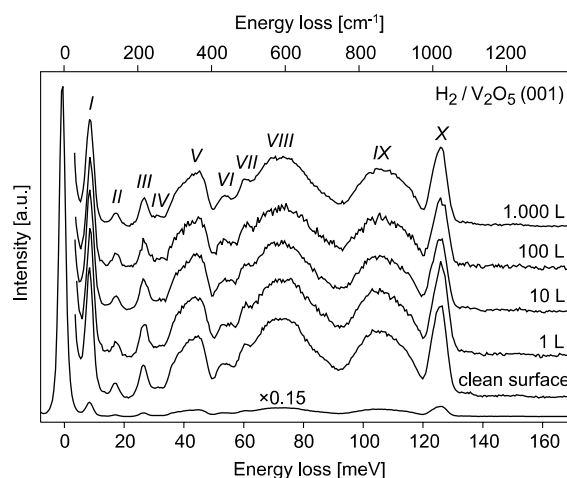
hydrogen. To learn about the interaction of V_2O_5-$(0\,0\,1)$ with hydrogen we studied the adsorption of hydrogen atoms and molecules. Fig. 4 shows spectra of $V_2O_5(0\,0\,1)$ taken after exposure to increasing amounts of molecular hydrogen at room temperature. The spectra are not significantly altered after hydrogen dosage, i.e. molecular hydrogen does not (or only very weakly) interact with the $V_2O_5(0\,0\,1)$ surface. In contrast to that, only a few Langmuirs of atomic hydrogen induce significant modifications of the loss spectra indicating a strong interaction (see Fig. 5). Details of the effect of atomic hydrogen will be discussed later.

The losses V, VIII and X, due to the vanadyl groups and the triply coordinated oxygen atoms O(3) are only little affected by atomic hydrogen. On the other hand, the loss IX, due to vibrations significantly involving the bridge-bonded oxygen atoms O(2) disappears already after small hydrogen doses. This means that atomic hydrogen affects the bridging surface oxygen atoms O(2) more strongly than the vanadyl oxygen atoms O(1) and the bridging oxygen atoms O(3). The strong modification of the spectra indicates that the surface is significantly modified upon interaction with atomic hydrogen.

The mode at 365 meV (2944 cm^{-1}) which is visible in the HREELS spectra of $V_2O_5(0\,0\,1)$ after
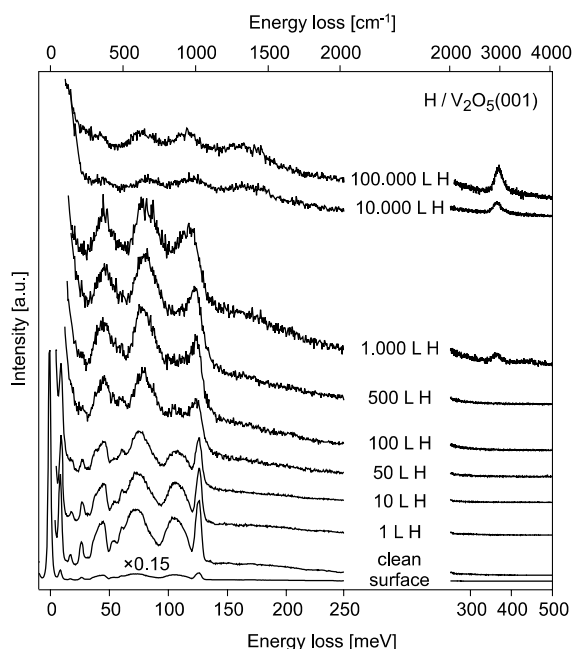
Fig. 5. Experimental HREEL spectra of $V_2O_5(0\,0\,1)$ after adsorption of increasing doses of atomic hydrogen: $E = 7.5$ eV, $\alpha_i = \alpha_r = 65°$, $T = 300$ K.
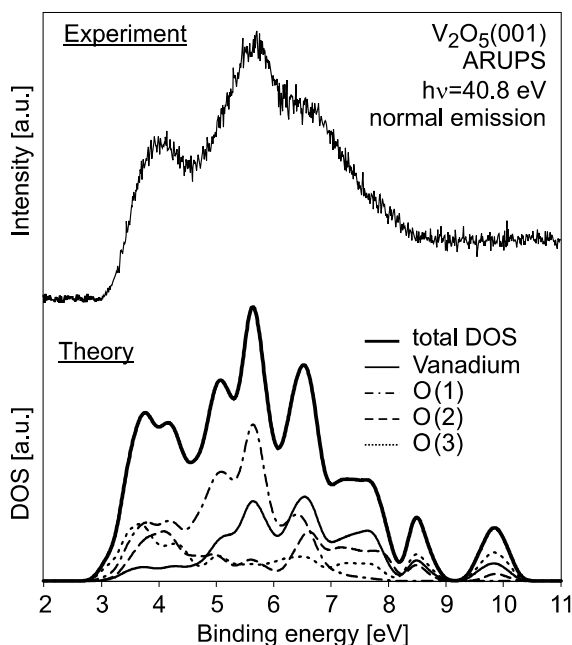

