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

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Water is the most extraordinary substance! Practically all its properties are anomalous, which enabled life to use it as building material for its machinery. Life is water dancing to the tune of solids.

Albert Szent-Györgyi (1893–1986)

# 5

## The interaction between $\text{H}_2\text{O}$ and pre-adsorbed O on the stepped Pt(533) surface

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**Abstract** We have investigated co-adsorption of  $\text{H}_2\text{O}$  and  $\text{O}_{\text{ad}}$  on the stepped Pt(533) surface using temperature programmed desorption (TPD) in combination with isotope exchange. Water desorption from both bare and oxygen pre-covered Pt(533) gives rise to three easily identifiable peaks in the TPD spectrum between 140–210 K. Only in co-adsorption experiments a desorption feature at  $\sim 270$  K appears, which we ascribe to recombinative desorption of  $\text{OH}_{\text{ad}}$  on step sites. If the surface is saturated with  $\text{O}_{\text{ad}}$ , we also observe a broadening of the desorption peak at 188 K, indicative of OH-formation on terrace sites. Oddly, the magnitude of the isotope exchange hardly varies with  $\text{O}_{\text{ad}}$  pre-coverage. Detailed analysis of the results suggest a strong bias for  $\text{OH}_{\text{terrace}}$  formation over  $\text{OH}_{\text{step}}$  formation. This is likely related to the extent to which  $\text{OH}_{\text{ad}}$  can be incorporated into a larger hydrogen bonded network. In spite of the observation that  $\text{OH}_{\text{step}}$  is more strongly bound than  $\text{OH}_{\text{terrace}}$ , the overall exchange on the Pt(533) surface is much lower than on Pt(111).

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## 5.1 Introduction

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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.<sup>6–8</sup> The interaction between H<sub>2</sub>O, O<sub>2</sub> 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 in oxidation reactions.<sup>132,133</sup> Another often studied process is the water formation reaction (WFR), where H<sub>2</sub> and O<sub>2</sub> react to form water via an OH intermediate. This reaction is also relevant for fuel cell catalysis and often studied as a prototype surface science reaction, because of its relative simplicity.<sup>26,85,134–137</sup>

Most studies investigating the platinum-water interaction have used the (111) surface as a model for the catalytically active surface. Although this is the least complex system, ultra high vacuum (UHV) studies already show significant complexity in adsorption and desorption phenomena.<sup>118–120</sup> 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.<sup>13</sup> Although some experiments have focused on the influence of steps and defects that are naturally present on a Pt(111) crystal,<sup>28,29</sup> more insight should result from studies employing a better defined model, such as a regularly stepped surface.<sup>26,27</sup>

The general consensus is that on Pt(111) water adsorbs molecularly at all coverages and temperatures (< 180 K). Even prolonged exposure to X-rays does not cause dissociation in the water layer.<sup>16</sup> Classically, water adsorbed on metal surfaces is thought to form an ice-like bilayer of hexagonal rings.<sup>6–8</sup> Low energy electron diffraction (LEED)<sup>17</sup> and helium diffraction<sup>18</sup> images show a ( $\sqrt{37} \times \sqrt{37}$ )R25.3° structure for H<sub>2</sub>O islands formed at submonolayer coverage on Pt(111), which is compressed into a ( $\sqrt{39} \times \sqrt{39}$ )R16.1° structure for the full bilayer. A combined scanning tunneling microscopy (STM) and density functional theory (DFT) study finds these “ $\sqrt{37}$ ” and “ $\sqrt{39}$ ” phases to also contain pentagon and heptagon structures.<sup>19</sup> An extensive high resolution electron energy loss spectroscopy (HREELS) study by Jacobi *et al.* shows distinct differences in the vibrational spectra for water monomer, bilayer, and multilayer structures.<sup>20</sup> Water dosed on Pt(111) at temperatures well below 135 K leads to the formation of amorphous solid water (ASW).<sup>21</sup> Temperature programmed desorption (TPD) studies of ASW show two peaks. One peak at 171 K is associated with monolayer desorption. This peak exhibits the characteristics of zero-order desorption kinetics<sup>22</sup> and has been attributed to the co-existence of a condensed phase and a 2-dimensional water-gas at submonolayer

coverages.<sup>21</sup> A second peak, associated with desorption from multilayers, starts at 154 K and increases in temperature with coverage.<sup>23</sup>

Only a few studies have been performed on the interaction between H<sub>2</sub>O and stepped platinum surfaces.<sup>26–29</sup> Scanning tunneling microscopy (STM) studies on an imperfect Pt(111) crystal show that water adsorbs preferentially on step sites, forming molecular chains.<sup>28</sup> TPD shows a stabilization of the water monolayer by the presence of step sites.<sup>26,27,124</sup> A two peak structure is observed for a monolayer of H<sub>2</sub>O desorbing from the stepped Pt(533) surface (Pt[4(111) × (100)]). At coverages below 0.13 ML a single peak is observed, which is reported to shift with coverage from 184 to 188 K.<sup>27</sup> This peak is associated with desorption from step sites. At higher coverage (above ~ 0.33 ML) a shoulder appears at 171 K, which is associated with desorption from terrace sites. The peak associated with desorption from the water multilayer appears at ~ 150 K.<sup>27</sup>

Oxygen adsorbs in three different states on Pt(111): physisorbed O<sub>2</sub> molecules are stable below 45 K,<sup>30</sup> chemisorbed O<sub>2</sub> molecules below 100 – 200 K,<sup>11</sup> and atomic oxygen below 575 – 900 K.<sup>11</sup> Subsurface oxygen is reported between 1000 and 1200 K if the sample is annealed between these temperatures at high oxygen pressures.<sup>11</sup> Oxygen dissociation is activated and atomic oxygen formation occurs via a precursor state of molecularly adsorbed oxygen. This precursor mechanism causes the sticking coefficient to decrease with surface temperature.<sup>10,31</sup> The maximum O<sub>ad</sub> coverage that can be reached via background dosing is 0.25 ML. LEED<sup>11,32–36</sup> and STM<sup>37</sup> pictures show a (2 × 2) pattern. Oxygen atoms bind preferentially in the fcc hollow sites.<sup>38,39</sup>

