Structure - activity relationships of Pt based model electrodes in electrocatalysis

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<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
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<tr>
<td>ATR</td>
<td>attenuated total reflection</td>
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<tr>
<td>CO</td>
<td>carbon monoxide</td>
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<td>CV</td>
<td>cyclic voltammogram</td>
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<td>CVD</td>
<td>chemical vapor deposition</td>
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<tr>
<td>DEMS</td>
<td>differential electrochemical mass spectrometry</td>
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<td>DFT</td>
<td>density functional theory</td>
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<td>DMFC</td>
<td>direct methanol fuel cell</td>
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<tr>
<td>DOS</td>
<td>density of states</td>
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<td>EBSD</td>
<td>electron backscatter diffraction</td>
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<td>EC</td>
<td>electrochemical</td>
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<td>ECSA</td>
<td>electrochemical surface area</td>
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<td>E-R</td>
<td>Eley-Rideal</td>
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<tr>
<td>fcc</td>
<td>face centered cubic</td>
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<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
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<tr>
<td>HOR</td>
<td>hydrogen oxidation reaction</td>
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<tr>
<td>HER</td>
<td>hydrogen evolution reaction</td>
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<tr>
<td>hcp</td>
<td>hexagonal close packed</td>
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IV
<table>
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<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>H_{upd}</td>
<td>underpotential deposited hydrogen</td>
</tr>
<tr>
<td>IRAS</td>
<td>infrared absorption spectroscopy</td>
</tr>
<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>LEED</td>
<td>low energy electron diffraction</td>
</tr>
<tr>
<td>L-H</td>
<td>Langmuir-Hinshelwood</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer</td>
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<tr>
<td>MOR</td>
<td>methanol oxidation reaction</td>
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<tr>
<td>MSCV</td>
<td>mass spectrometric cyclic voltammogram</td>
</tr>
<tr>
<td>NC</td>
<td>nanocluster</td>
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<td>NP</td>
<td>nanoparticle</td>
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<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
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<tr>
<td>PEM</td>
<td>proton exchange membrane</td>
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<tr>
<td>PEMFC</td>
<td>proton exchange membrane fuel cell</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>QMS</td>
<td>quadrupol mass spectrometer</td>
</tr>
<tr>
<td>rds</td>
<td>rate determining step</td>
</tr>
<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
<td>SAC</td>
<td>single atom catalyst</td>
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<tr>
<td>SECM</td>
<td>scanning electrochemical microscopy</td>
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<tr>
<td>SEM</td>
<td>secondary electron multiplier</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunneling microscopy</td>
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<tr>
<td>TOF</td>
<td>turnover frequency</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>-------------</td>
<td>----------------------------------</td>
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<tr>
<td>TPD</td>
<td>temperature programmed desorption</td>
</tr>
<tr>
<td>UHV</td>
<td>ultrahigh vacuum</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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1 Introduction

In 2020 the Kyoto protocol climate agreement has been superseded by the Paris Agreement, which is signed by 195 nations and aims at reducing the global average temperature by 2 °C compared to the value prior to the period of industrialization\[1\]. The requirements to achieve this goal are on the one hand the reduction of global carbon dioxide emissions from 40 billion tons in 2020 to 5 billion tons in 2050\[2\]. Simultaneously, the fraction of renewable energy sources from the worldwide energy mix should double every 5 to 7 years in order to achieve a ‘carbon dioxide free’ energy mix in the energy sector by the year 2040 as illustrated in Figure 1.1\[2\]. This includes also the augmentation of solar and wind power systems, which constitute, together with hydropower energy, the most important renewable energy sources. The strong dependence of these primary energy sources on weather fluctuations demands, however, strategies to efficiently store and convert excess produced electric energy. In this context a very suitable method is the storage of electric energy in chemical bonds, \textit{e.g.}, in molecular hydrogen (H\(_2\)) or methanol (MeOH) as proposed within the frameworks of the so-called hydrogen economy\[3,4\] and the MeOH economy\[5\]. While MeOH can be obtained from biomass, methane or synthesis from CO\(_2\) and H\(_2\), molecular hydrogen is produced in electrolyzers, where electric energy is employed to split water into H\(_2\) and molecular oxygen (O\(_2\)). A prominent system among such electrolyzers is the proton exchange membrane (PEM) electrolyzer, which can operate at higher current densities than other electrolyzer technologies such as the state-of-the-art alkaline electrolyzers\[6\], and thus constitutes a technology for H\(_2\) production with an excellent performance. The PEM electrolyzer consists of two half cells separated by a proton permeable polymer membrane where one half cell is equipped with an anode catalyst material which electrocatalytically accelerates the formation of O\(_2\) and protons from water. Subsequently, the protons diffuse through the membrane into the second half cell, where they react to H\(_2\) at the cathode catalyst in the so-called hydrogen evolution reaction (HER).

