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Summary

The application of catalytic processes was already important for man long before people had any knowledge about the molecular processes involved. Although the understanding of catalytic reaction has increased tremendously, and nowadays humanity heavily depends on applied catalysis, many details of processes have not been fully understood, yet.

The field of catalysis can be divided into several subcategories. Those are biocatalysis, homogeneous, and heterogeneous catalysis. In biocatalysis the catalytic reaction is generally performed by enzymes. For many enzymes their 3-dimensional structure and the structure of the active center is known. Still, it remains difficult to imitate the reactivity and selectivity artificially. Homogeneous catalysis commonly utilizes metal complexes which are in the same phase as the reactant(s). For many examples of these types of reactions entire mechanisms are known. For heterogeneous catalysis the catalyst and reactants are in different phases. Many industrially applied processes utilise catalyst particles which are dispersed over a substrate and gaseous reactants. Although those processes are very common, detailed knowledge about the molecular mechanisms is often not present. Factors generally influencing catalyst performance are reaction conditions (like pressure and temperature), catalyst structure, and the interactions of reactants and impurities in the feed gas with the catalyst. Increasing the understanding of those interactions at a molecular level will help to optimize existing processes and therefore save finite resources.

Research into aspects of heterogeneous catalysis very often takes advantage of so-called ‘model catalysts’ (e.g. single crystals) and ‘model reactions’ (e.g. hydrogen dissociation) This thesis focuses on the dissociation of deuterium on stepped platinum and nickel surfaces. Investigated are effects of site-blocking (see chapter 3), and surface structure sensitivity (chapters 4 and 6). To that end for the first time a cylindrical single crystal is employed in dynamic measurements (chapter 4), and the surface structure is analysed in detail (chapter 5).

In chapter 3 how CO poisoning effects hydrogen dissociation on Pt(533) is investigated. To that end the initial dissociation probability of deuterium with a very low kinetic energy was measured in dependence of CO precoverage. It turned out
that $S_0$ decreased linearly with CO precoverage up until $\theta_{CO} \approx 0.41$ ML. Above that coverage no reactivity was observed at that kinetic energy. Further, $S_0$ was measured for different kinetic energies of $D_2$ with a constant CO precoverage of 0.41 ML. It was observed that not only direct and indirect dissociation at the step edge were blocked, but also terrace reactivity was severely influenced. An addition barrier towards dissociation was introduced while the distribution of barriers remained unaffected.

Chapter 4 describes how for the first time a cylindrical single crystal is used to perform direct measurements in reaction dynamics. Technical details covering sample and holder, as well as experimental procedures are described. Initial results proof the power of this new combination of tools for investigating reaction dynamics.

The chapter explaining the detailed LEED analysis of the sample (chapter 5) proofs that over a wide range of the circumference of the crystal the surface structure consists of terraces with steps only one atom high. It as well discusses streaking in the LEED patterns which has been observed for many parts of the circumference. A possible explanation is provided. Further, a simple way to correct for the distortion caused by a projection error observed in our LEED pictures is introduced.

Chapter 6 systematically investigates the influence of step density and step geometry on dissociation probability. Surfaces with (111) terraces and (110) or (100) steps behave very similar and a model introduced for hydrogen dissociation on stepped platinum surfaces can be applied. Cross sections for direct non-activated adsorption and indirect non-activated adsorption are estimated. Surfaces with (100) or (110) terraces and (111) step edges behave differently. The first ((100) terraces, (111) steps) show a correlation between step density and reactivity but the model could not be applied as the (100) terraces provide a dissociation pathway which is not represented in the model. Unfortunately the model could not be adapted to this situation because of the limited amount of kinetic energies studied. For the latter, no dependence on step density was observed and all surfaces in the range from (110) towards (331) behave very similar when it comes to kinetic energy dependence. Here the model could not be applied/extended due to the same reasons mentioned before.

Chapter 7 discusses how the sample can be used for further investigations of
reactivity, especially methane dissociation. First data for methane dissociation are shown.