On stepped surfaces a similar (2 × 2) LEED-pattern is observed for O<sub>ad</sub> as on Pt(111).<sup>9,40</sup> However, Fiorin *et al.* state that no ordered structure of O<sub>ad</sub> atoms is formed on Pt(211) and Pt(411).<sup>44</sup> Dissociation takes place at 200 K<sup>45</sup> on the (111) terrace, but occurs predominantly on step sites<sup>10,46–48</sup> between 150 and 230 K.<sup>44,45,49</sup> Oxygen atoms adsorb preferentially on step sites.<sup>37,48</sup> A combined STM and density functional theory (DFT) study<sup>37</sup> shows that for (100) steps a twofold edge bridging site is favored, whereas for (110) steps the fcc hollow site behind the step edge is favored. O<sub>ad</sub> atoms bind stronger on (100) steps than on (110) steps.<sup>44</sup> TPD spectra on Pt(533),<sup>10,45,46,50</sup> other surfaces with (100) steps,<sup>49,51,52</sup> and surfaces with (111) steps<sup>9,32,40,53</sup> all show a three peak structure in the molecular oxygen regime and a two peak structure in the atomic oxygen regime. Equilibration between step and terrace sites happens only above 400 K.<sup>46</sup> Oxygen atoms do not diffuse onto the lower lying terrace.<sup>48</sup>

The co-adsorption of H<sub>2</sub>O and O<sub>2</sub> on Pt(111) is known to produce OH<sub>ad</sub> for 150 ≤ T ≤ 185 K.<sup>16,75,76</sup> When <sup>18</sup>O<sub>2</sub> and H<sub>2</sub><sup>16</sup>O are co-adsorbed at submonolayer coverages and subsequently annealed, the ratio <sup>18</sup>O : <sup>16</sup>O desorbing in H<sub>2</sub>O is 1 : 2, independent of the initial H<sub>2</sub><sup>16</sup>O coverage. Surface OH groups do not readily ex-

change H with unreacted O<sub>ad</sub>.<sup>77</sup> From this stoichiometry initially

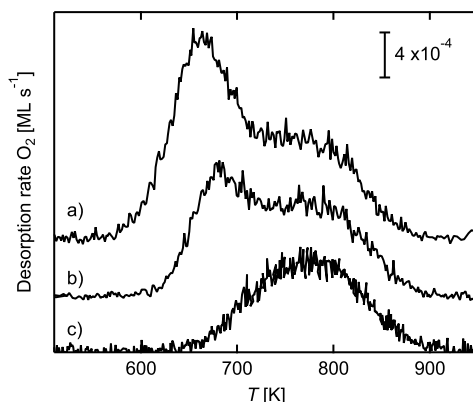


was deduced as the reaction equation.<sup>77,78</sup> However, recent DFT calculations found that this reaction does not go to completion and the H<sub>ad</sub> is actually incorporated in a hydrogen bonded network of H<sub>2</sub>O<sub>ad</sub> and OH<sub>ad</sub><sup>15,79</sup> via



All O<sub>ad</sub> participates in the OH formation.<sup>16</sup> This produces a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  LEED pattern with a weak  $(3 \times 3)$  superstructure.<sup>14,76,78</sup> H<sub>2</sub>O is needed to stabilize the formed OH species.<sup>16,80</sup> Different structures can be produced by different O<sub>ad</sub> : H<sub>2</sub>O ratios. The maximum number of H<sub>2</sub>O molecules that can participate in the reaction with one O adatom is four. However, the stoichiometry in equation (5.2) produces the most stable structure.<sup>14</sup> The hydrogen bonded network consists of hexagonal rings of coplanar O atoms bonded near atop sites with different O—O separations. 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.<sup>76,81</sup> 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.<sup>82</sup> The OH/H<sub>2</sub>O overlayer does not have H-bonds left to bind to a second layer, which makes the surface hydrophobic.<sup>83</sup> When H<sub>2</sub>O is removed, two OH react again to form immediately desorbing H<sub>2</sub>O (g) and O<sub>ad</sub>. Water desorption from the O-covered surface does not follow simple kinetics and happens through multiple channels: direct desorption, via OH recombination, as well as through proton transfer mediated transportation of water to the edges of an OH/H<sub>2</sub>O cluster.<sup>84</sup> Desorption happens primarily at low coordination and defect sites in the OH/H<sub>2</sub>O overlayer. HREELS studies on Pt(111) show three separate  $\delta(\text{OH}_{\text{ad}})$  peaks at 127, 113, and 102 meV, attributed to structurally different OH-groups. The two lower energy peaks are due to OH-groups which are hydrogen bond donors, but not acceptors.<sup>78</sup> The formed OH<sub>ad</sub> is also the intermediate in the WFR. In the presence of gas-phase H<sub>2</sub> it reacts readily to form H<sub>2</sub>O.<sup>85</sup>

We have studied the interaction between O<sub>ad</sub> and H<sub>2</sub>O on the stepped Pt(533) surface, which consists of 4 atom wide (111) terraces and a (100) step. The sample is studied under ultra high vacuum (UHV) conditions using TPD and LEED in combination with isotope exchange. We have discussed the main differences between this surface and the Pt(553) surface in chapter 4. Here we give a more elaborate account of the results for the Pt(533) surface.



**Figure 5.1** a) TPD spectrum of  $\text{O}_2$  desorbing from Pt(533) obtained by dosing 0.4 L  $\text{O}_2$  (enough to maximally cover the surface with  $\text{O}_{\text{ad}}$ ). b) After annealing for 5 min at 610 K. c) After annealing for 5 min at 640 K.

## 5.2 Experimental

All experiments were performed in POTVIS. General experimental details can be found in chapter 2.1.

During TPD experiments the sample was placed in a collinear geometry with the differentially pumped quadrupole mass spectrometer (QMS). Gee and Hayden<sup>10</sup> observed an angle dependence for the sticking probability of  $\text{O}_2$  on Pt(533). This could indicate that the angular distribution of  $\text{O}_2$  desorbing from Pt(533) is non uniform as well. Therefore, the use of the differentially pumped QMS might influence the relative intensities of oxygen desorbing from step and terrace sites. We tested this by comparing the TPD spectra from the differentially pumped QMS with spectra obtained with the QMS inside the main vacuum. No difference was observed in the spectra, indicating that the housing of the differentially pumped QMS is located close enough to the sample for angle dependent effects not to be of influence.

