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Water on well-defined platinum surfaces : an ultra high vacuum and electrochemical study

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A detailed TPD study of H₂O and pre-adsorbed O on the stepped Pt(553) surface

Abstract Water molecules desorbing from the bare Pt(553) surface desorb in a three peak structure, associated with, respectively, desorption from step and terrace sites and the water multilayer. Upon pre-covering the step sites with O_{ad} we likely observe OH formation on step sites. When terrace sites are also pre-covered with O_{ad}, OH_{terrace} formation is favored over OH_{step} formation, presumably because OH formed at terrace sites is more easily incorporated in a hydrogen bonded network of OH/H₂O. This is a gradual process: with increasing θ_O less OH_{step} is formed. Thus, in spite of the fact that OH at step sites has a higher binding energy than OH at terrace sites, the possibility of the formation of OH at terrace sites actually inhibits the formation of OH at step sites, leaving O_{step} as the most stable water dissociation product on the step.

6.1 Introduction

The interaction between water and platinum surfaces has been studied extensively because of its importance in electrochemistry, fuel cell catalysis, heterogeneous catalysis, and corrosion chemistry. Three extensive reviews have appeared that summarize the large body of knowledge on water-surface interactions that has been obtained using a variety of surfaces, co-adsorbates, and employed techniques.^{6–8} The interaction between H₂O, O₂ and platinum is especially interesting with regard to fuel cell catalysis, where OH adsorbed at platinum steps sites is considered to be a possible oxygen donor for the oxidation of, *e.g.*, CO, methanol, and ethanol at the anode. The structure sensitivity of these reactions is normally related to water activation,^{133,140} which is supposed to occur preferentially at step sites.

Most studies investigating the platinum-water interaction have used the (111) surface as a model. Although this is the least complex system, ultra high vacuum (UHV) studies already show significant complexity in adsorption and desorption phenomena.^{118–120} However, a real catalytic surface contains low coordination or defect sites in addition to (111) terraces. These defect sites are often thought to be more active for catalytic reactions involving bond breaking and making.¹³ Although some experiments have focused on the influence of steps and defects that are naturally present on a Pt(111) crystal,^{28,29} more insight should result from studies employing a better-defined model, such as a regularly stepped surface.^{26,27} In addition such studies could provide more insight into the nature of the step-bonded oxygen species that is active in electrocatalysis.^{133,140}

The general consensus is that on Pt(111) water adsorbs molecularly at all coverages and temperatures (< 180 K). Classically, water adsorbed on metal surfaces is thought to form an ice-like bilayer of hexagonal rings.^{6–8} A combined scanning tunneling microscopy (STM) and density functional theory (DFT) study finds that at submonolayer coverages water islands also contain pentagon and heptagon ring structures.¹⁹ Temperature programmed desorption (TPD) studies show two peaks. One peak at 171 K is associated with monolayer desorption. This peak shows the characteristics of zero-order desorption kinetics²² and has been attributed to co-existence of a condensed phase and a 2-dimensional water-gas at sub-monolayer coverages.²¹ A second peak, associated with desorption from multilayers, starts at 154 K and increases in temperature with coverage.²³ TPD shows a stabilization of the water monolayer by the presence of step sites.^{26,27,124} An additional peak is observed at ~ 188 K for (100) steps or at ~ 197 K for (110) steps, which suggests a stronger interaction of water with the (110) step (chapter 3).

TPD studies show that oxygen can adsorb in three different states on Pt(111):^{11,31,33,40,41,51,117} physisorbed O₂ is stable below 45 K,³⁰ chemisorbed O₂ up to 100–250 K,¹¹ and atomic oxygen up to 575–900 K. Oxygen dissociation is activated and atomic oxygen formation occurs via a precursor state of molecu-

larly adsorbed oxygen.^{10,31} The maximum O_{ad} coverage that can be reached via background dosing is 0.25 ML. Low energy electron diffraction (LEED)^{11,32–36} and scanning tunneling microscope (STM)³⁷ pictures show a (2×2) pattern. Oxygen atoms bind preferentially in the fcc hollow sites.^{38,39} On stepped surfaces a similar (2×2) LEED-pattern is observed for O_{ad} as on Pt(111).^{9,40} Dissociation takes place at 200 K⁴⁵ on the (111) terrace, but occurs predominantly on step sites^{10,46–48} between 150 and 230 K.^{45,49} Oxygen atoms adsorb preferentially on step sites.^{37,48} They are more strongly bound to (100) than (110) step sites.⁴⁴ A combined STM and density functional theory (DFT) study³⁷ shows that for (100) steps a twofold edge bridging site is favored, whereas for (111) steps the fcc hollow site behind the step edge is favored. TPD spectra on Pt(533),^{10,45,46,50} other surfaces with (100) steps,^{49,51,52} and surfaces with (111) steps^{9,32,40,53} all show a three peak structure in the molecular oxygen regime and a two peak structure in the atomic oxygen regime.

The co-adsorption of H_2O and O_2 on Pt(111) is known to produce OH_{ad} for $150 \leq T \leq 185$ K.^{16,75,76} When $^{18}O_2$ and $H_2^{16}O$ are co-adsorbed at sub-monolayer coverages and subsequently annealed, the ratio $^{18}O : ^{16}O$ desorbing in H_2O is 1 : 2, independent of the initial $H_2^{16}O$ coverage. Surface OH groups do not readily exchange H with unreacted O_{ad} .⁷⁷ OH_{ad} is incorporated in a hydrogen bonded network with H_2O_{ad} ^{15,79} in a reaction with the following stoichiometry:



All O_{ad} participates in the OH formation.¹⁶ H_2O is needed to stabilize the formed OH species.^{16,80} All H-groups participate in the hydrogen bonded network and OH is always bonded to the platinum substrate via the oxygen atom. All hydrogen bonds lie parallel to the surface.^{76,81} One third of the shared protons is delocalized between two O atoms, making them neither clearly covalently bound nor hydrogen bonded to the oxygen atoms.⁸² When H_2O is removed, the OH groups react to form H_2O and O_{ad} .

