Understanding the surface structure of catalysts and 2D materials at the atomic scale

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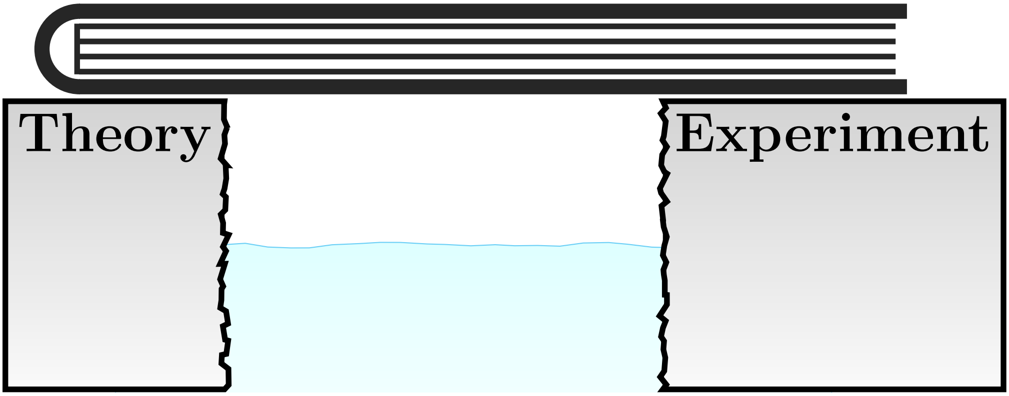
Chapter 1

Introduction



1.1 The Surface-Science Approach - a Success Story

Although catalysis is a fundamental part of all life, the discovery, and subsequent (industrial) application, of heterogeneous catalysis has had a tremendous impact on the development of humanity and currently serves as a cornerstone of modern society. The power of heterogeneous catalysis lies in the fact that the active catalyst subsists in a different (hence *hetero*) phase than the reactants. In most cases this means the catalyst consists of a solid, while reactants are either gaseous or (dissolved in) liquid. In comparison to biological or homogeneous catalysts, this means the lifetime of a heterogeneous catalyst is typically much higher, and separation of products and catalyst comparatively trivial. Naturally, since the catalyst and reactants are in different phases, catalysis occurs only at the solid-gas, or solid-liquid interface. As such, there is a natural scientific interest in the fundamental processes that occur at interfaces, as well as the properties of interfaces themselves. This interest has led to the development of the field of surface science, and has consequently led to the advancement of numerous scientific techniques.

Surface science focuses on the study of both the (atomic) structure of interfaces and the phenomena that occur at interfaces, which are, more often than not, closely related. Heterogeneous catalysis is obviously a focal point, but other facets of surface science involve the study of two-dimensional (2D) materials, and the functionalization of semiconductors and other nano-devices.[1–3] As such, surface science is literally at the interface between chemistry and physics.

Although surface science is not limited to solid-gas and solid-liquid interfaces, the vast majority of studies involves a solid constituent.[4] This makes adsorption of atoms and molecules on solids a primary focus, since it is a common avenue for catalytic function, as well as an obvious factor in thin film growth. In the second half of the 20th century, various techniques have been developed to detect and characterize both solid surfaces, and species adsorbed upon them. For the first time, this allowed for characterization of the geometric and electronic structure of surfaces at the atomic scale.[5]

Initially, experiments were mainly focused on vacuum conditions, which enables systematic reproducibility, by keeping the surface clean long enough to carry out experiments. In addition, many experimental techniques involve free electrons, and therefore, require low-pressure conditions to work. In an effort to further limit the number of entangled variables, the use of single crystals provides additional control over the surface structure. As a result, initial research was focused mainly on model systems, consisting of well-defined single-crystal surfaces in vacuum.[1,2,6]

In combination with the advancement of experimental techniques, theoretical approaches to model (phenomena on) surfaces at a submicroscopic scale have also been developed, in large part due to the exponential growth of computing resources since the second World War. Results from theory can be used to explain experimentally observed phenomena, while experiments, in turn, serve as a way to gauge the fidelity of the theoretical results.[7] Calculations on surfaces at an atomic level became tractable, since experiments initially targeted the adsorption of small molecules on clean, defect-free, low-index surfaces, which can be modeled efficiently using periodic boundary conditions.