The electric energy, which is stored in molecular energy carriers (H\(_2\), MeOH), can partly be recaptured by reversal of the operating principle of electrolyzers in fuel cell systems.
Accordingly, in fuel cells electric power is generated from the oxidation of H₂ (hydrogen oxidation reaction (HOR)) or MeOH (methanol oxidation reaction (MOR)) in one half cell, concomitant with the reduction of O₂ (oxygen reduction reaction (ORR)) from ambient air in the other half cell. Such generation of electric power from fuel cell systems is of special interest i) in the field of stationary applications, e.g., for emergency power systems, as well as ii) for electric mobility in cases of long distance transportation, e.g., in the shipping sector. Compared to other electric mobility solutions such as battery systems, which are more suitable for short distance transportation, the advantage of fuel cells are the higher energy density of the fuels and shorter fueling times[7]. The most prominent fuel cell type for transportation application is the proton exchange membrane fuel cell (PEMFC), which operates on gaseous H₂, usually compressed to 700 bar. Since the handling and long-term storage of H₂ is rather challenging, also alternatives such as the direct methanol fuel cell (DMFC), which is fueled with liquid MeOH, gained raising interest[8,9], also because the fueling infrastructure for liquid fuels already exists. However, a wide spread commercial availability of PEMFCs and DMFCs is hampered by the high production costs compared to internal-combustion engines[7]. For a large volume production of PEMFC stacks the catalyst material contributes significantly to the main costs[10]. Therefore, an attempt to save costs is to improve the catalyst activity which enables, e.g., to achieve similar or enhanced fuel cell performances with a reduced catalyst loading.

The state-of-the-art monometallic catalyst material used in PEM electrolyzers / fuel cells are carbon supported Pt nanoparticles (NPs), since among all transition metals Pt

![Figure 1.1](image-url): Global share of renewable energy sources from the overall global energy mix and its development over decades for different growth scenarios (From J. Rockström et al., *Science* **355**, 1269 (2017)[2]. Reprinted with permission from AAAS.).
exhibits the highest reactivity for the above mentioned electrocatalytic reactions. In DMFCs the carbon supported Pt NPs were superseded by bimetallic PtRu NPs as anode material, since the bimetallic combination exhibits a higher activity for the MOR and the electro-oxidation of carbon monoxide (CO). The latter reaction is relevant in DMFCs because CO is formed as reaction intermediate during the MOR and binds strongly to Pt. As a result CO blocks the Pt surface for adsorption of other reaction species which results in reduced performances of these systems.

An improvement of the catalyst performance can be achieved by the modification of shape, size or chemical composition of the Pt(Ru) NPs. To effectively improve the design of the catalyst materials in a way that they exhibit enhanced reactivities, it is beneficial to gain a fundamental understanding on the influence of specific structural parameters of the NPs on their electrocatalytic properties. This includes also the investigation of electronic and geometric effects which arise from changes in the structural properties due to i) the formation of local nanostructures or ii) modified compositions in the surface and the bulk of the catalyst material. The effects have to be investigated on an atomic scale level, since most catalytic reactions are structure-sensitive, which means that the catalyst activity is determined by the most active surface site. For instance, low coordination sites such as steps or kinks are often suggested to act as active centers for (electro-)catalytic reactions due to their different adsorption properties compared to higher coordination sites. Furthermore, the adsorption behavior and reactivity of Pt NPs is affected by introducing a guest metal in the bulk or at the surface of the NP which is rationalized by electronic effects and / or so-called ensemble effects, i.e., the formation of new adsorption sites at the surface. Additionally to these factors also varying the NP sizes can lead to different electronic properties: i) due to an increasing compressive strain with decreasing NP size, ii) changes in the equilibrium shapes of the NPs with decreasing NP size or iii) by approaching a size regime where the physicochemical properties of the NPs do not scale with the NP size any more, the so-called non-scalable regime.

