Surface Chemistry

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Co-adsorption of O and H_2O on Nanostructured Platinum Surfaces: Does OH Form at Steps?**

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Water activation is a prerequisite for CO, methanol, and ethanol oxidation in fuel cell catalysis,[1] in which platinum is often used as the anode material. To find better and cheaper catalysts, it is important to know the nature of the intermediate species in the reaction. Surface bonded OH is often suggested as the most important candidate for the electrochemical oxygen donor.[1] It has been shown to be stable under ultrahigh vacuum (UHV) conditions on Pt(111), where co-adsorbed H_2O and O_{ad} produce OH.[2] H_2O is necessary to stabilize the formed OH species[3,4] as it is incorporated in a hydrogen-bonded network of hexagonal rings of H_2O and OH[5] by Equation (1).

$$2H_2O + O_{ad} \rightleftharpoons H_2O + 2OH_{ad} \quad (1)$$

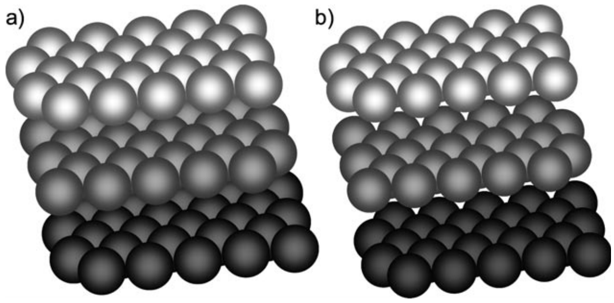

Figure 1. Surface structure of a) Pt(533), containing (100) steps, and b) Pt(553), containing (110) steps.

Real catalytic surfaces, however, have a more complex geometry, containing 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.[6] Electro-oxidation reactions on platinum show a structural dependency, which has been ascribed to preferential formation of OH at step and defect sites.[1] Herein we show that the tendency for O_{ad} to be hydrogenated to OH by H_2O depends crucially on whether it is bound to a (110) or (100) step site or to a (111) terrace site, which suggests oxygen adatoms as an alternative intermediate for step-mediated electrochemical oxidation reactions.

The simplest models for defect sites are regularly stepped single-crystal surfaces. Two different step sites can be distinguished: those with (100) geometry and those with (110) geometry. Oxygen adatoms and H_2O molecules adsorb preferentially on step sites, whereby O_{ad} favors (100) steps and H_2O (110) steps.[7–10] We previously studied the individual interactions of O_{ad} and H_2O on Pt(533) and Pt(553) surfaces, which consist of 4-atom wide (111) terraces with (100) and (110) steps, respectively (see Figure 1).[10] The samples were studied under UHV conditions using temperature-programmed desorption (TPD) in combination with isotope exchange. Herein, we precovered the surface with ^{18}O before dosing $H_2{}^{16}O$ to study co-adsorption. We refer to reference [10] and the Supporting Information for experimental details.

Figure 2a shows TPD spectra of $H_2{}^{16}O$ (lower panel) and $H_2{}^{18}O$ (upper panel) desorbing from Pt(533), in which the (100) steps were precovered with ^{18}O prior to dosing varying amounts of $H_2{}^{16}O$. Figure 2b shows similar data for Pt(553).

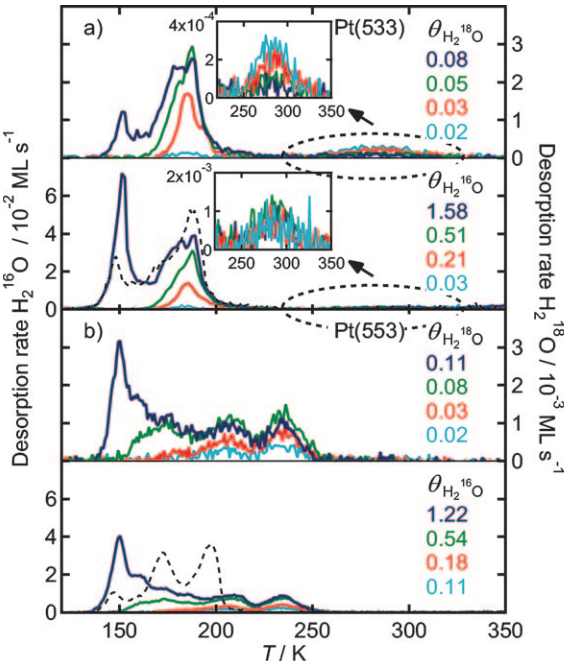

Figure 2. a) Desorption of $H_2{}^{16}O$ (bottom panel) and $H_2{}^{18}O$ (top panel) from a Pt(533) surface in which the step sites were precovered with $^{18}O_{ad}$. The dashed line shows desorption from the bare surface. b) Similar data for Pt(553).