A well-known 'success story' of surface science is the development of atomic models for the reconstruction of clean low-miller index Si surfaces, in particular the 2×1 reconstruction of Si(001). Diffraction and spectroscopy results on the reconstruction of Si(001) initially puzzled both theoreticians and experimentalists alike, leading to various conflicting hypotheses within the scientific community.[8–10] Eventually, advancements in scanning tunneling microscopy (STM) and density functional theory (DFT) resulted in a scientific consensus, namely that the dangling Si surface atoms in the Si(001) reconstruction form buckled dimers.[11] The seemingly inconsistent results between different experiments and theoretical models were, in part, a consequence of (temperature-dependent) changes in the buckling direction.[12] DFT calculations predicted asymmetric dimer buckling, while (room temperature) STM observed symmetric dimers, except near defects.[13–15] Low-temperature STM finally resolved this disagreement, by showing that the theory-predicted structure was correct, and the buckled dimers were able to switch orientation rapidly at room temperature, leading to an averaged symmetric appearance in STM images.[16]

1.2 The Gaps Between Theory and Experiment

Since the beginning of the field, catalysis has been a main focus of surface science, which means surface-adsorbate interactions are of great interest. Adding molecules onto a surface greatly increases the complexity, since, even on simple surfaces, there are typically many combinations of adsorption geometries possible. In practice, this often leads to compromises on the scale and scope of the theoretical models, due to the much higher computational cost of larger surface structures. In particular, larger surface reconstructions, which result in a loss of periodicity, are frequently disregarded by theoretical investigations.[17] This is an understandable compromise, but this "materials gap" between theory and experiment imposes limits on our understanding of surfaces, especially under dynamic conditions, such as during catalysis. In recent years, adaptations that allow many surface-science techniques to operate under high-pressure conditions, have made *in situ* experiments much more accessible, while yielding almost the same accuracy in results as their *ex situ* counterparts.[18–25] This allows experiments to transcend the so-called "pressure gap" between academic experiments and real catalysts, which has been a point of concern for catalysis since the inception of the surface-science field.[26]

One such technique, that links back to the work on silicon, is *in situ* STM. Since STM itself does not inherently necessitate vacuum conditions, it is possible to observe changes in the surface at temperatures and pressures relevant for catalysis in real time as long as the surface remains sufficiently flat and conducting.[27,28] Another example is (near) ambient-pressure (NAP) X-ray photoelectron spectroscopy (XPS), which allows for identification of the elements present on the surface, while simultaneously identifying their oxidation state.[29] For Pt(111), *in situ* STM and NAP-XPS have shown that at temperatures and oxygen pressures typical for catalytic processes involving platinum, the top platinum layers begin to oxidize, and these surface oxides eventually cover the entire surface.[30,31] Some of these observed surface oxides were shown to rapidly reduce in vacuum, which means they cannot be observed with an *ex situ* approach. In such cases, conventional zero-pressure and zero-temperature calculations fall short in describing the surface adequately, resulting in a secondary pressure gap of sorts between theoretical and experimental studies. While closing one “pressure gap” between experiments and real-world catalysis, it is important to prevent another “pressure gap” between theory and experiment from widening, which means theoretical methods are required to catch up with experimental developments.

1.3 Towards Closing the Gaps

1.3.1 A Comprehensive Description of the Surface

To reduce the “materials gap” between experiment and theory, it is necessary to improve the comprehensiveness of the atomic models, in order to better match them to the real situations in experiments. In the majority of computational surface-science studies, at least some aspects of the atomic surface model are simplified.[32] Modeling low-index surfaces of perfect crystals is particularly convenient, because this allows for periodic boundary conditions, which avoids (lateral) finite-size effects.[33,34] This is often a reasonable analogue for samples used in experiments, since the use of single-crystal surfaces for fundamental studies is popular, as explained in the previous section. Regardless of whether the lateral periodicity induced by a finite unit-cell size is a reasonable assumption, the direction perpendicular to the surface is, by definition, not periodic. This means that the bulk-terminated surface has to be approximated as a periodic “stack” of slabs, separated by some vacuum distance.[35] It is vital to ensure that the two surfaces on the slab do not interact with one another, either through the vacuum, or through the subsurface layers. Thicker slabs and larger slab-slab distances result in a more realistic approximation of a bulk-terminated surface, but this naturally results in higher computational costs.

Depending on the approach, the computational cost of *ab initio* electronic structure calculations scales differently with increasing number of electrons present in the atomic model. DFT is very popular due to the relatively favorable scaling of the computational cost, but in particular for metallic systems, the scaling of DFT is cubic with respect to the system size (computational cost $\propto n^3$, for an n-electrons system). Depending on the basis set used for periodic DFT, there is also a significant cost associated with increasing the vacuum distance between periodic slabs.[36] Another practical issue, when modeling experimentally observed surface structures at larger lenght scales, is the fact that the structures themselves inherently have more degrees of freedom. This not only makes convergence of geometric relaxations more tedious, but also vastly expands the configurational space that needs to be considered. These challenges exacerbate each other, since not only are more electronic structure calculations required, but the computational cost for each of them is also greatly increased.

