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## Steps in gas-surface reactions

Lent, R. van

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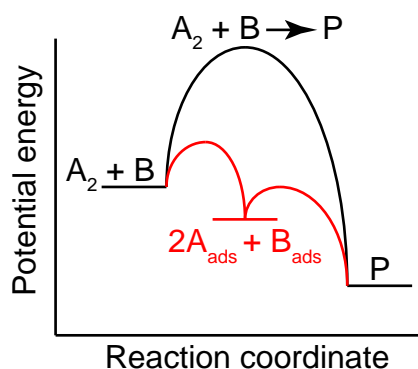
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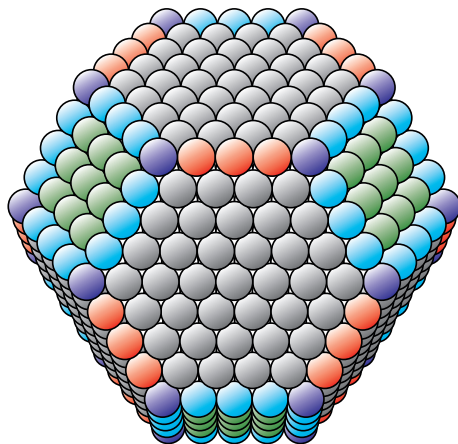
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200 years ago, Sir Humphry Davy worked on understanding combustion.[1] He theorized that flames required higher temperatures to glow than solids. To test his theory, he devised an experiment. He suspended a platinum gauze above a flame to heat the metal up. When he quenched the flame by adding too much gaseous fuel, the flame extinguished within seconds. However, the hottest part of the platinum gauze remained aglow for several minutes until all combustible gases were consumed. While limited in the number of metals he could test, the experiment only succeeded with platinum and palladium. This was the serendipitous discovery of what was not yet called catalysis.[2] Davy applied his discovery in a safety lamp for coal miners that could warn the user of highly flammable gases and asphyxiation. Soon after Davy's discovery, Henry identified the two chemical reactions responsible: combustion of hydrogen and carbon monoxide to form water and carbon dioxide.[3] The discovery that a platinum wire glows in the presence of combustible gases and oxygen literally and metaphorically sparked 200 years of heterogeneous catalysis research.

Nowadays, it seems impossible to imagine a world without catalysis. It is used at some point in almost every commercial product around us, e.g. in growing food, making plastics, or cleaning emissions from our car exhaust. It is a multi-billion dollar industry that will never disappear. So what does a catalyst, such as Davy's platinum wire, actually do? Figure 1.1 illustrates the principle. Reactions that occur without a catalyst generally have a significant reaction barrier (black). A catalyst (red) changes the reaction path, thereby reducing the reaction barrier and stabilizing key intermediate(s). The product P is subsequently released or desorbed. A good catalyst increases the reaction rate but is unaltered after the reaction is complete. It can repeat the catalytic process countless of times. The catalyst does not alter the equilibrium but does decrease the time it takes to reach equilibrium. Three general forms of catalysis are distinguished: homogeneous catalysis, heterogeneous catalysis, and biocatalysis. The difference between the three is the state of matter of the catalyst and the reactants that it acts upon. Homogeneous catalysts are in the same state of matter (gas, liquid, or solid phase) as the reactants and generally occurs in the liquid or gas phase. Biocatalysis is a biological variation on homogeneous catalysis, where proteins are the catalyst. Both proteins and homogeneous catalysts usually have a well-defined active site.



**Figure 1.1:** Schematic illustration how a generic catalyst (red) lowers the reaction barrier compared to the reaction taking place without a catalyst (black).



**Figure 1.2:** An exemplary nanoparticle with various surface sites: hexagonal (1 1 1) (grey) and square (0 0 1) (green) terraces. Different step edges and corners are depicted in blue, red, and purple.