Fig. 6. Comparison of the total (DOS) and the atom projected density (PDOS) of states calculated for a $V_{16}O_{49}H_{18}$ cluster [7] with a photoelectron spectrum of a freshly UHV-cleaved $V_2O_5(0\,0\,1)$ surface recorded with He(II) light (40.8 eV) in normal emission geometry. The energy scale of the calculated spectrum has been shifted to fit to the experimental spectrum. States close to 8.5 and 10 eV in the calculated spectra are due to hydrogen atoms which were introduced to saturate the bonds of the peripheral atoms of the cluster.

hydrogen doses of at least 1000 L (see Fig. 5) is likely due to a surface contamination. In most vibrational spectra of organic compounds CH stretching modes appear in the range between 354 meV (2855 cm^{-1}) and 365 meV (2940 cm^{-1}) [18] so that one is attempted to assign the loss at 365 meV (2940 cm^{-1}) to a contamination with a compound containing CH bonds. A hydrogen dosage higher than 1000 L requires a dosing time of several minutes. It can not be excluded that CH_x compounds form at the doser (for instance at the glowing tungsten tube or at the cooling shield) during this time and contaminate the sample surface.

3.3. UPS results

Fig. 6 compares an angular resolved photoemission spectra (ARUPS) spectrum of the $V_2O_5(0\,0\,1)$ surface with density of states (DOS) and partial density of states (PDOS) curves calculated for a $V_{16}O_{49}H_{18}$ cluster discussed in detail in Ref. [7]. Obviously the shape of the experimental intensity is well reproduced by the calculated total DOS. The valence band consists of oxygen 2p states hybridized with vanadium 3d levels. Fig. 6 reveals that the most prominent peak in the experimental data is to be assigned mainly to emission from vanadyl oxygen atoms whereas the weaker intensity around 7 eV is due to a mixture of vanadium 3d, O(2) and O(3) induced intensity. The feature at about 4 eV is due to emission from all three types of oxygen atoms which contribute in about equal amounts.

