

# Adsorption and Reaction Studies on Stepped Pt Surfaces Using In-Situ High Resolution XPS in Combination with a Supersonic Molecular Beam

Untersuchung zur Adsorption und Reaktion auf gestuften Platinoberflächen mittels hochauflösender in-situ XPS in Verbindung mit einem Überschall-Molekularstrahl

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#### Abstract

In this thesis, in-situ high-resolution X-ray photoelectron spectroscopy (XPS) is employed to study the adsorption and thermal evolution of various gases on single crystalline platinum surfaces, in particular, two regularly stepped surfaces, with the same terrace width but different step orientation, namely Pt(355) and Pt(322), were studied to elucidate the influence of defects on the surface properties.

The interplay between Ag decorated steps on Pt(355) and CO adsorption was studied by XPS and also by density functional theory (DFT); the calculations were performed by a collaborant. Decoration of the lower Pt step edges with Ag results in a blocking of the former Pt step sites for low CO coverages, attributed to a change in the electronic structure. Consequently, the C 1s binding energy of CO at the former Pt step sites is very similar to that for CO at terrace on-top Pt sites in the presence of Ag. Higher CO coverages induce the formation of embedded Ag clusters within the upper terraces.

The influence of sulfur, an effective poison for metal catalysts, on Pt(322) and Pt(355) was investigated: S preferentially adsorbs at the steps, passivating them for CO adsorption at low temperatures. Upon heating, step sites are populated by irreversible CO/S site exchange. At low S precoverages, the characteristic transition temperatures are 165 K for Pt(355) and 245 K for Pt(322). This significant difference indicates a higher activation barrier for the CO/S site exchange process on Pt(322), attributed to a high activation barrier and thus to a kinetic hindrance of the site exchange process at low temperatures.

In the study of the kinetics of the oxidation and removal of sulfur on stepped Pt(355) and flat Pt(111), SO<sub>3</sub> and SO<sub>4</sub> were identified as reaction intermediates. On Pt(355), the activation energy for the rate limiting step, the oxidation of S to SO, is less than half of that on flat Pt(111). This demonstrates the dominating role of steps and defects for the catalytic oxidation of sulfur. On the stepped surface, S is pushed away from the steps by oxygen strongly suggesting O at steps to be the catalytically active species.

Finally the adsorption and reaction of  $SO_2$  on clean and oxygen precovered platinum surfaces was studied. For the stepped surfaces, in addition to the known  $SO_2$  species for Pt(111), several step or oxygen induced  $SO_2$  species are observed. On all investigated surfaces, a hit and stick mechanism is observed for  $SO_2$  adsorption. On the oxygen free stepped surfaces, a higher reactivity towards  $SO_2$  dissociation/disproportionation is found compared to Pt(111). On the oxygen precovered Pt surfaces, some  $SO_3$  is formed directly upon adsorption of  $SO_2$  at low temperature. Heating the mixed  $O/SO_x$  layers results in oxidation of more  $SO_2$  to  $SO_3$  and the subsequent oxidation of  $SO_3$  to  $SO_4$ , which finally decomposes above 450 K.

#### Kurzzusammenfassung

In dieser Arbeit wurde mittels hochauflösender in-situ Röntgen-Photoelektronenspektroskopie (XPS) die Adsorption und das thermische Verhalten von verschiedenen Gasen auf Platin Einkristalloberflächen untersucht. Zwei regelmäßig gestufte Kristalle, Pt(355) und Pt(322), mit gleich breiten (111)-Terrassen aber verschiedener Stufenorientierung, sowie ungestuftes Pt(111) wurden als Substrate verwendet um den Einfluss von Defekten zu verstehen.

Die Wechselwirkung zwischen Ag-dekorierten Pt(355) Stufen und adsorbiertem CO wurde mit XPS untersucht und im Rahmen einer Kooperation mit Dichtefunktionaltheorie simuliert. Bei kleinen CO Bedeckungen zeigen die C 1s Spektren keinen Beitrag von an den ehemaligen Pt Stufen adsorbiertem CO mehr, sie scheinen blockiert zu sein. Durch die Änderung der elektronischen Struktur der ehemaligen Stufe weist dort adsorbiertes CO eine identische C 1s Bindungsenergie auf, wie linear auf den Terrassenplätzen gebundenes CO. Bei höherem CO Angebot wird die Adsorption von CO auf den Terrassen und die Bildung von Ag Inseln induziert.

Um die Auswirkungen des Katalysatorgiftes Schwefel zu analysieren, wurde dessen Einfluss auf die CO Adsorption auf den gestuften Oberflächen untersucht. S adsorbiert bevorzugt an den Stufenkanten und passiviert diese für die CO Adsorption bei niedrigen Temperaturen. Beim Heizen wird S durch CO von den Stufenplätzen auf die Terrassen verdrängt. Dies geschieht für kleine S Mengen auf Pt(355) bei 165 K und auf Pt(322) bei 245 K, was auf eine höhere Aktivierungsbarriere und damit auf eine größere kinetische Hemmung der Umlagerung auf Pt(322) hindeutet.

Weiterhin wurde die Oxidationskinetik von S auf Pt(355) und Pt(111) untersucht; dabei wurden lediglich SO<sub>3</sub> und SO<sub>4</sub> als Intermediate beobachtet, was auf die Oxidation von S zu SO als geschwindigkeitsbestimmenden Schritt schließen lässt. Auf Pt(355) verdrängt Sauerstoff S von den Stufen und ermöglicht dort als reaktive Spezies einen Oxidationsweg mit deutlich reduzierter Aktivierungsenergie.

Abschließend wurde das Verhalten von SO<sub>2</sub> auf sauberen und sauerstoffvorbelegten Pt-Oberflächen betrachtet. Auf den gestuften Oberflächen wurden, zusätzlich zu den von Pt(111) bekannten, mehrere neue durch die Stufen und/oder Sauerstoff induzierte SO<sub>2</sub> Spezies gefunden. Auf allen untersuchten Oberflächen adsorbiert SO<sub>2</sub> nach einem "hit and stick" Mechanismus. Die sauberen gestuften Oberflächen zeigen eine höhere Reaktivität als Pt(111). Auf allen drei mit Sauerstoff vorbelegten Oberflächen bildet sich selbst bei niedrigen Temperaturen während der SO<sub>2</sub> Adsorption etwas SO<sub>3</sub>. Beim Heizen dieser gemischten Schichten entsteht zunächst weiteres SO<sub>3</sub>, welches zu SO<sub>4</sub> weiteroxidiert wird und oberhalb von 450 K zerfällt.

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#### **1. Introduction**

Catalysis and catalytic processes are not only ubiquitous, but also of great economical and ecological importance: nine out of ten products from the chemical industry are produced using catalytic processes.<sup>[1]</sup> This does not only hold true for bulk and fine chemicals, but also for transportation fuels. Catalysts are also widely used to clean automotive and industrial exhausts.

A catalyst opens a new reaction pathway that exhibits a lower activation energy compared to the case without the catalyst. Three essential steps occur in such a catalytic reaction: the reactants bind to the catalyst, react there and then the product separates from the catalyst. The catalyst itself is not consumed during this reaction, but its presence enables to perform chemical reactions under more favorable conditions: typically lower pressures and/or temperatures are necessary to obtain the desired product compared to the noncatalyzed reaction. Two different kinds of catalytic processes are applied: homogeneous catalysis, in which the catalyst is in the same phase as the reactants, and heterogeneous catalysis, where the catalyst is in a different phase than the reactants. In heterogeneous catalysis the catalyst is usually in the solid phase, whereas the reactants and products are in the liquid or gaseous phase. The big advantage of heterogeneously catalyzed reactions is the easy separation of the catalyst from the products, while in homogeneous catalysis leaching of the catalyst is always an issue. In the following, we will focus on fundamental aspects of heterogeneous catalysis, which plays a major role in the production of the most important bulk chemicals as well as gasoline.<sup>[2]</sup> As catalysts decrease the activation energy of a specific pathway, they may also enhance the selectivity towards a desired product. Increasing the selectivity renders the reaction not only more efficient due to the higher yield, but also reduces the production of unwanted side products, i.e. less waste is produced.<sup>[1]</sup>

The most commonly known example for the application of heterogeneously catalyzed reactions is the automotive exhaust converter. In the three way catalyst (TWC), the three main pollutants CO, NO and hydrocarbons are removed from the exhaust: The toxic CO and unburnt hydrocarbons are oxidized to non-toxic CO<sub>2</sub> and H<sub>2</sub>O, while NO is reduced to harmless N<sub>2</sub>.<sup>[1-6]</sup> For the CO oxidation, Pt or Pd are effective catalysts, while Rh is used for the reduction of NO. The three way catalyst consists of a ceramic monolith, covered with a washcoat of Al<sub>2</sub>O<sub>3</sub> and other oxides and only a few percent of the aforementioned noble metals, which are present in the form of small clusters. For a better performance, numerous additives have been used, like cerium oxides, which stabilizes the structure of the Al<sub>2</sub>O<sub>3</sub> and serves as an oxygen storage.<sup>[7]</sup> In order to perform all three relevant reactions simultaneously, the air to fuel ratio has to be very close to the optimal stoichiometric value. Under fuel rich conditions, when less air and thus oxygen is available, the reduction of NO is still working, but the oxidation of CO and C<sub>x</sub>H<sub>y</sub> is not

efficient. Under lean conditions, CO and  $C_xH_y$  are oxidized completely but the reduction of NO fails. The development of feedback control systems for the air-fuel ratio in the 1980s and the implementation of cerium oxides as an oxygen storage material into the catalyst solved this problem. Nowadays, new tasks require further development of this technology. Since the resources of fossil fuels are finite and their combustion leads to the emission of greenhouse gases and thus contribute to global warming, fuel efficient cars become more and more important. Lean burn engines, operating at air to fuel ratios of 25:1 and above, effectively improve the fuel efficiency.<sup>[7]</sup> They produce oxygen rich exhaust gases and thus require new ways for NO removal. One approach to solve the problem of NO<sub>x</sub> reduction is the so called nitrogen-storage reduction (NSR) catalyst.<sup>[8]</sup> Here, NO is oxidized to NO<sub>2</sub> on Pt particles under lean conditions. Neighboring storage materials, typically alkaline and alkaline earth metal oxides, e.g. BaO, react with NO<sub>2</sub> and store it in form of nitrates. During short periods of fuel rich conditions, H<sub>2</sub>, C<sub>x</sub>H<sub>y</sub> and CO react with the NO<sub>3</sub><sup>-</sup> and reduce it to N<sub>2</sub> on the Pt particles.

