

Model reaction studies on vanadium oxide nanostructures on Pd(111)

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Deuterium desorption and reaction between deuterium and oxygen to water has been studied on ultrathin vanadium oxide structures prepared on Pd(111). The palladium sample was part of a permeation source, thus enabling the supply of atomic deuterium to the sample surface via the bulk. Different vanadium oxide films have been prepared by e-beam evaporation in UHV under oxygen atmosphere. The structure of these films was determined using low energy electron diffraction and scanning tunneling microscopy. The mean translational energy of the desorption and reaction products has been measured with a time-of-flight spectrometer. The most stable phases for monolayer and submonolayer VO_x are particular surface- V_2O_3 and VO phases at 523 and 700 K, respectively. Thicker films grow in the form of bulk V_2O_3 . The mean translational energy of the desorbing deuterium species corresponds in all cases to the thermalized value. Apparent deviations from this energy distribution could be attributed to different adsorption/desorption and/or accommodation behaviors of molecular deuterium from the gas phase on the individual vanadium oxide films. The water reaction product shows a slightly hyperthermal mean translational energy, suggesting that higher energetic permeating deuterium contributes with higher probability to the water formation. © 2006 American Institute of Physics. [DOI: [10.1063/1.2336770](https://doi.org/10.1063/1.2336770)]

I. INTRODUCTION

Many modern technologies take advantage of the specific physical and chemical properties of nanostructured surfaces. In particular, the catalytic activity of surfaces depends strongly on the chemical composition and the atomic scale structure of the surface. In this context ultrathin oxide films on metal supports have attracted considerable interest, because they represent a model system of an “inverse catalyst.” Vanadium oxide nanostructures in the monolayer regime have recently been studied extensively because they form a variety of interesting nanostructures with varying oxidation states.^{1–7} For the model systems $\text{VO}_x/\text{Pd}(111)$ and $\text{VO}_x/\text{Rh}(111)$ a number of experimental studies using low energy electron diffraction (LEED), scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), near-edge x-ray-absorption fine structure, and high-resolution electron-energy-loss spectroscopy (HREELS) have been performed to reveal the electronic and geometric structures of the individual oxides. Density functional theory (DFT) calculations have been carried out in this context and a quite comprehensive understanding of the oxide structures is available.^{5,6}

Evaporation of 0.5 ML vanadium on a Pd(111) surface at 523 K under oxygen pressure, typically 2×10^{-7} mbar, leads to a number of surface oxides with structures that are quite

different from that of bulk vanadium oxides. The most frequently observed surface oxide shows a 2×2 honeycomb structure. This structure has been identified by DFT calculations as a surface vanadium oxide (*s*- V_2O_3) phase and consists of a layer of two V atoms per unit cell located in three-fold palladium hollow sites and three oxygen atoms above V–V bridge sites.⁵ Exposing this surface to further oxygen changes the LEED pattern to a 4×4 structure. The structure of this phase has also been clarified by STM and DFT calculations and can be described by a surface oxide with V_5O_{14} stoichiometry. In this case the oxide layer is oxygen terminated at both the metal interface and the oxide surface and contains V atoms in tetrahedral O coordination. This layer is quite unstable and can easily be reduced to the so-called zigzag structure, as observed with STM. From DFT calculations a structure model for the zigzag phase is derived which contains V_6O_{14} units.⁴ Further reduction by hydrogen yields again the stable 2×2 *s*- V_2O_3 phase. In the case of higher vanadium coverage (1 ML) other vanadium oxide surfaces can be produced. The observed “flower LEED pattern” can be ascribed to a structure of rotational domains of rectangular unit cells and the formal stoichiometry of this phase is VO_2 .³ In addition, also a hexagonal oxide phase with formal VO_2 stoichiometry has been observed in the 1 ML range. For thicker oxide films (5 ML vanadium) a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern is found which can be described as being due to the (0001) face of the corundum V_2O_3 bulk phase.³ The reason for this LEED pattern is that the lattice mismatch between the V_2O_3 bulk lattice and the $\sqrt{3}$ direction of Pd(111) is only

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3.7%. The $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern of the vanadium oxide is therefore a pseudosuperstructure of the Pd(111) surface.

In this work we investigate the reactions of V oxide/Pd inverse catalyst surfaces by focusing on specific model reactions taking place on various surface vanadium oxides on Pd(111) and we explore the stability of these ultrathin oxide films under reaction conditions. In particular, we present experimental data on the desorption of deuterium and the reaction of deuterium with oxygen to form water. For these studies we use a Pd(111) sample which is part of a permeation source, that allows the supply of deuterium (or hydrogen) atoms by permeation from the bulk phase to the surface. This possibility opens new reaction channels to take place and both the reaction kinetics (reaction rates) as well as the reaction dynamics (energy distribution of the reaction products) may differ from those when deuterium (hydrogen) is supplied in the conventional way from the gas phase.^{8,9} Studies of this reaction type are relevant for heterogeneous catalysis, hydrogen storage, and solid fuel cell technology. The main emphasis of this work is to study the translational energy distribution of desorbing deuterium and of the reaction product water as a function of different vanadium oxide structures on Pd(111), and to analyze the stability of these oxides under reaction conditions. The energy distribution has been investigated with a time-of-flight spectrometer and the VO_x structures under reaction conditions have been verified by LEED. In addition, STM and LEED investigations on similarly prepared vanadium oxide films on a separate Pd(111) crystal have been performed to get a more complete picture of the real surface structures being involved.

II. EXPERIMENT

The reaction experiments were carried out in an ultra-high vacuum (UHV) chamber with a base pressure of 10^{-10} mbar, equipped with a LEED optics, an Auger electron spectrometer (AES), a multiplexed quadrupole mass spectrometer (QMS), and a time-of-flight (TOF) spectrometer. An extractor ion gauge and the QMS, calibrated with the help of a spinning rotor gauge, allowed the quantitative partial pressure determination in the vacuum system. A calibrated standard sample (tungsten filament) for thermal desorption allowed the quantitative measurement of deuterium desorption rates, as well as the determination of the effective pumping speed in the vacuum chamber.¹⁰ Thus, quantitative desorption and reaction rate measurements were possible. The time-of-flight spectrometer was used to determine the translational energy distribution of desorbing products, such as deuterium and water. The TOF spectrometer comprises two differentially pumped UHV chambers, housing the chopper motor and the QMS detector, respectively. A detailed description of the TOF spectrometer can be found elsewhere.¹¹ The STM measurements have been carried out in a second UHV system, at the University of Graz, also described elsewhere.²