A common approach to correlate NP structure and electrocatalytic activity is the systematic variation of macroscopic structural parameters, such as catalyst composition, structure, particle size, number of grains and grain boundaries, etc. However, from the complex three-dimensional NP structures it is rather complicated, if not impossible, to disentangle the different electronic / geometric effects or to identify the local electrocatalytic activity of a certain structural element at the surface, i.e., to derive an unambiguous structure-activity relationship. More detailed insights are accessible by em-
ploying two-dimensional model electrodes with lower complexity compared to their three-dimensional counterparts. For such 2D model catalysts it was already demonstrated that it is possible to visualize the local electrocatalytic activity of specific large scale surface structures such as grain boundaries or steps under reaction conditions, i.e., by in situ scanning tunneling microscopy (STM) or scanning electrochemical microscopy (SECM) in combination with electron backscatter diffraction (EBSD)\(^{40-43}\). Among 2D model electrodes single crystal based model systems are of special interest, since they allow for a systematic variation of surface nanostructures and additionally for comparison with computational data calculated on equally simple systems\(^{21,44-47}\). For instance, comparison of experimental electrocatalytic results with the electronic/adsorption properties obtained from theory offers valuable insights into the structure-activity relationship.

Single crystals for application in an electrochemical environment can be prepared under laboratory conditions, e.g., by flame annealing according to the method of Clavilier\(^48\). Laboratory conditions enable also surface nanostructuring, e.g., by electrodeposition of metals on the single crystal\(^49\). However, contaminants from the electrolyte solution and ambient air may hamper a controlled nucleation and growth of the metals under these conditions. Furthermore, the temperature window for surface nanostructuring is restricted to room temperature which reduces the amount of accessible nanostructures. A more versatile and controllable approach to obtain and systematically vary the amount of highly ordered and defined nanostructures, which are not accessible by other means, involves the preparation under ultrahigh vacuum (UHV) conditions\(^{50-55}\). UHV conditions enable also to use a variety of different surface science tools such as X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), STM etc., which allow for a detailed structural and chemical characterization of the 2D model electrodes. Among these tools, STM imaging is very powerful, since it allows for a direct visual inspection of the local surface structure, even at an atomic scale. Additionally, this technique provides the possibility to derive quantitative information on the abundance of specific nanostructures or atomic arrangements at the surface. Furthermore, for bimetallic systems STM imaging under UHV conditions allows to discriminate surface sites of different chemical composition on the atomic scale\(^{54,56,57}\) which is barely feasible under laboratory conditions.

In the present work nanostructured single crystals, which serve as 2D model electrodes for complex 3D NPs, were prepared under UHV conditions to study structure-activity relationships between structural parameters of 3D NPs and their activity for fuel cell
relevant electrocatalytic reactions. A specific structural parameter of interest was varied systematically at the surface of the nanostructured single crystals. STM imaging under UHV conditions enabled a direct visual control over the quality of the model electrode surfaces and provided quantitative information on the abundance of the specific structural parameter. Electrochemical /-catalytic measurements were performed on the electrodes in a newly designed electrochemical flow cell set-up. Comparing the reactivity of the electrodes with the abundance of the respective structural parameter allowed to derive an unambiguous structure-activity relationship. The structural integrity of the model electrodes was controlled by STM imaging under UHV conditions subsequent to the electrocatalytic measurements to avoid misinterpretations due to a possible restructuring of the electrode surface. Comparing the experimental results with previously reported theoretical studies on structural, chemical and electronic properties of respective 2D model systems helped for a stringent correlation between surface structure and activity.

Outline

This thesis is organized as follows. Chapter 2 provides an overview about the nanostructured model electrodes and electrocatalytic reactions investigated in this work. Furthermore, it briefly introduces the motivation to derive information about specific structure-activity relationships between certain structural parameters and electrocatalytic reactions. In Chapter 3, first general nucleation and growth concepts are addressed in Section 3.1, with focus on the preparation of nanostructured 2D model electrodes that are relevant for this work. The Sections 3.2-3.4 focus on general concepts related to the electronic / geometric properties of (bi)metallic catalysts and heterogeneous reaction mechanisms. Chapter 4 discusses in more detail the structure-activity relationships between certain structural parameters and electrocatalytic reactions relevant for this thesis. This includes the state-of-the-art knowledge on structure-activity relations and unresolved issues which are addressed in this work. The experimental set-up, the preparation procedure as well as the procedure for structural and electrochemical /-catalytic characterization of the model electrodes are described in Chapter 5. Chapter 6 presents publications listing me as first author, which present and discuss in detail new experimental results providing new insights into structure-activity relationships in electrocatalysis. Further publications listing me as co-author are the References\textsuperscript{[53,58]}. Finally, a summary of the key findings and their scientific value are presented in Chapter 7.
2 Objective