A mayor concern in catalysis is poisoning of the active sites.<sup>[1,2,4,9,10]</sup> Tetraethyl lead was added to automotive fuels as an octane enhancer and because of its beneficial tribological properties. As lead poisons the three way catalyst severely, lead-free fuels were developed.<sup>[2]</sup> Only the availability of these lead-free fuels made the breakthrough of the three way catalyst possible. Poisoning with sulfur was also an important issue, which led to the use of Pt instead of Pd, because of its higher tolerance towards S poisoning. Pd incorporates the S into the bulk, which makes its removal difficult.<sup>[1]</sup> Sulfur poisoning is even more problematic for NSR catalysts, because they are even more sensitive towards deactivation by sulfur.<sup>[7,8]</sup> S containing molecules in fuel are oxidized to SO<sub>2</sub>, which reaches the catalyst with the exhaust, during the combustion. There, it is oxidized to  $SO_3$ on Pt particles, which in turn forms BaSO<sub>4</sub> when it comes into contact with the storage materials. As sulfates are more stable than nitrates, it is not easy to remove the sulfates during fuel rich periods. This way, the catalyst gradually looses its NO<sub>x</sub> storage capacity with time. Under rich conditions, S accumulates on the metal particles, as there is not enough H<sub>2</sub> present in the exhaust for its reduction to H<sub>2</sub>S. This in turn deactivates the metal particles for the oxidation of CO and C<sub>x</sub>H<sub>y</sub>. All the above described effects make the NSR catalysts only available in regions, where fuel with a low sulfur concentration is available, e.g., Japan. The TWC and the NSR catalyst demonstrate that reactions on but also the heterogeneous catalysts themselves are very complex systems. A better understanding of the underlying principles of their behavior could lead to the development of catalysts with an improved performance. Due to their complex nature, it is very difficult to gain this insight from the study of the real systems.

One concept to study the underlying principles of heterogeneously catalyzed reactions is the so called "surface science approach": fundamental steps of these reactions, like adsorption, dissociation, diffusion, reaction of desorption of the reacting gases, are investigated using spectroscopy or microscopy on flat, low index plane surfaces of metals or oxides. Many of these techniques are using electrons as a probe and thus require ultra high vacuum conditions, which is in clear contrast to the reaction conditions under which the real catalysts work. This is the so called "pressure gap". In some cases, however, it is possible to predict the reaction rates of real catalysts by applying models based on the elementary steps investigated under high vacuum conditions (e.g. NH<sub>3</sub> synthesis<sup>[11]</sup>). There are also examples, in which investigations starting on single crystal surfaces with a combination of different surface science methods led to the development of an improved catalyst for industrial applications, like the steam reforming process<sup>[12]</sup> or hydrodesulfurization.<sup>[13]</sup> In order to bridge the pressure gap, new instruments, for example allowing to collect photoelectron spectra under pressures of up to 1 mbar, have been designed (<sup>[14]</sup> and references therein, <sup>[15,16]</sup>). Another possibility to allow to increase the pressure on the surface is a molecular beam setup, like in this work (see Chapter 2.4), that allows to study reactions at (local) pressures of up to 10<sup>-5</sup> mbar.

The aim of the surface science approach is to simplify the studied system to an extent, that different elementary steps can be investigated separately. This obviously calls for the investigation of the adsorption process of a reactant of interest, which constitutes the first step in a catalytic process (see above). Low index plane surfaces are used for such studies. One challenge is that the model systems do not exhibit the same complexity than the particles often used in the catalysts, which is commonly referred to as the "material gap". Small particles do not exhibit only one facet like flat surfaces, but a variety of them. Also, a high number of different defects like steps and kinks, which may play a decisive role, are present in such small particles rather than on flat single crystal surfaces used in the surface science approach. The (metal) atoms at these sites have a smaller number of neighboring atoms than the ones in flat areas. This different geometry is also reflected in a different electronic structure, which leads to a modified reactivity of defect sites;<sup>[2,17]</sup>

One approach to evaluate the differences in reactivity between flat areas and defect sites is to study regularly stepped or even kinked surfaces. On these surfaces, the exact number and orientation of defects is known. Via comparison with flat surfaces, the role of the steps is then elucidated. In this work, two stepped surfaces with the same defect density but with a different step orientation are used: Pt(355) and Pt(322) (description of the surfaces see Chapter 2.3). Platinum was chosen as substrate material, because it is widely used, not only in the TWC but also as a catalyst in many industrial processes, e.g., for hydrations or the oxidation of Ammonia to nitrous oxide, the first step in the production of nitric acid (Ostwald process).<sup>[10]</sup>

Real catalysts often contain more than one single metal. The investigation of bimetallic surfaces, as the most simple example of such multi-component systems, is most suitable for a surface science approach to study the fundamental properties of these systems. Ultrathin layers of one metal deposited onto a second one are two-dimensional systems,

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often exhibiting significantly different properties from either one of their pure components.<sup>[18,19]</sup> The bimetallic bonding can induce changes in the band structure of metals, which may lead to new chemical properties.<sup>[18,19]</sup> If the dimensionality is reduced further, regularly stepped surfaces can be used as a template for preparing nanowires, i.e., one dimensional structures. The prerequisite for their formation are the "right" kinetics and energetics to allow self assembly processes: the adsorbate atoms have to show a preference for high coordination sites, yet they should not form a surface alloy. Depending on the hybridization between the two metals, the diffusion barrier towards the steps and the tendency to form a surface alloy may differ significantly. One example is the late transition metal Nickel, which forms monoatomic wires on a stepped Rhodium surface, whereas the early transition metal Vanadium does not.<sup>[20]</sup> The strong hybridization of V and Rh leads to a very high diffusion barrier. The temperatures to overcome this barrier are high enough to induce surface allyoing rather than diffusion to the steps. In contrast, the weaker hybridization between Ni and Rh facilitates the diffusion to the steps, where the atoms assemble to monoatomic wires. In general, the right deposition temperature has to be found for each metal combination to allow diffusion to the steps, but at the same time prevent alloy formation.<sup>[19-24]</sup> The deposition rate is also an important parameter influencing the growth mode.<sup>[19]</sup>

The chemical properties of the adsorbed metals themselves can be interesting in itself. For example, in Ni nanowires on stepped Rh surfaces the center of the d-band is shifted towards the Fermi level. This leads to an enhanced reactivity of the Ni, which can be selectively oxidized.<sup>[24]</sup> The added metal can also be applied to passivate the step sites, which can be used to determine their special reactivity. This effect has been investigated for the dissociation of N<sub>2</sub> on a Ru(0001) surface with ~ 1% of steps, onto which a small amount of Au has been evaporated.<sup>[25]</sup> The adsorption rate at the steps was found to be at least 9 orders of magnitude higher than on the terraces at 500 K. This approach also allows to tune the reactivity of a surface. Along this line, the influence of small amounts of Ag on the CO adsorption on stepped Pt surfaces has been investigated in this thesis (see Chapter 3).

Another aspect of the bimetallic self-assembled systems that allows a precise control of the atomic coordination in 1D systems is the possibility to understand and tailor magnetic anisotropy energy barriers in nanosized systems. Because of the uniformity and elevated density of the monoatomic chain arrays prepared on vicinal surfaces as templates, integral spectroscopic methods can be used to address the electronic and magnetic structure in 1D systems. The understanding of these properties is desirable for improvements in the field of nanoelectronics. For example the magnetic properties of Co nanowires on Pt(997) have been examined.<sup>[26]</sup>

In a real catalytic system not only the substrate complexity is high, but also different gaseous reactants are present at the same time. After studying the adsorption of one gas

on a metal surface, an interesting step is to proceed with the investigation of the coadsorption and/or reaction of at least two gases. Especially the coadsorption of molecules, which act as poisons, holds great interest. The CO adsorption on regular surfaces has been studied by high-resolution photoelectron spectroscopy in our group <sup>[27,28]</sup>. This technique allows to get site selective in-situ information of the adsorbates like for example CO, <sup>[27,28]</sup> CH<sub>3</sub>, <sup>[29]</sup> and benzene<sup>[30]</sup> during the adsorption of molecules and also during heating of adsorbate layers.

In this thesis, this work is extended by investigating the influence of preadsorbed S on the CO adsorption on stepped surfaces, which is discussed in Chapter 4.1. The oxidation of S on Pt(111) and Pt(355) is the topic of Chapter 4.2. And finally the adsorption of  $SO_2$  first on flat and then on stepped surfaces is shown. Here also the coadsorption with oxygen and the reaction upon heating is of special interest (see Chapter 5).

#### 2. Fundamentals and techniques

# 2.1 X-ray Photoelectron Spectroscopy (XPS)<sup>[31-34]</sup>

#### Fundamentals

The fundamental principle of photoelectron spectroscopy is the photoelectric effect (also denoted as photoeffect): The sample is irradiated with photons of known energy hu, which leads to the emission of photoelectrons. The kinetic energy  $E_{kin}$  of the emitted electron can be determined by an electron energy analyzer.

From  $E_{kin}$  the binding energy  $E_B$  can be calculated by considering the work function of the analyzer  $\Phi$ :

$$E_B = h\upsilon - E_{kin} - \Phi$$

Corresponding to the electron configuration within the atoms, each element produces a set of signals at characteristic binding energies in the XP spectrum, allowing to analyze the chemical composition of the sample. As the intensity of these specific signals is proportional to the number of atoms probed, the XPS signal is a quantitative measure of the atoms probed in the sample. This led to the term "electron spectroscopy for chemical analysis" (ESCA), which was coined by K. Siegbahn. In addition to the chemical composition, XPS also allows to determine the chemical state of a sample. Although the core electrons of a molecule, which are probed by XPS, are not directly involved in a bond, they are nevertheless influenced by their chemical surrounding. As a consequence, the binding energy depends on the chemical state, which is also referred to as chemical shift. The "chemical surrounding" does not only refer to the oxidation state of atoms but in some cases also their coordination. Thus, in certain cases also the adsorption site of atoms or molecules can be probed (for an example, see below).