The Pd(111) sample was part of a permeation source, which allowed to study the deuterium or hydrogen desorption and water reaction in a continuous way. The high purity palladium disk (10 mm in diameter, 1 mm thickness) was

vacuum soldered with gold onto a high purity nickel cylinder. This cylinder was soldered onto a stainless steel disk, which in turn was welded to a stainless steel tube for gas inlet. The whole assembly was tightly covered by two concentric ceramic tubes containing a coil of molybdenum wire for resistive heating up to 1000 K. Several layers of tantalum foil were wrapped around the outer ceramics for radiation shielding. A NiCr–Ni thermocouple for temperature measurements was spot welded to the rim of the sample. The permeation source was attached to a LN_2 cooled sample holder which allowed the positioning of the sample in front of all necessary analytical devices.⁸ A continuous permeation/desorption flux of deuterium could be achieved with this device by applying a proper backpressure (typically 500–1500 mbars) and a convenient choice of the palladium sample temperature (typically 523–700 K). For pressure measurement in the gas inlet system of the permeation source a piezoelectric membrane gauge was applied. A Knudsen cell, used for calibration of the TOF spectrometer, was also mounted on the manipulator.

The Pd(111) surface was cleaned prior to the deposition of vanadium oxide by 600 eV argon ion sputtering at 300 K, followed by annealing at 900 K. The cleanliness was checked by AES and LEED. Vanadium oxide was prepared by electron beam evaporation of vanadium onto the Pd sample at 523 K in a background oxygen atmosphere of 2×10^{-7} mbar. The vanadium flux was measured by a quartz microbalance. The vanadium oxide layer is characterized by the amount of vanadium on the surface, which is given in monolayer equivalents (MLE). 1 MLE of vanadium oxide on the Pd(111) surface therefore is equivalent to 1.52×10^{15} V atoms/cm².

The TOF spectra have been obtained by using a chopper frequency of 200 Hz (yielding a pulse frequency of 400 Hz due to the double slit chopper) for water and a chopper frequency of 400 Hz (800 Hz pulse frequency) for deuterium. The time delay and the slit opening gate function (which are needed to obtain the fit temperature of the Maxwellians) were obtained from calibration with a Knudsen beam. For data evaluation it has been taken into account that the mass spectrometer is a density detector, which means that the measured signal is indirectly proportional to the velocity of the molecules. More details on the data acquisition and the fit procedures can be found elsewhere.¹¹

III. RESULTS

A. Stability of vanadium oxide on Pd(111)

The crucial question in the context of reaction studies on modified or nanostructured surfaces concerns the real structure of the surface layer under reaction conditions. In this work we have used LEED to follow the structure during reaction and we have compared the corresponding LEED patterns with those obtained at room temperature under vacuum conditions. We have studied the stability of vanadium oxides for 0.3, 1, and 5 MLE, respectively, for different temperatures and different reaction conditions:

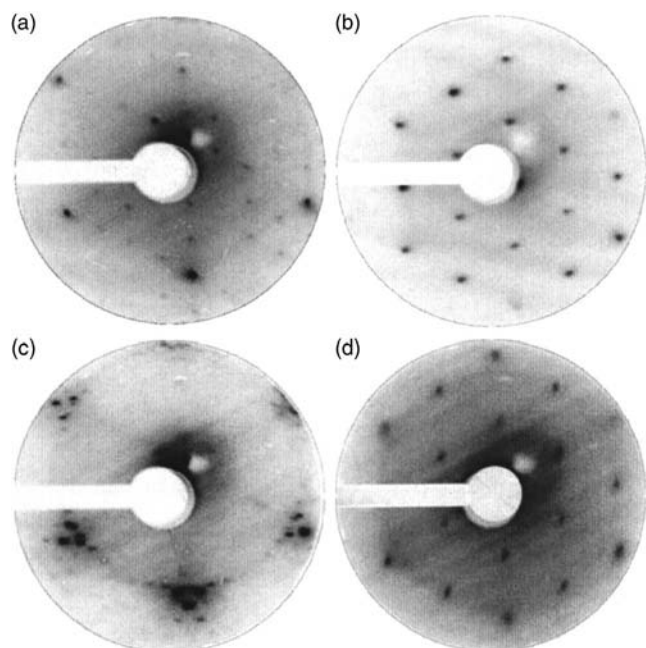


FIG. 1. LEED patterns for different 0.3 MLE VO_x structures on Pd(111): (a) after preparation at 523 K, 4×4 structure, $E=67$ eV; (b) during reaction of deuterium with oxygen at 523 K, 2×2 structure, $E=60$ eV; (c) during deuterium desorption at 700 K, VO structure, $E=56$ eV; (d) during reaction of deuterium with oxygen at 700 K, 2×2 structure, $E=64$ eV.

(a) permeation/desorption of pure deuterium yielding a typical D_2 pressure of 8×10^{-7} mbar and (b) permeation of deuterium and reaction with impinging oxygen (typically 1×10^{-6} mbar) to form water.

1. 0.3 MLE vanadium oxide

After the preparation of 0.3 MLE vanadium oxide at $T=523$ K in an oxygen atmosphere of 2×10^{-7} mbar we observed a 4×4 LEED pattern [Fig. 1(a)]. This pattern is very unstable and changes within a few minutes to a 2×2 structure. This is due to the fact that in our chamber the hydrogen and/or deuterium residual partial pressure is rather high. The 4×4 structure has been recently described as a rather open network structure where the surface unit cell consists of 5 V atoms and 14 O atoms, forming a honeycomb-like arrangement. A high-resolution STM image of the 4×4 structure is shown in Fig. 2(a). The 4×4 phase reduces easily by hydrogen.^{3,5} The stable structure which is quite resistant to hydrogen at 523 K is the 2×2 structure [Fig. 1(b)], which has also been described in detail in a previous paper;² see Fig. 2(b) for a STM image. In this case a V_2O_3 surface oxide is formed that also exhibits a honeycomb-like structure. Since at a vanadium coverage of 0.3 MLE the $s\text{-V}_2\text{O}_3$ layer covers only about 60% of the surface one is confronted with the coexistence of well ordered 2×2 phases and bare Pd(111) areas, as verified by STM measurements.^{3,4} Such a surface layer is particularly interesting for reaction investigations because one could expect a special influence of the island borders on the reaction. The 2×2 structure remains stable for deuterium permeation/desorption at 523 K for extended time (many hours) at a D_2 partial pressure of 8×10^{-7} mbar during permeation. This pressure corresponds

