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Steps in gas-surface reactions

Lent, R. van

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Summary and conclusion

Platinum is one of the best heterogeneous catalysts for hydrogenation and oxidation reactions. Throughout the first half of this thesis, we investigated how step edges at platinum surfaces influence surface reactivity. To this end, experimental techniques were adapted for use with curved single crystal surfaces. The chapters involve various steps relevant to oxygen reduction: hydrogen dissociation (chapter 3), hydrogen recombination (chapter 4), and overall oxygen reduction (chapter 5).

Chapter 3 investigates hydrogen dissociation on platinum. As one of the simplest heterogeneous catalytic reactions, hydrogen dissociation on Pt(1 1 1) has been described by two dynamical models that are fundamentally at odds. Whereas one model assumes predominant indirect dissociation at defects via diffusion, the other is based on direct or local dissociation at the site of impact. In chapter 3, we resolve this dispute by quantifying how reactivity depends on surface structure. We do this by employing a spatially resolved molecular beam in conjunction with a curved Pt single crystal surface with varying step density. We observe that reactivity varies linearly with step density and is step-type dependent. Only the model that relies on dissociation localized at the point of impact is consistent with these results and enables us to extract step-type specific reaction cross sections. These absolute reaction cross sections are a direct measure for dissociation at the clean surface.

In chapter 4, we discuss the simplest heterogeneously catalyzed reaction possible: isotopic scrambling of hydrogen. On Pt, this reaction occurs by dissociative adsorption of H_2 and D_2 , mixing of H and D atoms on the surface, and recombination to form the three isotopologues, H_2 , D_2 , and HD.

Full isotopic scrambling would lead to a product ratio of approximately 1:1:2. Step edges are well-known to enhance dissociative adsorption, especially at low impact energies. However, it is unknown whether subsequent diffusion and desorption only occurs along the steps or involves diffusion onto terraces. We study this by combining supersonic molecular beam techniques with a curved Pt single crystal surface with straight **A-** and **B-type** step edges, c-Pt(1 1 1)[1 $\bar{1}$ 0]31°. At a high surface temperature, we probe HD formation along the curved surface by dissociating equal amounts of low energy H₂ and D₂. HD formation tracks the trend in dissociation: higher step densities yield higher HD formation. However, HD formation is not enhanced at steps to the same extent as the dissociation probability. We explain why extended (1 1 1) terraces are more selective toward HD formation than highly stepped surfaces. At (1 1 1), diffusion is fast and isotropic. In contrast, diffusion at steps is slower and anisotropic. Consequently, steps exhibit lower selectivity in isotopic scrambling. A simple model that assumes isotropic mixing at terraces and anisotropic mixing at steps agrees well with our results.

In chapter 5, we investigate the step-type dependence for the overall oxygen reduction reaction using a double molecular beam system. We compare how overall oxygen reduction reactivity varies with the oxygen hydrogen ratio provided to the surface. Our results show that oxygen reduction on Pt is also step-type dependent. Under oxygen-lean conditions, oxygen dissociation probabilities are significantly higher at **B-type** steps than **A-type** steps. Despite higher reactivity for oxygen dissociation, the surface with **B-type** steps is depleted of adsorbed oxygen before the surface containing **A-type** steps. We argue that higher reactivity with **B-type** steps results from higher reaction probabilities for all relevant reactants: oxygen, hydrogen, and deuterium.

The second half of this thesis develops experimental techniques aimed at studying state-resolved CO₂ dissociation. First, chapter 6 adapts Reflection Absorption Infrared Spectroscopy (RAIRS) for use on curved single crystal surfaces. The curved sample and a coaxial collimator form an anamorphic beam expander. As proof-of-principle, we investigate how steps influence

CO adsorption on Pt. Initially, both wide and narrow terraces show narrow single absorption peaks, while intermediate widths exhibit broad features. These features are attributed to absorption by on-top bound CO at terrace and step sites. We explain our results in terms of single excitons that absorb IR radiation. $(1\ 1\ 1)$ and high step density surfaces form constant density islands that absorb at a single frequency. In contrast, the constant density island of the $(1\ 1\ 1)$ terrace are interrupted by steps for intermediate terrace widths, thereby broadening the absorbance features. Further improvements to the technique are suggested.