In the photoelectric effect electrons are emitted, which are used to probe the sample. The large cross section of electrons with matter leads to a low inelastic mean free path and consequently to an escape depth of only a few atomic layers, depending on the kinetic energy of the electron. Hence, they contain information that is mostly coming from the surface of the sample. These facts make XPS a valuable tool for investigating surfaces and molecules adsorbed on it.

#### Use of synchrotron radiation

With conventional X-ray sources commonly used in laboratories (Mg  $K_{\alpha}$  with h $\upsilon$  = 1253.6 eV or Al  $K_{\alpha}$  with h $\upsilon$  = 1486.3 eV), it takes minutes to even hours to record one XP spectrum, depending on the amount of the element under investigation present on the

sample. When studying reactions on surfaces in situ, however a much lower acquisition time is needed to be able to collect spectra that reflect the surface composition during the reaction. The shorter measurement time can be achieved with a high photon flux, which can be obtained by using radiation from a third generation synchrotron radiation source. All XPS experiments shown in this thesis were carried out at the synchrotron source BESSY II in Berlin, Germany. Synchrotron radiation is emitted from highly relativistic electrons (1.7 GeV at BESSY II) which are accelerated in a magnetic field and therefore emit radiation. At Beamline U94/2 PGM1, where the experiments for this thesis were performed, an undulator is used as the insertion device to deflect the electrons of the storage ring. It consists of an array of magnets with alternating polarity. This arrangement leads to a high intensity and brilliance of the produced photon beam. Between the insertion device and the end station a monochromator and apertures are mounted to achieve a high monochromaticity of the X-rays used.

Synchrotron radiation facilities provide a broad spectrum of intense light, ranging from IR to hard X-rays. The tuneability of the photon energy is another major advantage of synchrotron light. In our experiments, we used photon energies, at which the cross section for the photoemission is large and the substrate signals are attenuated. This further enhances the signal intensity from the molecules taking part in the surface reactions. A direct comparison shows a 30 times higher cross section for the carbon 1s core level at 380 eV photon energy compared to an energy of 1486.6 eV of an Al K<sub> $\alpha$ </sub> source.<sup>[35]</sup>

Other advantages of the synchrotron radiation, which were not used in this thesis, are, e.g., the high brilliance that can be used for microscopy, and well defined polarization, e.g. circularly polarized X-rays, that can be used for magnetic dichroism experiments.

One effect that can hamper the quantification of the XPS signal intensity is photoelectron diffraction, which is especially pronounced at low kinetic energies (i.e. when the electrons have a wavelength in the order of interatomic distances) This imposes a certain error on the absolute coverage values for the different species, because of their strongly differing local surrounding.<sup>[36]</sup>

#### In-situ measurements

Using synchrotron radiation allows to perform high resolution XPS experiments in a time dependent way. For example, it takes 6 s to record a typical 5 eV wide C 1s spectrum at a photon energy of 380 eV with a resolution of ~200 meV. For a typical 10 eV wide S 2p spectrum recorded at 260 eV with a resolution of ~140 meV, the data acquisition time is 10 s. We are thus able to obtain XP spectra in-situ, while dosing gases or while heating the sample. The latter method is called temperature programmed (TP)-XPS. Figure 2.1 shows an example of such an experiment. Selected S 2p spectra recorded during the

heating of a mixed layer of  $SO_2$  and O on Pt(111) are shown in panel a). In panel b), all spectra recorded during heating are displayed in a color coded density plot. This plot is obtained by "looking from the top" onto the spectra of Figure 2.1 a). The binding energy is plotted versus the temperature and the intensity is color coded with red referring to low and blue/purple to high intensity.

Several sulfur containing species are present on the surface. Due to the spin-orbit splitting, each species gives rise to a doublet in the S 2p region.<sup>[32]</sup> The S  $2p_{3/2}$  and S  $2p_{1/2}$  signals are always separated by 1.22 eV and their intensity ratio is 2:1. This can be easily seen in the spectra recorded at temperatures above 300 K (e.g. blue spectrum at 367 K,) where only two well separated doublets are present: The one at 162.2 (163.4) eV is assigned to elemental S, the one at 166.8 (168.0) eV to SO<sub>4</sub> (see [P5]). In Figure 2.1 a),



Figure 2.1: S 2p spectra of the TP-XPS experiment of SO<sub>2</sub> on the oxygen precovered Pt(111) surface: a) Selected spectra shown as waterfall plot and b) color coded density plot of all spectra. Photon energy: 260 eV; detection at normal emission. The long vertical lines indicate the energetic positions of the S 2p<sub>3/2</sub> peaks of the various species, the short ticks those of the S 2p<sub>1/2</sub> peaks. [P5]

the positions of the S  $2p_{3/2}$  peaks are marked with long vertical lines, the short ticks indicate the position of the S  $2p_{1/2}$  peaks. For lower temperatures, doublets due to the presence of SO, SO<sub>2</sub> and SO<sub>3</sub> are visible in the spectra. For SO<sub>2</sub> even species adsorbed in different geometries on the surface are distinguishable. The doublet at 164.5 (165.7) eV is assigned to a species bound to the surface in an upright standing configuration with the sulfur atom and one of the oxygen atoms bound to the surface. The doublet at 165.4 (166.6) eV is assigned to a SO<sub>2</sub> species adsorbed in a lying geometry, in which all three atoms bind to the surface. In addition a third SO<sub>2</sub> species in an oxygen modified geometry is found (doublet at 165.2 (166.4) eV). Due to the high photon flux, even species with a very low coverage give rise to a clearly detectable signal. The coverage of SO (at 163.5 (164.7) eV) is less than 2% of one monolayer.

In-situ HR-XPS is a valuable tool for studying processes on surfaces as it allows us to identify different surface species and to monitor their behavior in a time dependent way, during their adsorption, reaction and also during heating. In this thesis HR-XPS is applied to study the adsorption of CO on Ag (Chapter 3) and S (Chapter 4.1) precovered stepped Pt surfaces, of  $SO_2$  on flat an stepped Pt surfaces (Chapter 5) and to study the reaction of S and O on Pt(111) and Pt(355) (Chapter 4.2).

# 2.2 Low Energy Electron Diffraction (LEED)<sup>[2,33,37]</sup>

A widely used method in surface science is the diffraction of low energy electrons, typically between 20 and 500 eV, which have a wavelength on the order of Ångstroms (i.e. 1 Å at 150 eV). Due to their wavelike nature and the fact that their wavelength matches interatomic distances, they are scattered elastically at the periodically ordered atoms of crystalline samples. On a fluorescent screen the resulting reciprocal space image, consisting of spots, can be seen. Each of these spots on the fluorescence screen corresponds to a direction, in which constructive interference (diffraction) takes place. In this way, the unit cell of the sample can be determined. As the inelastic mean free path of low energy electrons in matter is low, LEED is a surface sensitive technique. As a consequence, also periodic adsorbate structures atop the surface of a crystal can also be investigated (see e.g. p(2x2) overlayer of 0.25 ML S in Chapter 4.1).

Another application of LEED is the determination of the terrace width of regularly stepped surfaces. The additional periodicity of the surface induced by the steps leads to additional spots in the LEED pattern. Figure 2.2 a) and b) show LEED patterns of the clean Pt(355) and Pt(322) surfaces, respectively. As the pattern is an image of the reciprocal space, the separation between the new spots and the integer LEED spots is large when the interatomic distances are small, and vice versa. Hence, a<sup>\*</sup> corresponds to the small distance a between two atoms along the steps (see Fig. 2,3) and b<sup>\*</sup> to the larger distance between two steps b.



Figure 2.2: LEED patterns of clean a) Pt(355) and b) Pt(322)

From the ratio of the reciprocal vectors  $a^*$  and  $b^*$  and the angle  $\eta$  (90° minus the cutting angle of the crystal), the terrace width z in atomic rows can be calculated:<sup>[37,38]</sup>

$$z = \frac{a^*}{b^*} \cdot \frac{2}{\sqrt{3}} \cdot \sin \eta$$

In this way, the terrace width of the clean Pt(355) surface was derived as 4.26 rows, which is in good agreement with the nominal 4.33 rows. For clean Pt(322), an average value of 5.29 rows is found, which is only in rough agreement with the nominal value of 4.66 rows. As the value of 5.29 is between the nominal values of 4.66 and 5.66 for five and six atom rows wide terraces, most likely this surface consists of five and six atom rows wide terraces. As the terrace width depends on the cutting angle which can not be adjusted with ultimate accuracy, some deviation from the nominal value is expected. Reconstruction of the surfaces, due to the adsorption of adsorbates can change this periodicity, as will be shown in Chapter 4.1.

#### 2.3 The stepped surfaces

In this work, two regularly stepped Pt surfaces, namely Pt(355) and Pt(322), were used as substrates. To obtain such vicinal surfaces, a single crystal is cut under a certain angle from one of its low index planes. Both stepped surfaces used here are cut under an angle of 12.28° from the (111) plane, but in different directions. This results in five atom rows wide (111) oriented terraces and monatomic steps for both surfaces. The main difference between the two is the step orientation. This can easily be derived from the notation for stepped surfaces which was introduced by Van Hove and Somorjai:<sup>[39]</sup> Pt(355) = Pt(S)-[5(111)x1(111)] and Pt(322) = Pt(S)-[5(111)x1(100)]. Figure 2.3 shows schematic drawings of the two surfaces. In the blow ups, the different step orientations are

highlighted. These also lead to differently coordinated step adsorption sites: On the (111) steps of Pt(355), three fold hollow sites are present, whereas on the (100) steps of Pt(322) four fold hollow sites exist.

