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Cover Page

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Issue Date: 2021-03-11

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INTRODUCTION

1.1. CHEMICAL REACTIONS AND THE EFFECT OF CATALYSTS

CHEMISTRY studies the properties and transformations of matter. It is impossible to imagine a world without chemical reactions, which transform substances into new compounds, often with completely new properties. Schematically, we can write a chemical reaction as:

$$A + B \longrightarrow C \tag{1.1}$$

One essential example is the formation of water from hydrogen and oxygen:

$$2\,H_2 + O_2 \rightleftharpoons 2\,H_2O \tag{1.2}$$

Two core aspects determine whether we actually see a reaction occur. Firstly, the energy balance between reactants and products determines if it is thermodynamically favorable for the reaction to take place, or if the reverse reaction is preferred. This energy balance can change depending on the chemical environment, e.g. temperature, pressure, or concentration. Secondly, kinetics describe the reaction rate, i.e. how fast the reaction ensues. For example, graphite and diamond are two allotropes made of the element carbon. Thermodynamically, graphite is the more stable structure under the conditions at the earth's surface, however, we do not commonly see diamonds freely transform into graphite. That is because the rate of the process is so low that the transformation is imperceivably slow.

The reaction rate is described by the Arrhenius equation:[1–3]

$$k = \nu e^{-\frac{E_a}{RT}} \tag{1.3}$$

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Here, k is the reaction constant, R is the universal gas constant, and T is the temperature. ν is the attempt frequency and E_a is the activation barrier. The last two terms are influenced by the conditions in which the reaction takes place. The activation energy is a barrier that needs to be overcome in order to go from the reactants to the products. Therefore, ν can be considered a descriptor of how frequently reactants attempt to overcome the barrier, and $e^{-\frac{E_a}{RT}}$ as the probability of successful attempts.
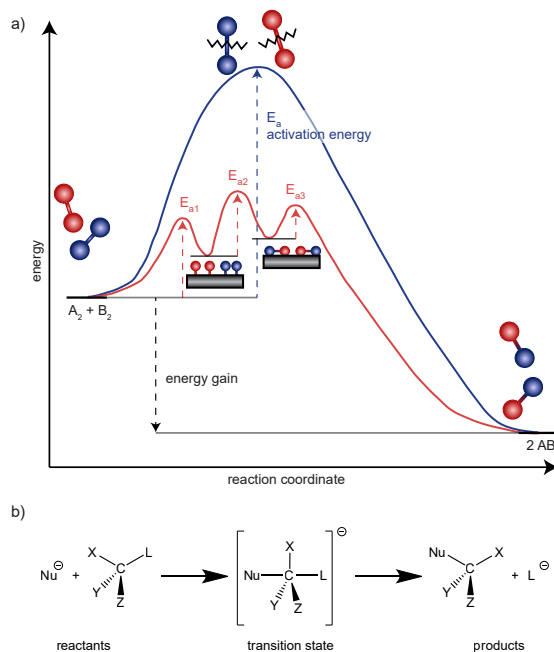

Figure 1.1: a) Schematic energy diagram of chemical reactions in the absence (blue) or presence (red) of a catalyst. The observed activation energy corresponds to the highest energy barrier that has to be overcome during the reaction path. b) Reaction mechanism of a S_N2 reaction, going through a transition state that is energetically less favorable than both reactants and products.

During the transformation of the reactants to products, they typically have to undergo a transition state that is less energetically favorable than both reactants and products. The blue line in figure 1.1a) illustrates this process. Figure 1.1b) shows an example where a nucleophilic substitution reaction undergoes a clearly unstable transition state. While the nucleophile (Nu^-) approaches the molecule and starts forming a bond and the leaving group (L) weakens its bond to the central carbon atom, a transition state is formed. As this transition state is energetically disfavored, the reactants need a certain amount of energy available to them, typically in the form of thermal energy, to reach this state. Once at the transition state, the reaction can then proceed towards the product while releasing energy.

