Water-Related Adsorbates on Stepped Platinum Surfaces

Kolb, Manuel Jerome

Chapter 7

Outlook

In this final section, we will discuss this research presented in this thesis in context with its relevant fields: water adsorbates at defect sites on platinum surfaces and the field of theoretical and computational electrochemistry.

The work presented here is part of the emerging field of study that deals with the interaction between reactants, intermediates and reaction products at and near low-coordinated or defect sites on heterogeneous catalysts in general, and on platinum surfaces in particular.

About twenty years ago, the study of the catalytic properties of the high-symmetry facets of catalysts from first principles started, due to the appearance of theoretical methods, appropriate density functionals as well as the computational capabilities that enable the description of these multi-atom systems. Since then our understanding of the gas-metal as well as the liquid-metal interface has grown tremendously, due to the interaction between experiment and the new insights created by theoretical calculations. However, the approach described above has typically focused on the aforementioned high-symmetry facets, while any realistic catalytic system contains large amounts of defect sites, which often dominate the overall catalytic activity.

For this reason, theoretical studies have started to appear in the last 5-10 years that deal with extended defect-containing surfaces. In this approach, surfaces with non-trivial Miller indeces are used as an approximation for the interaction between adsorbates and defect sites of any possible type. The timing of this development is mainly due to the advancement of computational power, which allows for a study of a reasonably complex stepped surface in the same timeframe as was common for the flat metal surfaces 20 years ago.

The work presented in this thesis has detailed the interaction between the electrochemically relevant adsorbates H, O, OH and H_2O and the simplest defect-

ive platinum surfaces which shows little defect-defect interaction, namely Pt(533) and Pt(553), in relation to experimental UHV work performed in the group of Ludo Juurlink.

Future research in this field of study should focus on extending our understanding of the adsorption properties of adsorbates on any type of defect. Larger terrace sizes can be treated using improved computational capabilities, made available in the last few years. This allows for a better understanding of long-range effects in these systems. In view of this the results shown in chapter 2 should be extended to consider higher coverages of oxygen on facets ranging from Pt(211) to Pt(977). The results obtained in such a future study will help explain UHV TPD results in the group of Ludo Juurlink, in which it was found that the total oxygen coverage present on these stepped surfaces follows an oscillating pattern for increasing terrace length. Furthermore, to better understand the limitations of using smaller terrace widths to model adsorption data, the results obtained in chapter 5 should be extended to include the adsorption on the Pt(211) and Pt(221) surfaces, which will enable a full systematic explanation of the influence of step edge type and terrace width on the desorption behavior of hydrogen from platinum surfaces, as studied experimentally by Cansin Badan in our group.

Step edges, as discussed here, should only form the starting point for these investigations, since kinks and corner sites also have the potential to show high catalytic activity and are also present on real-world catalysts. These model systems however require larger super-cell sizes to be employed, which leads to a great increase in computational cost.

Moore's law predicts a doubling of the number of transistors per square inch, which will lead to a smaller, but still comparable increase in computational capabilities. This development, combined with improved theoretical approaches such as the use of embedding schemes like QM-MM, will enable the treatment of very large systems with reasonable accuracy and computational costs. Furthering this goal, the results obtained in the chapters 3 and 4 are currently being used to test the quality of a REAX-FF empirical force field for the description of water adsorption on step edges as part of a research project in the group of Dr. Jörg Meyer. This will allow for an estimation of the quality of empirical force field data for the description of step-edge bound water, which is crucial for its use in embedded QM-MM approaches. This development may also eventually allow for the treatment of configurational entropy in water adsorption, an aspect that has so far been largely ignored in first-principles computational studies of water at defective surfaces.

In combination, these two factors will allow for the treatment of significantly larger systems, possibly up to the treatment of actual nano-particles in a full

aqueous environment.

Within the field of theoretical electrochemistry, this thesis gives a first idea of the complicated nature of the solvation environments encountered at defect sites. In the current state of the art, theoretical electrochemistry employs the computational hydrogen electrode scheme by Norskov and coworkers to estimate the thermodynamical reaction energies of separate reaction steps. From these, properties of the electrochemical reaction, such as onset potentials, can be calculated.

However, in this scheme usually the actual aqueous electrochemical environment is not considered. If needed, first-order estimates usually model the interaction between the reaction intermediates and a stylized hexagonal water layer which is used to estimate the solvation energy of the intermediates. However, since there is little to no understanding about the solvation environment at defect sites, such as steps, this approach cannot be used to correct electrochemical simulations of reactions on low-coordinated lattice sites.

The results from this thesis have made a first step in remediating this problem by providing an understanding of the structure of the first water layer near step sites, which now allows for the study of the interaction between solvated adsorbates and the solvating water environment. The results obtained in chapters 3 and 4 form a starting point for the calculation of solvation energies of OH situated at the two step edge types.