Fig. 7 exhibits ARUPS data for $V_2O_5(0\,0\,1)$ exposed to different doses of molecular and atomic hydrogen, respectively. In case of adsorption of molecular hydrogen significant modifications of the spectra occur only at very high doses pointing towards a very small sticking coefficient as observed before with HREELS (see Fig. 4). Hydro-
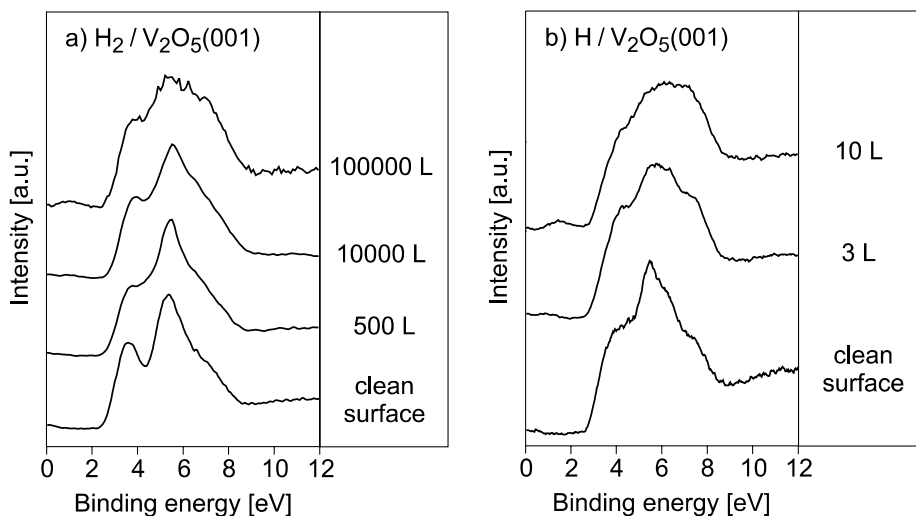
Fig. 7. ARUPS of $V_2O_5(0\,0\,1)$ for different doses of molecular (a) and atomic (b) hydrogen, respectively. The spectra have been recorded at 300 K with He(II) light ($h\nu = 40.8$ eV) in normal electron emission geometry.

gen doses in the order of 100 L require very long exposure times and it is possible that the surface modifications visible at high doses in Fig. 7a are due to atomic hydrogen produced by decomposition of molecules at the filament of the ion gauge. Adsorption of only a few Langmuirs of atomic hydrogen is sufficient to strongly alter the spectra (see Fig. 7b). The changes are more pronounced in the peripheral features at 3.5 and 7 eV than in the dominant central peak which may be viewed as another indication that the vanadyl oxygen atoms are relatively stable with respect to removal by atomic hydrogen.

Fig. 7b shows that intensity near to the Fermi level develops after dosage of atomic hydrogen. Since V_2O_5 is an isolating material with no d-electrons and a band gap of about 2.3 eV [19] there is no intensity in this energy regime expected for stoichiometric V_2O_5. With increasing amounts of atomic hydrogen the spectra become more and more similar to those of thin $VO_2(1\,1\,0)/$ $TiO_2(1\,1\,0)$ [20] and $V_2O_3(0\,0\,0\,1)/Au(1\,1\,1)$ films [21], respectively, as revealed by Fig. 8. In V_2O_3 and VO_2 the vanadium atoms possess 3d electrons which give rise to the intensity near to about 1 eV binding energy. From Fig. 8 the conclusion may be drawn that atomic hydrogen reduces the $V_2O_5(0\,0\,1)$ surface so that its electronic structure
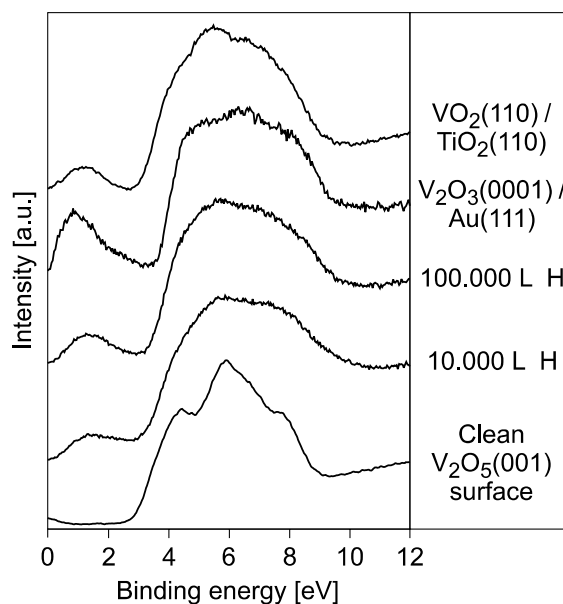