The unit cells of the two surfaces are also indicated by the base vectors a and b. From geometrical considerations, the nominal terrace width can be calculated from the cutting angle and the lattice constant of Pt. This yields a value of 4.33 atomic rows for Pt(355) and a slightly higher value of 4.66 for Pt(322). Figure 2.3 demonstrates this very clearly, as the fifth terrace row is overlapped by the first one of the next terrace by 2/3 on Pt(355) and only by 1/3 on Pt(322). Despite this difference in nominal terrace width, this presents the closest possible match in terrace width for two different step orientations. For more details see Ref [38].



Figure 2.3: Schematic drawings of left Pt(355) and right Pt(322), the unit cell with the base vectors a and b is also shown.

#### 2.4 The "synchrotron machine"

All XPS measurements in this thesis were performed at BESSY II (see Fig. 2.4) using a transportable UHV system, which is shown in Fig. 2.5. The "synchrotron machine", which was designed in our group, will be described briefly in the following section. Details can be found in Ref. [40] and [41].

Figure 2.5 shows a picture of the setup without any roughing pumps and cables attached to it. It consists of three main parts: the preparation chamber (on the right side), the analysis chamber (center) and the supersonic molecular beam setup (low left).

The preparation chamber is equipped with LEED optics, a background gas dosing facility, ports for evaporators, a quartz crystal micro balance (QCM) to calibrate the thickness of evaporated metal layers of, e.g., silver, and a sputter gun as cleaning facility for samples. The analysis chamber is equipped with an electron energy analyzer (Omicron EA 125 U7 HR), a quadrupole massspectrometer (Balzers QMA 200) for residual gas analysis and



Figure 2.4: Aerial view on the synchrotron radiation facility BESSY II in Berlin.

temperature programmed desorption (TPD) measurements, and a capillary array doser providing additional means of dosing gases. An independently pumped gas dosing system is connected to the analysis and preparation chamber. Using this dosing system and the supersonic molecular beam, two different gases can be dosed either subsequently or simultaneously without any cross contaminations. Sample temperatures of ~100 K can be achieved by cooling the sample with liquid nitrogen. A filament at the back of the sample is used for heating the sample during TPXPS experiments to temperatures of up to 600 K, without disturbing magnetic fields. For reaching even higher temperatures of up to 1500 K, e. g. during cleaning, direct resistive heating of the sample is employed. In contrast to the indirect heating with the filament, XPS measurements are not possible during the direct heating procedure, due to disturbances from magnetic stray fields resulting from the heating currents.

The molecular beam (MB) setup consists of three differentially pumped stages. In the first pumping stage, the nozzle is located. The first collimation of the MB is achieved with a skimmer, removing molecules only out of the zone of silence, allowing for supersonic conditions.<sup>[42]</sup> In the 2<sup>nd</sup> pumping stage, the molecular beam is further spatially confined by different apertures. A pneumatic valve is installed for fast switching of the molecular beam. Between the 2<sup>nd</sup> and 3<sup>rd</sup> pumping stage the molecular beam can be spatially confined by different apertures, so that the diameter of the beam fits to the diameter of the sample.

The width of the energy distribution of the molecules in a supersonic beam is much smaller than the Maxwell-Boltzmann distribution of an effusive source.<sup>[42]</sup> Especially for activated adsorption processes, e.g., the adsorption of methane,<sup>[29,43]</sup> it is interesting to change the kinetic energy of the molecules. This can be achieved by either heating the nozzle of the beam, by mixing another, lighter gas ("seeding") or by combining



Figure 2.5: Picture of the synchrotron machine without roughing pumps and cables. The main parts are labeled.

these two methods. Besides the defined kinetic energy, the supersonic molecular beam is spatially confined. This allows high local pressures at the sample (up to  $10^{-5}$  mbar), while the background pressure in the chamber is some orders of magnitude lower. In this thesis, a high oxygen pressure on the sample was needed during the study of the oxidation of sulfur. Thereby the surface oxygen coverage was raised in a short time and the saturation coverage could be kept constant during the reaction, which simplifies the analysis of the reaction kinetics (see Chapter 4.2). The supersonic beam can also be used for background dosing with a defined pressure. To achieve this, an aluminum flag located in the analysis chamber can be placed in the beam, such that the beam is scattered and does not directly impinge on the surface. This procedure was used in this thesis for dosing CO (Chapter 3 and 4.1).

# 3. CO adsorption on Ag/Pt(355) [P1]

Stepped surfaces can act as templates for the creation of bimetallic nanostructures. As the formation of bimetallic surfaces in general modifies the electronic properties of the parent metals<sup>[18,19]</sup> they can exhibit interesting magnetic<sup>[26]</sup> and in particular also chemical properties, like an enhanced reactivity or selectivity.<sup>[24]</sup> The addition of a noble metal can also be used to block step sites and thereby change the reactivity of the surface. In this way, the reactivity of the steps can be determined,<sup>[25]</sup> but also allows to tune the reactivity of a surface. Birchem et al. studied the influence of tin on the hydrogenation of 3-methylcrotonaldehyde on Pt(111) and Pt(355),<sup>[44]</sup> where the stepped Pt(355) surface is twice as reactive as the flat one. On Pt(355), small amounts of tin located in the vicinity of the steps lead to a preference of the saturated alcohol as a product. Higher amounts of tin, on the other hand, form islands on the terraces and lead to an improved selectivity towards the unsaturated alcohol. The latter effect is also observed on the tin modified Pt(111)surface. In a recent study, Stroppa et al. investigated the adsorption and dissociation of CO on clean and Ni decorated Rh(355) employing HR-XPS and density functional theory.<sup>[45]</sup> On the clean surface, the adsorption starts at step on-top sites. At only slightly higher coverages, the terrace on-top sites and higher coordinated sites at the step edges are occupied, and finally terrace hollow sites are filled. The experimentally observed XPS binding energies correlate very well with calculated surface core-level shifts. On the surface, decorated with a monorow of Ni, CO first adsorbs exclusively at the terrace ontop sites. At high total coverages, mixed Ni/Rh bridge and hollow sites are also occupied. CO adsorption on on-top sites on the Ni step atoms was not observed. In the calculations, the Ni/Rh hollow site is predicted to be equally stable as the terrace on-top site, but experimentally its occupation is observed only at higher coverages. The dissociation of CO was considered in this work, too. The theoretical results find a dissociation barrier of 1.05 eV on Rh(111), 0.03 eV on Rh(355) and -0.06 eV on Ni/Rh(355). The low calculated barrier for the clean Rh(355) surface implies that some dissociation could be possible at room temperature. However, dissociation was not experimentally observed by Stroppa et al. upon heating the CO covered surface.<sup>[45]</sup> Instead, the CO completely desorbed without dissociation. C 1s spectra of the same experiments on Ni/Rh(355) show a small amount of C left on the surface after heating and the majority of the CO still desorbs intact. The described study is an example how theory and HR-XPS experiments complement each other.

In this thesis, the combination of theoretical calculations and HR-XPS experiments is used to investigate the adsorption of CO on the Pt(355) surface decorated with varying amounts of Ag. It was chosen to modify the stepped Pt surface, because previous STM and thermal energy helium atom scattering (TEAS) measurements by Gambardella et al. showed that Ag monorows can be prepared on Pt(997) = Pt(S)-[9(111)x(111)].<sup>[22]</sup> The optimal temperature range for wire growth was found to be between 250 and 400 K.



Figure 3.1: a) Ag monorows ( $\Theta_{Ag} = 0.13$  ML) on Pt(997) deposited at 400 K, b) Ag islands at the lower step edges after deposition of 0.5 ML at 120 K<sup>[22]</sup>.

At these temperatures, up to 0.5 ML of Ag grow row by row along the step edges. Figure 3.1 a) shows one monorow of Ag deposited on Pt(997) at 400 K. For higher coverages, the step edges roughen. At lower temperatures, Ag islands grow at the bottom of the steps, since Ag has enough thermal energy to diffuse to the steps. But when it binds to a Ag cluster already sitting there, it has not enough energy to overcome the barrier to get around the corner to a free Pt step site. The resulting islands can be seen in Figure 3.1 b). At temperatures higher than 400 K, Ag has enough energy to migrate from one terrace to another. Ag diffusion to adjacent terraces then leads to step bunching.

Gambardella et al. also studied the adsorption of small amounts of CO on Pt(997) decorated with a monorow of Ag by STM. The CO molecules were found to adsorb at the former Pt steps, regardless of Ag decoration. The combination of Ag and Pt offers the

advantage that at the temperatures needed to investigate CO adsorption, Ag does not diffuse into the Pt crystal forming a bulk alloy nor does it form a surface alloy. This has not only been shown for flat Pt(111)<sup>[46]</sup>, but also for Pt(355).<sup>[47]</sup> In addition, Ag can be conveniently removed by heating the Pt crystal to 1100 K, which allows to perform experiments without time consuming cleaning of the surface using Ar ion bombardment. Furthermore TPD studies of CO on Ag single crystals show that the most strongly bound species desorbs with a rate maximum at 90 K,<sup>[48,49]</sup> i.e. at a much lower temperature than at Pt surfaces. Because of this, Ag was chosen to block the reactive Pt step sites for the adsorption and/or reaction of gases.

In the present thesis the influence of predeposited Ag on the adsorption of CO is shown, not only for low CO coverages as in the STM study of Gambardella et al.<sup>[22]</sup>, but for a wide range of CO coverages. Furthermore, the influence of the CO on the Ag is investigated. In order to do so, the results of our HR-XPS experiments are combined with ab initio density functional theory calculations from cooperation partners, which leads to a detailed understanding of the influence of Ag on CO and vice versa.

Using HR-XPS it could be verified, that Ag grows in a row by row mode also on Pt(355). Therefore, Ag 3d spectra of different amounts of Ag evaporated on the Pt(355) surface at 300 K were taken. The full width half maximum of the silver peaks stays constant up to a Ag coverage of 0.20 ML. Exceeding this coverage, which is equal to one row of Ag at the step edges, leads to an increase in width, which is attributed to the presence of two different kinds of Ag on the surface: one in the monorow, which has Pt and Ag neighbors in the same layer, and another in the second row, which has only Ag neighbors in the same layer.