This thesis particularly aims at gaining new fundamental insights into structure-activity relationships of Pt based NPs in fuel cell relevant electrocatalytic reactions. Such information is basis for a rational design of catalyst materials with improved catalytic activity and can be gained from suitable model catalysts. Figure 2.1 schematically illustrates complex NP structures (top row) and the respective 2D model surfaces (bottom row) with specific structural features that are relevant for the discussion in this thesis. They include i) NP sizes, ii) surface defect sites (step and kink sites), iii) the surface composition of NPs, and iv) the shell thickness of core-shell NPs, which consist of a metal NP surrounded by a thin film of another metal.

![Figure 2.1:](image)

**Particle size effects:** The performance of commercially used Pt NPs for the HER can be significantly enhanced if the Pt particle size is reduced to sizes between a few...
nanometer and single Pt atoms. It was proposed from theory that in this size regime the HER activity depends on the Pt particle size in a so-called volcano-like relation, if the activity is defined as Pt-mass-specific HER rate. This means that there should exist an optimum Pt particle size which exhibits higher mass-specific HER rates than smaller and larger particles. While experimentally for Pt NPs with sizes above 2 nm such a relation could not be identified, there is a lack of systematic quantitative data in the Pt nanocluster (NC) size regime (< 2 nm). In the present work Pt NCs with sizes between 0.3 nm and 2.0 nm were grown on a Ru(0001) supported chemically inert graphene layer (Pt-gr/Ru(0001), see Figure 2.1e) under UHV conditions, to quantitatively investigate if a volcano-like relation is present in this NC size regime. This experimental approach enabled to form uniform NC arrays with narrow size distributions and sizes below 2.0 nm, which are barely accessible under normal laboratory conditions. After structural characterization of the Pt NCs by STM imaging, their HER activity was correlated with their mean average size. This systematic approach allowed for a quantitative determination of a possible particle size effect in the NC size regime. The HER activity of the Pt NCs was discussed within the scope of the current theoretical models for the HER on metal surfaces and was compared with state-of-the-art commercial carbon supported Pt NPs. This study constitutes the first systematic electrocatalytic investigation of metal NCs grown on a gr/metal template and should serve as stimulus for further research on technically accessible Pt NCs with sizes below 2 nm.

**Surface defect sites:** Although often considered as active sites for the CO electro-oxidation on Pt electrodes, the exact role of defect sites, such as Pt steps, in this reaction is still highly debated. To investigate the role of these sites in the CO electro-oxidation, in this thesis hexagonally shaped Pt islands were grown epitaxially on a Pt(111) single crystal under UHV conditions to increase the Pt step density (Pt/Pt(111), see Figure 2.1f). Furthermore, CO adsorption at the Pt steps was inhibited by modifying the ascending Pt step edges with a narrow Au rim. The resulting structures, which are commonly known as 2D Pt-core Au-shell islands (see also Section 3.1.4), are only accessible under UHV conditions so far and the combination of Pt and Au to form 2D core-shell islands on Pt(111) was employed for the first time in this thesis. The increased number of step sites for Pt/Pt(111) compared to Pt(111) as well as the selective modification of the Pt step sites with a narrow Au stripe was verified by cyclic voltammetry, CO-TPD and furthermore visually examined by STM imaging under UHV conditions. Such a detailed structural characterization of electrode surfaces
with different amount of step sites with and without the selective modification of the step sites by another metal is barely achievable by similar studies performed under laboratory conditions. CO electro-oxidation measurements were performed on the electrodes to elucidate the role of step sites under reaction conditions and the results are compared to the current understanding of these sites in literature. Note that prior to this thesis 2D core-shell systems were solely investigated with respect to structure formation in the framework of thermodynamic and kinetic nucleation and growth theories\cite{74–77}. The present study demonstrates the high potential of employing these structures to determine the electrocatalytic activity of surface defect sites.