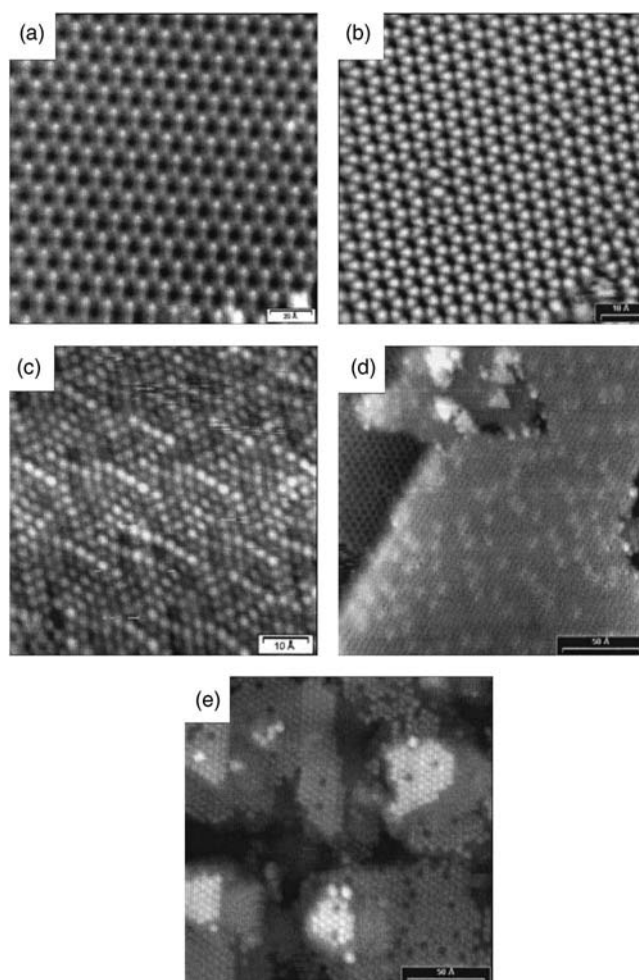


FIG. 2. STM images of various VO_x structures on Pd(111): (a) 4×4 V_5O_{14} ($160 \times 160 \text{ \AA}^2$, $U=2.0$ V, $I=0.1$ nA); (b) 2×2 $s\text{-V}_2\text{O}_3$ ($78 \times 78 \text{ \AA}^2$, $U=0.04$ V, $I=1.0$ nA); (c) “wagon-wheel” VO ($70 \times 70 \text{ \AA}^2$, $U=0.1$ V, $I=1.0$ nA); (d) rectangular VO_2 ($200 \times 200 \text{ \AA}^2$, $U=0.25$ V, $I=0.5$ nA); (e) bulk V_2O_3 (0001) ($200 \times 200 \text{ \AA}^2$, $U=-0.3$ V, $I=0.1$ nA).

to a deuterium desorption flux of about $6 \times 10^{15} \text{ D}_2/\text{cm}^2 \text{ s}$ (at a pumping speed of 140 l/s, effective surface area of 0.5 cm^2). After the oxygen partial pressure in the chamber is increased to 1×10^{-6} mbar (corresponding to an impingement rate of $2.7 \times 10^{14} \text{ O}_2/\text{cm}^2 \text{ s}$), water is formed on the vanadium oxide covered Pd(111) surface which desorbs immediately at this temperature. As the amount of permeating/desorbing deuterium is much larger than the amount of impinging oxygen, still a considerable amount of permeating deuterium desorbs associatively in the form of D_2 , in addition to the formation of water with the impinging and adsorbed oxygen. It is generally accepted that water formation on Pd(111) proceeds via the formation of hydroxyl intermediates.¹² In this reducing atmosphere the 2×2 structure is retained [Fig. 1(b)]. Heating the 0.3 MLE vanadium oxide surface to 700 K in vacuum or under reducing conditions leads to a change of the LEED pattern [Fig. 1(c)]. This structure can be assigned to a surface oxide of VO stoichiometry. Similar LEED patterns for vanadium oxide on Pd(111) and Rh(111) and corresponding STM investigations and DFT calculations have described this structure as the “wagon-wheel” structure.^{1,2,6,7} Figure 2(c) displays a high-

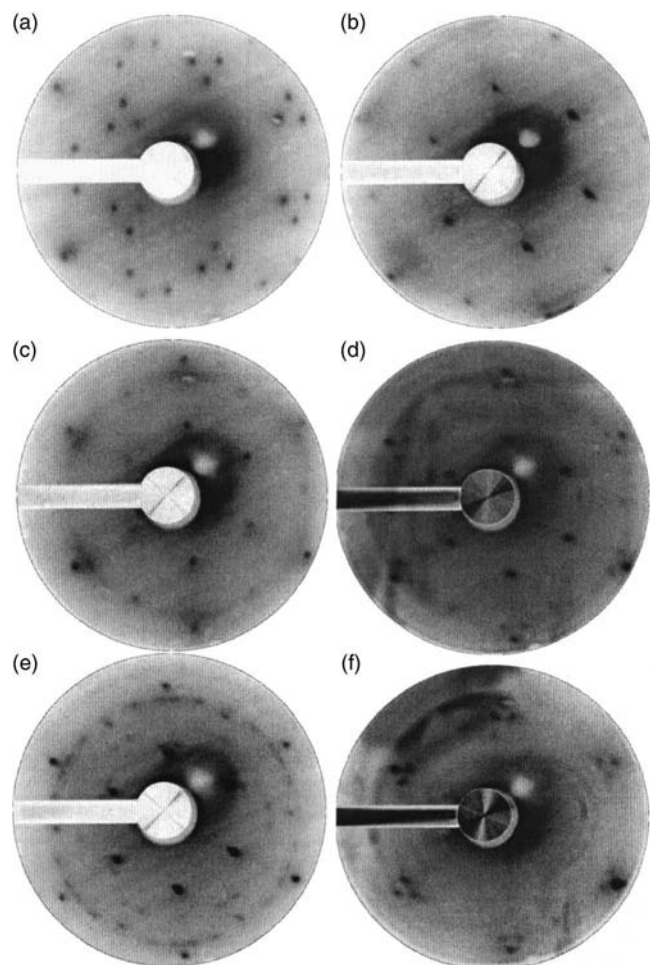


FIG. 3. LEED patterns for 1 MLE VO_x structures on Pd(111): (a) after preparation at 523 K, “flower pattern,” $E=39$ eV; (b) during deuterium desorption at 523 K, 2×2 structure, $E=40$ eV; (c) during reaction of deuterium with oxygen at 523 K, 2×2 structure, $E=60$ eV; (d) during oxygen exposure at 700 K, 2×2 structure+VO structure, $E=58$ eV; (e) during reaction of deuterium with oxygen at 700 K, 2×2 structure+rectangular structure, $E=57$ eV; (f) after reaction at 700 K, VO structure, $E=62$ eV.