Fig. 8. ARUPS of $V_2O_5(0\,0\,1)$ for high doses of atomic hydrogen and thin films of $VO_2(1\,1\,0)/TiO_2(1\,1\,0)$ [20] and $V_2O_3(0\,0\,0\,1)/Au(1\,1\,1)$ [21] respectively. The spectra have been recorded at 300 K with He(II) light ($h\nu = 40.8$ eV) in normal electron emission geometry.

becomes similar to that of VO_2. The comparison with V_2O_3 is less favorable since the V 3d peak of this oxide is too intense.

3.4. XPS results

The XPS spectrum of the O 1s and V 2p core levels of UHV-cleaved $V_2O_5(0\,0\,1)$ is shown in Fig. 9. The measured binding energies for the V $2p_{3/2}$, V $2p_{1/2}$ and O 1s levels are 517.4, 524.8 and 530.0 eV, respectively, which is in reasonable agreement with literature data [22].

The V 2p XPS peaks become significantly asymmetric after adsorption of atomic hydrogen. We have fitted the V $2p_{3/2}$ state as shown in the inset in Fig. 9. Comparison with literature data [22] reveals that the peak at 516.0 eV is to be assigned to V^{4+} or V^{3+} as found in VO_2 or V_2O_3. The feature at 517.2 eV is due to V_2O_5. In the case of the O 1s state at 530.1 eV only a small shift to higher energy is induced by atomic hydrogen which is in line with literature data [22]. These show that the
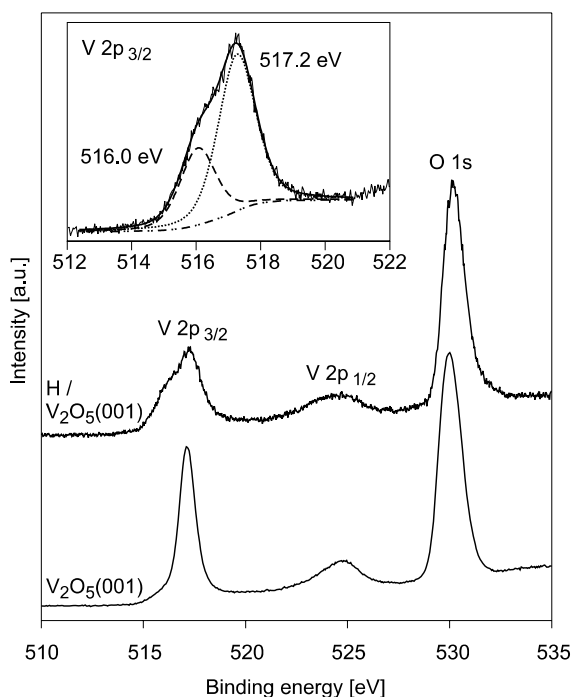
O 1s binding energy depends only weakly on the vanadium oxidation state.

3.5. Formation of OH groups

Contrary to expectations, after dosage of atomic hydrogen none of the spectra of V_2O_5 showed indications for the formation of OH groups. In the ARUPS spectra OH groups should induce structures in the region around 7 and 11 eV, as observed for NiO and Cr_2O_3, for example in Ref. [23].

However, no intensity at these energies is observed in the ARUPS spectra indicating that no hydroxyl groups have been formed. Similar conclusions may be drawn from the HREELS data (see Fig. 5) where hydroxyl groups should lead to an energy loss near to about 450 meV (3629 cm^{-1}). Contrary to $V_2O_5(0\,0\,1)$, both $VO_2(1\,1\,0)/$ $TiO_2(1\,1\,0)$ and $V_2O_3(0\,0\,0\,1)/Au(1\,1\,1)$ exhibit stable OH groups on the surface as revealed by Fig. 10. As shown before, reduction of the $V_2O_5(0\,0\,1)$ surface with high doses of atomic hydrogen leads to a surface with an electronic structure similar to that of VO_2 (see Fig. 8). However, this is not necessarily also true for the geometric structure. It may be assumed that after adsorption of atomic hydrogen *stable* OH groups do not form on $V_2O_5(0\,0\,1)$ for geometric reasons. However, there must be OH groups on the surface for short times since hydrogen dosage reduces the surface. These OH groups are possibly mobile enough to combine, forming water which may then desorb.