## 5.3 Results and discussion

### 5.3.1 $\text{O}_2$ adsorption/desorption

We have shown and discussed the TPD spectra of the single species ( $\text{O}_2$  and  $\text{H}_2\text{O}$ ) in chapter 3. Here, we only summarize our main findings. Figure 5.1a shows the  $^{16}\text{O}_2$  TPD spectrum with the maximum coverage we could obtain. The  $^{16}\text{O}_2$  was dosed at  $T_{\text{crys}} \approx 100$  K. The low temperature peak at 664 K is associated to the

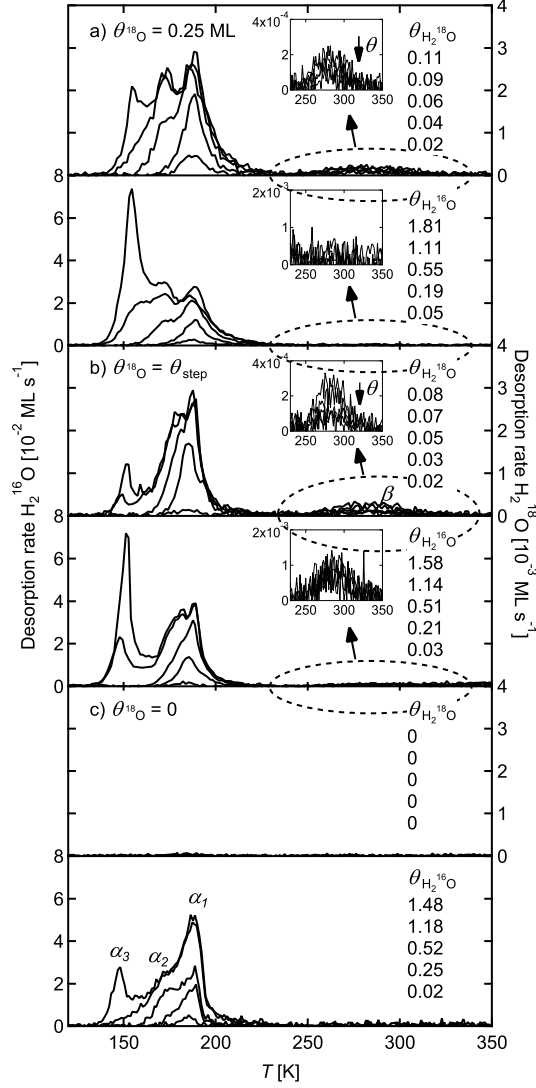
recombinative desorption of O<sub>ad</sub> on the (111) terraces.<sup>10</sup> The high temperature peak at 775 K is associated to the recombinative desorption of O<sub>ad</sub> from step sites.<sup>10</sup> The ratio O<sub>ad,step</sub> : O<sub>ad,ter</sub> as determined by Gaussian fits is approximately 0.11 : 0.14.

Flashing to 250 K removes all molecularly adsorbed oxygen from the Pt(533) surface and ensures that all remaining oxygen is dissociated into atomic oxygen. When the fully oxygenated surface is annealed at 650 K oxygen ad-atoms from terrace sites recombine into O<sub>2</sub> and desorb, leaving less O<sub>ad</sub> on the surface for the subsequent TPD, resulting in spectrum 5.1c, where only the step sites remain covered with O<sub>ad</sub>. Annealing at lower temperatures leaves intermediate amounts of O<sub>ad</sub> on the surface (*e.g.* 610 K results in spectrum 5.1b). Annealing between 650 and 735 K partially desorbs O<sub>ad</sub> from step sites as well. If the surface is annealed at T > 750 K, no desorbing O<sub>2</sub> can be detected in the subsequent TPD spectrum. Hydrogen TPDs taken after annealing the oxygen covered surface to 860 K (to just boil off the oxygen) show no change in the amount of step and terrace sites compared to the freshly prepared surface, indicating that no significant O-induced surface reconstruction has occurred.

In the isotope exchange experiments <sup>18</sup>O<sub>2</sub> was used instead of <sup>16</sup>O<sub>2</sub>. In this case 3% of the pre-dosed O<sub>ad</sub> on the surface is <sup>16</sup>O and 97% <sup>18</sup>O due to contamination from background gas. The isotope exchange data are uncorrected for this effect. When <sup>18</sup>O<sub>2</sub> is present on step sites only and consecutively <sup>16</sup>O<sub>2</sub> is dosed on the terrace sites, the O<sub>2</sub> TPD shows both species desorbing from both step and terrace sites. The ratio <sup>16</sup>O : <sup>18</sup>O is identical for both peaks, indicating that oxygen ad-atoms on the step and terrace sites have fully equilibrated. Equilibration between step and terrace O has previously been found to occur above 400 K only.<sup>46</sup> Since H<sub>2</sub>O is only present on the surface at temperatures below 320 K, we do not believe that this equilibration influences the exchange between pre-adsorbed O<sub>ad</sub> and H<sub>2</sub>O<sub>ad</sub>. However, it is not possible to tell whether the desorption of an oxygen isotope from a step or terrace site specifically is due to reaction at that site with H<sub>2</sub>O or due to the equilibration at higher temperatures. Therefore, we will only discuss the total oxygen signals and not the site specific contributions to the signal when discussing the oxygen exchange data.

### 5.3.2 H<sub>2</sub>O only

Figure 5.2c shows TPD spectra for *m/e* = 18 and 20 after dosing various amounts of H<sub>2</sub><sup>16</sup>O onto a bare Pt(533) surface. We have discussed these results in chapter 3. Briefly, H<sub>2</sub>O desorbs in three peaks, α<sub>1</sub>, α<sub>2</sub>, and α<sub>3</sub>, with peak temperatures of ~ 188 K, ~ 171 K, and ~ 148 K, respectively. The peak at highest temperature, α<sub>1</sub>, appears at the lowest H<sub>2</sub>O coverages. At coverages < 0.25 ML the peak desorption temperature shows a slight increase from 184 K to 188 K with increasing dose. For θ<sub>H<sub>2</sub>O</sub> > 0.25 ML, we observe no shift in desorption temperature until saturation of the α<sub>1</sub> peak. The second peak, α<sub>2</sub>, is clearly observed prior to saturation of α<sub>1</sub>. We



**Figure 5.2** TPD spectra of  $\text{H}_2^{16}\text{O}$  (left axis) and  $\text{H}_2^{18}\text{O}$  (right axis) dosed on Pt(533) with a)  $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$ , b)  $\theta_{^{18}\text{O}} = \theta_{\text{step}}$ , and c)  $\theta_{^{18}\text{O}} = 0$ .



interpret this observation as proof of limited mobility of H<sub>2</sub>O molecules adsorbed onto this surface. The lowest temperature peak,  $\alpha_3$ , is only observed when  $\alpha_1$  and  $\alpha_2$  have saturated. Following Grecea *et al.*,<sup>27</sup> we use the largest combined integral for  $\alpha_1$  and  $\alpha_2$  as a reference for the amount of adsorbed H<sub>2</sub>O and refer to this amount as  $\theta_{\text{H}_2\text{O}} = 1$  ML. The ratio  $\alpha_1 : \alpha_2$  as determined by Gaussian fits is roughly 5 : 4. Dosing larger quantities leads to the appearance of the  $\alpha_3$  peak, which is the result of multilayer desorption.<sup>27</sup> The spectra show a discrepancy in the absolute desorption temperatures compared to the ones reported by Grecea *et al.*,<sup>27</sup> which has been addressed in chapter 3. When we inspect the H<sub>2</sub><sup>18</sup>O signal, we observe that adsorbing H<sub>2</sub><sup>16</sup>O on bare Pt(533) leads to no measurable desorption of H<sub>2</sub><sup>18</sup>O.