resolution STM image of the wagon-wheel phase. Exposing this surface again to oxygen changes the LEED pattern back to the 2×2 structure [Fig. 1(d)]. The background signal in the LEED pattern is increased compared with Fig. 1(b) due to the Debye-Waller factor. Apparently, under these reaction conditions the surface vanadium oxide layer $s\text{-V}_2\text{O}_3$ is conserved at 700 K.

2. 1 MLE vanadium oxide

Evaporation of 1 MLE vanadium under oxygen atmosphere at 523 K leads to a LEED pattern as shown in Fig. 3(a). This “flowerlike” pattern has recently been described as being the superposition of diffraction from domains with rectangular unit cells of VO_2 stoichiometry and the 2×2 V_2O_3 structure.³ This is clearly apparent from the STM image in Fig. 2(d). After initiation of the deuterium permeation the LEED pattern changes to the pure 2×2 structure [Fig. 3(b)]. The VO_2 structure is reduced to the more stable V_2O_3 surface oxide.¹³ Adding oxygen at 523 K retains the 2×2 structure, but additionally a faint ringlike structure appears in the LEED pattern [Fig. 3(c)]. Heating the 1 MLE vanadium

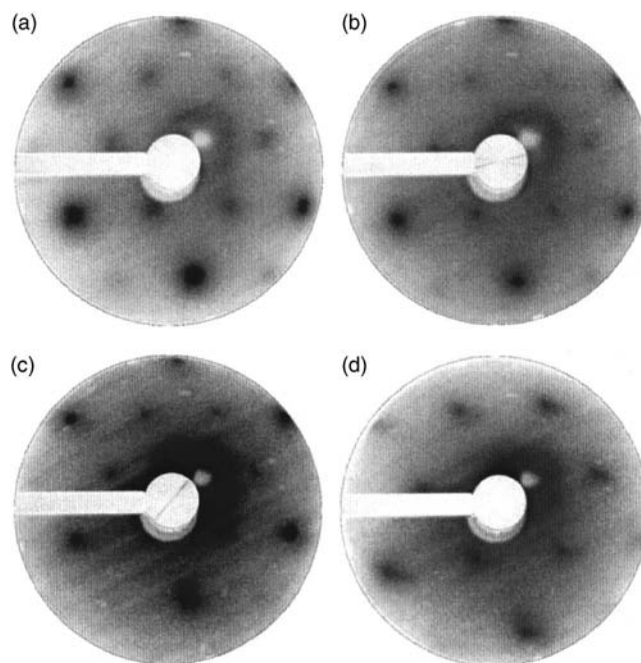


FIG. 4. LEED patterns of 5 MLE VO_x structures on Pd(111): (a) after preparation at 523 K, bulk V_2O_3 structure $(\sqrt{3} \times \sqrt{3})R30^\circ$, $E=57$ eV; (b) during reaction of deuterium with oxygen at 523 K, $(\sqrt{3} \times \sqrt{3})R30^\circ$, $E=56$ eV; (c) during deuterium desorption at 700 K, $(\sqrt{3} \times \sqrt{3})R30^\circ$, $E=63$ eV; (d) during reaction of deuterium with oxygen at 700 K, $(\sqrt{3} \times \sqrt{3})R30^\circ$, $E=42$ eV.

oxide surface to 700 K in vacuum leads to a LEED pattern similar to that in Fig. 1(c), which is again indicative of the wagon-wheel VO structure. Pure permeation of deuterium does not change this pattern. Exposing this surface to oxygen without permeation of deuterium leads to a LEED pattern which is a superposition of the VO structure and the 2×2 structure [Fig. 3(d)]. However, exposing oxygen to the surface when deuterium is permeated concomitantly, a change in the LEED pattern appears which has not been observed so far [Fig. 3(e)]. In addition to the 2×2 structure a new superstructure appears which can be explained by the superposition of rotational and mirror domains of a rectangular structure. This structure is similar to the flowerlike pattern but with a different size of the unit cell. A more detailed description of this phase will be given in the discussion. After the oxygen exposure has been terminated and only deuterium permeation still exists, the 2×2 structure and the rectangular structure disappear and the remaining pattern is again indicative of the VO structure [Fig. 3(f)].

3. 5 MLE vanadium oxide

Evaporation of 5 MLE vanadium under oxidative conditions at 523 K leads to a $(\sqrt{3} \times \sqrt{3})R30^\circ$ LEED pattern [Fig. 4(a)]. This pattern has been identified as being due to diffraction from the (0001) plane of V_2O_3 bulk phases.¹ No palladium signal is seen in the AES, indicating a continuous oxide film on the substrate. However, from the fact that the LEED spots are rather broad in this case we conclude that the film consists of quite small V_2O_3 crystallites. The STM measurements on such surfaces produced under similar conditions indicate a mean crystallite diameter of about 50–100 Å.¹

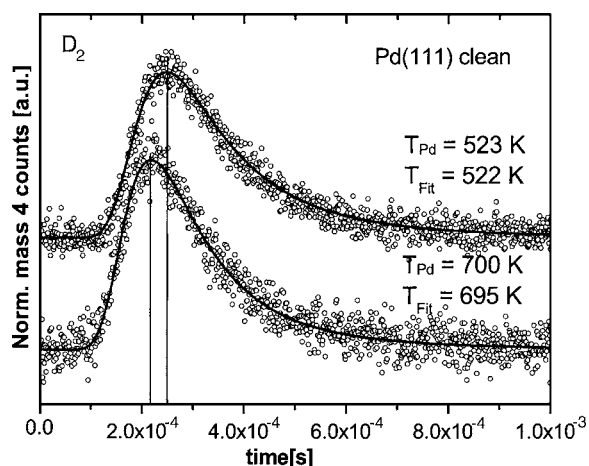


FIG. 5. Time-of-flight spectra for deuterium desorbing from clean Pd(111) at 523 and 700 K, respectively. The best fit temperatures for a Maxwellian distribution are also given, indicating a thermalized desorption.