H_2O adsorbs intact on the reconstructed Pt(110)- (1×2) surface.⁸⁶ Interestingly, on this surface OH_{ad} formed via the co-adsorption of O and H_2O is not incorporated in a hydrogen bonded network and OH_{ad} remains stable after water desorption up to ~ 205 K.⁸⁷

We have discussed the main differences between the co-adsorption of O_{ad} and H_2O at the Pt(553) surface and the Pt(533) surface in chapter 4. Here, we provide a more in depth study on the influence of the (110) step orientation on oxygen and water (co-)adsorption. Therefore, we (co-)adsorb O_{ad} and H_2O with various O_{ad} and H_2O coverages on the stepped Pt(553) surface, which consists of 4 atom-wide (111) terraces and a (110) step site. The sample is studied under ultra high vacuum (UHV) conditions using TPD and LEED in combination with isotope exchange.

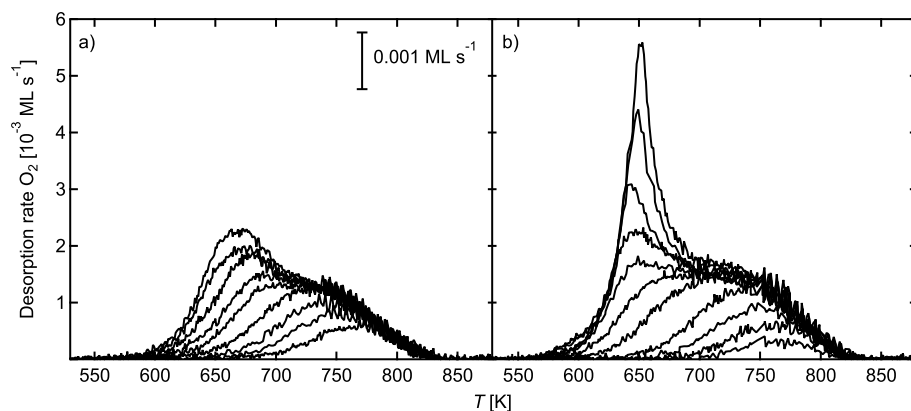


Figure 6.1 a) TPD spectra of O₂ desorbing from Pt(553) for varying O_{ad} coverages. b) The same spectra, but now without annealing the surface to 1200 K for 3 minutes in between experiments.

6.2 Experimental

All experiments were performed in Lion fish. Experimental procedures can be found in chapter 2.1.

6.3 Results and discussion

6.3.1 O₂ adsorption/desorption

We have discussed the desorption characteristics of the single species (O₂ and H₂O) in chapter 3 and will only discuss them briefly here. Figure 6.1a shows TPD spectra of various amounts of O_{ad} desorbing recombinatively from the Pt(553) surface. At the lowest coverage we observe a single peak at 765 K. With increasing coverage this peak shifts to 736 K, indicating second order desorption kinetics. We attributed this peak to recombinative desorption of O_{ad} from step sites. Above 0.11 ML a shoulder appears at 688 K, which also shifts to lower temperature with increasing coverage, indicating second order desorption kinetics, saturating at 663 K for 0.25 ML. We ascribe this peak to desorption from (111) terrace sites. The ratio of oxygen desorbing from step to terrace sites is 0.11 : 0.14 ML. We observed similar behavior on the Pt(533) surface, but the peak associated to desorption from step sites is located ~ 36 K higher on this surface, indicating that oxygen adatoms bind less strongly to (110) steps than to (100) steps as was concluded previously from microcalorimetry.⁴⁴

For the isotope exchange experiments we used ¹⁸O₂ instead of ¹⁶O₂. When dos-

ing $^{18}\text{O}_2$, the contamination level of ^{16}O was maximally 6%. The isotope exchange data are uncorrected for this effect. Figure 6.1b will be discussed in section 6.3.4.

6.3.2 H_2O desorption from the bare surface

Figure 6.2a shows TPD spectra of H_2^{16}O (lower panel, plotted vs. left axis) and H_2^{18}O (upper panel, plotted vs. right axis) from a Pt(553) surface that has been maximally pre-covered with ^{18}O . Figure 6.2b shows similar data, but for a surface where only the step sites have been pre-covered with ^{18}O . Figure 6.2c shows similar data from the bare surface. First, we shall discuss the data from the bare surface. The lower panel (plotted vs. left axis) of figure 6.2c shows TPD spectra of various amounts of H_2^{16}O desorbing from the Pt(553) surface. We see three peaks in the spectrum, α_1 – α_3 , at, respectively, 197 K, 171 K, and ~ 146 K. The upper panel of figure 6.2c shows the H_2^{18}O spectra ($m/e = 20$). We observe no significant signals at this m/e ratio, indicating that our mass to charge ratios between 18 and 20 have a sufficient baseline separation. At coverages below 0.28 ML we observe only the α_1 peak. When the total coverage reaches 0.42 ML, the α_1 peak develops a tail at the low temperature side, which develops into the α_2 peak at higher coverages. The development of the tail takes place before the α_1 peak saturates. The actual peak formation, however, only happens when the α_1 peak has saturated. Before α_2 saturates a third peak appears at coverages $\gtrsim 0.91$ ML. Both the α_1 and α_2 peak temperatures do not shift with increasing coverage, suggesting first-order desorption kinetics. The α_3 peak shows zero-order desorption kinetics starting at 147 K and slowly shifting towards 157 K for a coverage of 4.49 ML (coverages ≥ 1.15 ML not shown here). The ratio $\alpha_1 : \alpha_2$ is roughly 4 : 5. We ascribe the α_1 peak to desorption from step sites, α_2 to terrace sites, and α_3 to multilayer water. We define the combined integrals of α_1 and α_2 as a full monolayer water.