The vibrational spectrum of $V_2O_5(0\,0\,1)$ observed after dosage of more than 1000 L of atomic hydrogen is characterized by broad losses (see Fig. 11). Comparison with spectra of $VO_2(1\,1\,0)$ and $VO_2O_3(0\,0\,0\,1)$ (Fig. 11) reveals that these losses are found at energies where $VO_2(0\,0\,1)$ also exhibits losses. The comparison with $V_2O_3(0\,0\,0\,1)$ is less favorable. This observation is in line with the conclusions that has been drawn from the ARUPS and XPS data presented in Figs. 8 and 9, respectively.

The losses F and G in Fig. 11 are at energies typical for OH vibrations. Since $VO_2(1\,1\,0)$ and $V_2O_3(0\,0\,0\,1)$ both tend to form hydroxyl groups on their surfaces (see Fig. 10) this observation is
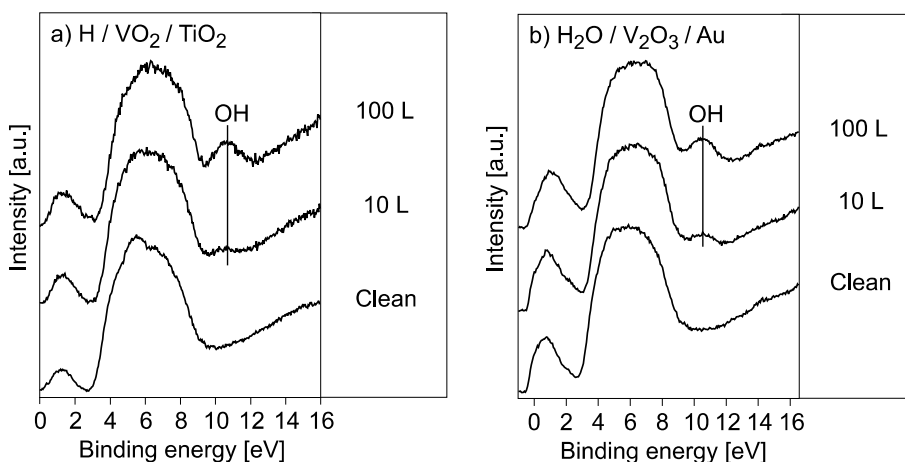

Fig. 9. XPS spectrum of the O 1s and V 2p core levels for UHV-cleaved $V_2O_5(0\,0\,1)$ before and after exposure to atomic hydrogen. In this case the hydrogen dose can not be given since the sample was mounted about 8 cm away from the doser: $hv = 625$ eV, $T = 300$ K.