**Surface composition – Ensemble effects:** It is widely accepted that mixed PtRu NPs exhibit higher activities for the CO electro-oxidation compared to pristine Pt NPs of similar size and shape. This is often ascribed to a synergistic bifunctional mechanism at neighboring Pt and Ru sites\cite{78}, which does, however, not take into account other electronic or geometric effects, although the latter were shown to modify the adsorption properties of adsorbates binding to PtRu surfaces\cite{79–86}. The role of electronic and geometric effects of PtRu electrodes beyond the bifunctional mechanism was addressed in this thesis for the CO electro-oxidation on \( \text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001) \) surface alloys which consist of a monolayer high \( \text{Pt}_x\text{Ru}_{1-x} \) alloy supported on a Ru(0001) single crystal (see Figure 2.1g). \( \text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001) \) electrodes with different surface compositions and thus different distribution of specific (mixed) atomic ensembles were prepared based on previous experimental reports\cite{87,88}. Comparing the reaction rates on these \( \text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001) \) electrodes for the CO electro-oxidation allowed to obtain insights in the role of geometric and electronic effects and to determine the most active \( \text{Pt}_n\text{Ru}_m \) ensembles at the surface. A similar study was already performed for the ORR on \( \text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001) \) electrodes\cite{89}. This thesis provides the first systematic investigation on the CO electro-oxidation on \( \text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001) \) surface alloys with different Pt contents.

**Vertical electronic and strain effects:** Ru-core Pt-shell NPs were shown previously to exhibit enhanced activities and a higher durability for/during the MOR and the CO electro-oxidation than pristine Pt NPs of similar size and shape\cite{90–98}. Since bimetallic sites are not present at the surface of these core-shell NPs, the improved properties are rationalized by the interaction of the Pt film with the Ru-core. The presence of such interactions was clearly demonstrated for Pt films grown pseudomorphically on a Ru(0001) single crystal (Pt\(_{X\text{-ML}}\)/Ru(0001)) (see Figure 2.1h) in gas phase\cite{99,100}, theoretical\cite{79,84,85} and electrochemical studies\cite{86}. This work demonstrates for the first
time that the theoretical concepts derived from these studies are transferable to an
electrocatalytic reaction, \textit{i.e.} the MOR, on the same type of model electrodes. The
activity of $\text{Pt}_{X\text{-ML}}$/Ru(0001) electrodes with different Pt film thickness was compared
with that of Pt(111) and correlated to the abundance of specific electronic effects in-
duced by Ru(0001). Additional information on the selectivity towards CO$_2$ formation
was gained from the detection of volatile species \textit{via} differential electrochemical mass
spectrometry (DEMS) measurements performed simultaneously to the electrochemcial
measurements.
3 General concepts

This Chapter provides a selected overview on concepts i) for the design of nanostructured bimetallic model electrode surfaces and ii) for the general description and interpretation of (electro)catalytic reactions on transition metal surfaces relevant for this work. Section 3.1 focuses on thermodynamic values and kinetic parameters that determine the nucleation and growth of nanostructures. In Section 3.2 electronic and geometric effects are discussed which are relevant for the understanding of adsorption processes on transition metals. The influence of adsorbate binding energies on transition metals for their electrocatalytic activity is discussed in Section 3.3. Finally, in Section 3.4 mechanisms for the heterogeneous reaction of two molecules on a metal surface are presented.

3.1 Nucleation and growth of nanostructured bimetallic model electrodes

This Section first focuses on basic concepts of nucleation and growth for the growth of a metal A on a substrate metal B. Subsequently, taking into account these concepts, examples for the design of nanostructured model electrodes relevant for this thesis are presented. In detail the focus lies on the growth of Pt NCs with different size on gr/Ru(0001), the modification of Ru(0001) single crystals by Pt and the preparation of metal supported 2D core-shell structures.

3.1.1 Basic concepts for nucleation and growth

Thermodynamic growth modes

Based on thermodynamic values, three different growth modes are distinguished for the growth of a metal A on another metal B as presented in Figure 3.1. These growth modes are (i) the Frank-van-der-Merwe growth (left column), which reflects a layer-by-layer growth of metal A on the substrate metal B, (ii) the Volmer-Weber growth (middle column), where 3D growth of metal A sets in on the substrate metal B before the
substrate is completely wetted by metal A, and (iii) the Stranski-Krastanov growth (right column), where metal A forms several or a single wetting layer on the metal substrate B, followed by 3D growth of metal A on this layer\cite{101-103}. Different thermodynamic growth modes can be rationalized by an optimization of the surface tension for the system, which depends on the surface and interface tensions $\gamma$ of both metals. A layer-by-layer growth (Frank-van-der-Merwe) is observed for

$$\gamma_B \geq \gamma_A + \gamma_I$$

(3.1)

where $\gamma_B$ and $\gamma_A$ denote the surface tensions of the substrate metal B and the guest metal A, respectively and $\gamma_I$ denotes the surface tension at the interface of metal A and metal B. Accordingly, isolated island growth (Volmer-Weber) is observed for

$$\gamma_B < \gamma_A + \gamma_I.$$  (3.2)

A Stranski-Krastanov growth is observed, if equation 3.1 is fulfilled for the first or first few layers, whereas with increasing film thickness equation 3.2 becomes dominant due to changes in the surface tensions\cite{102}.