In contrast, heterogeneous catalysts are in a different state of matter than the reactants – usually the solid phase. Heterogeneous catalysts generally consist of finely dispersed nanometer-sized metal particles on a porous support. An example of such a metal nanoparticle, with the face-centered cubic structure, is shown in figure 1.2. The surface of this nanoparticle comprises a variety of different types of surface atoms, indicated with different colors. Green and grey atoms represent a square (0 0 1) and hexagonal (1 1 1) terraces. Defect sites – shown in blue, red, and purple – have lower coordination numbers and generally bind reactants stronger. These different surface sites may each exhibit different catalytic activity. Catalytic reactions sometimes have an optimum particle size. These particle size effects are a trade-off between getting as much of a specific reaction site without significantly altering the electronic properties of the site. Changing the latter influences both the binding energies and catalytic activity according to the Brønsted-Evans-Polanyi principle.[4]

This thesis seeks to provide new insights in the fundamental processes that underlie heterogeneous catalysis. How defects such as those shown in figure 1.2 influence reactivity is still studied to this day, even to under-

stand the reactions that Davy already discovered 200 years ago. Since then, countless scientific advances were made that enable the work in this thesis. We would like to highlight some notable discoveries that have defined the field, starting with the work of Irving Langmuir that birthed the field of surface science and earned him the Nobel prize in 1932.[5] Langmuir studied light bulbs at General Electric and resolved a number of fundamental problems with some simple vacuum experiments. First, he showed that hydrogen molecules are dissociated by hot tungsten filaments and that these hydrogen atoms subsequently adsorb to the glass walls of the light bulb. The saturation coverage is approximately equal to the surface atoms available. Thereafter, he showed that oxygen also readily dissociates at tungsten filaments, thereby significantly reducing the emission current. The binding energy of oxygen to the tungsten surface is very high, comparable to covalent bonds. Finally, upon introducing a mixture of hydrogen and oxygen to the tungsten filament, oxygen poisons the surface. Catalytic activity towards hydrogen dissociation is negligible until adsorbed oxygen is removed from the surface. Upon oxygen removal, atomic hydrogen adsorption by the glass bulb proceeds as before. These observations were the basis for what is now known as the Langmuir-Hinshelwood reaction mechanism: reactants dissociatively adsorb at a catalytic surface and subsequently recombinationally desorb as the product.

Another noteworthy discovery in connection to the work in this thesis is that of electron diffraction, for which Thomson and Davisson were awarded the Nobel prize in 1937. We focus here on the Davisson-Germer experiment.[6] Although de Broglie[7] predicted the wave-particle duality for all particles, it had only been confirmed for photons. Unaware of this prediction, Davisson and Germer were scattering low energy electrons off a nickel surface. At some point in their experiments, they accidentally oxidized their polycrystalline nickel sample.[8] To resolve this problem, they decided to reduce the sample in hydrogen using a high temperature oven. In doing so, they annealed their polycrystalline nickel sample to temperatures sufficient to grow single crystalline grains that were larger than the size of their electron beam. Consequently, they effectively employed a single

crystal surface and showed that electrons exhibit wave-like behavior by diffracting.[8] Later, they purposely used a Ni(1 1 1) single crystal surface to perform their experiments.[6, 9] To this day, the surface science approach uses single crystal surfaces. Moreover, Low Energy Electron Diffraction is one of the most prominent surface science techniques for verifying the surface structure of single crystal surfaces.

A third technique essential to this thesis is that of molecular beams. Otto Stern was awarded the 1943 Nobel prize for his work on developing molecular beams. Although he was not the first to use atomic or molecular beams, he used them with Gerlach to show that atoms have angular momentum. In his Nobel lecture, Stern lauded the possibilities of molecular beams: "The most distinctive characteristic property of the molecular ray method is its simplicity and directness." [10] Molecular beams were used in those days to resolve problems related to classical and quantum physics. King and Wells[11] developed a surface science apparatus for directly measuring nitrogen sticking probabilities at tungsten single crystal surfaces using a molecular beam. Their approach is discussed in chapter 2. Auerbach et al.[12] showed that kinetic energy and incidence angle strongly affect the dynamics of N<sub>2</sub> dissociation at W(1 1 0). The observed dynamical behavior was unexpected and the field flourished. The dynamics of dissociative chemisorption were measured for various molecules at different surfaces.[13–18]