Upon CO adsorption on the clean Pt(355) surface first the step sites are occupied. At higher total coverages CO also adsorbs on terrace on-top and bridge sites (for details of CO adsorption on clean stepped Pt surfaces see [27,28] and references therein). C 1s spectra recorded during the initial stage of CO adsorption at 120 K for Ag coverages larger than 0.20 ML show only contributions with the characteristic binding energy of CO bound at terrace on-top sites. At first sight, this implies a site blocking by the preadsorbed Ag for CO on the previous step sites. However, DFT calculations show that CO still preferentially adsorbs at the former Pt step sites. The calculation of the surface core level shifts (SCLS) of CO adsorbed at these sites show a C 1s binding energy value similar to that of CO adsorbed at a terrace on-top site. This leads to the conclusion that Ag does not block the former Pt step sites for CO adsorption but only modifies the electronic structure. Also, the Ag 3d binding energies shift upon CO adsorption, which indicates that CO adsorbs at sites close to the Ag monorow, in line with an only apparent blocking of the former Pt step sites. Figure 3.2 a) shows the Pt(355) surface decorated with one row of Ag for a coverage of 0.10 ML of CO. This result also agrees with the finding of

Gambardella et al. that small amounts of CO adsorb at the former Pt steps on Pt(997) decorated with a monorow of Ag.<sup>[22]</sup>





Figure 3.2: 0.20 ML Ag on Pt(355): a) Ag monorows at low CO coverage, b) Ag peninsulas at the step edges at CO saturation, c) embedded Ag islands at CO saturation

The C 1s peak at the binding energy of the bare Pt step sites appears again in the spectra for CO coverages higher than 0.1 ML up to saturation. This shows that undecorated step sites become again available for CO adsorption. In this CO coverage regime also the width of the Ag 3d peaks is increasing. The latter finding also points to a rearrangement of Ag in a way that Ag atoms without Pt neighbors in the same layer are present on the surface. The Ag 3d spectra show no decrease in intensity, which would be expected for the formation of 3D clusters due to the damping of the photoelectrons from the then lower lying Ag atoms.

The experimental findings are in line with a formation of flat Ag islands that still have to be connected to the steps, as the full CO step coverage is not restored. Two different scenarios are possible, which can not be distinguished by the experimental data: Formation of peninsulas on the lower terraces or of embedded islands incorporated into the upper terrace, as shown in Figure 3.2 b) and c), respectively. At this point, the DFT calculations are again beneficial, which show that the only the embedded islands scenario is energetically preferred over the monorow scenario at CO saturation. This observed displacement is consistent with previous results, which found that the difference of the binding energies of a Ag-Ag bond and a Ag-Pt bond<sup>[22,47,P1]</sup> is smaller than the difference of the binding energy of a CO molecule bound to step and terrace sites.<sup>[50-52]</sup> Thus, the

formation of the embedded islands is plausible and must be driven by the adsorption of CO.

For high total CO coverages also the adsorption of some CO on the embedded Ag islands was observed, which leads to peaks in the C 1s and O 1s spectra that are well separated from the CO species on Pt. As CO does not adsorb on clean Ag surfaces at the temperatures of 120 K used here,<sup>[49]</sup> this is an example on how the bimetallic binding to the Pt influences the binding of CO to Ag. Upon heating, the CO species bound to Ag is removed at ~170 K. The coverage of CO adsorbed on Pt sites is found to decrease roughly linearly with increasing Ag coverage.

Comparison of the thermal evolution of the adsorbed layers on Ag/Pt(355) to the one on a clean surface shows that Ag also influences the desorption of CO. The TP-XPS data reveal that bridge sites on the terraces are depleted at lower temperatures with increasing Ag coverage. On the clean and Ag covered surface CO bound to Ag free step sites is the last species present. This shows that at least some parts of the steps remain Ag free also for low CO coverages. With increasing temperature, the amount of CO on Ag free Pt step sites even increases. That means that for higher temperatures occupation of CO on Ag free step sites is preferred over Ag adsorption there, also for low CO coverages. This is in contrast to the presence of monorows at CO coverages < 0.10 ML during adsorption. In a TPD study by Davies et al.,<sup>[47]</sup> a high temperature desorption feature, assigned to CO desorbing from the step sites, was observed for Pt(355) precovered with various amounts of Ag. The authors concluded from the data that the step sites would also be Ag free at low temperatures. Our TPXPS data show, however, that not only the amount of CO on Ag free step sites increases with temperature, but also some CO exhibiting the XPS binding energy of terrace on-top sites is still present at higher temperatures than on the Ag free surface. These CO molecules also contribute to the high temperature TPD peak assigned to Ag free Pt steps.

In summary the study of CO adsorption on Ag/Pt(355) shows how valuable the combination of DFT calculations and HR-XPS data is to get insight in the complex underlying energetic effects. It is also an example for how important in-situ measurements are for a clear understanding of the surface processes.

#### 4. Interaction of sulfur with stepped surfaces

Poisoning is a major issue in large scale applications of heterogeneously catalyzed reactions.<sup>[2,4,9,53]</sup> A number of different effects can lead to deactivation of a catalyst:<sup>[2,54]</sup> If the poison is stronger bound to the metal surface than the reactant, it blocks the overall available adsorption sites. Since adsorption is the first necessary step in the catalytic cycle, this can decrease the reaction rate. As the reactivity of a catalyst can be governed by a small amount of active sites, the effect can be even stronger, when these active sites are blocked. Then, a small amount of poison can have a dramatic effect on the reaction rate. Besides these direct site-blocking effects, long range electronic effects can also play a role. The adsorption of the poison on the substrate can change its electronic structure and can thus induce a change in the binding strength between catalyst and reactant. Considering the case of a significantly reduced binding between catalyst and reactant, the reaction may become completely impossible, because the reactant does not adsorb at the chosen reaction conditions. In addition, the adsorption of the poison might induce a restructuring of the surface. Thereby the active sites might be eliminated.

# 4.1 Passivation of steps by sulfur <sup>[P2, P3]</sup>

A better understanding of the underlying principles and mechanisms of poisoning can lead to the development of catalysts that exhibit a higher resistance towards poisoning or enable effective strategies to remove the poison from the surface. Sulfur is known to be a very efficient poison for metal catalysts. In this thesis, the influence of S on the adsorption and desorption of CO on Pt(355) and Pt(322) was investigated, as well as the removal of S from Pt(355) and Pt(111) by oxidation.

On Pt(111), S occupies threefold hollow sites.<sup>[55-60]</sup> TPD studies of CO adsorbed on Pt(111) precovered with S showed that the total adsorption capacity is decreased with increasing S precoverage. In addition, the desorption maximum shifts to lower temperatures indicating that the binding energy of CO is lowered by S adsorption <sup>[56,57,61,62]</sup>. A p(2x2) S overlayer forms on Pt(111) with a coverage of  $\Theta_S = 0.25$  ML. When CO is coadsorbed with this overlayer, it can only adsorb in the on-top geometry with a maximum coverage of  $\Theta_{CO} = 0.25$  ML. A sulfur precoverage of  $\Theta_S = 0.33$  ML completely suppresses the adsorption of CO on Pt(111).<sup>[56,57]</sup> TPD studies in the presence of S on stepped and polycrystalline surfaces also revealed a lower CO desorption temperature. From the absence of the high temperature peak in the TPD spectra assigned to CO desorption.<sup>[63-65]</sup> XP spectroscopy showed a doublet with the 2p<sub>3/2</sub> peak at a binding energy of 162.2 eV at a S coverage of  $\Theta_S = 0.1$  ML on Pt(111). When the S coverage is increased to  $\Theta_S = 0.3$  ML the binding energy is lowered by 0.2 eV.<sup>[58,59]</sup>

Using LEED it was shown, that the Pt(S) – [6(111)x1(100)] surface reconstructs in the presence of very small amounts of S. Terraces with double width separated by steps width double height are formed. This reconstruction occurs faster at higher temperatures.<sup>[66]</sup> Formation of double steps on stepped Pt crystals covered by a (2x2) overlayer of S was also observed in STM studies.<sup>[67,68]</sup> Excessive dosing of CO at room temperature can lift the reconstruction.<sup>[67]</sup> Because of these observations, the Pt(355) and Pt(322) surfaces covered with different amounts of S have been studied by LEED, to check if these surfaces also reconstruct. As described in Chapter 2.2, the terrace width can be calculated from the spot splitting. Figure 4.1 a) shows a LEED pattern of the Pt(355) surface with  $\Theta_S = 0.14$  ML. The distance between the splitted spots is approximately the same as for the clean Pt(355) surface. This value was also found for all  $\Theta_S < 0.25$  ML. At  $\Theta_S = 0.25$  ML or higher, the distance is halved, as is evident from Figure 4.1 b). Thus, the formation of double steps, as depicted in Figure 4.2 d), on the Pt(355) surface could only be observed for very high sulfur coverages. The additional spots in Figure 4.2 b) are attributed to the p(2x2) S overlayer. Figure 4.2 c) shows the LEED pattern for a small amount of



Figure 4.1: LEED patterns of a) unreconstructed Pt(355) with  $\Theta_s = 0.14$  ML, b) reconstructed Pt(355) with  $\Theta_s = 0.25$  ML, c) reconstructed Pt(322) with  $\Theta_s = 0.03$  ML. d) shows a schematic drawing of the unreconstructed and reconstructed surfaces.

S ( $\Theta_S = 0.03$  ML) adsorbed on Pt(322). Here, the spot splitting is halved compared to the one for the clean surface. In contrast to Pt(355), the Pt(322) surface already reconstructs for very low S coverages. LEED patterns after dosing CO and also after heating to various temperatures were also acquired without any detectable changes.