Catalysts are substances that increase the rate of a reaction but are neither consumed

nor permanently changed by the reaction, or in the words of Friedrich Wilhelm Ostwald: "A catalyst is a substance which affects the rate of a chemical reaction without being part of its end products".[4, 5] The red line in figure 1.1a) shows a typical reaction path of a catalyzed reaction. The thermodynamic balance between reactants and products is not changed by catalysts, as the free energy of a reaction does not depend on the reaction path. For this reason, a catalyst cannot change the direction in which a reaction occurs. However, catalysts do lower the activation barrier of the reaction, e.g. by stabilizing intermediates and making transition states less unfavorable. The fraction $e^{-\frac{E_a}{RT}}$ in equation 1.3 therefore becomes larger, i.e. more "attempts" of the reactants are successful at overcoming the barrier, and as a result the reaction rate increases. In a laboratory setting, it can therefore appear as if a catalyst "makes the reaction happen", by increasing the reaction rate to a perceivable timescale.

Generally, two types of catalysis are distinguished: homogeneous catalysis, where catalyst and reactants are in the same (often liquid) phase, and heterogeneous catalysis, where reactants in the liquid or gas phase interact with a solid catalyst. Homogeneous catalysis finds application, e.g. in organic synthesis. There, catalysts can be mere protons in acid-catalyzed reactions, or complex structures of metal ions coordinated by organic ligands. A specific type of homogeneous catalysts are enzymes. All living organisms use catalyzed molecular modifications in their metabolic processes. Enzymes are large protein clusters that perform these highly targeted modifications on biological substrates under the mild conditions present in cells.

The work presented in this thesis relates to heterogeneous catalysis, and specifically catalytic reactions of small gas-molecules on solid surfaces.
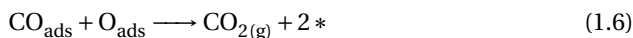
1.2. HETEROGENEOUS CATALYSIS

The role of heterogeneous catalysis in today's world cannot be overstated. Finding a catalyst for the conversion of molecular nitrogen and hydrogen to ammonia, was crucial to the development of modern fertilizer. This conversion is now known as the Haber-Bosch process.[6, 7] Two Nobel prizes in chemistry were awarded for its development. Today, 50% of the global food production relies on synthetic nitrogen fertilizers.[8] In daily life, a heterogeneous catalyst in car exhausts reduces the amount of carbon monoxide and nitric oxide in the exhaust fumes. Fuel cells vehicles, which apply electrocatalysts, are nowadays commercially available.

Heterogeneous catalysis is crucial to today's economy due to the wide range of chemicals it has made available. Industrial processes in chemical manufacturing depend 80-90% on catalysis.[9] Catalysts can improve yields but also selectivity towards the

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desired products by improving the reaction rate of certain reaction pathways more than others. Industrial catalysts often consist of metallic nanoparticles supported on oxide materials.

Schematically, reactions involving a heterogeneous catalyst can be described as reactants from the gas or liquid phase adsorbing at the surface, reacting (possibly in several steps) to form new compounds, and the products finally desorbing from the surface. The exact sequence of the reaction steps, i.e. the reaction mechanism, can vary. Different reaction mechanisms have been observed in gas-surface reactions. For example, CO oxidation on Pt can be described by the Langmuir-Hinshelwood mechanism:[10]

$$CO_{(g)} + * \rightleftharpoons CO_{ads} \tag{1.4}$$

$$O_{2(g)} + 2* \rightleftharpoons 2O_{ads} \tag{1.5}$$

$$CO_{ads} + O_{ads} \longrightarrow CO_{2(g)} + 2* \tag{1.6}$$

Here, CO adsorbs molecularly at an active surface site (*). Oxygen, on the other hand, undergoes dissociative adsorption, leading to two O atoms adsorbed at active sites. One adsorbed CO molecule can then recombine with an adsorbed O atom to form a CO_2 molecule, which desorbs from the surface. Adsorption on the surface stabilizes intermediate states during the reaction path, resulting in a lower activation energy compared to the uncatalyzed gas-phase reaction of CO and O_2.

