

This work discusses the adsorption properties of water and the water related adsorbates H, O and OH on the regularly stepped Pt(533) and Pt(553) surfaces. Understanding the influence of defect sites, such as the two types of step edges present on these two surfaces, can help to improve our understanding of the (electro)catalytic properties of platinum surfaces under realistic conditions, where defect sites are abundant.

Most theoretical studies to date have focused on the high-symmetry facets of platinum in order to predict its catalytic properties. While this can certainly help in gaining insight into this subject, real catalytic platinum surfaces will contain defect sites, which are known to exhibit significantly altered catalytic behavior. For this reason, studies were performed that use regularly stepped metal surfaces, on which the step edges are used as model systems for the edges of nano-particles. In this study we present density functional theory calculations on the adsorption properties of the electrocatalytically relevant adsorbates water, OH, O and H in order to gain insight into their adsorption properties on the step edges present on the regularly stepped Pt(533) (4 atom wide (111) terrace and a (100)-type step edge) and Pt(553) (5 atom wide (111) terrace and a (111)-type step edge).

In chapter 2, the discussion starts with an investigation of the adsorption properties of isolated adsorbates on the two model surfaces. We establish a framework for the investigation by choosing the exact parameters of the model surfaces and the computational settings. On this basis we calculate the adsorption properties of the four adsorbate species that are the focus of this thesis. We find that the (100) step edge of the Pt(533) surface binds the adsorbates OH, H and O more strongly than the (111)-edge on Pt(553). For water we find little to no difference in adsorption energy at the step edge. We use these results for a comparison to previous results of ultra-high-vacuum temperature programmed desorption studies performed in our group, in which we find that, with the exception of the hydrogen desorption on Pt(553), all TPD spectra can be qualitatively explained by our theoretical results. The chapter concludes with an estimation for thermodynamic reaction barrier for the dissociation of water into H and OH and the reaction of water and oxygen to form two OH adsorbates. We find that on the Pt(533) step edge, both reactions are thermodynamically favorable, while on the Pt(553) surface the reaction with oxygen is thermoneutral, and the dissociation reaction is endothermic.

In chapter 3 we propose high-coverage water adsorption structures along the step edge of the Pt(533) surface. We find that if only the step edge is covered with water, the so-called zig-zag configuration is most stable geometry, in accordance to earlier studies. Increasing the coverage to form isolated ring structures leads to a preference of pentagonal and hexagonal ring structures. Increasing the coverage even further to form double-stranded structures, we find 6 almost iso-energetic structures that can cover the step edge. We observe a general trend for a hydrogen-down orientation of the lower-step-edge water molecules, which we rationalize by the Smoluchowski effect. Furthermore, we conclude that the step edge will be a nucleation point for the growth of water structures and will most likely have long-range influences on the adsorption structure for more than 10 Angstrom.

In chapter 4 we present a combined scanning tunneling microscopy and density functional theory study on the adsorption structures on the Pt(553) surface. On this surface we find a very strong preference for tetragonal water structures, both for isolated ring structures, as well as for the double-stranded case. We explain this by a pronounced templating effect of the underlying platinum lattice. The Smoluchowski effect is used to rationalize the orientation of the lower-step-edge water molecules, as was seen on the Pt(533) surface. The results of the theoretical study are confirmed by STM imaging, in which we find double-stranded water structures on the step edges.

Chapter 5 links together with chapter 2 in trying to elucidate the still unexplained hydrogen desorption

spectra of the Pt(553) surface by studying the interaction effects present at higher hydrogen coverages. We find that for the Pt(553) surface the interaction effects are limited in range, with a very small attractive interaction for the sites along the step edge and a very weak interaction for the terrace sites. Furthermore, we observe that the adsorption energies fall into two general regimes, one for the step edge adsorption which is more strongly adsorbed and one for all terrace adsorption sites. From these results we conclude the origin of the two peaks in the TPD spectrum for Pt(533) to be the terrace sites for the low-temperature peak and the step sites for the high-temperature peak. For Pt(553) we find a completely different picture. The adsorption energy for the step edge shows a (for hydrogen) rather large attractive interaction, while the adsorption energy for all sites on the terrace decreases with increasing coverage. For this surface we find four general regimes of adsorption energies, namely the step edge adsorption, which leads to the highest-temperature peak, the two most favorable sites on the terrace, which lead to the second-highest-temperature peak in the spectrum and the two next-most-favorable sites on the terrace which are the origin of the lowest temperature peak. At this coverage we reach the experimentally observed step-to-terrace ratio of 1:2.25, which means that there will be no additional hydrogen atoms adsorbed in the real system. Additionally, the other possible adsorption sites at higher coverages in the DFT calculations also showed a significantly reduced adsorption energy compared to the ones discussed above, which leads us to conclude that these sites will not be occupied.

In summary this thesis has shown that DFT calculations on the GGA level can be used to study water related adsorbates on regularly stepped platinum surfaces. We link our results to experimental observations, which we are able to explain and, in the case of the water structures, even predict. DFT studies can therefore be used to further improve our insight into the solvation of defective platinum surfaces to further our understanding of electrocatalysis.