The ratio $\alpha_1 : \alpha_2$ is much larger than would be expected on geometric arguments alone. STM shows that water adsorbs on both sides of the step edge.²⁸ Therefore, it seems likely that molecules desorbing in the α_1 peak originate from both the upper and lower side of the (110) step, and probably also at least in part from the (111) terrace. Terrace sites further away from step sites seem unaffected. A DFT study on (100) steps indicates that steps bind water much more strongly than locations in the middle of the terrace.²⁷ The α_2 peak has not yet saturated before the appearance of α_3 . This indicates that there are still patches of bare platinum when the multilayer starts to form on Pt(553).

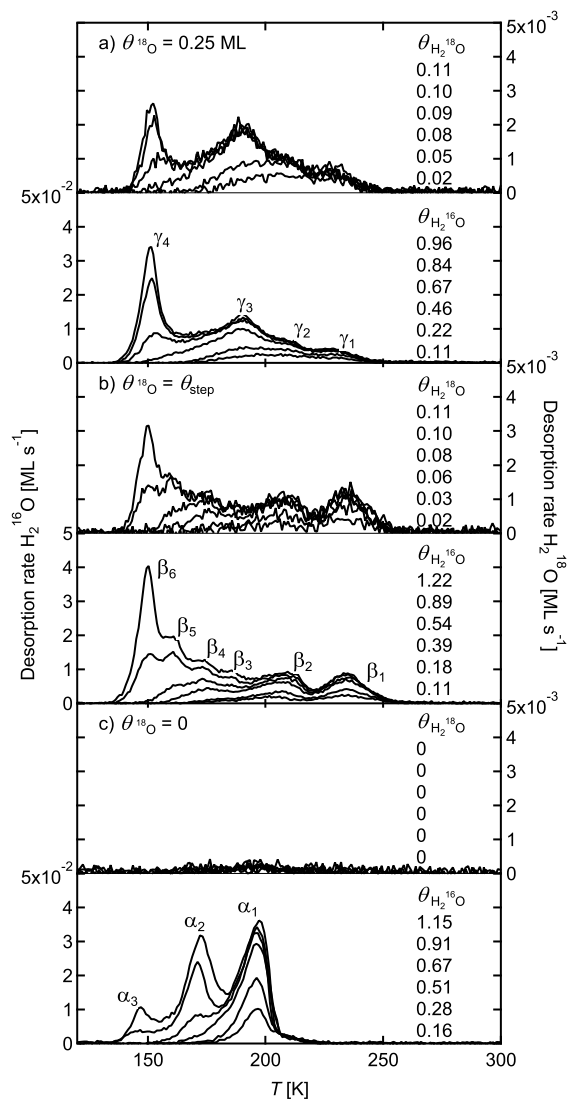


Figure 6.2 TPD spectra of H₂¹⁶O (left axis) and H₂¹⁸O (right axis) dosed on a) Pt(553) with $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$, b) $\theta_{^{18}\text{O}} = \theta_{\text{step}}$, and c) $\theta_{^{18}\text{O}} = 0$.

6.3.3 Co-adsorption of $^{18}\text{O}_{\text{ad}}$ and H_2^{16}O

$$\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$$

Figure 6.2b shows TPD spectra of various amounts of H_2O desorbing from a Pt(553) surface on which the step sites have been pre-covered with $^{18}\text{O}_{\text{ad}}$ prior to H_2^{16}O adsorption. First we focus on the H_2^{16}O signal (lower half, plotted vs. left axis). At the lowest coverages we observe a two peak structure, β_1 and β_2 , shifting from 235 to 233 K and from 204 to 209 K with increasing coverage, respectively. These two peaks grow in simultaneously and have a similar integral. Already at the lowest coverages a small shoulder is visible at ~ 185 K. Above 0.22 ML (before β_1 and β_2 saturate), this shoulder develops into a two peak structure, β_3 and β_4 , with peak temperatures of, respectively, ~ 185 K and ~ 173 K. At 0.62 ML another shoulder at the low temperature side starts to develop, eventually resulting in a peak, β_5 , at 161 K. At coverages $\gtrsim 0.86$ ML we reach the maximum number of six peaks with β_6 starting at 150 K and shifting to higher temperatures with increasing coverage (higher coverages not shown here). All peaks start to emerge before all higher temperature peaks have saturated. The β_1 – β_3 peaks saturate above ~ 1.15 ML, whereas the other peaks keep increasing in intensity above this coverage. The continuing increase in β_4 and β_5 is likely to be an optical illusion caused by the increase in β_6 , which increases the baseline for the β_4 and β_5 peaks.

The number of observed peaks makes it difficult to assign each peak separately based on TPD alone. Nonetheless, we will attempt to give a tentative assignment to the peaks. The β_6 peak is last to appear and its leading edge is located at the same position as the α_3 peak, which we attributed to desorption from the multilayer on the bare Pt(553) surface. We attribute the β_6 peak to multilayer desorption.

On Pt(111), the co-adsorption of O and H_2O is known to cause OH formation. The resulting hydrogen bonded OH/ H_2O network has various stable structures, depending the O : H_2O ratio.¹⁴ During a TPD experiment, H_2O molecules are slowly titrated off the surface. This results in a continuously changing O : H_2O ratio. It is likely that, similar to the Pt(111) surface, different ratios have different structures, some of which are more stable than others. Therefore, it seems likely that the β_1 – β_5 peaks observed for $\text{O}_{\text{step}}/\text{Pt}(553)$ are due to H_2O desorption and re-combinative desorption of 2OH_{ad} as H_2O from different stable $\text{H}_2\text{O}/\text{OH}$ hydrogen bonded networks.

