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Exploring structure dependencies of gas-surface interactions with curved single crystals

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SUMMARY

CURVED CRYSTALS with their variable, but well-defined surfaces have enormous potential for applications in surface chemistry, to unravel the role of specific sites in the reaction mechanism. Measurements can be repeated on the same crystal with incremental changes of the surface structure. Because effects of sample heterogeneity are avoided, curved crystals make it possible to detect even subtle differences in surface reactivities and assign them to specific surface sites. They were used throughout this thesis to study effects of surface structure on elemental chemical reaction steps.

In chapter 2 we introduce the different types of curved crystals that have been used in literature. We expand on their advantages and challenges in different types of applications. Most standard surface science techniques require adaptations to improve spatial resolution to benefit from the variable surface structure. Improving the spatial resolution by limiting the exposed area, in turn can lead to reduced signal-to-noise ratios; a noteworthy exception is STM, where inherently only a small surface area is probed.

We introduce a nomenclature for crystals in the shape of domes ($d\text{-M}(hkl)\text{-x}^\circ$), cylinders ($cyl\text{-M}[abc]$), and cylindrical slices ($c\text{-M}(hkl)[abc]\text{-x}^\circ$). These are the three shapes that have been used in recent studies involving curved crystals. Depending on the crystal shape, lattice type and crystallographic orientation, curved crystals expose a range of surface structures, with different types of high-symmetry planes, separated by steps and kinks. In this context, LEED provides a useful means to examine overall surface structures across curved surfaces and detect large-scale reconstructions or faceting, by analyzing spot splitting observed in diffraction patterns of vicinal surfaces. Complementary STM studies can give insight into local fluctuations to the average structure.

In regards to surface chemistry, curved crystals have in recent years been used to study the relation between surface structure and chemical reactivity. Prominent examples include the use of cylindrical sections in the study of CO adsorption and oxidation at near-ambient pressures and the use of dome-shaped crystals to investigate the enantioselective adsorption and decomposition of chiral organic molecules on Cu surfaces. In our own group, a fully cylindrical crystal has been employed to study hydrogen dissociation on Ni. More recently, a cylindrical slice of single-crystalline Pt has been used to investigate the surface dynamics of dissociative hydrogen chemisorption, and molecular oxygen adsorption on Pt surfaces, as well as the sites of adsorption of CO. New studies involving curved crystals to examine structure dependencies of elemental chemical reactions, are presented in this thesis.

In chapter 3, we thoroughly study the surface structure of a *c*-Pt(111)[11 $\bar{2}$]-31° crystal. Its apex is oriented to expose the (111) surface. With increasing curvature towards the sides of the crystal, kinked step edges forming {210} microfacets are introduced, resulting in chiral surface structure. The kinked steps consist of short segments in the direction of A- and B-type steps.

The overall surface structure is confirmed by LEED spot splitting analysis. A subsequent STM study then examines in detail local variations in surface structure. At the apex, (111) planes that are >100 nm wide and freely meandering step edges are found. To a small extent, vacancy islands remain after sputtering and mild annealing. The equilibrium shape of these vacancy islands reveals the direction of A- and B-type steps on the (111) terrace, and consequently lets us assign short segments of these step types within the kinked {210} steps. This in turn determines the handedness of the chiral stepped surfaces on the two sides of the crystal.

With increasing angle from the apex, steps align along the direction dictated by the crystal's curvature. Terrace width distributions are narrow and symmetric, with a single peak maximum at high step densities. At lower step densities distributions are asymmetric and exhibit, besides the main peak, secondary local maxima at larger terrace widths. Fitting the distributions with a Gaussian function therefore results in better fits at narrowly stepped arrays than wider arrays. Plotting the Gaussian width of these fits against mean terrace width has displayed a non-linear trend in a previous STM study by Walter *et al.* of a similar curved Pt crystal with close-packed steps, which was attributed to a transition in step-step interactions. For the crystal with kinked {210} steps this transition cannot be observed, but also not excluded with certainty.

The highly kinked {210} steps can assume a large range of configurations with varying corrugation, while maintaining their overall orientation as given by the surface curvature of the crystal. The two extremes of this are firstly, the perfect bulk

termination, featuring fully kinked steps consisting of only inner and outer kinks, and secondly the full reconstruction into long segments of A- and B-type steps, separated by only few kinks. To which degree this reconstruction happens is highly relevant if gas-surface reactions are investigated. Chapter 3 therefore includes a thorough analysis of the varying segment lengths along the step. No significant variation of kink densities, nor consistent changes in the distribution of segments, are found for surface arrays with mean terrace widths ranging from <1 nm to >100 nm, showing that the step morphology does not change with step density across the curved crystal. Additionally, the majority of segments along the kinked step edges are 1-3 atoms wide. Long segments, which may behave as $\{001\}$ or $\{110\}$ microfacets, rather than $\{210\}$ microfacets occur only rarely.

The detailed surface characterization of the c -Pt(111)[11 $\bar{2}$]-31° crystal is an important prerequisite for the chemical reactivity measurements described in chapters 4 and 5.

A molecular beam study of the dissociative chemisorption of D₂ at low kinetic energy is described in chapter 4. It involves both the crystal described above, as well as a c -Pt(111)[1 $\bar{1}$ 0]-31° crystal, exhibiting A- and B-type steps on the two sides respectively. Initial sticking probabilities (S_0) are increased on vicinal surfaces compared to (111). Fitting the increase of S_0 with step density reveals small differences between the three different step types on the two curved crystals.

