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Structure dependence of molecular reactions on surfaces

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Cover Page



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Chapter 7

Summary and outlook

7.1 Summary

Heterogeneous catalysis has been applied throughout human history even when people had no knowledge about the processes involved. To investigate the mechanisms of chemical reactions, simple “model systems” are generally used. Chemical reactions in model systems occur with the same elementary steps as catalytic processes under realistic conditions. Although such systems have been studied extensively, many details are not yet clear. In this thesis we focus on simple systems, such as hydrogen dissociation on Pt and Cu surfaces and oxygen dissociation on Pt surfaces.

Hydrogen dissociation on Pt surfaces is a model system for weak (non) activated diatomic molecule dissociation. It has been studied extensively using both experiments and theoretical calculations. The potential energy surface (PES) shows both energetic and geometric corrugation. Using an adjustable Specific Reaction Parameter (SRP) approach to DFT, calibrated by Ghassemi et al. on data of D_2 dissociation on Pt(111) by Luntz et al., good agreement between theory and experiment[22, 39] has been obtained. Their results predict a weak difference in sticking probabilities for two different azimuthal angles at high polar angle incident and high kinetic energies. In chapter 3 we studied hydrogen dissociation on Pt(111) surface. Our data agree well with the earlier experimental work. The reaction only depends weakly on the azimuthal orientation of the incidence plane, which is consistent with the SRP-DFT calculations.

Hydrogen dissociation on Cu surfaces is a model system for strongly

activated dissociative adsorption of diatomic molecules on a metal surface. It is also important as the first step of hydrogenation of CO_2 to methanol over a $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst. Understanding of elementary reaction steps may help development of new catalysts. To mimic the edges on real catalyst particles, macroscopic flat surfaces with atomic steps are introduced. The lower coordination of step atoms usually lowers dissociation barriers by increasing the binding energy. In chapter 4 we studied hydrogen adsorption and desorption on the $\text{Cu}(111)$ and $\text{Cu}(211)$ surfaces. The latter contains A-type steps and the (111) terraces. Here, we find that the $\text{Cu}(111)$ surface is more reactive than the $\text{Cu}(211)$ surface. A-type steps cause a - to our understanding unique - upward shift in the distribution of activation barriers to adsorption and a downward shift in barriers to desorption. Furthermore, the barrier distributions, which are weakly dependent on hydrogen pre-coverage and saturation coverages, are shown to depend on incident energy. Lateral interactions between adsorbed hydrogen atoms must be weak, especially in the lower coverage regime.

In chapters 5 and 6 we moved onto a curved $\text{Pt}(111)$ single crystal. The apex of this crystal is $\text{Pt}(111)$. The crystal contains monoatomic A-type steps on one side and B-type steps on the other. The step density increases linearly with the distance from the apex. This crystal can mimic a series of stepped surfaces with A or B steps. To some degree, this overcomes the materials gap between a single crystal surface and real catalysts.

In chapter 5 we studied HD formation on the curved $\text{Pt}(111)$ single crystal surface. At low incident energy, HD formation on Pt surfaces is known to be depended on the step density. Using a proper cleaning procedure and a final annealing at 850 K, we observed a linear increase of HD formation with distance from the apex. This indicates the step density increases linearly with distance from the apex. A LEED study confirms this linear increase through the spot splitting observed in LEED patterns. When the crystal is cleaned using the same procedure but followed by a final annealing at 1200 K, HD formation is reduced on both sides. For A-type steps, HD formation is reduced over the entire range, especially near (655). For B-type steps, HD formation is reduced locally at (443). The reduction indicates the presence of faceting, but LEED fails to show this ostentatiously. HD formation as a chemical probe is more sensitive than LEED. More details about the reconstruction need to be studied by STM. Our data also show

that faceting occurs at (443), not at (997). The Pt(997) surface was previously shown to reconstruct and studied by He atom diffraction, LEED and STM.

The dissociation of oxygen on Pt is more complex than that of hydrogen. The process involves at least four states: a molecular physisorbed state, at least two molecular chemisorbed states and an atomic oxygen chemisorbed state. Previous studies have shown that step edges induce a dominance of the indirect dissociation mechanism - presumably proceeding via the physisorbed molecular state, and more reactive in dissociating O₂ than (111) terraces. In chapter 6 we studied O₂ dissociation on Pt surfaces using the same curved Pt(111) single crystal. The sticking probability of O₂ increases linearly with the distance from the apex for both A- and B-type step sides at the lowest incident energy, 65 meV. The steepness of the slopes and the nearly identical absolute values on both sides indicate that the dynamic processes leading to sticking is dominated by steps and insensitive to the step type. At higher incident energies, this dependence clearly starts to lose its linear character. This indicates that the dynamical processes leading to sticking at higher incident energies are not dominated by steps alone. By using an alignment-controlled O₂ beam, sticking of oxygen on flat Pt(111) surfaces preferentially occurs when the internuclear axis is aligned parallel to (111) surface. For the Pt(553) surface, the preference for O₂ sticking with a molecular axis parallel to the surface entirely disappears at low incident energy. At higher incident energy, the sticking probability ratios $S_0(H)/S_0(C_z)$ for the (553) and (111) surfaces converge to the same value. The results of R and L experiments indicate that dissociation on both A- and B-type steps is clearly favored for molecules impacting with their internuclear axis parallel to the step's (100) or (110) facets.