Fig. 10. Angular resolved photoemission spectra of (a) VO$_2$(1 1 0)/TiO$_2$(1 1 0) dosed with atomic hydrogen [20] and (b) V$_2$O$_3$(0 0 0 1)/Au(1 1 1) exposed to water [21]. The spectra have been recorded at 300 K with He(II) light ($hv = 40.8$ eV) in normal electron emission geometry.
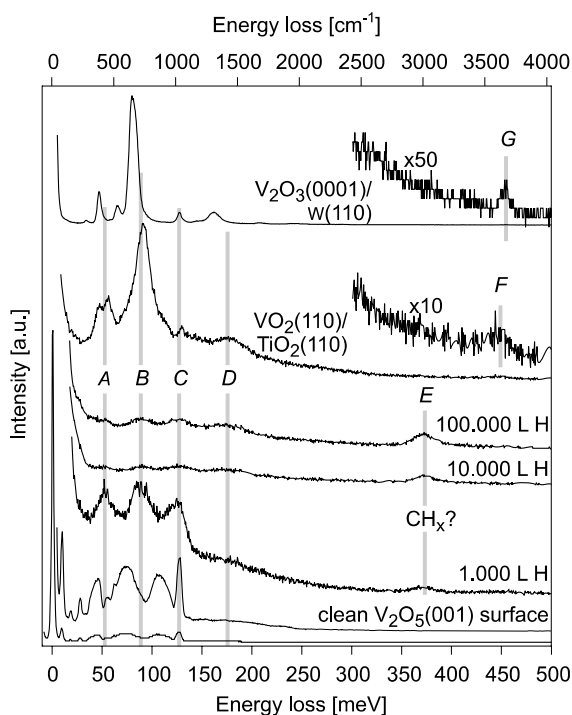

Fig. 11. HREEL spectra of V$_2$O$_5$(0 0 1) after admission of high doses of atomic hydrogen in comparison with loss spectra of VO$_2$(1 1 0)/TiO$_2$ [20] and V$_2$O$_3$(0 0 0 1)/W(1 1 0) [21]: $E = 7.5$ eV, $\alpha_i = \alpha_r = 65°$, $T = 300$ K.

not unexpected. In both cases the energies are near to 450 meV which gives additional support to the

assumption that the loss at 365 meV in Fig. 11 is not due to OH groups.

One interesting point to note is that the loss C is found in all spectra in Fig. 11. In the case of V$_2$O$_5$(0 0 1) this loss is due to the O–V vibration of vanadyl groups (see Table 1). From Fig. 11 it may be concluded that vanadyl groups are found also on VO$_2$(1 1 0) and V$_2$O$_3$(0 0 0 1). For the case of V$_2$O$_3$(0 0 0 1)/Pd(1 1 1) the existence of vanadyl groups at the surface has been verified by Netzer and co-workers [24] and for V$_2$O$_3$ clusters deposited on Al$_2$O$_3$/NiAl(1 1 0) V–O vibrations of vanadyl groups have been observed with IR spectroscopy by Bäumer and co-workers [25]. Vanadyl groups are not a part of the corundum structure of V$_2$O$_3$; their existence is likely confined to the surface. For the (0 0 0 1) surface of Cr$_2$O$_3$ which is isostructural to V$_2$O$_3$ similar results have been obtained before. The interaction of the surface with oxygen leads to the formation of chromyl groups as revealed with vibrational spectroscopy [26].

4. Conclusions

We have studied the interaction of atomic and molecular hydrogen with V$_2$O$_5$(0 0 1). Molecular hydrogen interacts only very weakly with

$V_2O_5(0\,0\,1)$ whereas atomic hydrogen strongly reduces the surface. In contrast to observations made for $V_2O_3(0\,0\,0\,1)$/Au(1 1 1), $V_2O_3(0\,0\,0\,1)$/ W(1 1 0), and $VO_2(1\,1\,0)$/TiO$_2$(1 1 0) no surface hydroxylation could be detected even after interaction with atomic hydrogen, although the electronic structure of strongly reduced $V_2O_5(0\,0\,1)$ is similar to that of VO_2. Geometric reasons may be responsible for this observation. However, since $V_2O_5(0\,0\,1)$ is strongly reduced after dosage with atomic hydrogen there must be an interaction with hydrogen atoms. It may be assumed that mobile OH groups form which combine to form water which desorbs from the surface.

As indicated by HREELS and ARUPS data the reduction of the $V_2O_5(0\,0\,1)$ surface by atomic hydrogen occurs most likely mainly via removal of the bridging oxygen atoms O(2) whereas the vanadyl oxygen atoms O(1) and the bridging oxygen atoms O(3) are more stable with respect to removal by atomic hydrogen.

Acknowledgements

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