### 5.3.3 Co-adsorption of <sup>18</sup>O<sub>ad</sub> and H<sub>2</sub><sup>16</sup>O

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

Figure 5.2b shows TPD spectra for  $m/e = 18$  and 20 after dosing various amounts of H<sub>2</sub><sup>16</sup>O onto a Pt(533) surface where all step sites have been pre-covered with <sup>18</sup>O. First we focus on the H<sub>2</sub><sup>16</sup>O spectra (lower part, plotted versus left axis). Similar to the bare surface, we observe a three peak structure. The peak temperatures are roughly the same as well. The  $\alpha_1$  desorption temperature slightly increases from 184 K to 188 K between 0 and 0.25 ML. The  $\alpha_2$  peak starts to appear at 182 K as a shoulder to  $\alpha_1$ , before  $\alpha_1$  saturates, at  $\theta_{\text{H}_2\text{O}} > 0.50$  ML. The multilayer peak,  $\alpha_3$ , appears at  $\sim 150$  K for  $\theta_{\text{H}_2\text{O}} > 0.90$  ML, after saturation of  $\alpha_1$  and  $\alpha_2$ . Thus,  $\alpha_1$  and  $\alpha_3$  have not shifted compared to the bare surface, whereas  $\alpha_2$  has shifted from 171 to 182 K. This indicates an extra stabilization of terrace water by the O ad-atoms on step sites. If we look closely at the peak shapes and integrals we notice that these have changed compared to  $\theta_{18\text{O}} = 0$ , *i.e.* the ratio  $\alpha_1 : \alpha_2$  is smaller in the  $\theta_{18\text{O}} \approx \theta_{\text{step}}$  case. The  $\alpha_2$  peak has broadened slightly at the low temperature side. This could either be explained by relatively more H<sub>2</sub>O desorbing from terrace sites or a decrease in the difference in adsorption energy for step and terrace sites. We also observe that the water multilayer forms at lower water coverages than for the bare surface. This is probably due to competition between O ad-atoms and H<sub>2</sub>O molecules for adsorption on step sites. This would lead to less H<sub>2</sub>O on step sites and would thus explain the decrease in magnitude of  $\alpha_1$ .

Next we turn to the H<sub>2</sub><sup>18</sup>O signal (upper part of figure 5.2b, plotted versus right axis). Here, we first note that we have not unambiguously determined the integral for 1 ML H<sub>2</sub><sup>18</sup>O desorbing from the surface, we have used the integral for 1 ML H<sub>2</sub><sup>16</sup>O as our reference in calculating  $\theta_{\text{H}_2^{18}\text{O}}$ . We feel this is justified since the ionization efficiency in our QMS, the transmission through the quadrupole, and the amplification by the channeltron are not expected to vary significantly for these isotopes. Turning to the data, we observe that the  $\alpha_1$  and  $\alpha_2$  peaks behave similar to the H<sub>2</sub><sup>16</sup>O signal, though the  $\alpha_2$  peak appears to be slightly smaller than in the

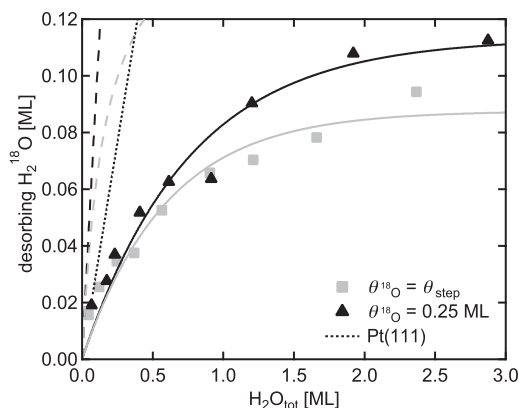
$\text{H}_2^{16}\text{O}$  signal. The main difference is that the signal is lower by a factor of ten. The  $\alpha_3$  peak is relatively much smaller.  $\text{H}_2^{18}\text{O}$  desorption starts at 142 K, indicating that reaction (5.2) occurs reversibly at (and quite possibly below) this temperature. The small amounts of  $\text{H}_2^{18}\text{O}$  in  $\alpha_3$  show that the exchange between the first and second water layer is poor.

A new broad feature ( $\beta$ ) is observed at  $\sim 270$  K. The  $\beta$  peak is hardly discernible in the  $\text{H}_2^{16}\text{O}$  signal in the figure. However, here we would like to point out the scale difference of a factor of ten in the spectra. The feature has to be due to an attractive interaction between  $\text{H}_2\text{O}$  and the adsorbed O-atoms on step sites. Possible species formed are  $(\text{H}_2\text{O})_x\text{—O}_y$ , OH, or  $\text{O} + \text{H}$ . OH is known to be stable on  $\text{Pt}(111)^{14-16,75,76}$  and is thus a likely candidate for the species formed at step sites.

OH has to be stable on a surface for the WFR to occur. It is an intermediate species in the reaction, but it has been shown on  $\text{Pt}(111)$  that its stability makes the WFR occur efficiently, since it catalyzes the reaction.<sup>85,135,138,139</sup> On  $\text{Pt}(111)$  all  $\text{O}_{\text{ad}}$  is completely removed by the WFR when the oxygenated surface is kept at 135 K (well below the desorption temperature of atomic oxygen (700 K)<sup>40</sup>) in a hydrogen atmosphere.<sup>134</sup> Therefore, we can test whether OH is stable on the  $\text{Pt}(533)$  surface by use of the WFR. We have held a  $\text{Pt}(533)$  surface with  $\theta_{\text{O}} \approx \theta_{\text{step}}$  under a  $\text{H}_2$  pressure of  $2 \times 10^{-7}$  mbar at 200 K. The surface temperature of 200 K was chosen to desorb all formed  $\text{H}_2\text{O}$  immediately. The subsequent oxygen TPD shows no desorbing oxygen. The  $\text{O}_{\text{ad,step}}$  can only have been removed by the WFR if the formed  $\text{OH}_{\text{ad}}$  is stable. Therefore, we conclude that OH has to be stable at step sites. On  $\text{Pt}(111)$  the stable OH causes  $\text{H}_2\text{O}$  to desorb at higher temperatures, *i.e.* 200 K instead of 170 K for the bare surface.<sup>14,90</sup> On the stepped  $\text{Pt}(533)$  surface this effect is more dramatic, showing an increase of 80 K from 188 K to 270 K. Therefore, a plausible albeit tentative explanation for the high temperature  $\beta$  peak is that it is due to reaction of  $\text{OH}_{\text{step}}$  to form  $\text{H}_2\text{O}$ . Spectroscopic techniques should provide more definitive insight in this matter.

