Water adsorption on polycrystalline vanadium from ultra-high vacuum to ambient relative humidity

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ABSTRACT

We have studied the reaction of water vapor with a polycrystalline vanadium surface using ambient pressure X-ray photoelectron spectroscopy (AP-XPS) which allows the investigation of the chemical composition of the vanadium/water vapor interface at $p(H_2O)$ in the Torr range. Water dissociation on the vanadium surface was studied under isobaric conditions at $p(H_2O)$ ranging from 0.01 to 0.50 Torr and temperatures from 625 K to 260 K, i.e. up to a relative humidity (RH) of ~15%. Water vapor exposure leads to oxidation and hydroxylation of the vanadium foil already at a pressure of 1×10^{-6} Torr at 300 K (RH ~ 4×10^{-6}%). The vanadium oxide layer on the surface has a stoichiometry of V_2O_3. Initial adsorption of molecular water on the surface is observed at RH > 0.001%. Above a RH of 0.5% the amount of adsorbed water increases markedly. Experiments at increasing temperatures show that the water adsorption process is reversible. Depth profile measurements show a thickness for the vanadium oxide layer of 3–5 mono layers (ML) and for vanadium hydroxide of 1–1.5 ML over the whole RH range in the isobar experiments. The thickness of the adsorbed water layer was found to be in the sub-ML range for the investigated RH's.

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1. Introduction

The interaction of water vapor with solid surfaces at ambient conditions of temperature and relative humidity plays a major role in technological applications and in the environment and is thus a highly interdisciplinary field. Hitherto research has focused on the role of interfacial water in heterogeneous catalysis [1–3], atmospheric chemistry [4,5], environmental science [6], corrosion chemistry [7] and electrochemistry [8,9]. The mechanism and kinetics of surface chemical processes are strongly influenced by the presence of adsorbed water [10,11]. Water can be a participant or product in surface chemical reactions, as in the water gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) or it can be a spectator and still influence the reaction through blocking of active sites or hindering the adsorption of reactants. On the other hand, trace amounts of H_2O can promote CO oxidation on Pt(111) [12] and Au nanoparticles supported on TiO_2 [13,14]. Most surfaces, in particular the polar ones, are covered by a water layer with thicknesses from a few Å (aerosol particles in troposphere) to infinite thickness (particles in solution) under ambient relative humidities [15–17]. Despite its importance the growth mechanism of water and water layers on different

materials (metallic, mineral, oxide) is still not fully understood for all surfaces.

The interaction of water with solid surfaces has been intensively studied by using surface science techniques in ultrahigh vacuum (UHV) and at low temperatures. These studies provide detailed information on the water/solid interface at a molecular level [18–20]. Most processes of interest in real systems take place at elevated temperatures and at ambient or even higher pressures, as in heterogeneous catalysis. The fundamental question is if the information that is gained under UHV and low temperatures can be extrapolated to realistic conditions. The structure and chemical composition of the surface in equilibrium with gases at ambient pressure can be different from those in UHV. Furthermore, chemical reactions can be kinetically hindered at low temperatures. This is often referred to as the "pressure gap". In order to close this gap, surface chemical reactions – including those involving water – have to be investigated in situ at as close to realistic operating conditions as possible.

Synchrotron based in situ ambient pressure XPS (AP-XPS) is an excellent experimental tool for water adsorption studies on surfaces at ambient relative humidities since it allows the investigation of surfaces at water vapor pressures in the Torr range (equilibrium water vapor pressure at 273 K is 4.6 Torr) and up to a RH of 100% [21]. Furthermore it provides information on the elemental composition at the sample surface as well as on the local chemical environment (e.g., oxidation

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states and functional groups) [22]. Recently, AP-XPS has been used to investigate the interaction of water with Cu metal [23] and metal oxide surfaces, including α-Fe$_2$O$_3$(0001) [24], Fe$_3$O$_4$(001) [25], MgO(100)/Ag(100) [26], Cu$_2$O [27], Al$_2$O$_3$ [27], TiO$_2$ [15] and SiO$_2$ [28]. Here we discuss the interaction of water vapor with a polycrystalline vanadium surface.

Vanadium is used in a wide range of applications. Aside from steel production, vanadium metal is used as a coating material, an alloy component in functional materials [29] and it is also a promising alternative to more costly metals (such as Pd) in H$_2$ purification processes [30]. Vanadium oxides are part of electrical and optical switching devices, light detectors, sensors and in heterogeneous catalysis. The high variety of oxidation states of vanadium (V^0–V^{5+}) make it suitable for numerous catalytic reactions [31,32].

Extended research has focused on the properties of vanadium oxide, as described in the review of Surnev et al. [33]. There is, however, not much information yet on the interaction of vanadium metal with water vapor, although this is highly relevant for hydrogen purification processes, including vanadium membranes, and for catalytic reactions. Jaeger et al. [34] studied the chemisorption of water on vanadium clusters by infrared photodissociation (IR-PD) spectroscopy. On the basis of their measurements they postulated that on the V$^+$-clusters (3 to 18 atoms) water is mainly adsorbed as intact molecule; it could not be excluded, however, that some dissociative chemisorption of water is present on the clusters because hydroxyl groups would not exhibit any bending mode resonance in IR-PD [34].

Here we report on the interaction of water vapor with a polycrystalline vanadium foil, which we have studied using AP-XPS by measuring uptake and desorption isobars at water pressures of 0.05, 0.10, 0.25 and 0.50 Torr. The quantitative analysis of the peak areas due to adsorbed water molecules, hydroxide groups and vanadium oxide provides information on the degree of oxidation and hydroxylation of the vanadium surface as well as the thickness of the adsorbed water layer as a function of RH. We show that hydroxylation occurs at RH < 10^{-6}%, while molecular water is already present at RH as low as 10^{-3}%. These results imply that the vanadium surface is covered by a significant amount of hydroxyl groups and molecular water molecules under most realistic operating conditions, which need to be taken into account in models of the heterogeneous surface chemistry of vanadium in catalytic reactions.