Herein the adsorption of CO was investigated with in-situ HR-XPS, which allows to determine the adsorption sites of CO and S. Figure 4.2 a) and d) show selected C 1s spectra collected during the adsorption of CO on clean Pt(355) at 130 K and Pt(322) at 150 K, respectively. Small S precoverages block the step sites for CO adsorption. This can be seen by the decreased intensity of the step peaks (at 286.4 eV and 285.8 eV) in Fig. X b) and e). On Pt(355),  $\Theta_S = 0.10$  ML block the steps sites completely. On Pt(322), a significantly lower amount of S suffices to block all step sites, because their number is halved due to the reconstruction of the surface. For intermediate S precoverages only the terrace on-top and terrace bridge contributions are present in the spectra, as shown in Figure 4.2 c) and f). In the presence of sulfur, the strong preference of on-top sites for low



Figure 4.2: selected C 1s spectra recorded during adsorption of CO at 130 K and  $p_{CO} = 1.5 \times 10^{-9}$  mbar on a) clean Pt(355), b) Pt(355) with  $\Theta_S = 0.03$  ML, c) Pt(355) with  $\Theta_S = 0.13$  ML, at 150 K on d) clean Pt(322), e) Pt(322) with  $\Theta_S = 0.02$  ML and f) Pt(322) with  $\Theta_S = 0.14$  ML.

CO terrace coverages is relaxed. The adsorption starts simultaneously on both terrace sites. High amounts of sulfur effectively block the adsorption of CO in the bridge geometry on the terraces. This is in agreement with earlier experiments on Pt(111) where only on-top sites are occupied for  $\Theta_{\rm S} = 0.25$  ML.<sup>[56,57,67]</sup>

Figure 4.3 shows a color coded density plot of the spectra recorded during heating the CO covered Pt(355) surface precovered with  $\Theta_S = 0.14$  ML. Upon heating, the peak assigned to CO bound to the step sites at 286.4 eV reappears, which means that the step sites are repopulated by CO. Simultaneously the peak at 286.1 eV assigned to CO bound to terrace bridge sites looses intensity. In the same temperature range the S 2p binding energy shifts to the value characteristic for S on terrace sites. These findings are attributed to a CO/S sites exchange process. Cooling the surface down after heating below the onset of CO desorption does not lead to a depletion of the repopulated step sites. This shows that the site exchange process is irreversible. For Pt(355) the transition temperature for low S coverages is at 165 K and finally the same CO step coverage as for the clean surface is reached. A significantly higher transition temperature (245 K for low S coverages) is found for Pt(322). Here, only roughly half of the CO step coverage as for the clean surface is reached, due to S-induced formation of double steps.

From the irreversible lifting of the step passivation by sulfur upon heating for both surfaces we conclude that, under the experimental conditions applied, an occupation of step sites by CO is energetically favored over occupation with S, with the CO/S site exchange process being kinetically hindered at low temperatures. In a simplified picture and neglecting that lateral interactions in the pure and mixed phases are not taken into account, this indicates that in the coadsorption situation the effective energy difference  $\Delta E_{CO}$  between step and terrace sites for CO is larger than the corresponding energy difference for sulfur,  $\Delta E_s$ . But if CO is dosed at low temperatures, the activation barrier to



Figure 4.3: Color coded density plot of S 2p spectra recorded during heating of a CO covered Pt(355) surface with  $\Theta_S = 0.14$  ML

move the S atoms away from the steps is too high. It can only be overcome by providing thermal energy, i.e., via heating. The different characteristic temperatures indicate a different barrier height for the two surfaces. This is related to differences in the binding energy of S and CO on the (100) and (111) steps.

The TP-XPS experiments also show that sulfur coadsorption lowers the desorption temperature of CO at both terrace and step sites, with CO at step sites being the most stable species. Our in-situ results show that the S-induced lowering of the CO desorption temperature found by TPD can not be attributed to a blocking of the step sites by S, as was proposed in the literature.<sup>[63-65]</sup> In fact, it is due to a lowering of the binding energy of CO at step sites, due to S at nearby terrace sites.

#### 4.2 Sulfur Oxidation: It's the steps! <sup>[P3]</sup>

Up to now, there are only very few studies for the direct measurement of kinetic parameters such as activation energies for surface reactions.<sup>[69,70]</sup> In most cases, they are determined by TPD, where only the desorbing species can be detected. Thereby important reaction intermediates can easily be missed, which can hamper the correct determination of kinetic parameters. Sulfur oxidation on Pt(111) was studied by TPD.<sup>[71,72]</sup> But as no information about the surface intermediates was available, only an apparent activation energy could be derived.<sup>[72]</sup>

In this thesis, in-situ HR-XPS measurements are used to derive the activation energy of sulfur oxidation on Pt(355) and on Pt(111). This method allows to identify and quantitatively analyze even small amounts of the reacting species in a time-dependent fashion. Theoretical calculations indicate that at the oxygen saturation limit, S is oxidized to SO<sub>x</sub> (x = 1-4) and that the total energy increases with x.<sup>[73]</sup> For the oxidation of SO<sub>2</sub> to SO<sub>3</sub> by a Langmuir-Hinshelwood mechanism an activation energy of 46 kJmol<sup>-1</sup> was calculated,<sup>[74]</sup> which is, however, not the rate limiting step of the S oxidation reaction (see below). To identify the reaction intermediates, studies of SO<sub>2</sub> adsorption on Pt surfaces were used as reference <sup>[75-79]</sup> and in Chapter 5 (P5).

To get an overview of the relevant reaction steps, the thermal evolution of a coadsorbed layer of atomic oxygen and a small amount of preadsorbed sulfur on Pt(355) was investigated. It was found that the binding energy of the S 2p doublet of S coadsorbed with O exhibits the typical value for S at terrace sites. This means that oxygen displaces S from the step sites of Pt(355), where it preferentially adsorbs in the absence of coadsorbates (see above). Upon heating the mixed overlayer to above 260 K first a new S 2p doublet at higher binding energies assigned to SO<sub>3</sub> shows up in the spectra that reaches maximum intensity around 340 K. Further heating decreases its intensity and a new doublet at again higher binding energies evolves which is assigned to SO<sub>4</sub>. The SO<sub>4</sub>-species decomposes above 500 K, into SO<sub>3</sub>, which desorbs, and O. The fact that oxidation



Figure 4.4: Arrhenius plot of the rate constants as determined from the isothermal S oxidation experiments on Pt(355) (red) and Pt(111) (blue) at different pressures (as noted).

of S directly yields  $SO_3$  and that no intermediate SO or  $SO_2$  species are found indicates that the rate-determining step is the first oxidation step, i.e. the oxidation of S to SO.

To determine the activation energy, isothermal experiments, in which the sulfur precovered Pt(355) surface ( $\Theta_S = 0.02 - 0.035$  ML) is exposed to a constant oxygen pressure via the supersonic molecular beam, were performed. For all investigated temperatures (250 – 450 K) an exponential decay of the S coverage was observed, after induction periods of shortening length with increasing temperatures. As expected, S is oxidized faster at higher temperatures. The displacement of S from step to terrace sites was found at all temperatures. This shows that the catalytically active species on the stepped surface must be oxygen at the step sites. Logarithmic plots of the normalized S coverage versus time yield straight lines in all cases. This indicates pseudo first order reaction kinetics with respect to sulfur. Only during the induction period, in which the O coverage on the surface is much higher than the S coverage. This excess of oxygen explains the observed pseudo first order behavior. The slope of the straight lines correspond to the reaction rate *k*. The Arrhenius equation describes the temperature dependence of the reaction rate k on the activation energy E<sub>a</sub>:

$$\mathbf{k} = \mathbf{k}_0 \cdot \mathbf{e}^{-\frac{\mathbf{E}_a}{\mathbf{R}T}}$$

Following this equation  $E_a$  of the reaction can be derived by plotting  $\ln k$  versus  $T^{-1}$  as shown in Figure 4.4.

To verify that the reaction is indeed pseudo first order and the activation energy does not depend on the oxygen pressure, similar experiments were performed at a different oxygen pressure. As can be seen in Figure 4.4, both red lines have the same slope, thus yielding the identical activation energies for both oxygen pressures. From the slope of the red lines

the activation energy can be calculated to  $34 \pm 2 \text{ kJmol}^{-1}$  for the oxidation of S to SO on Pt(355).

To elucidate the role of the steps in the reaction, similar experiments were also performed for the flat Pt(111) surface. Again, pseudo-first-order reaction kinetics are found. However, the activation energy of  $74 \pm 4$  kJmol<sup>-1</sup> is more than twice the value found on the stepped surface. This value demonstrates the importance of the steps in the oxidation process.

Summing up, we presented HRXPS data that allowed the identification of reaction intermediates and the possibility of quantitative time resolved measurements also for very low coverages allows to get a detailed insight in the complex reactions occurring during sulfur oxidation.

#### 5. Adsorption and reaction of SO<sub>2</sub> on Pt surfaces

Not only sulfur but also its oxides, which are both common impurities in crude oil, are known to be poisons for platinum containing catalysts. The resulting decrease of activity, e.g. in automotive catalysts,<sup>[4,9,10,80,81]</sup> is of great economic and ecological importance. A number of surface science studies aimed at a fundamental understanding of the underlying processes concerning the poisoning of platinum catalysts by studying the adsorption and reaction of SO<sub>2</sub> on flat Pt single crystal surfaces <sup>[71,73-79,82,83]</sup>. However, SO<sub>2</sub> can not only lead to poisoning of catalysts. In some cases it can even enhance the reactivity and act as a promoter. For example addition of SO<sub>2</sub> into the gasfeed poisons the oxidation of CO and propene, but promotes the oxidation of propane over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>[84]</sup> At first the promoting effect was proposed to rely on the formation of sulfates on the support. Then Wilson et al. showed a Pt(111) surface precovered with oxygen and  $SO_2$  is active for the dissociative adsorption and combustion of propane.<sup>[83]</sup> Oxygen and SO<sub>2</sub> form a SO<sub>x</sub> species on the Pt surface, which enhances the sticking probability of the hydrocarbon and appears to form a complex with the carbon containing reaction intermediates. Thus no support mediated effects are necessary to promote the oxidation of alkanes. This promoting or poisoning effect of  $SO_x$  species on the oxidation of hydrocarbons was studied in detail for different hydrocarbons on Pt(111).<sup>[75,85,86]</sup> Also the catalytic destruction of trichloroethane was investigated on SO<sub>x</sub> precovered Pt(111).<sup>[87]</sup>

Despite these efforts and the importance of the sulfur/sulfur oxide chemistry on surfaces the complex reaction on platinum surfaces was not completely understood. Some of the results were even contradictory. This is mainly due to the fact that a number of different  $SO_x$  (x = 0-4) species can be formed on Pt, from which some can even adapt several different stable conformations, e.g. SO<sub>2</sub> on the flat Pt(111) surface <sup>[73,88]</sup>. Moreover, no studies had been published on stepped surfaces, although these could help to elucidate the relevant sites for adsorption and reaction of SO<sub>2</sub>. Because of contradicting results on Pt(111) first a detailed in-situ HR-XPS study of SO<sub>2</sub> adsorption on the clean and oxygen precovered flat surface was performed. To identify the role of defects, in our case steps, the adsorption of SO<sub>2</sub> was then also studied on Pt(322) and Pt(355).