During the Langmuir-Hinshelwood mechanism, the reacting species adsorb at separate sites, and subsequently react. The adsorption site may in some cases differ from the site of reaction. In this case, diffusion across the surface also has to be considered as part of the reaction. Other mechanisms have also been observed for surface reactions. For example, after one species pre-adsorbs, the second reactant may react directly from the gas phase (Eley-Rideal mechanism).[3] Alternatively an intial reaction with a reactive surface layer may occur, and a second species later replenishes the catalyst (Mars-van Krevelen mechanism). [11]

1.3. SURFACE SCIENCE APPROACH

The activity of heterogeneous catalysts is predominantly due to atomic layers at, or close to, the surface. The bulk material remains mostly unaffected. Understanding the reactivity of different types of surfaces in catalytic reactions is therefore of economic, as well as fundamental scientific interest. Surface chemistry, and specifically gas-surface dynamics, aim at unraveling how chemical reactions take place at surfaces, and how they are influenced by, e.g. catalyst material, surface structure, or the state of the reacting molecules. Reactants, reactions conditions, and the surface are controlled simultaneously for that reason. Theoretical and experimental studies

often go hand-in-hand in order to interpret observations and resolve details of the reaction mechanism.

Industrial heterogeneous catalysts are commonly composed of different materials and phases, with limited control over the exact surface structure. In contrast, surface science frequently makes use of single crystalline materials - a difference that is referred to as the material's gap.[12] The atomic arrangement in crystalline materials is defined by their lattice structure. Well-defined surfaces can be exposed, their structure depending on the orientation at which they are polished. Certain high symmetry planes result in atomically flat surface planes, while at a 'miscut' angle steps and kinks are introduced that separate high-symmetry terraces. Surfaces are generally described by their Miller indices (*hkl*), which indicate their orientation relative to the 3D lattice unit cell.[13] Figure 1.2 demonstrates the position of (111) and (001) planes within an *fcc* lattice.

Typically, flat single crystals exposing a defined plane are used to study surface reactions. Throughout this thesis, however, we make use of curved crystals cut from single crystalline materials. These type of samples are currently only employed by few research groups worldwide. Curved crystals provide a range of surface structures across their curvature, which is determined by the bulk lattice. We can therefore smoothly vary the composition of surface sites - terraces, steps and kinks - and determine their specific reactivity in gas-surface reactions. A thorough discussion of curved crystal surfaces is given in chapter 2.
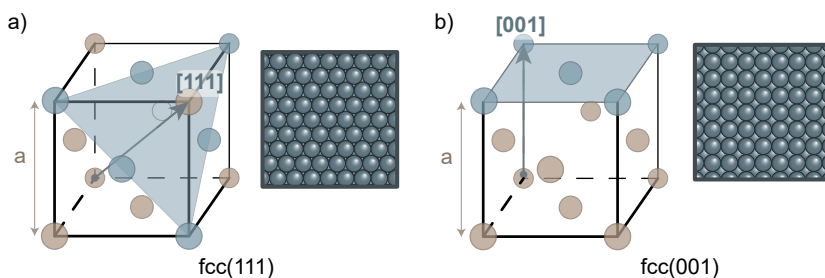

Figure 1.2: a) Unit cell of the *face-centered cubic* lattice with the atomically flat (111) plane indicated and atomic arrangement of a *fcc*-(111) surface. b) Unit cell of the *face-centered cubic* lattice with the atomically flat (001) plane indicated and atomic arrangement of a *fcc*-(001) surface.

Before experiments examining chemical reactions are carried out, single-crystalline surfaces are typically prepared by ion-bombardment (sputtering) to eliminate surface contamination and subsequent annealing at moderate temperatures to restore the surface structure. While this treatment may lead to almost perfect bulk-termination at the surface, in some cases surface reconstructions or faceting occur. Several methods are available to characterize the actual structure after surface preparation.