One method to reduce the overall computational cost of developing a large-scale atomic surface model is to improve the accuracy of the initial guess of the overall structure, by first investigating key features, such as preferred adsorption sites or bonding geometries, in simplified model systems. Although the results from these model systems do not necessarily hold when transitioning to the large-scale atomic model, they at least aid in discerning which segments of the configurational space are worth exploring further. This prior screening of the configurational space (via either calculations or literature research) is sometimes referred to as applying "chemical intuition".[37]

Regardless of the accuracy of the (initial) geometry, the scale of some surface features found in experiment is simply not tractable for electronic structure calculations, such as DFT. If the primary goal is to attain a reasonable atomic model for these kinds of systems, the use of a force field may be warranted, typically sacrificing accuracy for orders of magnitude lower computational cost.[38–41] In a force field approach, the electrons are not considered explicitly. Instead, energies and forces are calculated directly as a function of the atomic positions and the lattice vectors (when using periodic boundaries). Consequently, the computational cost scales approximately linearly with the number of atoms in most cases, since only interactions between atoms in close proximity have to be considered explicitly. This is in stark contrast to *ab initio* methods, like DFT. Since these force-field parametrizations are normally fitted to the results of *ab initio* calculations, they can at best approach the accuracy that these respective *ab initio* methods would have.[42–44] Modern developments in "reactive" force-field parametrizations are able to qualitatively, and in some cases quantitatively, reproduce key results from DFT.[45–47] Although, the fitting process of such force-field parametrizations can be rather arduous, they provide a tool to narrow the gaps between theory and experiment, since investigation of larger surface features found in experiments, such as the spoke wheels in Chapter 5, might otherwise be inaccessible when relying solely on *ab initio* electronic structure calculations.

1.3.2 Considering Finite Temperature and Pressure

To accompany the departure from the historical surface-science approach towards *in situ* experiments, theoretical models need to include (non-zero) temperatures, as well as interactions with gas- (or liquid-) phase molecules in the description of the surface. The most conceptually straightforward approach to model these dynamic processes is to make use of molecular dynamics (MD) simulations.[48] In the case of molecular dynamics, pressure and temperature are included explicitly by adding gas (or liquid) molecules to the vacuum above the surface and by giving all atoms an explicit kinetic energy. In a typical approach, the time is discretized, and the forces on all atoms have to be calculated at the start of each time step. The subsequent movement of all atoms during the time step is determined according to Newton's equations of motion, based on the calculated forces and initial momenta.[49] The maximum length of each time step is typically in the femtosecond range, while the time scales reported in *in situ* experiments range from minutes to hours.[50–52] This means that to model such an *in situ* experiment at appropriate time scales with *ab initio* molecular dynamics, more than 10^{13} *ab initio* calculations would be required, which is simply not feasible, especially for the aforementioned large surface structures. To circumvent this problem, MD simulations commonly utilize force fields. Nevertheless, bridging thirteen orders of magnitude on the time scale remains non-trivial and such MD simulations remain computationally costly, especially for large systems.[53–56]

Because adsorption and desorption of gases on and from the surface at *in situ* pressure and temperature is orders of magnitude faster than the time a typical *in* *situ* measurement takes, an often reasonable assumption is that the surface structure observed in such a measurement is the result of a (quasi-)equilibrium between the surface and gas phase.[57,58] If the gas phase and surface are in equilibrium, atomistic thermodynamics can be employed to compare the relative stability of various surface structures, as a function of temperature and (partial) gas pressures, based on the result of conventional (zero-pressure, zero-temperature) electronic energy calculations.[59–61] This provides a means to bridge the gap between the computational conditions and the *in situ* experimental conditions for negligible additional computational cost.

Chapters 4-6 contain three different model systems, whereby agreement between (*in situ*) experiments and theory is achieved using the various gap-bridging methods discussed above. First, Chapter 4 in this thesis illustrates how gas-phase calculations alone are not sufficient when searching for novel low-dimensional materials using DFT, as for 2D cobalt sulfide on Au(111), theory and experiment only agree when the substrate is considered explicitly in DFT calculations. The second model system consists of Pt(111) during *in situ* STM experiments, in which a platinum oxide spoke-wheel structure was observed previously.[31] This spoke wheel had not yet been investigated theoretically, likely due to the large scale of the structure and its poor stability in vacuum. Atomistic thermodynamics is combined with force-field calculations in Chapter 5 to investigate the structure and stability of the spoke wheels, and to explain why they are formed during the initial oxidation of Pt(111). Lastly, an atomistic thermodynamics approach is used in combination with *ab initio* electronic structure calculations (DFT) in Chapter 6 to construct a phase diagram for the adsorption of NO and CO on the Rh(100) surface during *in situ* STM experiments, which gives insights into the role of NO and CO in the *in situ* roughening of the surface.

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