The STM image presented in Fig. 2(e) shows the hexagonal pattern of the corundum V_2O_3 (0001) top facets of these crystallites. The LEED structure remains stable at 523 K, both under reducing conditions as well as under reaction conditions [Fig. 4(b)]. This is also true for a sample temperature of 700 K, without [Fig. 4(c)] and with [Fig. 4(d)] oxygen exposure. It should be noted that after the reaction experiment AES revealed a significant palladium signal, but the LEED pattern still shows the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, albeit with increased spot size. Apparently, the crystallites have changed their shape and size during the reaction.

B. Permeation of deuterium and reaction with O_2 on the surface VO_x on Pd(111)

Hydrogen or deuterium permeates easily through palladium samples, even at relatively low temperature.¹⁴ It therefore offers a convenient way to expose a surface to atomic H or D, which originates from the interior of the sample. One could imagine that this permeating deuterium or hydrogen reacts quite differently with other adsorbed species than molecular H_2 or D_2 impinging from the gas phase. This is also expected to hold for modified palladium surfaces, e.g., modified by chemical additives or by a nanostructuring of the surface.⁹ Surface vanadium oxides, which exhibit a large variety of different stoichiometries and form different nanostructures on Pd(111), are excellent model systems which can be taken to study the permeation and desorption of deuterium and its reaction with impinging oxygen to water. We have focused particularly on the translational energy distribution of the desorption flux and the reaction products, which have been measured by TOF spectroscopy.¹¹ In Fig. 5 TOF spectra of permeating/desorbing deuterium from a clean Pd(111) surface at two different surface temperatures are depicted for comparison. Least squares fits to the data points using Maxwellian distributions yield mean translational energies of the desorption flux, $\langle E \rangle = 2kT_{fit}$, where the fit temperature T_{fit} is close to the sample temperatures. This shows that associative desorption of deuterium from Pd(111) is largely unactivated, as already described for hydrogen desorption in previous work.^{9,15} The error of the Maxwellian

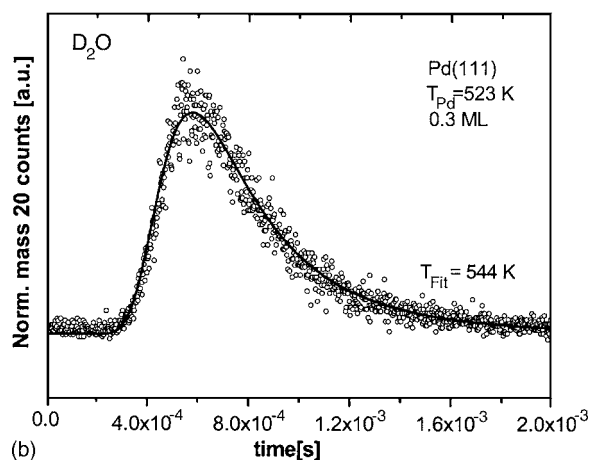
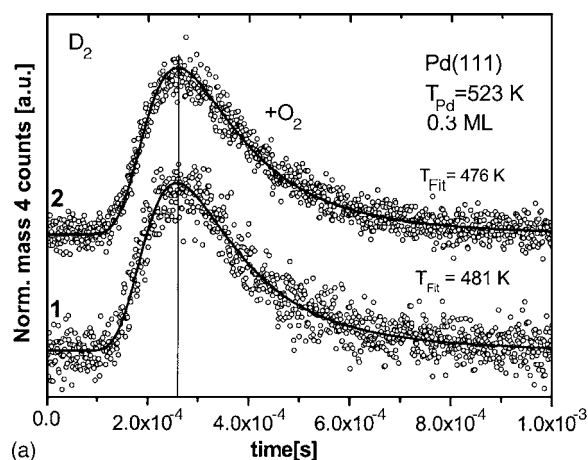


FIG. 6. (a) Time-of-flight spectra for pure deuterium desorption (curve 1) and deuterium desorption during concomitant oxygen exposure (curve 2) from 0.3 MLE VO_x on Pd(111) at 523 K. (b) Time-of-flight spectrum of D_2O resulting from the reaction of permeating D and impinging O_2 on 0.3 MLE VO_x on Pd(111) at 523 K.

fits to the data points is approximately 5% throughout the experiment and will not be cited explicitly for all the individual fit temperatures in the following.

1. 0.3 MLE vanadium oxide

The TOF spectrum for deuterium from a Pd(111) sample covered with 0.3 MLE vanadium oxide at 523 K is shown in Fig. 6(a) (curve 1). The surface vanadium oxide film in this particular case is characterized by the s - V_2O_3 2×2 structure. A least squares fit of a Maxwellian TOF distribution to the experimental data points leads to $T_{fit} = 481$ K. Although this value is not far off the surface temperature of 523 K, this decrease in the mean translational energy was reproducibly measured within the margin of error. The TOF measurement of D_2 during molecular oxygen exposure (1×10^{-6} mbar) leads to a TOF spectrum as depicted in Fig. 6(a) (curve 2). As already outlined above not all deuterium atoms react with oxygen to water. In addition, due to the much higher deuterium permeation rate compared to the oxygen impingement rate, associative desorption of deuterium molecules still takes place. The best fit temperature is now $T_{fit} = 476$ K. Apparently the TOF spectrum is not changed significantly. In the latter case we have also measured the TOF distribution of