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In this thesis low-energy electron diffraction (LEED), Scanning tunneling microscopy (STM), and Auger electron spectroscopy (AES) are used to characterize the surface across our curved crystals. LEED is a technique commonly applied to obtain information about the average structure probed by an electron beam. It makes use of the phenomenon that well-ordered surfaces can cause diffraction by elastically scattering electrons. Regularly stepped surfaces cause additional diffraction, resulting in split spots. STM, or other scanning probe techniques, can image the surface on a smaller scale, revealing local variations in surface structure. Electron spectroscopy techniques, e.g. AES, or x-ray photoelectron spectroscopy (XPS), are sensitive to the chemical nature of atoms at or near the surface, rather than the structure.[14] They can thus be used to examine the surface composition and reveal contamination.

At ambient pressure, gas molecules from the background would rapidly adsorb on the prepared surfaces. In order to maintain a clean surface, preparation and experiments must be carried out in ultra-high vacuum (UHV), i.e. at pressures $< 10^{-9}$ mbar. In this way, surface reactions of specific reactants can be observed almost exclusively. Gas-phase reactions are mostly avoided at such low pressures, as the large mean-free path of >60 km makes inter-molecular collisions unlikely. Additionally, signal detection for electron- or mass spectrometry-based techniques is much improved in vacuum. However, gas-surface reactions in UHV do not always reflect catalytic reactions in industrial applications; different reactions mechanisms or surface reconstructions may occur at higher pressures. This contrast is referred to as the pressure gap.

While the surface structure plays an important role in understanding gas-surface reaction mechanisms, a multitude of variables in the state of the reacting molecules also have to be considered.[15] Gas molecules are never completely still, they can move by translation, vibration, and rotation, and can be electronically excited. The exact state in which a molecule approaches the surface influences the subsequent reaction steps. Normally, the distribution of states is governed by temperature and pressure of the gas. Supersonic molecular beams, create a very narrow distribution of kinetic and rotational states, which can be modified among others by (anti-)seeding into other gasses, or heating the nozzle where the supersonic expansion takes place.[16] In this thesis (chapters 4 and 5), we use molecular beams to study dissociation and recombination of hydrogen on well-defined Pt surfaces. Similarly, the state in which a molecule desorbs from a surface can be influenced, e.g. by the way that it was adsorbed on the surface, surface coverage by other adsorbates, the reaction site and reaction kinetics. In the work presented in chapter 6, we use temperature-programmed desorption to explore differences of water nucleation on different Ag surfaces.

1.4. EXPERIMENTAL TECHNIQUES IN THIS THESIS

1.4.1. LOW-ENERGY ELECTRON DIFFRACTION

Low-energy electron diffraction (LEED) uses an electron beam with relatively low energy ($20 - 200$ eV), which is impinged on a surface. In this range, the wavelength of the electrons is on a similar length scale as the interatomic spacing of many crystalline materials. Well-ordered surfaces can thus cause diffraction of low-energy electrons. Experimentally, the diffraction pattern caused by elastically scattered electrons is visualized on a (hemispherical) fluorescent screen, while inelastically scattered electrons are filtered out by a series of hemispherical grids. The diffraction pattern displayed on the screen corresponds to the reciprocal lattice of the surface structure. For high-symmetry surface planes, the diffraction pattern is easily identified. Regularly stepped surfaces produce diffraction patterns with spot splitting, caused by the superlattice of steps.[17, 18] LEED can thus be employed to determine the average surface structure of the area probed by the electron beam.

1.4.2. SCANNING TUNNELING MICROSCOPY

Scanning tunneling microscopy can be used to investigate microscopic details of the local surface structure. An atomically sharp tip is placed close a conducting surface, and a potential is applied between them. Subsequently, the tip is further approached towards the surface, until the tunneling probability for electrons becomes large enough that a tunneling current can be measured. The tip is then scanned across an area of the surface. As the tunneling current decreases exponentially with sample-to-tip distance, even small variations in surface topography can be detected. With STM, atomic resolution of the surface structure can be achieved. However, STM images only probe a small fraction of the surface. In order to confirm the overall structure, several places across the surface need to be imaged.