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For $H_2^{16}O$ we show also desorption spectra of more than 1 monolayer (ML) $H_2^{16}O$ adsorbed on the bare surfaces (dashed lines).

We focus first on the $H_2^{16}O$ spectra. For the bare Pt(533) surface (dashed line), the three-peak structure has been assigned previously: the 188 K peak results from desorption from step sites, the peak at 171 K from desorption from terrace sites, and the peak at around 146 K from desorption from the H_2O multilayer.[10] We define the sum of the 188 and 171 K peaks in the dashed spectrum as 1.0 ML. Upon precovering the steps with $^{18}O_{ad}$, the peaks stay roughly at the same position, while the sum of the integrals of the 188 and 171 K peaks diminishes slightly relative to those of the bare surface. These results suggest that precovering the (100) step with oxygen hardly affects water adsorption other than blocking some adsorption sites for water. The Pt(553) surface shows very different behavior. In this case, H_2O desorption from the bare surface also occurs in three peaks, attributed to step (197 K), terrace (171 K), and multilayer (ca. 146 K) desorption.[10] However, in contrast to (100) steps, precovering (110) steps with oxygen results in large changes in the desorption features, including new desorption peaks appearing up to 240 K.

To shed light on what causes the apparent apathy of Pt(533) toward the precovering of the step with O_{ad} and the large changes observed for Pt(553), we turn to the $H_2^{18}O$ TPD spectra. Note that the axes are 20-fold larger for $H_2^{16}O$ than for $H_2^{18}O$. For Pt(533), all peaks show the same structure as their $H_2^{16}O$ TPD equivalents. The only difference is observed for the multilayer peak, which is relatively small for $H_2^{18}O$. This result indicates that isotopic equilibrium between the first and second water layers has not been reached. Its presence, however, testifies that isotope exchange has occurred below the desorption temperature for the multilayer (i.e. 140 K). The stunning appearance of an additional desorption feature at 280 K provides more clues as to why the TPD spectrum from the Pt(533) surface is hardly influenced by the presence of O_{ad} on step sites. First, we notice that this peak is the largest feature when very small amounts of water are dosed. Second, this feature decreases in size with increasing water dose. Third, upon scrutinizing the $H_2^{16}O$ TPD spectra, we observe the same peak, although much less well-resolved because of the higher background signal and associated noise. In contrast to the peak at 280 K in the $H_2^{18}O$ signal, the peak in the $H_2^{16}O$ signal does not show a significant dependence on water dose. As the desorption temperature is too high for any interpretation based on desorption of chemisorbed H_2O, we ascribe this feature to the reversible occurrence of Equation (1) on step sites, without implying the stoichiometry given in Equation (1). Apparently, OH on the otherwise O-saturated step is very stable, but only a small concentration of OH is allowed. With this interpretation, all other observations are simply explained: the (100) step prefers to keep a low OH/O ratio, which does not interfere much with adsorbed water on the (111) terrace because of a lack of H atoms. The oxygen covered (100) step hesitatingly allows for some isotope exchange at low temperatures. This results in leaching of ^{18}O from the steps, which causes the $H_2^{18}O$ TPD signal at 280 K to decrease with increasing $H_2^{16}O$ dose.

Steps with a (110) orientation behave differently. The H_2O TPD spectra for Pt(553) with the step sites precovered with O_{ad} show two initial desorption peaks around 202 and 228 K, which grow in simultaneously for both isotopes. Contrary to spectra from Pt(533), all $H_2^{18}O$ desorption features track the desorption of $H_2^{16}O$ with increasing water dose. Since the peaks at 202 and 228 K appear for the lowest H_2O coverages and at high temperatures, we associate them with desorption from step sites. We speculate that they result from the decomposition of hydrogen-bonded H_2O/OH mixtures at the (110) step, similar to those formed on Pt(111).[11] It is conceivable that the 228 K feature results from a pure recombination of 2 OH in the absence of H_2O, which then occurs at much lower temperature than on (100) steps (228 vs. 280 K). This conclusion is in accordance with density functional theory (DFT) calculations, which show that for various elements (including O) the binding energy for moieties with an extra H atom scales with the binding energy of the central atom:[12] both OH and O bind stronger to (100) steps than to (110) steps.[10] Our assignment of the peaks to an H_2O/OH mixture suggests that hydrogenation of O_{ad} to OH by H_2O on (110) step edges is considerably more facile than on (100) steps, even if OH alone binds stronger to the latter steps. It also explains why the entire TPD spectrum is influenced by the presence of O_{step} on Pt(553); mixed H_2O/OH structures at the (110) step edges may easily connect to a hydrogen-bonded network at the adjacent (111) terrace and thereby affect its desorption characteristics.