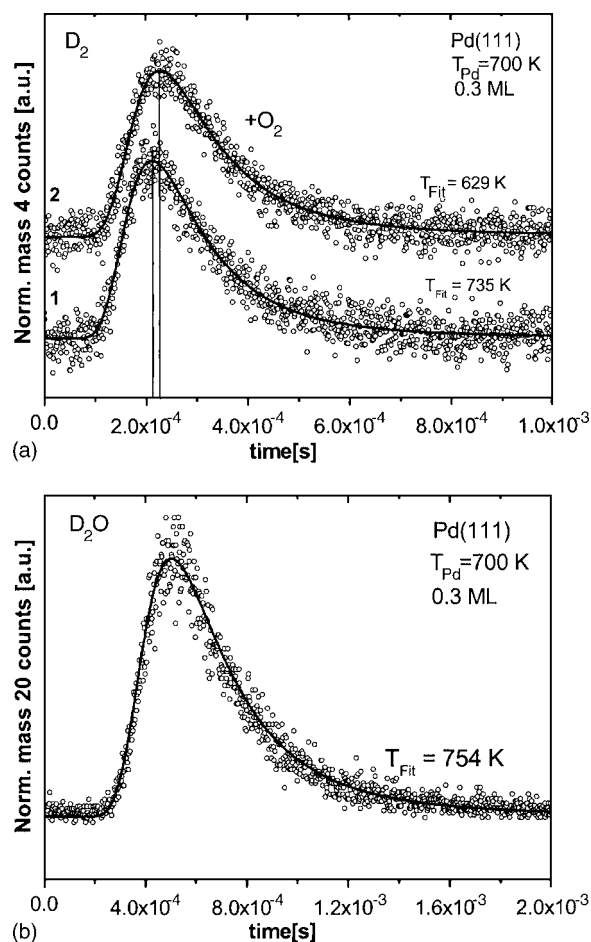


FIG. 7. (a) Time-of-flight spectra for pure deuterium desorption (curve 1) and deuterium desorption during concomitant oxygen exposure (curve 2) from 0.3 MLE VO_x on Pd(111) at 700 K. (b) Time-of-flight spectrum of D₂O resulting from the reaction of permeating D and impinging O₂ on 0.3 MLE VO_x on Pd(111) at 700 K.

the water reaction product [Fig. 6(b)]. A best fit temperature $T_{\text{fit}}=544$ K is obtained, indicating that water desorption is close to thermal, but slightly hyperthermal.

The same experiments were performed at a sample temperature of 700 K. The backpressure of deuterium in the permeation source was changed in such a way that the permeation flux was approximately the same as for the 523 K situation. The TOF spectrum for pure deuterium desorption is depicted in Fig. 7(a) (curve 1). A best fit yields $T_{\text{fit}}=735$ K. From the LEED investigations we know that in this case the surface consists of a surface vanadium oxide with VO stoichiometry. After adding the appropriate oxygen pressure the surface is changed to the 2×2 vanadium oxide structure with s -V₂O₃ stoichiometry. Deuterium desorption during oxygen impingement yields a TOF spectrum which now indicates a significantly smaller value for the mean translational energy of $T_{\text{fit}}=629$ K [Fig. 7(a), curve 2]. Apparently, the specific oxide layers which are stable at the individual reaction conditions influence the TOF spectra. The corresponding water-TOF spectrum [Fig. 7(b)] yields a best fit temperature of $T_{\text{fit}}=754$ K, again slightly hyperthermal.

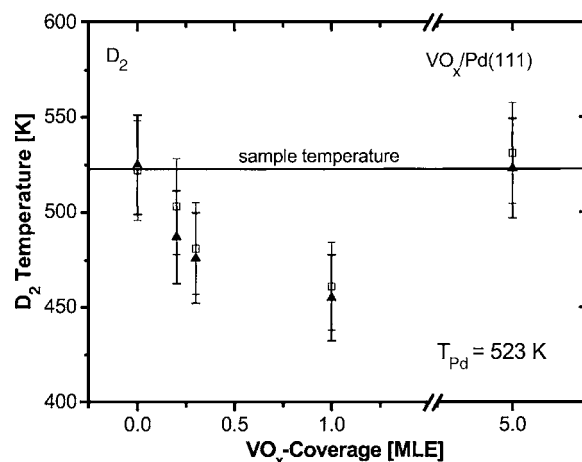


FIG. 8. Maxwellian fit temperatures for desorbing deuterium as function of VO_x coverage on Pd(111) at 523 K: (□) pure deuterium desorption and (▲) deuterium desorption during oxygen exposure.

2. 1 and 5 MLE vanadium oxides

The 1 MLE surface vanadium oxide at 523 K is characterized by a 2×2 structure, with additional spots in the LEED pattern, resulting in the flowerlike pattern. From STM measurements it is known that this surface consists of a full layer of surface V₂O₃ with additional islands of VO₂ stoichiometry.⁵ This surface should exhibit only few border lines between oxide islands and bare Pd(111). We have carried out pure deuterium desorption as well as deuterium + oxygen reaction TOF studies on this surface, both at 523 and 700 K. Since the shape of the spectra and the signal to noise behavior are similar as in the above described circumstances we will not present all the individual TOF spectra but quote only the determined fit temperatures. The data are compiled, together with the data for the 0.3 and 5 MLE surface vanadium oxides in Figs. 8–10. Pure deuterium desorption from the 1 MLE surface at 523 K (LEED shows the 2×2 structure) yields a mean translational energy corresponding to a temperature of $T_{\text{fit}}=461$ K, which is again significantly smaller than the surface temperature (Fig. 8). In the case of concomitant oxygen exposure the D₂ TOF yields

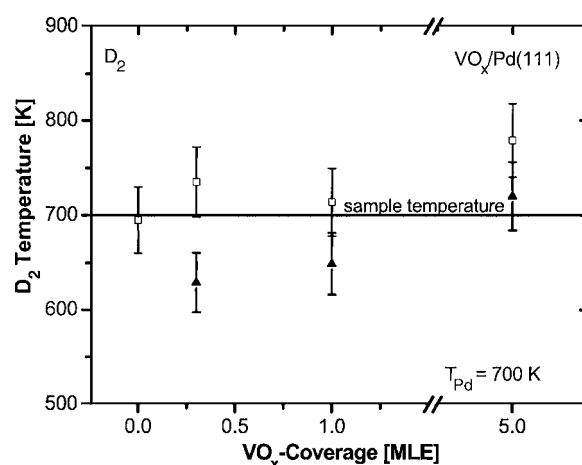


FIG. 9. Maxwellian fit temperatures for desorbing deuterium as function of VO_x coverage on Pd(111) at 700 K: (□) pure deuterium desorption and (▲) deuterium desorption during oxygen exposure.