The highest temperature peaks, β_1 and β_2 , appear simultaneously, indicating that the species can not exist independently. When we sum the H_2^{16}O and H_2^{18}O TPD spectra, the combined integral of these two peaks is roughly 0.4 ML, which is slightly less than the integral of the α_1 peak. However, the total integral of the H_2O TPD spectra before the multilayer peak appears has decreased as well, compared to the bare surface, since H_2O and O_{ad} compete for adsorption sites on the steps. Analogous to the bare surface, it is likely that these peaks are the result of desorp-

tion from step sites. Both the β_1 and β_2 peak are strongly stabilized compared to desorption from step sites from the bare surface, *i.e.* they appear at higher desorption temperatures. Similar to oxygen pre-covered Pt(111), this could be due to OH formation. On reconstructed Pt(110)-(1 × 2) OH_{ad} is stable up to ~ 205 K without co-adsorbed H₂O,⁸⁷ a similar temperature as the location of the β_2 peak.

The β_3 – β_5 peaks have a desorption temperature that is more reminiscent of the terrace desorption peak from the bare surface. These peaks would then be the result of desorption from terrace sites, suggesting that the α_2 peak splits into a three peak structure in the presence of O_{ad} on the steps. In spite of the fact that no O, and therefore no OH, is present on terrace sites, the presence of O adatoms on step sites influences H₂O desorption from terrace sites significantly. The simultaneous appearance of all peaks could be a sign of the limited mobility of H₂O molecules on this surface.

Next, we focus on the H₂¹⁸O signal (upper half of frame in figure 6.2b, plotted vs. right axis). We observe the same six peak structure as in the H₂¹⁶O signal. All spectra seem to image their H₂¹⁶O counterparts. Only β_1 is relatively larger than β_2 in the two spectra with the lowest amount of water, in contrast to the corresponding H₂¹⁶O spectra. This could indicate that most OH-recombination via the reverse of reaction (6.1) happens in β_1 and that β_2 actually contains the H₂O molecules needed to stabilize the formed OH_{ad}. We realize this last explanation is highly speculative, and for instance DFT, Monte Carlo simulations and/or spectroscopy should provide more insight in the nature of the various peaks.

On Pt(553) we observed that the multilayer peak was relatively smaller in the H₂¹⁸O signal compared to the H₂¹⁶O signal for $\theta_{18O} \approx \theta_{step}$ (see chapters 4 and 5). We attributed this to poor coupling between the first and second adsorbed layer. We observe this effect to a much smaller extent on the Pt(553) surface. This indicates that the interaction between the first and second layer is strongly dependent on the structure of the substrate. Apparently the Pt(553) surface facilitates H₂O exchange between the first and second water layer, whereas Pt(533) is more resilient to exchange.

The gray data in figure 6.3 show the amount of desorbing H₂¹⁸O, *i.e.* water molecules that have exchanged their oxygen atoms with the pre-adsorbed O_{ad}, as a function of the total H₂O coverage for a Pt(553) surface where only the step sites have been pre-covered with ¹⁸O adatoms. The dashed line shows how much H₂¹⁸O would desorb if complete isotopic scrambling were to occur, assuming the same 0.25 ML as a maximum coverage for O_{ad} on Pt(553) as Gee and Hayden did for Pt(533),¹⁰ and a Pt : H₂O ratio of 3 : 2 for 1 ML H₂O. We observe an increase in the amount of desorbing H₂¹⁸O with increasing θ_{H_2O} . This may be expected, since there is simply more H₂O present to participate in the exchange. The amount of exchange is much smaller than the complete scrambling scenario. We will discuss this data further in the next subsection.

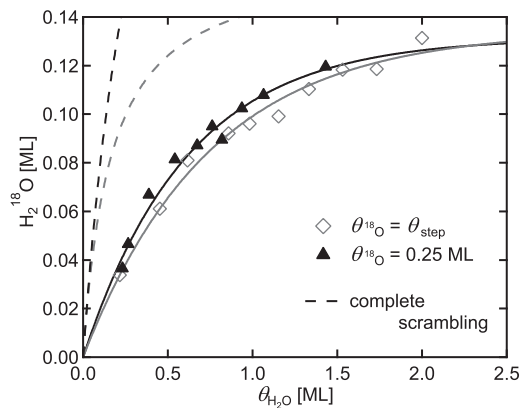


Figure 6.3 Amount of desorbing H_2^{18}O vs. the amount of adsorbed H_2^{16}O for Pt(553) with $\theta_{^{18}\text{O}} = \theta_{\text{step}}$ (■) and $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$ (▲). The dashed lines show the calculated amounts of formed H_2^{18}O for complete isotopic scrambling. The lines fitted through the data are only to guide the eye.

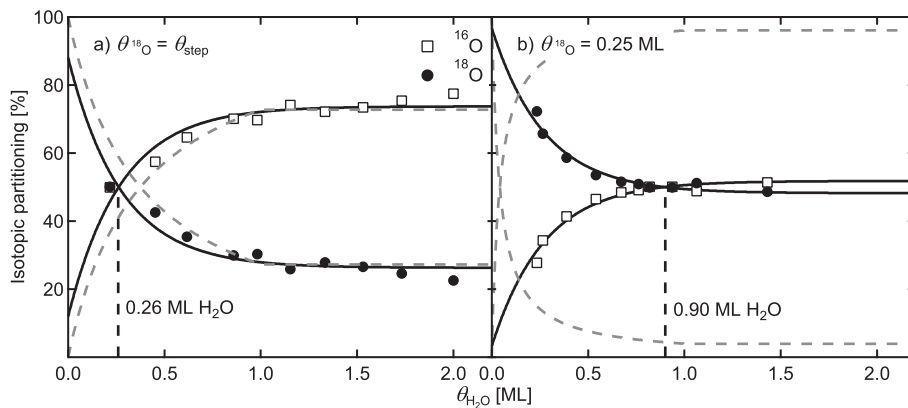


Figure 6.4 Isotopic partitioning in oxygen TPD spectra for varying amounts of H_2^{16}O dosed on Pt(553) pre-covered with $\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$ a) or $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$ b). The dashed lines show the calculated isotopic partitioning assuming complete isotopic scrambling.