The thorough STM analysis of the kinked steps, in combination with the site-specific reactivities of A- and B-type steps, allows us to conclude that kinks aid dissociation more than atoms in straight steps. However, the measured reactivity difference for the three step types is not adequately captured by models that rely on the (generalized) coordination number of various types of surface atoms. We believe that the origin of the discrepancy is the dynamical nature of the interaction. For a light-weight molecule interacting at low collision energy with a surface that is characterized by (at most) modest barriers to dissociation, molecular wells close to the dissociation site increase the dissociation probability. We therefore describe the interaction in terms of a cross section, σ_0 . It reflects the physical area near the step where impingement leads to trapping and dissociation as found in earlier theoretical dynamics studies. The average length of this area, Σ_0 , measured normal to the step, is derived directly from the experimentally determined dependence of reactivity on step density. We believe that the reactivities determined here provide a useful tool for modeling dissociation on vicinal surfaces with potentially large unit cells. Furthermore, they allow careful prediction of reactivities on industrially relevant catalyst sites by bridging the whole range of stepped Pt surfaces.

In chapter 5, surfaces close to the apex of the c -Pt(111)[11 $\bar{2}$]-31° crystal are re-

examined. Meandering step edges, as well as vacancy islands that remain after the gentle last cleaning cycle of surface preparation, are found instead of a perfect (111) surface. We manually extract defect densities at, and close to, the apex and compare them to the step densities expected from the angle of curvature. Only in a range of $\pm 100 \mu\text{m}$ from the apex are the defect densities increased.

We can thus revisit sticking probabilities of D_2 on the kinked vicinal surfaces. We also probe HD formation from a mixed beam of H_2 and D_2 . Data close to (111) is corrected according to the actually probed defect density, but the difference does not affect our previous finding in chapter 4 significantly. However, by fitting the increase of S_0 with step density, we can now extrapolate towards zero and extract the sticking probability for a perfect 'defect-free' (111) surface. This closes a common gap between theoretical studies that compute a perfect (111) unit cell, and experimental results where, even in case of perfect surface preparation, entropy creates a residual defect density.

Both D_2 dissociation probabilities and HD formation probabilities increase nearly linearly with step density. Measured reactivity can thus be approximated as a linear sum of individual contributions by steps and terraces. However, a slight curvature of the data may indicate diffractive scattering of the small molecules at highly ordered step arrays. The lower dependence on step density for HD production than D_2 dissociation may indicate anisotropic diffusion caused by higher binding of H (D) atoms at steps sites.

Further expanding on the advantage of curved crystals, we investigate water desorption from hydrophobic surfaces using two curved Ag single crystals in chapter 6. The crystals are two slices of the same cylinder, centered at (111) and (001) respectively: $c\text{-Ag}(111)[1\bar{1}0]-31^\circ$ and $c\text{-Ag}(001)[1\bar{1}0]-31^\circ$. Besides the two high-symmetry planes, surfaces with three types of steps are probed, A-type, B-type, and A'-type ($\{111\}$ microfacets on (001) terraces).

Subtle differences in desorption of submonolayer water coverages point toward structure dependencies in water cluster nucleation. Within the interpretation that desorption reflects binding, on the $c\text{-Ag}(111)$ crystal water molecules are bound measurably stronger by steps than (111) terraces, resulting in a desorption temperature shift as the step density increases. We detect changes in binding energy that vary less than 1 kcal/mol, which is considered 'chemical accuracy'. The binding energy at the two step types can also be shown to not be the same. The A'-type steps bind water approximately equally strong as the (001) terrace. As a result the desorption temperature at very low coverages does not change significantly with step density. We predict that on (001) terraces water cluster nucleation is not dominated by steps.

Water desorption both from surfaces with A-type steps and surface with A'-type steps is extrapolated towards the maximally stepped (311) surface. We conclude that the

A- and A'-steps themselves have the same binding energy for water and can in fact be seen as the same type of step, where facets forming the step edge and terrace are inverted. However, here we can clearly see the influence of the different terrace types. When extending the (111) facets from (311), we see a decrease in desorption temperature, indicating a weaker binding at the (111) terraces. On the other hand, extending the (001) facets from (311) doesn't result in a change in desorption temperature, indicating that the (001) terraces have a very similar binding energy. The difference indicates the fundamental difference between (111) and (001) terraces and illustrates the influence of terrace type on adsorption at steps. Controlling the combination of terraces and steps in terms of terrace type, step type and step density thus provides an extremely sensitive tuning mechanism for the location of water nucleation.

Beyond the work in chapters 3-6, we emphasize the potential of curved crystals in surface science in chapter 7. When studying adsorbates on vicinal surfaces by STM, curved crystals provide a wide range of surface structures, which are exposed to the adsorbing molecule at the same time. Samples do not need to be exchanged to study different surfaces, and different experimental conditions can be avoided. Therefore, gradual changes, e.g. in terrace coverage or adsorbate structure, can be tracked. With regards to gas-surface dynamics, surface-dependent changes in reaction probabilities can be determined, even when these effects are subtle.

Different materials, shape, and orientation may be chosen for curved crystals, allowing to study surface-sensitive reactions, e.g. on alloys or oxides, and opening the door towards efficient chiral heterogeneous catalysis.