Figure 3.1: Thermodynamic growth modes for the growth of a metal A (orange) on another metal B (blue).
Kinetically controlled growth

For metal film growth far from thermodynamic equilibrium the nucleation and growth of a metal A on a substrate metal B is determined by the kinetics of the microscopic processes on the surface during and after the evaporation of metal A as, reviewed in References \[104–106\]. The deposition of metal A on the substrate metal B proceeds with a specific evaporation rate $F$, which is defined as the number of metal atoms hitting the surface per unit cell and second$^{[105]}$. As soon as an atom of metal A reaches the surface of metal B it either sticks directly to the site where it hits the substrate or diffuses isotropically along the surface$^{[104–106]}$. Additionally, desorption or interdiffusion processes might appear where metal A desorbs from B or segregates into the bulk of metal B, respectively$^{[104–106]}$. For the present study desorption processes are not considered, since the thermal energy in the experiments is too low to activate metal desorption.

The diffusion rate for metal adatoms migrating on the substrate surface depends on the diffusion coefficient $D$. This coefficient is defined as the number of sites/unit cells visited by an adatom per unit time and is given by the following expression$^{[105]}$:

$$D = D_0 \cdot \exp \left\{ - \frac{E_D}{k_B T} \right\}.$$  \hspace{1cm} (3.3)

In this equation $E_D$ denotes the diffusion barrier, $D_0$ is a diffusion prefactor which includes the attempt frequency to overcome the diffusion barrier, $k_B$ is the Boltzmann constant and $T$ is the substrate temperature. The motion of a mobile adatom continues along the surface until it is stabilized either (i) by forming a nucleation center with another diffusing adatom or (ii) by attaching at an immobile low coordination site such as a step, kink or vacancy, which are in this case also called trap sites. The distance covered by an adatom prior to its stabilization at the surface is defined as mean free path of diffusion $\lambda_M$, which depends, in a simplified picture, on the diffusion rate $D$ as well as on the deposition rate $F$ in a power law relation$^{[105,107]}$:

$$\lambda_M \approx \left( \frac{D}{F} \right)^{1/6}. \hspace{1cm} (3.4)$$

According to equation 3.4, a small $\lambda_M$ – which is equivalent to a high nucleation probability if desorption is neglected – is achieved for low diffusion rates and/or high deposition rates (and vice versa). Since the nucleation probability strongly affects the metal island nucleation and growth behavior, $D$ and $F$ are thus key parameters that determine the island density. Furthermore, the diffusion rate for a specific system can be varied by changing the temperature, as evident from equation 3.3.
Another relevant parameter is the evaporation duration $t_{\text{evap}}$, since it determines – at constant $F$ – the total amount of metal A deposited on the substrate metal B. Examples for nanostructured surfaces relevant for the present work are presented in the following, also discussing the influence of the above described parameters, i.e., $F$, $t_{\text{evap}}$ and $T$, on the surface structure.

### 3.1.2 Pt NCs supported on gr/Ru(0001)

Graphene supported on a transition metal (gr/metal) can be employed as template for the growth of metal NC arrays with NCs of controlled size, as reviewed in detail in Reference[51]. Suitable templates are gr/Cu(111)[108,109], gr/Rh(111)[110], gr/Ir(111)[111,112] and gr/Ru(0001)[113–122]. For gr/Ru(0001) the nucleation and growth behavior of NCs was studied previously for Ru[120], Rh[117], Pd[117] and Pt[113,114,119,120,122] NCs. Since Section 6.1 focuses on the electrocatalytic properties of Pt NCs supported on gr/Ru(0001), only the properties of gr/Ru(0001) and the nucleation and growth behavior of Pt on this template are discussed in the following.