Figure 6.4a shows the isotopic partitioning of ^{16}O and ^{18}O desorbing as O_2 for $\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$, based on the simultaneously measured $m/e = 32, 34$, and 36 spectra. We also show the calculated isotopic partitioning if complete isotopic scrambling were to occur. At the lowest H_2O coverages measured (0.22 ML), we observe that half of all pre-adsorbed $^{18}\text{O}_{\text{ad}}$ has exchanged with an ^{16}O from H_2^{16}O . The exchange levels off at coverages $> 1 \text{ ML}$ at $\sim 74\%$ of all original ^{18}O having exchanged with ^{16}O from water. Apparently, not all water molecules or O atoms have participated in the reversible formation of an $\text{OH}/\text{H}_2\text{O}$ network. Water adsorbed on terrace sites probably does not interact with the oxygen atoms on step sites and is therefore not likely to participate in the oxygen exchange reaction. STM shows that at low H_2O coverages most molecules are located at step sites.²⁸ Therefore, below 0.25 ML most water is likely located at the steps. An isotopic partitioning of more than 50% ^{16}O could be caused by more than one H_2O molecule interacting with one O_{ad} . It could also be caused by reaction (6.1) occurring reversibly at low temperatures, moving $^{18}\text{O}_{\text{ad}}$ as H_2^{18}O to terrace sites or to the multilayer, effectively leaching the $^{18}\text{O}_{\text{ad}}$. If the first explanation is true, one O_{ad} atom on step sites interacts with up to three H_2O molecules. This is less than on $\text{Pt}(111)$, where up to four H_2O molecules can interact with one O adatom.¹⁴ The difference could be due to the broken symmetry of the (553) surface, introduced by the presence of step sites.

$\theta_{^{18}\text{O}} = 0.25 \text{ ML}$

Figure 6.2a shows TPD spectra of various amounts of H_2O desorbing from a $\text{Pt}(553)$ surface which has been maximally pre-covered with $^{18}\text{O}_{\text{ad}}$ (0.25 ML) prior to H_2^{16}O adsorption. Again, we focus on the H_2^{16}O spectra first (lower half, plotted vs. left axis). From the lowest coverages onwards we observe a small peak, γ_1 , starting at 232 K and finally stabilizing at 228 K for $\theta_{\text{H}_2\text{O}} \gtrsim 0.39 \text{ ML}$. Simultaneous to the appearance of this peak we observe the appearance of a broad feature, centered at 204 K . At coverages $\gtrsim 0.23 \text{ ML}$ this feature splits up into two peaks, γ_2 and γ_3 , located at 208 and 191 K . For coverages $\gtrsim 0.39 \text{ ML}$, the γ_3 peak is the most prominent feature in the spectrum in the monolayer desorption regime. When $\theta_{\text{H}_2\text{O}}$ becomes larger than 0.67 ML , a peak γ_4 starts to appear at 152 K . Thus, at the largest H_2O coverages we observe a four peak structure. The γ_1 – γ_3 peaks grow in simultaneously, but the γ_1 peak saturates at $\sim 0.33 \text{ ML}$. The γ_2 and γ_3 peaks have almost saturated when γ_4 starts to appear.

The γ_4 peak appears at the same temperature as the α_3 and β_6 peaks, which we attributed to desorption from the second water layer. We associate the γ_4 peak with the same process. The γ_1 and γ_2 peaks appear at similar temperatures as, respectively, the β_1 and β_2 peak. Therefore, it is likely that the γ_1 and γ_2 peaks originate from recombinative desorption of OH and H_2O desorption on step sites. The peak temperature of γ_1 , however, has decreased by $\sim 4 \text{ K}$ compared to β_1 . OH on step sites is bound less strong on the $\text{Pt}(553)$ surface when the terrace sites are covered

with O_{ad} compared to when it has bare (111) terraces. Only one peak appears to be resulting from desorption from terrace sites: γ_3 . This shows that the energy differences between various structures of the OH/H₂O hydrogen bonded network have increased compared to the $\theta_{18O} \approx \theta_{step}$ case, favoring one structure. TPD spectra of H₂O molecules desorbing from a Pt(111) surface with an O pre-coverage of 0.25 show a desorption peak from terrace sites around 192 K,¹⁴ which is the same temperature as the γ_3 peak. We attribute the γ_3 peak to the formation of a hydrogen bonded OH/H₂O network on the (111) terraces, with a similar stability as the one formed on the Pt(111) surface. The γ_1 – γ_3 peaks start to appear simultaneously. This could indicate that the electronic corrugation of the surface for H₂O adsorption flattens when O adatoms are adsorbed on terrace sites, reducing the driving force for H₂O molecules to find an adsorption site where they are bound more strongly, once they are incorporated in the OH/H₂O hydrogen bonded network. Therefore, diffusion to the steps is more difficult.

Next, we turn to the H₂¹⁸O signals (upper half of panel, plotted vs. right axis). At the highest H₂O coverages, we observe a similar four peak structure as in the H₂¹⁶O spectra. The main difference is that all spectra are a factor of ten less intense compared to the H₂¹⁶O signals. Another difference is that the γ_1 peak saturates earlier, at 0.14 ML, compared to 0.33 ML for the H₂¹⁶O spectra. The γ_2 and γ_3 peaks appear to saturate earlier as well. This indicates that after 0.39 ML dosing more H₂O does not lead to more water molecules interacting with the pre-adsorbed ¹⁸O at step sites. The ratio H₂¹⁸O : H₂¹⁶O for the γ_4 peak compared to the ratio for the total spectrum has decreased relative to the $\theta_{18O} \approx \theta_{step}$ case. This shows that the OH/H₂O layers have a different coupling to the second layer for different θ_{18O} .