1.4.3. AUGER ELECTRON SPECTROSCOPY

Auger electron spectroscopy (AES) is a technique used to characterize the chemical composition at (or near) the surface of a material. It makes used of the Auger effect, which is illustrated in figure 1.3. The surface is bombarded with high-energy electrons from an electron gun. This can cause the ejection of an core electron from surface atoms, creating an electron hole. The hole is subsequently filled with an electron from a higher energy level in the atom. The associated energy gain can lead to the emission of a third electron, the Auger electron. During AES, Auger electrons emitted from surface atoms are detected and their kinetic energy analyzed. The energies of Auger transitions are specific to the element and chemical environment of the surface atoms that the electron originated from. Auger spectra therefore give insight into the

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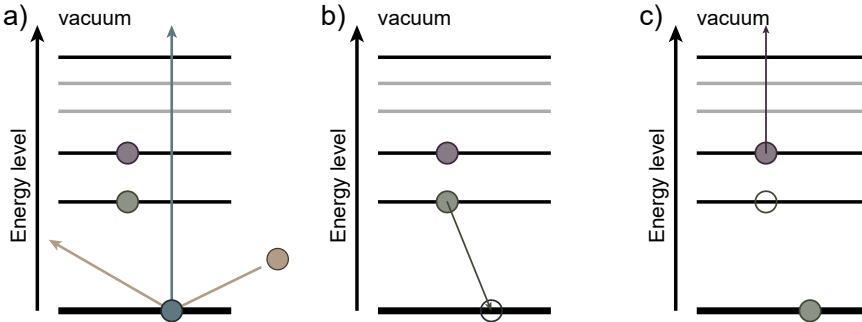chemical elements present at (or near) the surface.

Figure 1.3: Auger emission process. a) An incident electron (beige), hitting a surface atom, causes the ejection of a core electron. b) A second electron (green) is de-excited from a higher energy to fill the electron hole. c) The transition energy is transferred to a third electron (purple), which is emitted into vacuum.

1.4.4. KING-AND-WELLS METHOD

The King-and-Wells method (KW) is used to determine sticking probabilities of gas molecules on surfaces.[19] In a source chamber, a (supersonic) molecular beam is created by the expansion of a high pressure gas mixture into vacuum. This expansion causes cooling, and a narrow distribution of kinetic and rotational states of molecules in the beam. The expanding gas plume is then shaped into a beam by skimmers. In this thesis, where curved crystal surfaces are employed, the last skimmer is a rectangular orifice that limits the footprint of the beam along the curvature to improve spatial resolution.

During a KW experiment, two flags initially block the molecular beam from entering the main chamber of a UHV system and hitting the sample surface. A quadrupole mass spectrometer (QMS) is used to determine the partial pressure of the gas species under investigation. Figure 1.4 shows a typical QMS signal during a KW experiment. Initially, the background signal in the main chamber is low. When the first flag is removed, the molecular beam enters into the main chamber. The partial pressure increases abruptly and then stabilizes. At this point the beam is still prevented from hitting the sample surface by the second flag. Once this second flag is removed, the molecular beam impinges on the sample, and a portion of the molecules in the beam stick to the surface. The initial sticking probability (S_0) is defined as the ratio between the pressure drop when flag 2 is opened (p_{drop}) and the pressure rise when flag 1 was initially opened (p_{rise}):

$$S_0 = \frac{p_{drop}}{p_{rise}} \tag{1.7}$$

S_0 can be used to describe the chemical reactivity of the surface towards adsorption of molecules. Different parameters, e.g. incident angle, kinetic energy (and energy distribution) of the beam, surface structure, and surface temperature. Varying these parameters and recording S_0 can therefore give insight into the underlying mechanism during adsorption.
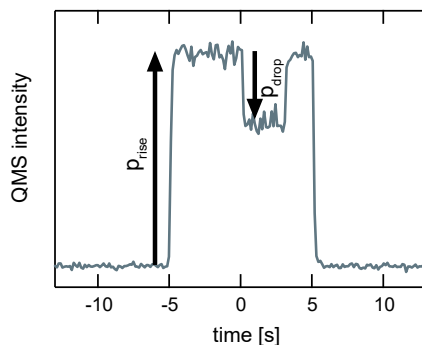