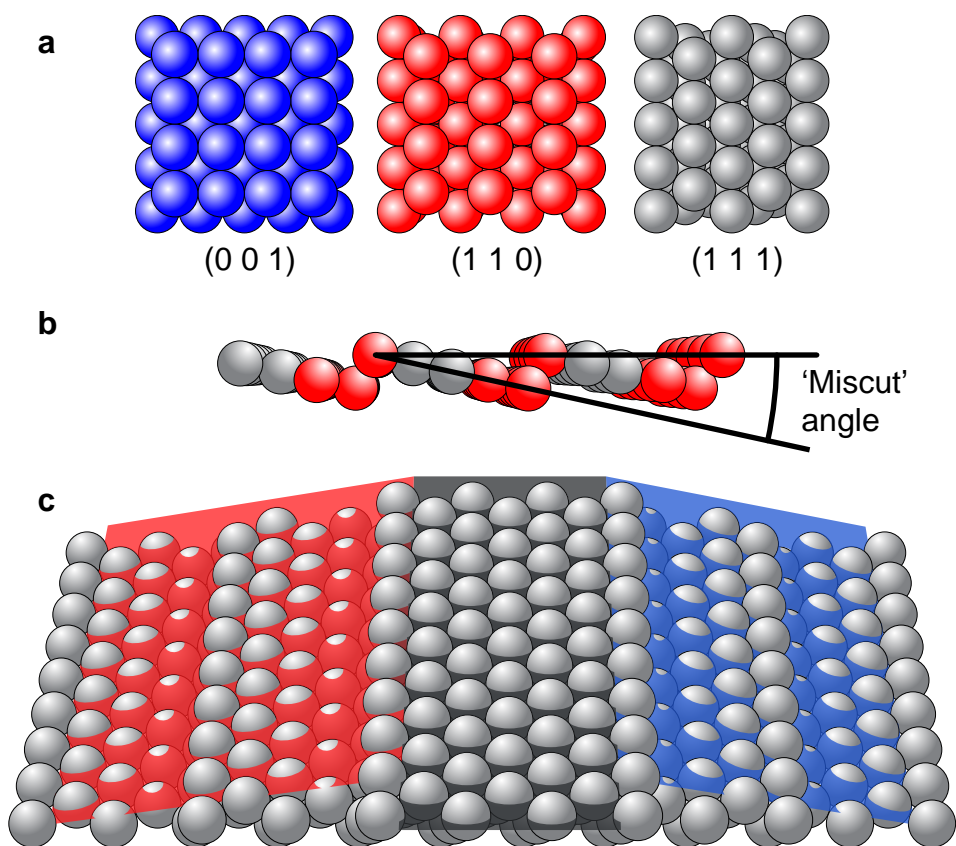
Throughout the years, many developments have enabled experimentalists to control virtually every aspect of molecule-surface collisions by using molecular beams. We highlight some notable examples. Early surface science experiments used nozzle heating or plasma beam sources to increase the internal state distribution of molecules.[17] Combining molecular beams with lasers opened up new possibilities, e.g. stimulated Raman pumping enabled incident hydrogen molecules to be vibrationally tagged for state-resolved dissociation and resonance enhanced multi-photon ionization (REMPI) detection for state-resolved scattering.[19] Molecules such as methane or water had to wait for the advent of tunable coherent in-

frared light sources for state-resolved dissociation.[20, 21] For methane, vibrational excitation opened up many new possibilities. As a polyatomic molecule, it has a lot more vibrational degrees of freedom than diatomic molecules. The vibrational efficacy, which compares vibrational and kinetic energy in breaking the bond, varies for different normal mode vibrations (and their overtones).[20, 22, 23] Using isotopologues, it is possible to also show bond specificity in  $\text{CHD}_3$  dissociation.[24] Even more recently, hexapole alignment gives stereo-dynamic control over incident  $\text{O}_2$  molecules, showing what molecular orientation is most beneficial for dissociation.[25–27]