The intensity of the  $\beta$  peak in the  $\text{H}_2^{18}\text{O}$  signal is dependent on  $\text{H}_2\text{O}$  coverage, being larger for lower  $\theta_{\text{H}_2\text{O}}$ . In the  $\text{H}_2^{16}\text{O}$  signal this effect is not observed, but the absolute magnitude of the peak is five times larger, which probably masks this subtle effect. The appearance of the  $\alpha_3$  peak in the  $\text{H}_2^{18}\text{O}$  spectra indicates that reaction (5.2) occurs reversibly at low temperatures. As the reversible reaction (5.2) already occurs below 140 K, we expect that  $^{18}\text{O}$  is leached by  $\text{H}_2^{16}\text{O}$ , leading to a decrease of the  $\beta$  peak in the  $\text{H}_2^{18}\text{O}$  signal with increasing  $\text{H}_2^{16}\text{O}$  coverage.

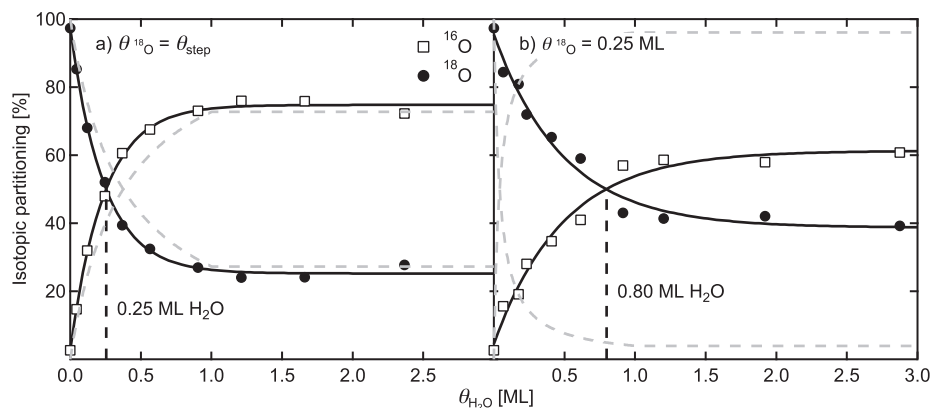
The gray data in figure 5.3 show the absolute amount of desorbing  $\text{H}_2^{18}\text{O}$  as a function of the total amount of desorbing  $\text{H}_2\text{O}$  for  $\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$ . We compare this to the amount of  $\text{H}_2^{18}\text{O}$  formed on  $\text{Pt}(111)^{77}$  as well as to complete isotopic scrambling, assuming a  $\text{Pt} : \text{H}_2\text{O}$  ratio in 1 ML  $\text{H}_2\text{O}$  of 3 : 2. The amount of exchange taking place on the  $\text{Pt}(533)$  surface is far less than if complete isotopic scrambling were to occur. The amount of  $\text{H}_2^{18}\text{O}$  formed increases with increasing  $\text{H}_2^{16}\text{O}$  dose, whereas



**Figure 5.3** Isotopic partitioning versus the amount of adsorbed H<sub>2</sub><sup>16</sup>O for Pt(533) with  $\theta_{18\text{O}} = \theta_{\text{step}}$  (■) and  $\theta_{18\text{O}} = 0.25 \text{ ML}$  (▲). The inset shows the absolute amount of desorbing H<sub>2</sub><sup>18</sup>O. The lines fitted through the data are only a guide for the eye. The dashed lines show calculated traces for complete isotopic scrambling, whereas the dotted line shows the same data for desorption from a Pt(111) surface pre-covered with 0.25 ML O taken from ref.<sup>77</sup>

the relative amount of H<sub>2</sub><sup>18</sup>O drops with increasing H<sub>2</sub>O coverage to 6% (not shown here). This is consistent with the fact that  $\alpha_1$  and  $\alpha_2$  do not increase in size in the H<sub>2</sub><sup>18</sup>O signal in figure 5.2b when  $\theta_{\text{H}_2\text{O}} > 0.90 \text{ ML}$ . Since the coupling to the second layer was shown to be poor, the relative exchange as a function of  $\theta_{\text{H}_2\text{O}}$  levels off. We will discuss these data further in section 5.3.3.

Figure 5.4a shows the isotopic partitioning of <sup>16</sup>O and <sup>18</sup>O in the TPD spectra of the recombinative desorption of O<sub>ad</sub> from step sites. The dashed line shows the calculated partitioning if complete scrambling occurs. This is clearly not the case. At low H<sub>2</sub><sup>16</sup>O coverages most O<sub>ad</sub> on the surface after water desorption is still <sup>18</sup>O. When the H<sub>2</sub><sup>16</sup>O coverage reaches 0.25 ML 50% of the <sup>18</sup>O<sub>ad</sub> has been exchanged with <sup>16</sup>O from H<sub>2</sub><sup>16</sup>O. The exchange saturates at ~ 75% of all O<sub>ad</sub>. STM shows that at low H<sub>2</sub>O coverages most molecules are located at step sites.<sup>28</sup> Therefore, below 0.25 ML most water is likely located at the steps. Oxygen adatoms are not mobile on the surface below 400 K<sup>46</sup> and all O<sub>ad</sub> is also located at the step. At low coverages all extra adsorbed water is in direct contact with the oxygen adatoms adsorbed at the steps. At higher coverages additional water will be adsorbed at terrace sites and probably not interact with the oxygen atoms on step sites. Therefore, this additional water is not likely to contribute to the isotope exchange. An isotopic partitioning of more than 50% <sup>16</sup>O indicates that each oxygen adatom has interacted with more than one H<sub>2</sub>O molecule, either by direct contact or by reaction (5.2) occurring reversibly at low temperatures, moving <sup>18</sup>O in water to terrace sites or the multilayer, allowing further exchange with H<sub>2</sub><sup>16</sup>O molecules at these sites. The presence of the



**Figure 5.4** Isotopic partitioning in oxygen TPD spectra for varying amounts of  $\text{H}_2^{16}\text{O}$  dosed on Pt(533) pre-covered with a)  $\theta_{^{18}\text{O}} = \theta_{\text{step}}$  or b)  $\theta_{^{18}\text{O}} = 0.25 \text{ ML}$ . The dashed gray lines show calculated traces for complete isotopic scrambling.