7.2 Outlook

Besides our studies presented above, there are two ways to improve our current understanding of the relationship between surface structure and chemical reactivity. The first improvement is by using STM to probe the local structure with (near) atomic resolution. The second improvement is preparing reactants in the molecular beam in a more controlled fashion, e.g. dividing the reactants into two well-controlled

molecular beams.

7.2.1 STM

As shown in chapter 5, local structures on the curved Pt(111) single crystal surface change with the annealing temperature. By using HD formation as a chemical probe, we clearly observed a reactivity difference with two different annealing temperatures, 850 K and 1200 K. However, this method cannot directly demonstrate the difference of the micro-structure on the surface. LEED is usually a good technique to study the local surface structure. However, in our studies of the curved Pt(111) single crystal, it proved to be less sensitive to local reconstructions than HD formation. The origin of this is that LEED is an averaging technique, which averages the step densities over the probed area. For a flat single crystal, this averaging is not a problem because the probed surface area is uniform. For a curved single crystal with a smooth gradient of step densities, this averaging makes LEED less sensitive to local structure changes. Hence a technique with (near) atomic resolution is needed to probe the local structure.

Scanning tunneling microscopy (STM) is an appropriate technique for this purpose. STM has been used to study the local structures of curved single crystals by other groups[104, 105, 135, 142]. The technique could reveal the local terrace width distribution across the curved crystal and identify the reconstructions. Therefore the chemical reactivity and the local structure can be correlated to one another.

We can also study the types of reconstruction, e.g., step-doubling, faceting and step bunching, on the A- and B-type step sides of the curved Pt(111) single crystal. Furthermore, the dynamics of reconstruction can be studied by varying the annealing temperature, annealing time and cooling rate. This provides a physical aspect of surface reconstruction and can be used to design the geometry of real catalytic nanoparticles.

7.2.2 Double beam

All experiments in this thesis were carried out by using a single supersonic molecular beam (SMB). For experiments with multiple reactants, we usually mixed the reactants into one beam. To prevent reactions from taking place in the nozzle, we avoided heating the nozzle too

much. This limited the energy range we could probe. As an example, we have attempted to increase the kinetic energy of D_2 by seeding D_2 in H_2 . When the nozzle was heated to high temperatures, like $800\text{ }^\circ\text{C}$, most of the D_2 was converted to HD. This made the D_2 signal too low to be measured by QMS. We have also tried to measure the hydrogenation of CO_2 by seeding CO_2 in H_2 . A large amount of H_2O and CO were generated in the nozzle when heated to high temperature. To overcome this problem, a possible method is pre-adsorbing other reactants through background dosing and providing the main reactants by the SMB. The possible drawback of this method is that the coverage of the background adsorbing reactants may be very small which will probably limit the reaction. The other method is dosing several reactants continuously from the background. In both methods, the main issue is that the reactants supplied from background dosing are barely controlled.

There are two molecular beams connected to our UHV apparatus. One is a supersonic molecular beam and the other is an effusive molecular beam (EMB). In the future we hope to be able to study reactions by using these two beams simultaneously. We can then separate reactants that may react. The ratio of reactants in SMB and EMB can be adapted by changing the flow rates of the flow controllers or by chopping the SMB or EMB. With the usage of these two molecular beams, a series of reactions can be investigated, for example, the HD formation by using H_2 and D_2 , CO oxidation by using CO and O_2 and CO_2 reduction by using CO_2 and H_2 .

7.2.3 Lock-in amplified detection

In chapter 4 we showed that the small sticking probability can be directly measured by averaging multiple KW measurements. This method improves the signal-to-noise ratio. The KW technique can also be improved by using lock-in amplification. The second flag in our UHV chamber is a wheel with a 50% duty cycle divided over two “open” sections of equal size. It is firmly attached to the axis of a UHV-compatible stepper motor (Arun Microelectronics). Previously we only used it to control impingement of the beam onto the crystal within the UHV chamber in an “on/off” fashion by a single quarter turn of the wheel. However, we can also turn it continuously to chop the beam. In this way, the sticking probability can be detected by

combing with the lock-in amplifier. There is another way to apply lock-in amplifier. The nozzle of the EMB can be moved along the beam axis backward and forward periodically by using a motor. This periodic movement can change the distance between the nozzle and the first skimmer, and thus change the intensity of the EMB periodically. This can also be combined with the lock-in amplifier.