Chapter 7 presents an outlook for performing state-resolved CO_2 dissociation experiments. We provide a basic explanation of CO_2 spectroscopy and develop an optical excitation setup. The optical setup resolves around an Optical Parametric Oscillator that is actively stabilized to the Lamb dip of the transition of interest. We present initial results that show excited CO_2 in the molecular beam.

The work throughout this thesis paves the way for future work studying dynamics at surfaces. By combining curved single crystal surfaces with molecular beams, we can extract absolute reaction cross sections for defects. Thus far, we have only applied this to low kinetic energy hydrogen dissociation. In future work, this combination can be used to resolve the kinetic energy dependence of hydrogen dissociation at defects. This combination can be applied to other model systems as well. Curved surfaces are particularly well-suited to investigate whether specific reactions require diffusion toward an active site. The absolute reaction cross sections that are extracted from this technique provide new benchmarks for DFT. In particular, they test how well van der Waals corrections work for these model system.

Double beam experiments are similarly powerful, but were only applied to flat single crystal surfaces in this thesis. We highlight four questions that remain unanswered. First, the kinetic energy dependence for the two reactants was not touched upon in this work. Studies involving oxygen dissociation suggest that the step-type dependence inverts at higher O_2 incidence energy. Second, OH and OOH intermediates have been suggested

for the reaction. Reflection Absorption Infrared Spectroscopy may be employed to perform *in operando* catalysis under UHV conditions, potentially identifying these key intermediates and their adsorption site. Thirdly, the effect of step density has not been resolved in this work, nor have we been able to study the actual overall kinetics of the reaction. If Molecular Beam Relaxation Spectroscopy can be applied to curved surfaces, we can resolve how the overall oxygen reduction kinetics depend on step density. Our previous results from desorption experiments suggest **B-type** steps are kinetically favorable. These experiments can unequivocally confirm this, as well as the nature of the active site. Finally, this combination can resolve whether diffusion towards an active site is rate limiting, as is suggested in literature.

The work presented throughout this thesis also open up a great number of experiments involving CO₂. In addition to the combination of techniques discussed above, we also have control over the quantum state of CO₂. This opens up many new possibilities of studying gas-surface dynamics. Mechanistic insights made for methane can also be investigated for CO₂. We highlight five notable experiments for future work. First and foremost, we can compare the kinetic and vibrational energy dependence of CO₂ dissociation to extract the vibrational efficacy. Reactivity is expected to be quite low, so RAIRS can be applied to quantify reactivity. Second, RAIRS can identify the reaction site(s) (steps vs terraces). Third, experiments that rotate the polarization of the infrared radiation can resolve whether CO₂ dissociation depends on vibrational alignment of the molecule. Fourth, state-resolved CO₂ scattering is of interest as well. We know that methane scattering is non-adiabatic. Vibrational energy is efficiently redistributed from the antisymmetric stretch to the symmetric stretch in the collision. These vibrational modes are separated by only 131 cm⁻¹. (3025.5 cm⁻¹ vs 3156.8 cm⁻¹) Similar experiments would be of great interest for CO₂. The antisymmetric stretch vibration for CO₂ is significantly higher in energy than the other two normal modes. (Chapter 7) Finally, state-resolved experiments can be applied to other polyatomic molecules. Of particular interest is acetylene, C₂H₂, which is also a linear molecule. Unlike

CO₂ however, it has more vibrational degrees of freedom than CO₂ and is thermodynamically unstable. Direct comparison between state-to-state scattering of these two molecules would give fundamental insight in how energy is redistributed during gas-surface collisions.