The surface science approach uses single crystal surfaces as model catalyst. These model catalysts are generally studied under ultrahigh vacuum (UHV) conditions. New surface science techniques are usually first applied to so-called low Miller index surfaces. For metals with the face centered cubic structure, such as platinum, these are  $(1\ 1\ 1)$ ,  $(1\ 1\ 0)$ , and  $(0\ 0\ 1)$  shown in figure 1.3a. Single crystal boules are cut to expose one of these low Miller index surfaces. Since it is impossible to cut metal single crystals with subnanometer accuracy, small miscuts always result in long planes of low Miller index surfaces separated by step edges. These step edges can dominate overall reactivity at the surface if the low Miller index surface exhibits little to no reactivity. The influence of step edges can be studied systematically by purposely ‘miscutting’ the single crystal boule at a larger angle, as schematically shown in figure 1.3b. The surface then exposes high Miller index surfaces with shorter terraces separated by step edges, such as the  $(5\ 5\ 3)$  surface shown. Throughout this thesis, surfaces with **A-type** or  $\{0\ 0\ 1\}$  steps are marked in blue. Surfaces containing **B-type** or  $\{1\ 1\ 0\}$  steps are marked in red.

UHV allows for a large range of surface sensitive techniques.[28] However, the use of separately polished flat surfaces to probe the influence of different step types and/or terrace widths imposes difficulties:[29] sample-to-sample variation in the quality and purity of the surface and bulk of individual single crystals; the need to break vacuum; initial cleaning of new crystals,





**Figure 1.3:** a) Low Miller index surfaces for face-centered cubic crystals. b) High Miller index surfaces can be exposed by cutting the single crystal at an angle with respect to the low Miller index surface, shown here for the  $(5\ 5\ 3)$  that occurs at approximately  $12.3^\circ$  with  $(1\ 1\ 1)$ . c) Illustration how a curved surface exposes surfaces that vary from  $(5\ 5\ 3)$  along  $(1\ 1\ 1)$  to  $(3\ 3\ 5)$ .

which may take months of sputtering-annealing cycles; and differences in absolute temperature measurement resulting from minor variations in thermocouple connections. Some problems can be overcome. Repetitive breaking of UHV conditions can be eliminated through the use of a load-lock system, but exchangeable sample mechanisms usually compromise heating and/or cooling efficiency. The effect of different impurities between crystals can be removed (at least in part) by cutting all samples from the same single crystal boule. However, the expense and time necessary to work with multiple individual crystals remains. In our experience, the experimental time requirement is proportional to the number of surfaces studied.

An alternative to this traditional surface science method of studying the influence of steps is to use a curved surface. Various shapes have been utilized, including fully cylindrical crystals, which exhibit at least two regions of each low Miller index structure on their circumference;[30–32] and dome-shaped crystals, which also include kinked step edges.[33, 34] For a nickel cylinder with its rotational axis along  $(1\ 0\ \bar{1})$ , we found mostly smooth variations in step density between the three low Miller index surfaces  $(0\ 0\ 1)$ ,  $(1\ 1\ 1)$  and  $(1\ 1\ 0)$ . [35] In contrast, faceting of high Miller index planes was observed on a cylindrical Pt crystal oriented with its rotational axis along  $(0\ 0\ 1)$ . [32] Limitations of working with a full cylindrical crystal include the thermal inertia of a large sample, and the difficulty of adapting sample holders to this shape. A compromise solution is to fashion a section of curved crystal into the approximate size and shape of a typical flat sample. Although the range of surface structures available on such a partial section is more limited, such crystals have been employed successfully in standard UHV systems.[36, 37] In these cases, they expose surfaces ranging from  $(5\ 5\ 3)$  along  $(1\ 1\ 1)$  to  $(3\ 3\ 5)$ , as indicated in figure 1.3c. Generally, the direction of curvature is chosen such that the curvature results from atomically straight step edges. Dome-shaped crystals offer a continuous range of surface structures, including straight and kinked step edges. Cu crystals were employed in studies of surface structure and chemical reactivity[33, 34]. Spherical single crystals were also employed in electrochemistry to resolve the roughening of Pt electrodes upon scanning

to oxidative potentials.[38]