In the literature, there is consensus that at 120 K SO<sub>2</sub> adsorbs molecularly in two different conformations on clean Pt(111). The two species have been identified from their different binding energies in high resolution x-ray photoelectron spectroscopy (HR-XPS) <sup>[76]</sup>. By near edge X-ray absorption fine structure (NEXAFS) measurements they have been assigned as flat lying and upright standing SO<sub>2</sub> <sup>[76]</sup>. These results have been confirmed by DFT based calculations by Lin and coworkers. <sup>[88]</sup> TPD measurements of SO<sub>2</sub> on Pt(111) show that SO<sub>2</sub> desorbs around 370 K for small initial coverage. For higher initial coverage the main desorption peak is found at ~320 K.<sup>[71,78,82]</sup> The formation of SO and SO<sub>4</sub> species upon heating SO<sub>2</sub> multilayers to room temperature, has been proposed by

high resolution electron energy loss spectroscopy (HREELS).<sup>[77]</sup> Under comparable conditions, the formation of S and SO<sub>4</sub> has been reported from HR-XP spectra,<sup>[76]</sup> with the SO<sub>4</sub> species being stable up to at least 370 K.

The results for SO<sub>2</sub> adsorption on the oxygen precovered surface are controversial. Two SO<sub>2</sub> species with binding energy values corresponding well to those on clean Pt(111)<sup>[76]</sup> have been identified by HR-XPS also on oxygen precovered Pt(111).<sup>[75]</sup> In the same study the formation of a SO<sub>x</sub> species is found at ~200 K, which the authors assign to SO<sub>4</sub>. However this species starts to decompose already at 280 K, leaving only atomic S on the surface at 340 K and its S  $2p_{3/2}$  binding energy is not consistent with values reported in the literature.<sup>[76,79]</sup> TPD studies of the thermal evolution of SO<sub>2</sub> on O-precovered Pt(111) showed a SO<sub>2</sub> desorption peak at 320 K. In addition, significant desorption of SO<sub>2</sub> and/or SO<sub>3</sub> was found above 500 K.<sup>[71,78,83]</sup> This high temperature peak was associated with the decomposition of SO<sub>4</sub>. Note that identification of SO<sub>3</sub> is difficult in mass spectrometry, as the dominating cracking fragment is SO<sub>2</sub>.<sup>[89]</sup> The TPD results differ significantly from the conclusions of the HR-XPS study by Lee et al, where SO<sub>4</sub> decomposition was assumed to be completed at much lower temperatures.

## 5.1 SO<sub>2</sub> on Pt(111) <sup>[P5]</sup>

The S 2p spectra recorded in the thesis during adsorption of SO<sub>2</sub> on Pt(111) show the two well known doublets assigned to upright standing and flat lying SO<sub>2</sub>. Interestingly the two species adsorb simultaneously with a constant ratio. Also on oxygen precovered Pt(111) a constant ratio of the SO<sub>2</sub> species is observed. Here, more upright standing SO<sub>2</sub> is found and additionally a third, oxygen induced SO<sub>2</sub> species is present. The fact that a significant amount of SO<sub>2</sub> reacts to SO<sub>3</sub> directly upon adsorption, at temperatures as low as 130 K, shows the high reactivity of the system.

Figure 5.1 a) shows S 2p spectra recorded during heating of the SO<sub>2</sub> covered Pt(111) surface in a color coded density plot (details see Chapter 2.1 and P5). The intensity of the doublet at higher binding energies grows at the expense of the one at lower binding energies. This means that a conversion of flat lying into upright standing SO<sub>2</sub> takes place, which was also observed by Polčik and coworkers.<sup>[76]</sup> By a simple Redhead analysis<sup>[90]</sup> of the interconversion (self-diffusion) of SO<sub>2</sub> from the inflection point in our data at 193 K an activation energy of ~52 kJ/mol can be calculated, which agrees well with the barrier for self diffusion of 42kJ/mol calculated by Lin and coworkers.<sup>[74]</sup> Heating to temperatures higher than 220 K leads to desorption of most of the SO<sub>2</sub>. Only a small amount of S and a minor amount of SO<sub>3</sub> are found on the surface, indicating that not more than 6 % of the SO<sub>2</sub> dissociate on the flat surface. This is in line with results from Polčik et al. who found only small amounts of S after heating a layer formed by adsorption at 212 K. Only upon heating thick multilayers they observed the formation of SO<sub>4</sub>.<sup>[76]</sup>



Figure 5.1: Color coded density plots of the S 2p spectra collected during heating the SO<sub>2</sub> covered surface on a) Pt(111), b) Pt(111) precovered with 0.25 ML of oxygen and c) Pt(355)

The spectra recorded during the TP-XPS experiments on oxygen precovered Pt(111) are shown in Figure 5.1 b). In contrast to clean Pt(111) significant amounts of the initially adsorbed SO<sub>2</sub> are converted to SO<sub>3</sub> which subsequently reacts to SO<sub>4</sub>. During this process also some elemental S is formed. Some SO is present on the surface, which results from beam damage, due to the intense synchrotron radiation. Above 450 K the SO<sub>4</sub> specie decomposes to SO<sub>3</sub>, which desorbs, and to O. This oxygen reacts with the S on the surface to form SO<sub>x</sub> which desorbs and leaves a S free surface at the end of the TP-XPS experiment. Our data shows that SO<sub>4</sub> is stable up to 450 K. This is in agreement with the results of earlier TPD experiments.<sup>[71,76,78,83]</sup> However it is in contrast to the low thermal stability of the SO<sub>x</sub> species assigned to SO<sub>4</sub> observed by Lee et al. In fact, the thermal behavior fits well to the one of SO<sub>3</sub> in the present study. Also the difference in binding energy between the lying SO<sub>2</sub> and the SO<sub>x</sub> species of Lee et al. is similar to the distance to  $SO_3$  in the present study. These facts lead us to the conclusion that  $SO_3$  is formed in the experiment conducted by Lee et al. Maybe the initial oxygen coverage in this study of Lee et al. was too low to form  $SO_4$ . Our results were confirmed in a recent IR study of Happel and coworkers.<sup>[91]</sup> They also observed the formation of a  $SO_x$  species that was stable up to 450 K upon adsorption of  $SO_2$  on Pt(111) precovered with 0.25 ML of atomic oxygen.

After having a completed and unified picture of  $SO_2$  adsorption and reaction on clean and oxygen precovered Pt(111), the behavior on Pt(322) and Pt(355) was investigated.

### 5.2 SO<sub>2</sub> on stepped Pt surfaces <sup>[P6]</sup>

In addition to the two known SO<sub>2</sub> species on Pt(111), upright standing and flat lying, new step induced SO<sub>2</sub> species were found on the stepped surfaces. On these surfaces also a constant ratio of the different SO<sub>2</sub> species was found during adsorption. This indicates a hit and stick mechanism, due to the large energy barrier for the conversion form one species to the other (see above). Fig. 5.1 c) shows the S 2p spectra recorded during heating the SO<sub>2</sub> covered Pt(355) surface. On this surface a lying SO<sub>2</sub> species at the (111) steps is the thermally most stable species. A thermally induced conversion of the other SO<sub>2</sub> species into the lying SO<sub>2</sub> step species is observed, as can be seen from the shift in binding energy of the SO<sub>2</sub> around 200 K. In contrast to that, no interconversion of species upon heating is observed on Pt(322) and the thermally most stable SO<sub>2</sub> species is the standing one at the (100) steps. On both stepped surfaces, a significant proportion of SO<sub>2</sub> dissociates/disproportionates upon heating and forms S and SO<sub>3</sub>, as can be seen from the shift is intensity at 162.2 and 166.0 eV above 300 K in Figure 5.3 c). This is in contrast to the flat surface where only small amounts of SO<sub>2</sub> dissociate.

On the oxygen precovered stepped Pt surfaces, also additional  $SO_2$  species induced by steps and/or oxygen are observed. As on the flat surface some  $SO_3$  is formed directly upon adsorption. Upon heating more of the  $SO_2$  is oxidized to  $SO_3$ . Subsequently oxidation of  $SO_3$  to  $SO_4$  occurs. Above 450 K,  $SO_4$  decomposes and leads to S-free surfaces on which only oxygen is left. The comparison to the data obtained on Pt(111) shows that in the clean and oxygen precovered case the stepped surfaces show a higher reactivity towards  $SO_2$  dissociation and/or reaction. This indicates the important role of steps and defects in catalytic processes.

#### 6. Summary

Highly dispersed particles used in heterogeneous catalysis often exhibit a variety of defect sites. These are proposed to have a higher reactivity, compared to flat low index surfaces. In order to elucidate the differences in reactivity between flat areas and defect sites, regularly stepped surfaces can be studied. In this thesis two vicinal Pt crystals have been used as substrates: Pt(355) and Pt(322). Both exhibit five atom rows wide (111) oriented terraces and monatomic steps with (111) and (100) orientation, respectively. To model complex reactions and reaction conditions that usually occur in heterogeneous catalysis, the Pt surfaces were modified with a second metal and coadsorption situations, especially with poisons, were created to study their respective effects.

To study the adsorption and thermal evolution of various gases on single crystalline platinum surfaces in-situ high resolution X-ray photoelectron spectroscopy was employed. The measurements were performed at the third generation synchrotron BEESY II, which provides highly intense X-rays with a high resolution, allowing site selective in situ measurements. Thereby, the temperature and coverage occupation of adsorption sites can be studied, in order to obtain a detailed description of the adsorbate layers.