For gr/Ru(0001) the large lattice mismatch between graphene ($a_{\text{gr}} = 2.46\,\text{Å}$[123,124]) and Ru(0001) ($a_{\text{Ru}} = 2.71\,\text{Å}$[123]) leads to a periodic corrugation of the graphene layer apparent as Moiré pattern[123–125] with a $(25 \times 25)\text{C}/(23 \times 23)\text{Ru}(0001)$ superstructure consisting of four almost identical $(12.5 \times 12.5)\text{C}/(11.5 \times 11.5)\text{Ru}(0001)$ subunits[126,127]. The vertical corrugation of the graphene layer is $\Delta h = 1.5\,\text{Å}$[123,128] and the $(12.5 \times 12.5)\text{C}/(11.5 \times 11.5)\text{Ru}(0001)$ Moiré unit cell spans an area of $30\,\text{Å} \times 30\,\text{Å}$[123,128,129]. A high-resolution STM image of gr/Ru(0001) is shown in Figure 3.2a, where the Moiré unit cell is labeled by a blue rhombus. Three different regions are discernable as labeled by $\alpha$, $\beta$ and $\gamma$. The carbon atoms in the $\gamma$ regions interact only via van der Waals forces with Ru(0001). Therefore, these carbon atoms appear topographically higher than those in the $\alpha$ and $\beta$ region, where every second carbon atom forms a covalent-like bond with the substrate[128]. Furthermore, different types of hollow site adsorption of the carbon atoms in the $\alpha$ (fcc) and $\beta$ (hcp) regions result in different electronic interactions with the underlying Ru atoms and thus in higher electron densities in the $\alpha$ region[128].

As displayed by a blue triangle in the STM image of a Pt-gr/Ru(0001) surface in Figure 3.2b, Pt atoms nucleate preferentially in the $\alpha$ region and form a single Pt NC per $\alpha$ site due to the higher density of states (DOS) in this region[113,114,120]. For gr/Ru(0001) the periodicity of the Moiré pattern, the corrugation as well as the strong electronic interactions between carbon and Ru are thus very suitable for a controlled growth of
3.1 Nucleation and growth of nanostructured bimetallic model electrodes

![Figure 3.2](image.png)

**Figure 3.2:** (a) High-resolution STM image of gr/Ru(0001) (9 nm x 9 nm, $I_T = 63$ nA, $U_T = -70$ mV). The regions labeled with $\alpha$ and $\beta$ are topographically lower than the region labeled with $\gamma$. The different apparent heights in the $\alpha$ and $\beta$ regions are due to adsorption at face centered cubic (fcc) and hexagonal close packed (hcp) Ru(0001) sites, in the respective regions. (b) STM image of a Pt-gr/Ru(0001) sample (25 nm x 25 nm, $I_T = 89$ pA, $U_T = 1.75$ V). The Pt NCs preferentially nucleate in the $\alpha$ regions as indicated by the blue triangle.

A periodic Pt NC array$^{[51,113,114,120]}$. As described in Section 3.1.1, the nucleation and growth behavior of Pt NCs on gr/Ru(0001) should depend on the evaporation rate and the diffusion rate of Pt on the surface. For this system it was, however, shown that for deposition rates between 0.005 ML min$^{-1}$ and 0.012 ML min$^{-1}$ the nucleation probability is not affected by the evaporation rate but solely by surface diffusion of Pt$^{[116]}$. The diffusion barrier for Pt on gr/Ru(0001) is higher than on other gr/metal templates due to the strong corrugation of the graphene layer$^{[51]}$ and a strong C–Pt bond at the $\alpha$ sites$^{[117,120,122]}$ ($E_{ads} = -2.8$ eV$^{[119]}$). The high diffusion barriers in these regions result in a high nucleation probability for Pt adatoms. As a result the amount of $\alpha$ regions occupied with Pt NCs increases if the amount of Pt deposited increases$^{[113,114,120]}$. At a certain critical Pt amount the NC density is, however, saturated and 3D growth of existing NCs sets in$^{[113,117,120,122]}$. At room temperature the occupation of $\alpha$ sites by Pt NCs saturates at ca. 30%$^{[120]}$. A higher occupation (up to 100%) is obtained for the growth at sample temperatures between 120 K and 140 K$^{[114]}$ due to the lower diffusion rate (see equation 3.3). Ripening of the NCs was observed between 450 K and 920 K.
leading to large Pt NCs and a low NC density\textsuperscript{[116]}. This was suggested to proceed \textit{via} Smoluchowski ripening, where entire NCs diffuse along the surface and coalesce with other NCs\textsuperscript{[116]}.

Based on this knowledge, it is possible to prepare Pt NCs with uniform sizes below 2 nm on gr/Ru(0001)\textsuperscript{[113,114,116,120]}, where the Pt NC size and density on gr/Ru(0001) can be tuned by varying the Pt coverage\textsuperscript{[113,116]} as well as the sample temperature\textsuperscript{[114,116]}. This will be employed to investigate size effects of gr/Ru(0001) supported Pt NCs with sizes below 2 nm for the HER activity in Section 6.1.