$\alpha_2$  and  $\alpha_3$  peaks in the  $\text{H}_2^{18}\text{O}$  spectra makes it impossible to fully exclude the latter explanation. However, we have already argued that coupling to the multilayer is inefficient. The  $\alpha_2$  peak is present in the  $\text{H}_2^{18}\text{O}$  spectra, but it is smaller compared to the  $\text{H}_2^{16}\text{O}$  spectra. Therefore, we think most O is exchanged via a direct interaction between  $\text{O}_{\text{ad}}$  and  $\text{H}_2\text{O}$ . If this is the case, one  $\text{O}_{\text{ad}}$  atom on step sites interacts with up to three  $\text{H}_2\text{O}$  molecules. This is less than on Pt(111), where up to four  $\text{H}_2\text{O}$  molecules can interact with one O adatom.<sup>14</sup> This could be due to the broken symmetry of the surface, introduced by the presence of step sites. Since the  $\text{O}_{\text{ad}}$  is located at the top of the step and is slightly puckering out of the step edge,<sup>37</sup> it is conceivable that some of these  $\text{H}_2\text{O}$  molecules are located at the bottom of the step.

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

Figure 5.2a shows TPD spectra for  $m/e = 18$  and 20 after dosing various amounts of  $\text{H}_2^{16}\text{O}$  onto a Pt(533) surface where both step and terrace sites have been pre-covered with  $^{18}\text{O}$ . We still observe three peaks in the  $\text{H}_2^{16}\text{O}$  signal (lower half, plotted vs. left axis). The peak temperatures are identical to the ones on the bare surface:  $\alpha_1 \sim 188 \text{ K}$ ,  $\alpha_2 \sim 171 \text{ K}$ , and  $\alpha_3 \sim 155 \text{ K}$ . However, the  $\alpha_1$  peak has become somewhat broader at the high temperature side compared to both  $\theta_{^{18}\text{O}} = 0$  and  $\theta_{\text{step}}$ . It is located at a similar position as the feature caused by oxygen-induced OH-formation on Pt(111), which varies between 195 and 205 K for different  $\text{O}_{\text{ad}}$  pre-coverages.<sup>90</sup> Therefore, it would be difficult to observe separate peaks for recombinative desorption of  $\text{H}_2\text{O}$  from OH on terrace sites and  $\text{H}_2\text{O}$  desorbing from step sites, but the sum of these peaks could be observed as a broadened  $\alpha_1$  peak. Thus the broadening of the  $\alpha_1$  peak suggests OH formation at terrace sites. The

multilayer peak,  $\alpha_3$ , is already present at coverages well below 0.9 ML, which is a lower coverage than in the  $\theta_{18\text{O}} \approx \theta_{\text{step}}$  case, where we ascribed this to competition between  $\text{O}_{\text{ad}}$  and  $\text{H}_2\text{O}$  on step sites. We ascribe the further lowering of the combined  $\alpha_1$ - $\alpha_2$  integral to a similar competition of  $\text{O}_{\text{ad}}$  with  $\text{H}_2\text{O}$  for adsorption sites both on steps and terraces. The  $\text{H}_2^{18}\text{O}$  signal (upper half of figure 5.2c, plotted vs. right axis) behaves similar to the  $\theta_{18\text{O}} \approx \theta_{\text{step}}$  case: the  $\alpha_1$  and  $\alpha_2$  peaks are smaller versions of the ones in the  $\text{H}_2^{16}\text{O}$  signal, whereas the  $\alpha_3$  feature is relatively small. We do not observe the slight decrease in the  $\alpha_2$  peak, as was the case on the  $\theta_{\text{O}} \approx \theta_{\text{step}}$  surface. The appearance of  $\text{H}_2^{18}\text{O}$  in the multilayer peak indicates that  $^{18}\text{O}$ - $^{16}\text{O}$  exchange has begun below  $\sim 155$  K but  $\text{H}_2\text{O}$  exchange between the first and second  $\text{H}_2\text{O}$  layers remains limited.

Also in this case we observe a small  $\beta$  peak at  $\sim 270$  K, albeit slightly smaller compared to the  $\theta_{\text{step}}$  case. In the  $\text{H}_2^{16}\text{O}$  signal it may be lost in the noise. This indicates that the extra O adatoms on terrace sites disfavor OH formation at step sites. Possibly,  $\text{H}_2\text{O}$  molecules near the step edge are more inclined to interact with  $\text{O}_{\text{ad}}$  on terrace sites than with  $\text{O}_{\text{ad}}$  on step sites as we argued before for Pt(553) (see chapters 4 and 6).

The black triangular data points in figure 5.3 show the absolute amount of  $\text{H}_2^{18}\text{O}$  desorbing as a function of the total amount of desorbing  $\text{H}_2\text{O}$  for  $\theta_{18\text{O}} = 0.25$  ML. The amounts formed are far less than in case of complete isotopic scrambling, or desorption from the Pt(111) surface. At  $\text{H}_2\text{O}$  coverages  $< 0.25$  ML, the amount of  $\text{H}_2^{18}\text{O}$  formed is independent of oxygen pre-coverage (the black and the gray traces are identical). The step sites were always fully covered with  $\text{O}_{\text{ad}}$  in both sets of experiments. At these low coverages water preferentially adsorbs at step sites, as has been shown previously for the bare surface by STM.<sup>28</sup> All adsorbed water is in contact with  $\text{O}_{\text{ad}}$  at low coverages. As the amount of  $\text{H}_2\text{O}$  increases the traces start to differ. For  $\theta_{18\text{O}} = 0.25$  ML the maximum amount formed is  $\sim 0.11$  ML or 5%. This is only 1.2 times the amount we measured for  $\theta_{18\text{O}} \approx \theta_{\text{step}}$ . However, from the ratio  $\text{O}_{\text{ad,step}} : \text{O}_{\text{ad,ter}}$  obtained from figure 5.1a it is clear that there is over twice as much  $^{18}\text{O}$  present on the surface. The increase in formed  $\text{H}_2^{18}\text{O}$  upon also pre-covering terrace sites with  $^{18}\text{O}$  is far less than would be expected based on this ratio. This could suggest that on the Pt(533) surface  $\text{O}_{\text{ad,terrace}}$  is less active in the isotope exchange with  $\text{H}_2\text{O}$  than  $\text{O}_{\text{ad,step}}$ . For the Pt(553) surface, however, we have argued that at high  $\text{O}_{\text{ad}}$  pre-coverages not  $\text{O}_{\text{ad,terrace}}$  is inactive in the oxygen exchange, but  $\text{O}_{\text{ad,step}}$ . We based this on two observations. First, in TPD spectra with  $\theta_{\text{O}} = \theta_{\text{max}}$  a peak is present at 193 K, which is a similar position as the recombinative OH desorption peak on Pt(111).<sup>14</sup> Second, the peak associated with recombinative desorption of OH from step sites decreases in both size and desorption temperature compared to  $\theta_{\text{O}} \approx \theta_{\text{step}}$  (see chapters 4 and 6). Even though these effects are much more subtle on the Pt(533) surface, we do observe them; the  $\alpha_1$  peak has broadened if we compare the  $\theta_{\text{O}} = 0.25$  ML to the  $\theta_{\text{step}}$  spectra, which could very well be