Figure 3 shows the absolute amounts of desorbing $H_2^{18}O$ as a function of the total H_2O coverage for Pt(533), Pt(553), and Pt(111)[13] for both $\theta_{^{18}O} = \theta_{max}$, that is, the entire surface precovered with O_{ad}, and $\theta_{^{18}O} \approx \theta_{step}$. We also plot the amount of desorbing $H_2^{18}O$ in case complete isotopic scrambling were to occur, assuming a Pt/H_2O ratio of 3:2[14] for 1.0 ML H_2O and a Pt/O ratio of 4:1 for the fully oxygen covered surface with an $O_{step}/O_{terrace}$ ratio of 0.11:0.14.[10] For all three surfaces it is clear that complete scrambling does not occur. For stepped surfaces, exchange occurs to a lesser degree than for Pt(111) and is dependent on step type. Less exchange is

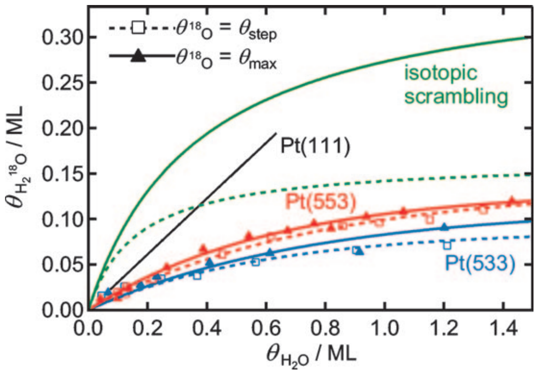

Figure 3. Amount of $H_2^{18}O$ desorbing from Pt(553) (red), Pt(533) (blue), and Pt(111) (black) as a function of the total amount of H_2O for $\theta_{^{18}O} \approx \theta_{step}$ (dashed) and θ_{max} (solid). The Pt(111) data are taken from reference [13], assuming a H_2O/Pt ratio of 2:3 for the full monolayer.

observed for Pt(533) than for Pt(553). This observation supports our claim that hydrogenation of O_{ad} on (110) steps is more facile than on (100) steps. On the stepped surfaces, slightly more O_{ad} is exchanged for $\theta_{^{18}O} = \theta_{max}$ than for $\theta_{^{18}O} \approx \theta_{step}$. However, in the $\theta_{^{18}O} = \theta_{max}$ case, over twice as much ^{18}O is available for the exchange. Clearly, the increase in exchange is not as large as would be expected on the basis of the amount of extra ^{18}O available. One might conclude that most exchange happens at step sites and terrace sites are relatively inactive in OH formation, but this is in contradiction with the notion that on Pt(111) all O adatoms participate in the OH formation.[4]

In Figure 3, we find no significant increase in isotope exchange when increasing the amount of oxygen on the surface by a factor of two. Figure 4 compares the desorption of H_2O for a total coverage of approximately 1 ML H_2O from Pt(553) for the surface on which only the steps (dashed line) and the entire surface (solid line) are precovered with O_{ad}. The high-temperature desorption features, ascribed to OH recombination at the step, decrease in magnitude and shift to a lower temperature. The most prominent feature in the $\theta_O = \theta_{max}$ spectrum (other than the multilayer peak at around 146 K) is a peak at 193 K. This temperature is very similar to the peak attributed to recombinative desorption of OH from a Pt(111) surface with $\theta_O = \theta_{max}$ (192 K).[11] We observe similar effects on the Pt(533) surface, although they are more subtle. Therefore, this result strongly suggests that if O_{ad} is available at terrace sites, OH formation at terrace sites is favored over OH formation at step sites. The preference of OH formation on terrace sites leaves unreacted O adatoms at step sites. Therefore, the total amount of exchange hardly increases in Figure 3, when terrace sites are also precovered with O_{ad}.