Studies employing curved single crystal surfaces require experimental techniques with sufficient spatial resolution; a detail that is generally unimportant with macroscopically flat surfaces. Various techniques have been applied to study the continuously varying surface structure with high spatial resolution. Early studies employed Low Energy Electron Diffraction (LEED),[35, 39] Auger Electron Spectroscopy[40, 41] and Photoelectron emission microscopy.[32] More recently Scanning Tunneling Microscopy[36, 42, 43] and probes using electromagnetic radiation, e.g., Angle Resolved Photoemission Spectroscopy,[42, 44] and X-ray Photoelectron Spectroscopy (XPS),[36] have been shown to be applicable with high spatial resolution. These techniques mostly probe the chemical identity, oxidation state, and electronic states of the surface and its adsorbates. The dynamics of chemical processes were studied using supersonic molecular beams. In this way, the King and Wells technique was used to determine the absolute probability of molecular and dissociative adsorption as a function of incidence angle and kinetic energy.[30] Also, spatially-resolved temperature programmed desorption has demonstrated differences in the desorption of  $\text{H}_2\text{O}$  from different step types of a curved  $\text{Ag}(1\ 1\ 1)$  single crystal.[37] Planar Laser-Induced Fluorescence showed that light-off temperatures for CO oxidation on a curved  $\text{Pd}(1\ 1\ 1)$  sample are lower at  $\{1\ 1\ 0\}$  steps than  $\{0\ 0\ 1\}$  steps.[45]

How defects influence reactivity is actively studied to this day.[27, 46–48] Platinum is one of the best catalysts for oxidation reactions. It is used for hydrogen oxidation in fuel cell applications, but also for CO oxidation in the three-way car catalyst. Throughout this thesis, we study processes relevant to these two applications using stepped surfaces. We use both curved and traditional flat single crystal surfaces to study how defects influence reactivity in surface reactions relevant to hydrogen fuel cells. We systematically unravel mechanistic details by studying the catalytic steps individually. In chapter 3, we elucidate how defect density and defect type affect initial hydrogen dissociation. Dissociation occurs at the site of im-

pact and does not require a highly mobile precursor. For the first time to our knowledge, we extract site-specific reaction cross sections for the  $\{0\ 0\ 1\}$  and  $\{1\ 1\ 0\}$  steps. The  $\{1\ 1\ 0\}$  step type has a larger reaction cross section than the  $\{0\ 0\ 1\}$  step type. In chapter 4, we show that while defects increase reactivity, they lower selectivity in isotopic scrambling of dihydrogen. We attribute this to poor diffusive mixing at steps. In chapter 5 we show using two molecular beams that  $\{1\ 1\ 0\}$  steps are also more reactive in oxygen reduction than  $\{0\ 0\ 1\}$ . This is a result of both higher  $O_2$  and higher  $H_2$  sticking. In chapter 6, we adapt reflection absorption infrared spectroscopy so it may be applied to curved single crystal surfaces. We then use this technique to study CO adsorption on platinum as proof of principle. Finally, we present an outlook in chapter 7. There, we describe the spectroscopy of  $CO_2$ . Throughout this thesis work, we developed an optical excitation setup to prepare  $CO_2$  in a vibrationally excited state for state-resolved  $CO_2$  dissociation experiments. We present initial characterization of the optical setup and  $CO_2$  excitation in the supersonic molecular beam.