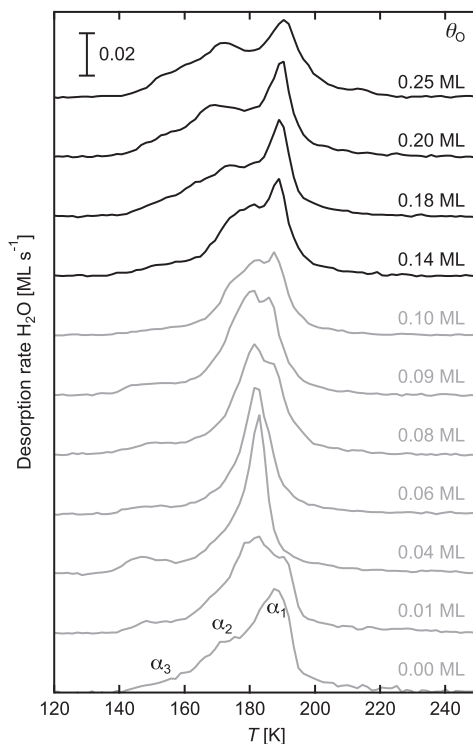
due to an overlap between the original  $\alpha_1$  peak and a peak due to recombinative OH desorption around 192 K. We also observe a decrease in the magnitude of the  $\beta$  peak compared to the  $\theta_{\text{step}}$  case. On Pt(111) it has been shown that  $\text{OH}_{\text{ad}}$  has to be incorporated in a hydrogen bonded OH/ $\text{H}_2\text{O}$  network.<sup>16,80</sup> On Pt(533) this can be done more easily on terrace than on step sites, favoring  $\text{OH}_{\text{terrace}}$  formation over  $\text{OH}_{\text{step}}$  formation, even though for a single OH (*i.e.* in the absence of water) step sites may be more favorable adsorption sites. This also explains why stepped surfaces are far less reactive for reaction (5.2) than Pt(111).

Figure 5.4b shows the isotopic partitioning in  $\text{O}_2$  for  $\theta_{^{18}\text{O}} = 0.25$  ML. At the lowest  $\text{H}_2\text{O}$  coverages the isotopic partitioning is similar to when  $\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$ . However, the isotopic partitioning of  $^{16}\text{O}$  desorbing as  $\text{O}_2$ , *i.e.* O adatoms that have exchanged with the O atoms in  $\text{H}_2^{16}\text{O}$ , rises less steeply than was the case when only the step sites were pre-covered with  $^{18}\text{O}$ . When  $\theta_{\text{H}_2^{16}\text{O}} \approx 0.80$  ML half of the  $^{18}\text{O}_{\text{ad}}$  on the surface has been exchanged with  $^{16}\text{O}$ . The isotopic partitioning levels off at  $\sim 61\%$ , showing that on average only two  $\text{H}_2\text{O}$  molecules interact with one O adatom. This is less than when only the step sites were covered with  $\text{O}_{\text{ad}}$ , where it was three. The isotopic exchange saturates earlier for  $\theta_{^{18}\text{O}} \approx \theta_{\text{step}}$  than for  $\theta_{\text{O}} = 0.25$  ML. This shows that when terrace sites become occupied with oxygen adatoms, at higher water coverages, not all  $\text{O}_{\text{ad}}$  interacts with  $\text{H}_2\text{O}$ . Possibly, also for the fully oxygenated Pt(533) surface not all  $\text{H}_2\text{O}$  molecules are participating in the OH/ $\text{H}_2\text{O}$  network. This is in contrast with findings for Pt(111), where all adsorbed  $\text{H}_2\text{O}$  is part of the OH/ $\text{H}_2\text{O}$  network.<sup>83</sup> On stepped platinum surfaces, in the presence of water, terrace OH is favored over  $\text{OH}_{\text{step}}$ . On terraces it is possible to form hexagonal water rings, incorporating the  $\text{OH}_{\text{ad}}$  formed. In spite of more favorable energetics for forming a single OH on step sites, the possibility of being incorporated in a large network appears to favor the formation of OH on terrace sites for the system as a whole.

The (111) terrace on our Pt(533) crystal is only just large enough to form one water hexagon. This is probably too little to form an entire stable OH/ $\text{H}_2\text{O}$  structure, causing the presence of step sites to form a break in this network, excluding some O (and  $\text{H}_2\text{O}$ ) from participating in the oxygen exchange. The stability of the formed OH/ $\text{H}_2\text{O}$  structure is likely to vary with terrace width. A study on the amount of exchange on surfaces with different terrace widths could provide more insight.