The black data in figure 6.3 show the amount of desorbing H₂¹⁸O, *i.e.* the amount of water molecules that have exchanged their oxygen atoms with the pre-adsorbed O_{ad} , for a Pt(553) surface where the full surface has been covered with oxygen adatoms as a function of the total amount of H₂O. Similar to the $\theta_{18O} \approx \theta_{step}$ case, we observe an increase in the amount of desorbing H₂¹⁸O with increasing θ_{H_2O} . The data obtained for the maximum obtained oxygen pre-coverage are remarkably similar to the data obtained when only the step sites were pre-covered with ¹⁸O_{ad}. This indicates that an equal amount of H₂O molecules participates in the interaction with O_{ad} as in the $\theta_{18O} \approx \theta_{step}$ case. However, from figure 6.1 we know that there are over twice as many O adatoms present on the surface for H₂¹⁶O molecules to interact with. An explanation could be that the extra O, *i.e.* O_{ad} on terrace sites, does not interact with post-dosed water. However, this would not agree with the observation of the γ_3 peak in figure 6.2a, which we attributed to recombinative desorption of OH from terrace sites. It also does not agree with the H₂¹⁸O TPD spectra. They show H₂¹⁸O desorption from the lowest temperature peak onwards, indicating that the reaction (1.4) occurs reversibly below ~ 145 K. Furthermore, we observed a decrease in the integral of γ_1 and γ_2 compared to β_1 and β_2 . Therefore, we think

that on the step sites fewer O adatoms participate in OH formation when the terrace sites are also covered with O adatoms. On terrace sites it is probably easier to incorporate the formed OH in the preferred hydrogen bonded network. Therefore, OH formation on terrace sites competes with OH formation on step sites, even though by itself OH on step sites is more strongly bound. A possible explanation would be that H₂O molecules participating in the OH/H₂O network on the terraces are less capable of also interacting with oxygen adatoms on step sites, leading to a decrease in the amount of formed OH on those sites. In any case, it seems that O adatoms are left unreacted at step sites.

Figure 6.4b shows the isotopic partitioning of ¹⁶O and ¹⁸O desorbing as O₂ of $\theta_{18\text{O}} = 0.25$ ML. At the lowest H₂O coverages measured, we observe a steep rise in the amount of exchange with the oxygen atom from H₂¹⁶O. The exchange levels off at coverages > 0.90 ML, where about half of all pre-adsorbed O_{ad} has participated in the oxygen exchange reaction. This indicates that one oxygen adatom interacts with up to two H₂O molecules. This is similar to what we observed on the Pt(533) surface.

Varying ¹⁸O pre-coverages

Figure 6.5 shows TPD spectra of ~ 1 ML H₂O desorbing from a Pt(553) surface that has been pre-covered with varying amounts of O_{ad}. The lowest spectrum corresponds to H₂O desorbing from the bare Pt(553) surface. We observe the three peak structure, α_1 – α_3 , with peaks at 197, 171, and 145 K, corresponding to, respectively, H₂O desorbing from step (stabilized) sites, terrace sites, and other H₂O molecules. When we start to pre-cover the step sites with O_{ad}, the α_1 peak disappears and the β_1 and β_2 peaks appear instead, both at higher surface temperatures than the original α_1 peak. The α_2 peak at 171 K is reduced to a shoulder to the newly formed β_5 peak at 163 K. The β_1 peak shifts to lower temperatures and has a decreasing integral with increasing O_{ad} pre-coverage, until it ends up being the γ_1 peak. The desorption temperature of the β_2 peak, increases slightly with increasing O_{ad} coverage. However, it is difficult to say whether β_2 is actually shifting or if it is an artifact due to the shift of β_1 . We attributed mainly β_1 to OH at step sites. The decrease in β_1 desorption temperature shows that filling more (than half) of the step sites with O destabilizes OH formation on these step sites. The γ_3 peak, around 191 K becomes visible when ~ 25% of the terraces sites is pre-covered with O_{ad}. The equilibrium of



shifts to the left with increasing $\theta_{\text{O, terrace}}$. Instead OH is formed on terraces.

The change in α_2 shows that the presence of only a little bit of oxygen (at step sites), influences H₂O molecules at terrace sites drastically. Around the coverage where all step sites are pre-covered with O_{ad} the profile of the TPD is the most

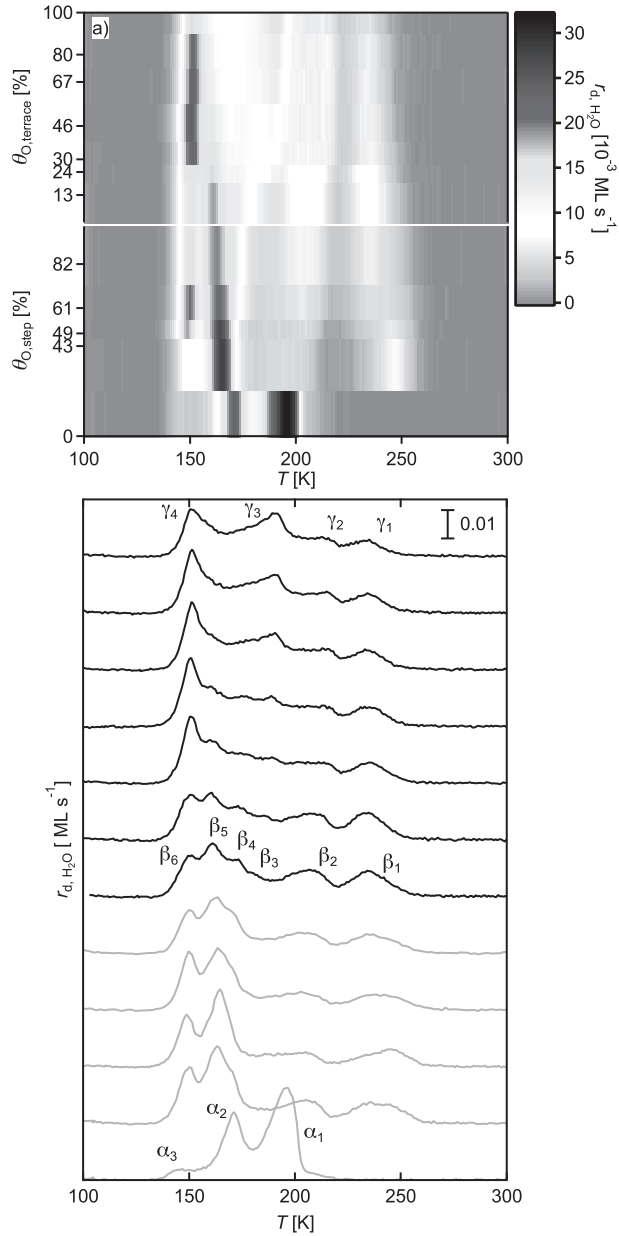


Figure 6.5 TPD spectra of ~ 1 ML H_2O desorbing from Pt(553) with varying O_{ad} pre-coverages of the steps sites (bottom half) and the full step and part of the terrace sites (top half).