One topic is the interplay between Ag decoration of the steps on Pt(355) and CO adsorption. Depositing various amounts of Ag at 300 K initially leads to a row-by-row growth starting from the lower Pt step edges. This decoration of the step sites results in a change in the CO adsorption behavior. The combination of XPS with DFT calculations shows - in contrast to conclusions from TPD studies in literature - only an apparent blocking of step sites occuring for low CO coverages, which is attributed to a change in the electronic structure. As a consequence, in the presence of Ag, the C 1s binding energy of CO at the former step sites is equal to that for CO at terrace on-top sites. Higher CO coverages induce the formation of embedded Ag clusters within the upper terraces. Thus part of the original Pt step sites are free again for CO adsorption.

To study the influence of poisons on the platinum surface the influence of sulfur, which is an effective poison for metal catalysts, was investigated on Pt(322) and Pt(355). S preferentially adsorbs at the steps and passivates them for CO adsorption at low temperatures. The required S precoverage for step passivation is significantly lower for Pt(322), because of the lower number of steps as a result of the S-induced double-step formation. Upon heating, population of step sites with CO occurs due to irreversible CO/S site exchange. At low S precoverages, the characteristic transition temperatures are 165 K for Pt(355) and 245 K for Pt(322). This significant difference indicates a higher activation barrier for the CO/S site exchange process on Pt(322). For medium to high S precoverages the transition temperature stays unchanged for Pt(322) but increases for Pt(355). The observed behavior is attributed to a kinetic passivation of the steps by sulfur at low temperatures, which is lifted upon heating. The kinetics of the oxidation and removal of sulfur on stepped Pt(355) and flat Pt(111) were also studied. SO<sub>3</sub> and SO<sub>4</sub> were identified as reaction intermediates. The fact that no SO and SO<sub>2</sub> species were found indicates that the rate-limiting step is the oxidation of S to SO. On Pt(355) the activation energy of  $34 \pm 2$  kJ/mol for this step is found to be less than half of the value of  $74 \pm 4$  kJ/mol for flat Pt(111). This documents the dominating role of steps and defects for the catalytic oxidation of sulfur. On the stepped surface S is pushed away from the steps by oxygen. Thus the catalytically active species on the Pt(355) surface must be oxygen at step sites.

Furthermore, we studied the adsorption and reaction of sulfur dioxide on clean and oxygen precovered platinum surfaces and discuss earlier contradicting results. On the clean Pt(111) surface flat lying and upright standing SO<sub>2</sub> were found, adsorbing in similar amounts at low temperature. Upon heating, the ratio changes strongly, favoring the standing SO<sub>2</sub> species; subsequently almost all SO<sub>2</sub> desorbs. On the oxygen precovered surface the standing SO<sub>2</sub> species is preferably populated and even at low temperatures a direct reaction of SO<sub>2</sub> to SO<sub>3</sub> occurs. Upon heating, SO<sub>2</sub> oxidation to SO<sub>3</sub> and subsequently to SO<sub>4</sub> is found. The adsorption and reaction of SO<sub>2</sub> was also studied on clean and oxygen precovered Pt surfaces. For Pt(322) and Pt(355), in addition to the known SO<sub>2</sub> species for Pt(111), several SO<sub>2</sub> species induced by the steps and/or oxygen are observed. On all investigated surfaces a hit and stick mechanism is found for the adsorption. The oxygen free stepped surfaces have a higher reactivity towards SO<sub>2</sub> dissociation/disproportionation, compared to Pt(111). On all three oxygen precovered Pt surfaces some SO<sub>3</sub> is formed directly upon adsorption of SO<sub>2</sub> at low temperatures. Heating of this mixed O/SO<sub>x</sub> layers first results in oxidation of more SO<sub>2</sub> to SO<sub>3</sub>, then in subsequent oxidation of SO3 to SO4, which finally decomposes above 450 K.

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# 9. Curriculum Vitae

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### School

1987/09 - 1991/07	Elementary School in Nürnberg Reichelsdorf, Germany				
1991/09 - 2000/06	Sigmund Schuckert Gymnasium in Nürnberg, Germany				
2000/06	Abitur at the Sigmund Schuckert Gymnasium in Nürnberg, Germany				
<u>University</u>					
2000/10 - 2006/02	Diplom (Dipl.) degree course in Chemistry at the Friedrich- Alexander University of Erlangen-Nürnberg				
2003/02	Vordiplom				
2005/05	Diplom				
2005/06 - 2006/02	Diploma thesis at the Chair of Physical Chemistry II in the research group of PD Reinhard Denecke, Friedrich-Alexander University Erlangen-Nürnberg				
	Title: In-situ-Untersuchungen des Einflusses von Silber auf die CO-Adsorption auf gestuften Platinoberflächen				
Since 2006/03	Dissertation at the Department of Physical Chemistry II in the Group of Prof. Hans-Peter Steinrück, Friedrich-Alexander University of Erlangen-Nürnberg				

## **10. Abbreviations**

Silver	NEXAFS		Near Edge X-ray
Aluminum			Absorption Fine Structure
Gold	Ni	Nickel	
Barium	NSR	Nitroge	en-Storage Reduction
Carbon	υ	Freque	ncy
Cobalt	0	Oxyger	1
Binding Energy Difference	Pt	Platinu	m
Density Functional Theory	QCM	Quartz	Chrystal Microbalance
Activation Energy	QMS	Quadru	pole Mass Spectrometer
Binding Energy	R	Gas Co	nstant
Electron Spectroscopy for	Ru	Ruthen	ium
Chemical Analysis	S	Second	
Electronvolt	S	Sulfur	
Planck Constant	SCLS	Surfac	e core level shift
Hydrogen	STM	Scannin	ng Tunneling Microscopy
High-Resolution	Т	Temper	rature
Joule	TEAS	Therma	al Energy Helium Atom
Kelvin		Scatteri	ing
Reaction Rate	TPD	Temper	rature Programmed
Boltzmann Constant		Desorp	tion
Low Energy Electron Diffraction	TPXPS	Temper	rature Programmed XPS
Molecular Beam	TWC	Three V	Way Catalyst
Magnesium	XPS	X-ray F	Photoelectron Spectroscopy
Monolayer			
Nitrogen			
	Silver Aluminum Gold Barium Carbon Carbon Cobalt Binding Energy Difference Density Functional Theory Activation Energy Binding Energy Binding Energy Electron Spectroscopy for Chemical Analysis Electron Spectroscopy for Chemical Analysis Electronvolt Planck Constant Planck Constant Hydrogen High-Resolution Joule Kelvin Reaction Rate Boltzmann Constant Low Energy Electron Diffraction Molecular Beam Magnesium Monolayer	SilverNEXAAluminumGoldNiBariumNSRCarbonvCobaltOBinding Energy DifferencePtDensity Functional TheoryQCMActivation EnergyRuBinding Energy DifferenceRuChemical AnalysisSElectron Spectroscopy forRuChemical AnalysisSPlanck ConstantSCLSHydrogenSTMHigh-ResolutionTJouleTEASKelvinTLow Energy Electron DiffractionTPXPSMolecular BeamXPSMonolayerXPS	SilverNEXAFAluminumGoldNiNickelBariumNSRNickelBariumVFrequenceCarbonVFrequenceCobaltOOxygenBinding Energy DifferencePtPlatinuDensity Functional TheoryQCMQuartzActivation EnergyQMSQuartzActivation EnergyRuGas ConElectron Spectroscopy forRuRuthenChemical AnalysissSecondElectronvoltSSulfurPlanck ConstantSCLSSurfaceHydrogenTEASThermeJouleTEASThermeKelvinScatterScatterReaction RateTPDTempeBoltzmann ConstantTPXPJesorpLow Energy Electron DiffractionTWCThree YMonelayerXPSX-ray FMonolayerStragenStragen

### 11. Appendix:<sup>1</sup>

- P1: Interaction between silver nanowires and CO on a stepped platinum surface
  R. Streber, B. Tränkenschuh, J. Schöck, C. Papp, H.-P. Steinrück, J.-S. McEwen,
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- P2: Kinetic passivation of steps with sulfur and CO/S site exchange processes on stepped Pt surfaces:
  R. Streber, C. Papp, M.P.A. Lorenz, A. Bayer, R. Denecke, H.-P. Steinrück Chem. Phys. Lett. 452, 2009, 94
  http://dx.doi.org/10.1016/j.cplett.2007.12.038
- P3: Site blocking and CO/sulfur site exchange processes on stepped Pt surfaces
  R. Streber, C. Papp, M.P.A. Lorenz, S. Wickert, M. Schöppke, R. Denecke and H.P. Steinrück
  J. Phys.: Condens. Matter 21, 2009, 134018
  <a href="http://dx.doi.org/10.1088/0953-8984/21/13/134018">http://dx.doi.org/10.1088/0953-8984/21/13/134018</a>
- P4: Sulfur Oxidation on Pt(355): It Is the Steps!
  R. Streber, C. Papp, M.P.A. Lorenz, A. Bayer, R. Denecke, H.-P. Steinrück Angew. Chem. Int. Ed. 48, 2009, 9743 <u>http://dx.doi.org/10.1002/anie.200904488</u>
- P5: SO<sub>2</sub> adsorption and thermal evolution on clean and oxygen precovered Pt(111) R. Streber, C. Papp, M.P.A. Lorenz, O. Höfert, E. Darlatt, A. Bayer, R. Denecke, H.-P. Steinrück Chem. Phys. Lett. 494, 2010, 188 http://dx.doi.org/10.1016/j.cplett.2010.06.007
- P6: Influence of steps on the adsorption and thermal evolution of SO<sub>2</sub> on clean and oxygen precovered Pt surfaces
  R. Streber, C. Papp, M.P.A. Lorenz, O. Höfert, W. Zhao, S. Wickert, E. Darlatt, A. Bayer, R. Denecke, and H.-P. Steinrück submitted to J. Phys. Chem. C
- <sup>1</sup> This Ph.D. thesis was written in a cumulative form with the full text of the scientific publications in the appendix. Due to copyright protection, the internet version of the dissertations pdf file must not contain the full text but the citations of the publications.