### Varying $^{18}\text{O}$ pre-coverages

Figure 5.5 shows the TPD spectra for  $\sim 1$  ML  $\text{H}_2\text{O}$  adsorbed on the Pt(533) surface with varying  $\text{O}_{\text{ad}}$  pre-coverages. In the lower half (gray traces) of figure 5.5 the amount of pre-adsorbed O on step sites has been varied. When no oxygen is adsorbed we observe the three peak structure ( $\alpha_1$ – $\alpha_3$ ) shown in figure 5.2c. As step sites become covered with pre-adsorbed oxygen the  $\alpha_1$  peak initially decreases in

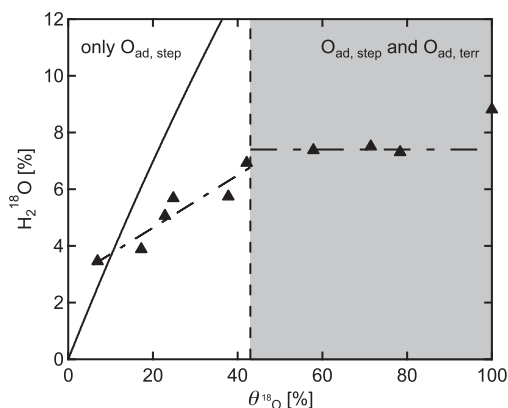


**Figure 5.5** TPD spectra of  $\sim 1$  ML H<sub>2</sub>O desorbing from Pt(533) with varying  $O_{ad}$  pre-coverages of the steps sites (gray) and the full step and part of the terrace sites (black).

size, whereas the  $\alpha_2$  peak increases in size. Some H<sub>2</sub>O<sub>step</sub> is converted into OH<sub>step</sub> and desorbs in the  $\beta$  peak (not shown in figure 5.5). This (partially) lifts the step induced stabilization of other H<sub>2</sub>O molecules that now desorb in  $\alpha_2$ . H<sub>2</sub>O is pushed from the  $\alpha_1$  into the  $\alpha_2$  peak, resulting in a two peak structure (a single  $\alpha_1 + \alpha_2$  peak and a separate  $\alpha_3$  peak) at  $1/3 \theta_{step} \lesssim \theta_O \lesssim 2/3 \theta_{step}$ . At higher coverages the three peak structure emerges again. However, initially the  $\alpha_2$  peak is larger than the  $\alpha_1$  peak and very sharp. The  $\alpha_1$  peak becomes larger than  $\alpha_2$  again only when the step sites are almost fully covered with oxygen ( $> 0.09$  ML). The dis- and re-appearance of the  $\alpha_1$  peak with increasing  $O_{ad}$  pre-coverage corroborates the theory that at high  $\theta_O$  this peak is actually due to a different processes than at low  $\theta_O$ , *i.e.* at high  $\theta_O$  it is due to recombinative desorption of OH from terrace sites.

The top half of figure 5.5 shows the TPD spectra for the Pt(533) surface where the terrace sites are also pre-covered with varying amounts  $O_{ad}$ . A three peak structure is visible in all spectra. At coverages  $\gtrsim 1/2 \theta_{terrace}$  the TPD features broaden towards the high temperature side, showing the onset of OH formation on the (111)





**Figure 5.6** Isotopic partitioning of  $\text{H}_2^{18}\text{O}$  versus the amount of pre-adsorbed  $^{18}\text{O}_2$  when Pt(533) is covered with  $\sim 1$  ML  $\text{H}_2^{16}\text{O}$ . The dashed line marks the coverage from which the (111) terrace starts to become occupied with  $^{18}\text{O}_{\text{ad}}$ . The straight line shows the amount of exchange if complete isotopic scrambling were to occur.

terraces. Initially less  $\text{H}_2\text{O}$  desorbs in the  $\alpha_2$  peak. When the surface is fully oxygenated the  $\alpha_1$  peak also corresponds to less  $\text{H}_2\text{O}$ . This illustrates the increasing competition of  $\text{H}_2\text{O}$  with  $\text{O}_{\text{ad}}$  for adsorption sites.

The percentage of  $\text{H}_2^{18}\text{O}$  desorbing as a function of the surface  $^{18}\text{O}_{\text{ad}}$  pre-coverage for  $\sim 1$  ML post-dosed  $\text{H}_2^{16}\text{O}$  is given in figure 5.6. The straight line shows the calculated amount of exchange for complete isotopic scrambling. For  $\text{O}_{\text{ad}}$  coverages up to 43% of the surface only the step sites are covered with  $\text{O}_{\text{ad}}$  (white area). The relative amount of  $\text{H}_2^{16}\text{O}$  that has exchanged an oxygen atom with  $^{18}\text{O}_{\text{ad}}$  increases linearly in this regime from  $\sim 3\%$  to  $\sim 7\%$ . The gray area in the graph shows the regime where the terrace sites become occupied with pre-adsorbed  $^{18}\text{O}_{\text{ad}}$ . In this regime the percentage of exchanged O stays roughly constant at 8%. With increasing oxygen pre-coverage, O adatoms have to compete with one another for interaction with  $\text{H}_2\text{O}$  molecules. This causes the amount of exchange in  $\text{H}_2\text{O}$  to be constant with increasing  $\text{O}_{\text{ad}}$ , whereas the percentage desorbing as  $\text{O}_2$  decreases slightly (not shown here). Except for the lowest  $\theta_{\text{O}}$  the amount of exchange is far less than if complete isotopic scrambling were to occur, suggesting again that  $\text{O}_{\text{ad}}$  in steps is much more stable (against  $\text{OH}_{\text{ad}}$  formation) in steps than it is on terraces.

## 5.4 Conclusion

We have shown that the co-adsorption of  $\text{H}_2\text{O}$  and  $\text{O}_{\text{ad}}$  on the Pt(533) surface gives rise to a small new feature at  $\sim 270$  K in the  $\text{H}_2\text{O}$  TPD spectra, tentatively ascribed



to OH<sub>ad</sub> on step sites. If the full surface is pre-covered with O<sub>ad</sub> we also observe a broadening of the  $\alpha_1$  peak, which we ascribe to OH-formation on terrace sites. Varying the O<sub>ad</sub> : H<sub>2</sub>O ratio shows that different ratios give rise to various structures in the TPD spectra, indicating that there are different stable structures possible on the surface, similar to Pt(111).<sup>14</sup> We believe that hexagonal ring structures on terraces are favored whenever possible, at the expense of the formation of step-bonded OH that is energetically more favorable if only that species is taken into account. Isotope exchange data show that when only the step sites have been pre-covered with O<sub>ad</sub> the O<sub>ad</sub> interacts with up to three H<sub>2</sub>O molecules. The exchange does not increase much when more <sup>18</sup>O is present on the surface. We attribute this to competition between OH formation on step and terrace sites. Terrace sites are favored, because there the formed OH can be incorporated in a larger hydrogen bonded structure. A discontinuity in this surface structure by the presence of the step causes the overall reactivity toward the formation of OH to be lower than on Pt(111).

Generally it is found that reactivity increases with the amount of defects.<sup>13</sup> The formation of OH on step sites is a counterexample to this common observation. This shows that experiments on Pt(111) surfaces are a poor model for the reactivity of catalytic particles, since they do not take into account these defect sites. The stability of the formed OH/H<sub>2</sub>O structure is likely to vary with terrace width. A study on the amount of exchange on surfaces with different terrace widths could provide more insight into this issue.