Figure 1.4: QMS trace of a gas species during a King-and-Wells experiment. Initially, the residual partial pressure is low. It increases rapidly, when the first flag is opened and the molecular beam enters the main chamber (p_{rise}). Once the second flag is removed and the beam hits the sample surface, the partial pressure decreases (p_{drop}). In this example, the subsequent closing of the two flags is also shown, the partial pressure then returns to the initial background.

1.4.5. Temperature-programmed desorption

For temperature-programmed desorption (TPD), a gas is first adsorbed on the surface, which is kept at a stable temperature. Subsequently, the sample is heated with a defined (programmed) temperature ramp. At the same time, the desorption of molecules from the surface is monitored with a QMS. TPD spectra contain information about desorption energy, rate, kinetics, as well as the surface coverage, making temperature-programmed desorption a useful technique in surface science. In order to correctly interpret results, thorough analysis is required. Different analysis methods are available to extract kinetic information.

A variation of TPD is temperature-programmed reaction (TPR), where reactant molecules are adsorbed at a temperature below the onset of reaction. During the temperature ramp, reaction eventually sets in and the desorbing product can be detected.

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1.5. SCOPE OF THIS THESIS

In this thesis, we study reaction steps of small molecules on catalytic surfaces and unravel their structure dependencies by employing well-defined surfaces of curved crystals.

Chapter 2 lays out the design of curved crystals, which are used throughout this thesis. The macroscopic curvature of these types of single crystals grants microscopic control over the available surface sites. They can be oriented to precisely expose a desired range of tuneable surface structures. However, spatial resolution has to be considered when adapting standard surface science techniques to curved crystals. We discuss recent advances and applications of curved crystals in surface physics and chemistry, and particularly in research aimed at bridging the material's gap in heterogeneous catalysis.

Chapter 3 details the surface structure characterization of a curved Pt crystal, with fully-kinked steps that produce chiral surfaces. By low-energy electron diffraction, scanning-tunneling microscopy, and Auger electron spectroscopy, overall structures are confirmed, chiralities determined, and microscopic insight into the behavior of step arrays and atomic structure of step edges is obtained. This allows us to link chemical reactivities to specific surface sites in the following chapters.

In **chapter 4**, we use two different Pt crystals curved around the (111) plane to study hydrogen dissociation on vicinal surfaces featuring three types of steps. We use insights into the atomic composition of the kinked step edges to extract site-specific reactivities and define reactive cross-sections for all three types.

Chapter 5 revisits the surface structure of the curved crystal in chapter 3, focusing on areas near the apex without well-ordered arrays. We determine the range on the crystal where vacancy islands and freely meandering steps cause defect densities to deviate from those predetermined by the miscut angle. Extrapolating D_2 sticking probabilities to zero step density allows us to extract the dissociation probability on a perfect (111) surface. In addition to hydrogen dissociation, we measure H-D exchange on the crystal and discuss the relation between them.

In **chapter 6**, two curved Ag crystals are combined for H_2O desorption experiments from stepped surfaces. We explore differences in water nucleation on surfaces with three step- and two terrace types by quantifying changes in the desorption temperature of sub-monolayer coverages of H_2O. Linear relationships of desorption energy with step density are identified. The potential of combining curved crystals with different orientations is emphasized.

Chapter 7 discusses prospective applications of curved crystals in surface chemistry. We present preliminary results of studying CO_2 adsorption on Pt and characterize the

surface of a novel curved crystal of a bimetallic alloy.

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