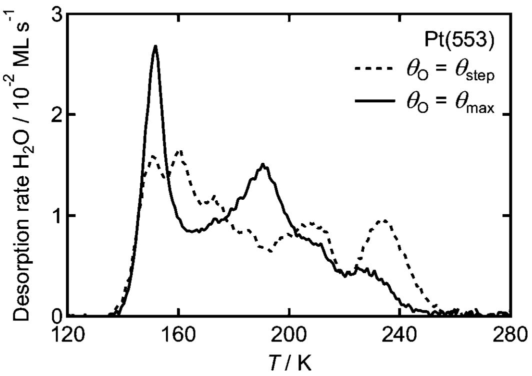

Figure 4. Desorption of approximately 1 ML H_2O from Pt(553) with $\theta_O \approx \theta_{step}$ (dashed) and θ_{max} (solid).

The $O_{ad} + H_2O$ activity series we observed has the following order: Pt(533) < Pt(553) < Pt(111). We put forward a possible origin of this series in Figure 5, which shows a schematic representation of the energy levels for the different co-adsorption systems. The O binding strength varies as $Pt(533)_{step} > Pt(553)_{step} > Pt(111)$. We found an identical series for OH. This order is expected on the basis of reference [12], which reports a general trend for various metal surfaces that if the central atom binds stronger to a particular surface the hydrogenated species will bind stronger as well, even though reference [12] did not study the exact same surfaces as used in this study. On Pt(111), the formed OH_{ad} is incorporated in a large hydrogen-bonded network,[3,4] resulting in an extra stabilization of adsorbed species. Therefore, the formation of OH_{ad} on (111) terraces is energetically downhill relative to $Pt(111){-}O + x H_2O$. Across steps, the hydrogen-bonded networks are, at least to some extent, disrupted. Our data suggest that on the two stepped surfaces the formation of OH_{ad} is energetically uphill or neutral (in the case of Pt(553)) on the step sites. Consequently, the energy levels on the $OH + (x-1) H_2O$ side are grouped closer together than on the $O + x H_2O$ side. The relative positions of the energy levels for the three surfaces shift the equilibrium towards the $O_{ad} + H_2O$ side for the steps or towards the OH_{ad} side for the (111) terraces.

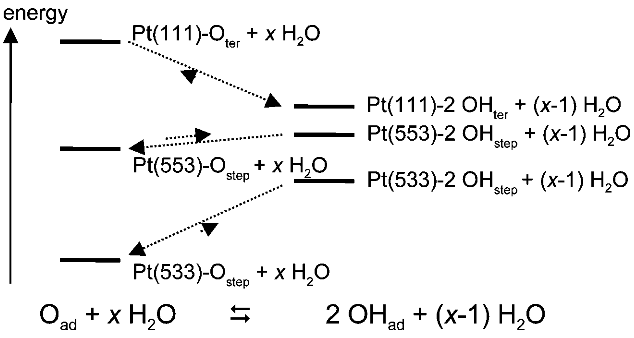

Figure 5. Energy levels for the co-adsorption of O_{ad} and H_2O on Pt(111), Pt(553), and Pt(533).

These experiments show that on stepped platinum surfaces OH_{ad} might not be as readily formed as one would assume on the basis of the energetics of OH adsorption alone, which would suggest an OH affinity series of Pt(533) > Pt(553) > Pt(111). In fact, we found that the amount of OH_{ad} formed follows the reverse trend. We attribute this trend to the fact that, although step-bonded OH by itself has a higher stability, on Pt(111) OH_{ad} can actually be incorporated in a three-dimensional OH/H_2O hydrogen-bonded network, which favors $OH_{terrace}$ formation over OH_{step} formation, leaving unreacted oxygen adatoms at the step sites. For the electrochemical situation, it would imply that O would be a more likely species to form at steps than OH. This in fact agrees with the electrochemical observation that Pt(111) is the only surface on which a clear OH_{ad} formation feature can be decoupled from O_{ad} formation.[15] Our UHV modeling experiments suggest that atomic oxygen may well be a more likely candidate for the step-bonded oxygen donor than OH, which would imply a whole new paradigm for electro-oxidation reactions. Finally, we note that the current tendency, both among theorists and experimentalists, to decouple reactivity at terraces and step sites may lead to important omissions, as it ignores the necessity to properly account for solvation and long-range order effects.

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