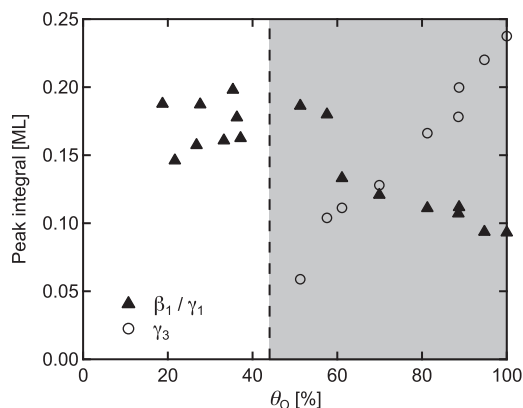


Figure 6.6 Peak integral of β_1/γ_1 and γ_3 as a function of oxygen pre-coverage

flat, with a high number of relatively small peaks. This could indicate that many stable structures which vary only slightly in adsorption energy exist around this temperature.

When terrace sites become filled with O_{ad} γ_3 increases in intensity. In contrast to what is observed on Pt(111),^{14,90} the peak temperature of γ_3 does not shift with O_{ad} pre-coverage. The γ_3 peak is located at a similar temperature as the peak associated with recombinative desorption of OH from Pt(111) that has been pre-covered with 0.25 ML O_{ad} . The increase in γ_3 indicates that more H₂O is incorporated in the OH/H₂O hydrogen bonded network at the (111) terraces at the expense of OH formation on step sites, as we already argued in the previous subsection. To substantiate this statement, we deconvolute the TPD spectra by fitting a total of six Gaussians to all TPD spectra. Gaussians do not describe the peak shape of the data perfectly, but give a reasonable approximation. Moreover, the number of overlapping peaks can make deconvolution of the data difficult, but we find that by keeping some peaks relatively constant, a reasonable fit can be obtained and peak integrals can be quantified. However, we shall only use them for comparison to spectra that have been fit using similar parameters. The resulting peak integrals are shown in figure 6.6. When only the step sites are pre-covered with O_{ad} the peak integral of β_1 is more or less constant. When the terrace sites become pre-covered with O_{ad} γ_3 emerges and the integral of β_1 decreases. Both figure 6.5 and 6.6 show that this is a gradual process. This situation appears comparable to electrochemistry, where it is possible to control the amount of O_{ad} or OH_{ad} on step and terrace sites by varying the electrode potential, *i.e.* the driving force of the reaction. In UHV, however, this is accomplished by varying the particle concentrations, θ_O in this particular case.

Figure 6.7 shows the isotopic partitioning in ~ 1 ML H₂O vs. the amount of pre-

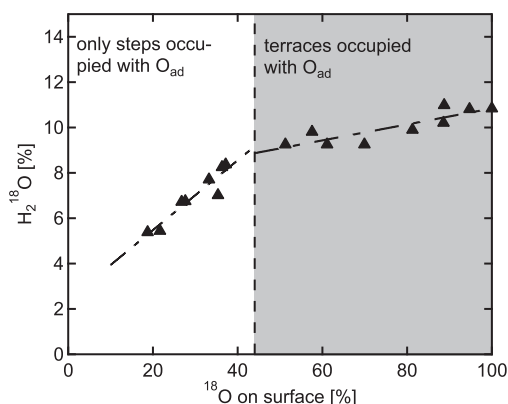


Figure 6.7 Isotopic partitioning of H_2^{18}O vs. the amount of pre-adsorbed $^{18}\text{O}_2$ when Pt(553) is covered with ~ 1 ML H_2^{16}O . The dashed line marks the point where the (111) terrace starts to become occupied with $^{18}\text{O}_{\text{ad}}$.

adsorbed O_{ad} on the surface. The white side of the panel shows the $\theta_{^{18}\text{O}}$ coverages at which only the step sites are (partially) covered with O_{ad} . We observe an increase in the relative amount of water molecules desorbing as H_2^{18}O from 5 to 9%. At coverages larger than 44% $^{18}\text{O}_{\text{ad}}$, the terraces start to become occupied with O_{ad} as well. This is shown by the dashed line and the gray area. Here the isotopic partitioning rises much less steeply from 9 to 11%. This indicates that when only step sites are being pre-covered with $^{18}\text{O}_{\text{ad}}$, all extra $^{18}\text{O}_{\text{ad}}$ is likely to participate in the oxygen exchange reaction. When terrace sites become occupied with $^{18}\text{O}_{\text{ad}}$ as well, not all $^{18}\text{O}_{\text{ad}}$ atoms participate in the oxygen exchange reaction. The extra O adatoms compete with the O_{ad} on step sites for H_2O molecules. H_2O molecules favor O adatoms on terrace sites, which are more easily incorporated in a hydrogen bonded network, whereas this probably leaves some unreacted H_2O molecules as well.

Figure 6.8 shows the isotopic partitioning of oxygen atoms desorbing as O_2 . We observe most exchange for the lowest oxygen coverages. A small amount of oxygen is more active in the oxygen exchange reaction. All extra oxygen is less active, though we do not observe a clear discontinuity in the trend when terrace sites start to become filled as well. This is consistent with the observation β_1 and β_2 decrease with increasing oxygen pre-coverage and that this is a gradual process.