2. Materials and methods

The experiments were performed at the Molecular Environmental Science beamline (11.0.2) at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory [21], using the ambient pressure X-ray photoelectron spectrometer endstation [35]. AP-XPS is based on a differentially-pumped electrostatic lens system, which minimizes the path length of electrons through the high-pressure region and thus scattering of electrons by gas molecules, as well as maintains high vacuum conditions in the electron energy analyzer [21,36].

Polycrystalline vanadium foil (Alfa Aesar, 99.5% purity, 0.15 mm thickness) was cleaned prior to the experiments by several sputter-anneal cycles (10^{-5} Torr of Ar, 1.5 keV, 4 mA) followed by annealing to 1200 K for 2 min. The cleaning progress was monitored by XPS. All impurities could be removed except for small traces of oxygen (less than ~0.15 ML equivalent, chamber base pressure was ~8 × 10^{-10} Torr). The high reactivity of vanadium towards oxygen and water vapor in the residual gas makes the preparation of oxygen-free surfaces extremely difficult. The required equipment for the preparation of oxygen-free vanadium, a titanium sublimation pump and a cooling trap held at liquid nitrogen temperature as it is described in the literature [37], is not compatible with the experimental setup used in the present investigations.

After cleaning, the vanadium foil was transferred from the preparation chamber to the spectroscopy chamber for XPS analysis of the initial

state of the foil prior to water vapor exposure. XPS data were collected for V 2p, O 1s and C 1s core levels at a kinetic energy (KE) of ~210 eV with incident photon energies of 720 eV, 735 eV and 490 eV, respectively. For the depth profiling the O 1s and V 2p spectra were taken in sequence with kinetic energies between 115 eV and 715 eV in 100 eV increments. All binding energies were referenced to the V Fermi edge, which was measured after every change of the incident photon energy.

Water vapor from HPLC grade water was introduced into the measurement chamber through a precision leak valve. Prior to the experiments the water was purified in multiple freeze–pump–thaw cycles followed by direct pumping on the water source at room temperature. The relative humidity is defined by RH = 100(p/p_0), where p is the water vapor pressure in the spectroscopy chamber and p_0 the equilibrium water vapor pressure (calculated from Eq. 2.5 of Wagner and Pruss [38]) with respect to the sample temperature [26].

For the measurement of the different isobars (0.05, 0.1, 0.25 and 0.5 Torr) the sample was first heated to ~630 K and spectra of the nominally clean surface were recorded. Subsequently, water vapor was introduced at this elevated sample temperature and then the sample was cooled slowly to as low as 260 K at constant water vapor pressure (maximum deviation 5%) while simultaneously recording O 1s, C 1s and V 2p XPS spectra (for more details see supporting information). To investigate the desorption of water from the surface the sample was heated after the 0.25 and 0.5 Torr uptake isobars. The experimental results of the four isobar measurements are displayed versus RH to make them comparable to each other. It has to be mentioned here that for the calculation of RH a simplified model was used were sample surface and gas phase are in equilibrium although they might vary in temperature (relevant at high temperature differences between gas and sample). In the supporting information it is explained how to calculate the RH's in a more accurate way (with respect to the different temperature between sample and gas phase), although for our results there is only very small difference between both medoths.

The XPS spectra were analyzed using the commercial software package CasaXPS 2.3.16 PR 1.6. The integrated V 2p and O 1s peak intensities were determined after Shirley background subtraction. For C 1s peaks a linear background was subtracted. All peaks were fitted with Gaussian–Lorentzian (G–L) shapes. As a reference for the peak fitting parameters the works of Biesinger et al. [39] and Siversmit et al. [31] were used. For the V 2p metal peak a G–L mix of 0.62 and an asymmetry of 0.9 was used. The spin-orbit splitting for V 2p was kept constant at 7.62 eV [40]. The peak positions, full width at half-maximum (FWHM) and intensities for all peaks were left unconstrained except for the O 1s peak of the oxygen impurities, which were calculated from the C 1s signal, and the O 1s peak of adsorbed water below RH of ~0.01%, where the FWHM was set to 1.67 eV and the position was constrained to ≥ 532.75 eV. These values were determined from the peak parameters obtained from unconstrained fits at high RH.

For the calculation of the O 1s peak intensity due to carbonaceous impurities on the surface the C 1s peak areas were utilized. According to the compilation of C 1s binding energies by Briggs and Beamson [41] the binding energy of the adsorbed carbon species is consistent with an acid group (~288.9 eV). From the integrated C 1s peak area of the acid group-related peak, the corresponding O 1s peak area was calculated using an experimentally determined O/C sensitivity factor from gas phase CO$_2$ measurements using the same spectrometer/beamline settings. The peak area for the O-impurity (2 peaks, one each for C=O and C–OH in the acid group) was set to the corresponding calculated values, with the FWHM held between 1.9 and 2.1 eV and the position constrained to 532.15–532.20 eV and ≥ 533.5 eV. During the isobar experiments the total amount of carbon impurities remained nearly the same with typical values of ~10% ML equivalent.

Care was taken to avoid electron or photon induced reactions at the sample surface, especially hydroxylation. This effect has been reported in earlier XPS studies [26,42]. We have observed that the vanadium-water system is relatively insensitive to beam-induced effects. To