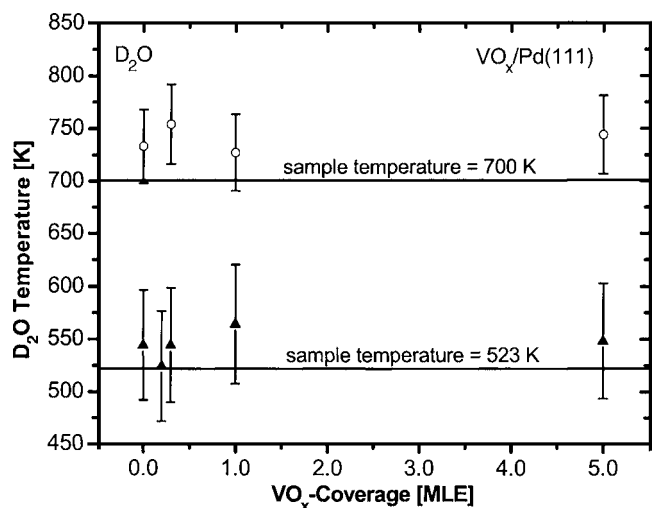


FIG. 10. Maxwellian fit temperatures for desorbing D_2O as function of VO_x coverage on Pd(111) at (▲) 523 K and (○) 700 K.

a mean desorption temperature of $T_{\text{fit}}=455$ K. The TOF spectrum for D_2O can be approximated by a mean desorption temperature of 567 K (Fig. 10). The TOF measurements at 700 K yield the following best fits to the spectra: pure deuterium desorption (LEED shows VO structure), $T_{\text{fit}}=714$ K; deuterium during oxygen exposure [LEED shows (2×2) +rectangular VO_2 structure], $T_{\text{fit}}=649$ K (Fig. 9); water desorption, $T_{\text{fit}}=727$ K. Again, for 1 MLE vanadium oxide different structures are stable under different reaction conditions which have an influence on the TOF spectra.

In the case of the 5 MLE vanadium oxide the structure is characterized by the LEED pattern indicating bulk V_2O_3 . The desorption and reaction studies yield the following results: At 523 K pure deuterium desorption gives $T_{\text{fit}}=531$ K, deuterium concomitant with oxygen yields a best fit temperature $T_{\text{fit}}=523$ K (Fig. 8), and the water TOF can be described by $T_{\text{fit}}=548$ K (Fig. 10). At 700 K pure deuterium desorption gives $T_{\text{fit}}=779$ K, deuterium concomitant with oxygen yields $T_{\text{fit}}=720$ K (Fig. 9), and the water TOF can be described by $T_{\text{fit}}=744$ K (Fig. 10).

IV. DISCUSSION

The 0.3 MLE vanadium oxide prepared under oxidizing conditions at 523 K forms a layer of 4×4 V_5O_{14} which fully covers the Pd(111) surface [Figs. 1(a) and 2(a)]. However, under our experimental conditions, where a quite high deuterium (hydrogen) partial pressure exists, the 4×4 phase quickly reduces to the 2×2 s - V_2O_3 phase. This phase covers about 60% of the Pd(111) surface⁴ and is stable at 523 K, both under reducing conditions as well as under reaction conditions (deuterium+oxygen). Note, however, that the reaction conditions are also largely reducing conditions ($p_{O_2}=1 \times 10^{-6}$ mbar equals 2.7×10^{14} O_2/cm^2 s impinging on the surface, deuterium pressure increase during permeation of 8×10^{-7} mbar equals about 1.2×10^{16} D/cm^2 s emanating from the bulk). It is known from STM that at this temperature under reducing conditions the s - V_2O_3 phase forms compact two-dimensional islands on the bare Pd(111) surface.⁴ The TOF spectrum for deuterium desorbing from this surface

at 523 K can be approximated by a Maxwellian of $T_{\text{fit}}=481$ K. It would be tempting to ascribe this feature of a “cooled” deuterium flux to particular changes of the potential energy surface (PES) for the desorption process. However, careful examination of the experiment leads to a different and quite simple explanation of this result. As outlined above the deuterium permeation/desorption flux of about 6×10^{15} D_2/cm^2 s leads to a pressure increase in the chamber of 8×10^{-7} mbar (at a pumping speed of 140 l/s as determined with the desorption standard¹⁰). This pressure equals an impingement rate of D_2 on the surface of 6×10^{14} D_2/cm^2 s. This means that about 10% of the deuterium flux which leaves the surface originates from reflected or adsorbed/desorbed deuterium. On the bare Pd(111) surface the sticking coefficient for hydrogen (deuterium) is quite high [$S_0=0.45$ (Ref. 16)]. In this case the permeated/recombined deuterium molecules and the adsorbed/desorbed deuterium molecules are close to thermal, as observed experimentally (Fig. 5). In the case of the 0.3 MLE vanadium oxide about 60% of the surface is covered by the oxide. We assume that deuterium molecules impinging on the oxide areas do not adsorb but are reflected without losing much of their kinetic energy, corresponding to 300 K. This contribution to the total desorption flux yields on the average a mean translational energy which is equivalent to a smaller temperature than the corresponding sample temperature (Fig. 8).

For the 1 MLE oxide surface at 523 K, which is composed of a full layer of 2×2 s - V_2O_3 and islands with the rectangular oxide structure, no bare palladium is exposed and the contribution of reflected molecules with 300 K Maxwell temperature is even larger, as seen in Fig. 8. The result of these considerations is that the mean translational energy distribution of permeating/desorbing deuterium, which is thermalized on the Pd(111) surface, is also largely thermalized for the vanadium oxide layer. In the case of concomitant oxygen exposure the kinetic energy distribution of deuterium is not changed significantly. The reaction product water is also close to thermal, but slightly hyperthermal (by about 10%).

On the 5 MLE vanadium oxide at 523 K, which consists of small islands of bulk vanadium V_2O_3 , pure deuterium desorption and D_2 desorption during water reaction are again thermalized (Fig. 8). This is somewhat puzzling because this would mean that impinging deuterium is fully thermalized either by dissociative adsorption/recombinative desorption or by inelastic scattering with a high accommodation coefficient. Apparently, the deuterium adsorption behavior on the surface vanadium oxide and the bulk vanadium oxide is quite different. Here the question of the influence of the surface morphology at the accommodation process has to be considered. The morphology of the 5 MLE bulk-type V_2O_3 [Fig. 2(e)] is quite rough at the atomic scale, compared to the monolayer surface vanadium oxide [Fig. 2(d)]. Multiple collisions in the interaction region on the bulk V_2O_3 surface may give rise to the more pronounced accommodation. We will investigate this particular feature with more appropriate adsorption techniques in the future.