6.3.4 Unannealed Pt(553) surface

A final point of consideration is the treatment of the Pt(553) surface, since it is more prone to reconstruction than surfaces with (100) step sites.

Figure 6.1b shows TPD spectra of varying O_{ad} coverages desorbing from a

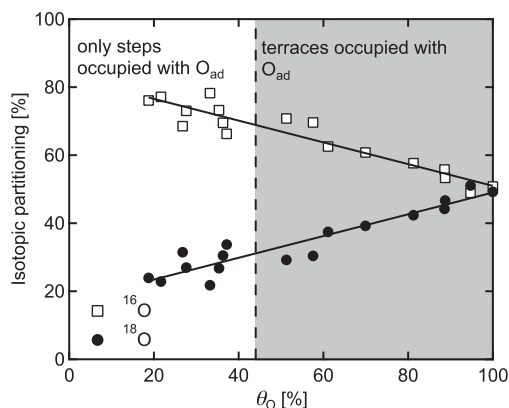


Figure 6.8 Isotopic partitioning of ^{16}O and ^{18}O desorbing in O_2 as function of the amount of pre-adsorbed $^{18}\text{O}_2$ when Pt(553) is covered with $\sim 1 \text{ ML H}_2^{16}\text{O}$. The dashed line marks the point where the (111) terrace starts to become occupied with $^{18}\text{O}_{\text{ad}}$.

Pt(553) surface, that has not been annealed for 3 minutes at 1200 K following an experiment where oxygen had been adsorbed at the surface. The eight traces with the lowest coverage have been obtained by first saturating the surface and then heating it to 662 – 750 K before cooling down again and subsequently taking the TPD. The three traces with the highest coverage are all from surfaces with the maximum coverage, taken subsequently without any annealing above 1000 K in between. At the lowest coverages we observe one peak. It starts at 767 K and shifts towards lower temperatures (722 K) with increasing coverage, indicating second order desorption kinetics. The behavior of this peak is similar to what we observe with the properly treated surface. At coverages above 0.19 ML a new shoulder appears at 649 K. If we try to obtain the surface with the maximum amount of O_{ad} , this spectrum turns out to be not reproducible. Every subsequent TPD will give more O_{ad} in the peak associated with desorption from terrace sites. This peak shows zero order desorption behavior, which indicates that this peak is no longer due to the recombinative desorption of O_{ad} . Zero order desorption kinetics are typical of concentration independent processes. A conceivable mechanism would be that sub-surface oxygen comes to the surface and reacts immediately with O_{ad} , leaving the O surface coverage constant. Another option would be the formation of oxide clusters which are stable at high temperatures, as is observed on the chiral Pt(531) surface.¹⁴¹

Figure 6.9 shows $\sim 1 \text{ ML H}_2\text{O}$, desorbing from a Pt(553) surface with $\sim 0.06 \text{ ML}$ oxygen pre-adsorbed, *i.e.* about half of the step filled with O_{ad} . The dashed line shows the spectrum with the properly handled surface. It shows the same structure as we observed in figure 6.5. The solid line shows a spectrum where we did not perform the annealing step in between consecutive experiments. It still shows

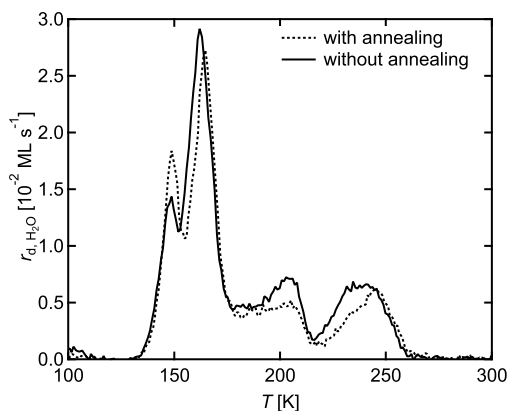


Figure 6.9 TPD spectra of H_2O desorbing from a Pt(553) surface with $\theta_{\text{O}} = 0.06$ ML with annealing for 3 min at 1200 K between experiments (dashed line) and without annealing (solid line).

a four peak structure, but the integrals of the β_1 and β_2 peaks have increased by $\sim 23\%$ compared to the properly treated surface. All peak temperatures, except from the multilayer peak, have shifted slightly towards lower temperatures. The increased integrals of the non-multilayer peaks indicate an increase in effective surface area for the surface without the annealing step. This observation is consistent with the idea that a sub-surface oxide or oxide cluster is formed, that roughens the surface upon desorption.

6.4 Conclusion

Water molecules desorbing from the bare Pt(553) surface desorb in a three peak structure. When the step sites are pre-covered with O_{ad} this turns into a six peak structure. On step sites we likely observe OH formation, desorbing in a two peak feature, which has to be stabilized in a hydrogen bonded network of H_2O molecules. The desorption temperature and intensity of these peaks decrease with increasing O_{ad} pre-coverage. Not only H_2O desorption from step sites is influenced, but from terrace sites as well. The many different peaks in the spectrum could be due to different stable structures at different $\text{O} : \text{H}_2\text{O}$ ratios. When the terrace sites are also covered with O_{ad} we observe a sharp feature at ~ 193 K which we attribute to recombinative desorption of OH_{ad} from terrace sites. At these higher $^{18}\text{O}_{\text{ad}}$ pre-coverages the amount of exchange is similar to that when only the step sites are pre-covered with $^{18}\text{O}_{\text{ad}}$. We attribute this not to inactivity of terrace O adatoms to interact with H_2O , but to the competition between terrace and step O adatoms to react with H_2O molecules. OH formed at terrace sites is more easily incorporated

in a hydrogen bonded network of OH/H₂O, and is, therefore, favored over the formation of OH on step sites. Thus, in spite of the fact that OH at step sites has a higher binding energy than OH at terrace sites, the possibility of the formation of OH at terrace sites actually inhibits the formation of OH at step sites, leaving O_{ad,step} unreacted. This is probably due to the fact that on terrace sites more extensive hydrogen bonded networks can be formed.