The permeation experiments at 700 K yield some differences compared to the 523 K case. Under reducing condi-

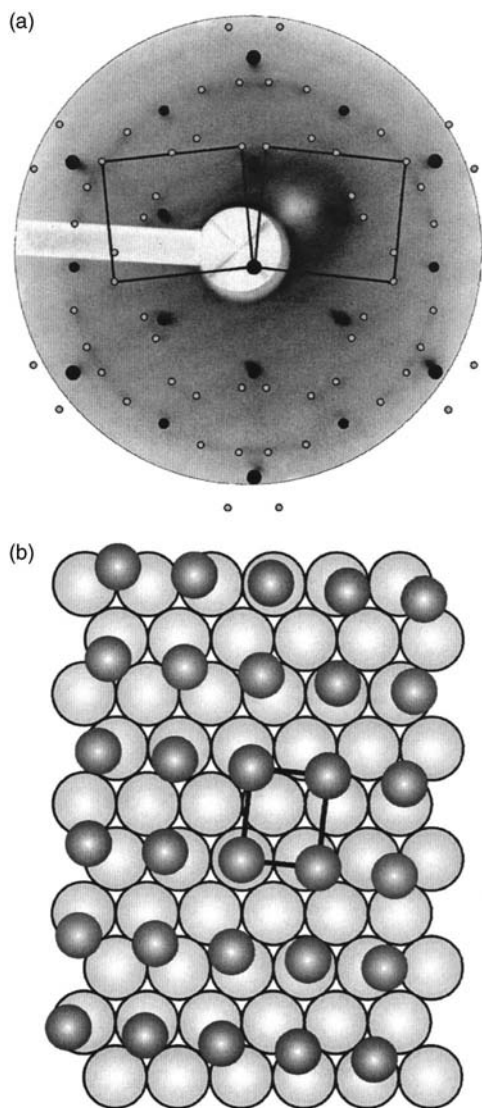


FIG. 11. (a) LEED pattern of Fig. 3(e) with calculated LEED spots and rectangular reciprocal unit cells and (b) corresponding geometrical model.

tions, i.e., for pure deuterium desorption, the LEED patterns indicate the existence of the VO structure, both for 0.3 and 1 MLE. In this case the mean translational energy distribution of deuterium is close to thermal (Fig. 9). Following the considerations made above leads to the conclusion that deuterium molecules impinging from the gas phase on the VO surface leave the surface fully accommodated, either due to adsorption/desorption or due to a large accommodation coefficient for the inelastically reflected molecules. Under reaction conditions, i.e., permeation of hydrogen during exposure to oxygen, LEED reveals the existence of the 2×2 s - V_2O_3 phase, both for 0.3 and 1 MLE. On this vanadium oxide layer with higher oxidation state again a cooled kinetic energy distribution is observed, due to the negligible sticking coefficient for deuterium on this oxide phase. For the 5 MLE case at 700 K the desorption features are similar to those for the 523 K, case showing that the bulk vanadium oxide is less influenced by temperature and oxygen pressure. The D_2O desorption flux at 700 K is for all VO_x phases slightly hyperthermal, as for the 523 K case (Fig. 10). This behavior suggests that those deuterium atoms with higher kinetic en-

ergy in the energy distribution react with higher probability with the intermediate hydroxide species on the surface, to form water.

Finally, we would like to address a special feature of the 1 MLE structure at 700 K under reaction conditions. In addition to the 2×2 LEED pattern extra diffraction spots appear which have not been observed so far [Fig. 3(e)]. These additional spots can be fully explained by rotational and mirror domains of a rectangular structure with similar surface unit cell as that proposed for the flowerlike pattern. The schematic LEED pattern together with a schematic geometric model is depicted in Fig. 11. The direction of the short axis of the superstructure is rotated with respect to the (01) direction of the substrate unit cell by $\pm 6^\circ$ and the length ratio of the rectangular unit cell is 1:1.2. This is close to the ratio of the unit cell axes of the flowerlike pattern. The only difference is a contraction of the reciprocal unit cell by about 10%, equivalent to an expansion of the geometric unit cell by 10%. This leads to a better matching of the atoms of the rectangular structure along the diagonal with respect to the $\langle 110 \rangle$ rows of the palladium substrate. On the other hand the direction of the diagonal is 3.5° off the $\langle 110 \rangle$ direction [Fig. 11(b)]. Apparently, at 700 K the VO_2 rectangular structure relaxes to an energetically more favorable expanded structure. In this case a larger number of oxygen atoms can occupy on-top positions which have been shown to be the energetically most favorable ones.³

V. SUMMARY AND CONCLUSION

Various vanadium oxides in different oxidation states have been prepared on a Pd(111) surface and their stabilities under specific reaction conditions have been analyzed. The palladium sample was part of a permeation source, thus enabling the permeation of deuterium through the sample onto the surface. The permeation/desorption of deuterium from the surface oxide layer and the reaction of permeating deuterium with impinging oxygen on the oxide layer has been investigated, using LEED and TOF spectroscopy. The main results of our study can be summarized as follows.

- (1) The stable phase of a 0.3 MLE vanadium oxide at 523 K, during deuterium desorption as well as during reaction between deuterium and oxygen, is the 2×2 s - V_2O_3 surface oxide. The experimentally obtained mean translational energy for desorbing deuterium is smaller than the thermal value. However, this is just due to a considerable contribution of reflected (nonaccommodated) deuterium molecules that are at room temperature. The translational energy distribution of associatively desorbing deuterium itself is thermal.
- (2) The stable 0.3 MLE vanadium oxide at 700 K is the “wagon-wheel” VO phase. TOF shows a thermal distribution of deuterium from this surface, indicating

that the reflected contribution is also thermal. The adsorption and accommodation behaviors of impinging deuterium are apparently quite different on the *s*-V₂O₃ surface and on the VO surface. Concomitant oxygen adsorption changes the vanadium oxide to *s*-V₂O₃. The TOF spectrum is again “cooled” due to the changed adsorption behavior of deuterium.

- (3) For the 1 MLE VO_x scenario more different stable oxide phases exist as a function of temperature and deuterium and/or oxygen pressures. However, the main feature is again that the different oxides existing at 523 and 700 K exhibit different adsorption behaviors for deuterium, resulting in different apparent TOF distributions.
- (4) The 5 MLE vanadium oxide forms a bulklike V₂O₃. Deuterium desorption from this surface yields thermalized TOF spectra, both for 523 and 700 K. This shows that the adsorption behavior for deuterium is different on the surface vanadium oxide and the bulk vanadium oxide. The influence of the different surface morphologies may be a possible reason.
- (5) The mean translation energy distribution of the water reaction product is on the average slightly hyperthermal. A possible explanation for this behavior is that those deuterium atoms which possess higher kinetic energy after permeation react more easily with the hydroxyl intermediate and channel their energy into the reaction product.

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