### 3.1.3 Pt modified Ru(0001)

The influence of the sample temperature during deposition of Pt on a Ru(0001) single crystal is displayed in Figure 3.3. Figure 3.3a shows a representative STM image of a Ru(0001) surface with Pt islands deposited at room temperature. At this temperature the diffusion rate of Pt adatoms along the island edges is low, resulting in the formation of small dendritic pseudomorphic grown Pt islands\textsuperscript{[130,131]}. For temperatures between $T = 600$ K - 730 K diffusion along the island edges is facilitated and a thermodynamically more favorable hexagonal arrangement of the Pt islands is observed as shown in Figure 3.3b and described in more detail in References\textsuperscript{[130,131]}.

**Figure 3.3:** STM images of (a) small dendritic Pt islands grown on Ru(0001) at room temperature (130 nm x 130 nm, $I_T = 1.8$ nA, $U_T = 0.4$ V) and (b) compact hexagonal Pt islands on Ru(0001) formed by subsequent annealing of the sample in a) to 600 K-730 K (130 nm x 130 nm, $I_T = 0.4$ nA, $U_T = 0.8$ V). (c) Upper panel: Schematic illustration of the surface shown in b) as top view (left) and side view (right). Lower panel: Schematic illustration of a Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloy formed by annealing a Pt island modified Ru(0001) sample to 750 K - 1350 K, shown as top view (left) and side view (right).

At temperatures above 750 K vertical exchange processes of Pt island atoms and Ru atoms of the topmost Ru(0001) layer are activated\textsuperscript{[87,88]}, as schematically illustrated in
3.1 Nucleation and growth of nanostructured bimetallic model electrodes

Figure 3.3c (STM images are shown in Section 5.2.2). This results in a Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloy where the Pt$_x$Ru$_{1-x}$ alloy is confined to the topmost surface layer with a random distribution of the surface atoms. Segregation of Pt atoms into the Ru(0001) bulk is negligible for Pt coverages $\theta_{Pt} < 0.80$ monolayer (ML) and temperatures up to 1350 K. This is ascribed to the high energy barrier for diffusion of Pt into the Ru(0001) bulk. For a more detailed structural analysis of the Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys and surface alloys in general the reader is referred to References [87,88,133]. Deposition of Pt on Ru(0001) at sample temperatures between 600 K and 680 K with low evaporation rates and long evaporation duration leads to the growth of a multilayer thick pseudomorphic Pt film, as described previously and shown in Sections 5.2.2 and 6.4. The morphology of the resulting Pt films points to a Frank-van-der-Merwe growth mode (see Section 3.1.1) under these conditions, in agreement with the lower surface energy of the (111) facet of Pt ($\gamma_{Pt} = 1.00$ eV atom$^{-1}$) compared to Ru(0001) ($\gamma_{Ru} = 1.57$ eV atom$^{-1}$). Due to different lattice constants of Pt(111) (next neighbor distance $NN_{Pt} = 2.77$ Å) and Ru(0001) ($NN_{Ru} = 2.70$ Å), the pseudomorphic grown Pt film is laterally compressed by 2.5% compared to a Pt(111) single crystal plane. This compressive strain is present for Pt films with a thickness up to 7 MLs. For Pt films of 8 ML thickness and above the surface starts to relax, which is apparent from the formation of dislocation patterns on the surface as it was observed by STM.

3.1.4 2D core-shell structures

2D core-shell structures are compact metal islands with edges modified by a guest metal rim. A schematic illustration is given in Figure 3.4, where islands consisting of metal B are supported on a metal A and are modified by a narrow rim of a metal C.

**Figure 3.4:** Schematic illustration of 2D core-shell structures supported on a metal A.

For a controlled growth of 2D core-shell islands, interlayer diffusion of metal C into the island core or into the substrate have to be avoided. Thus, during deposition of metal C
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the sample temperature should be below the respective surface alloy formation temperatures. On the other hand the sample temperature should be sufficiently high to avoid nucleation of new islands of metal C in between or on top of the core islands. The latter process is also determined by the Ehrlich-Schwoebel barrier for adatoms of metal C that hit the surface on top of the core islands and descend across the island edge. Furthermore, a reduced nucleation probability is achieved by deposition of metal C at low evaporation rates (see equation). Accordingly, the preparation of 2D core-shell structures is rather demanding and has so far only been studied for a limited number of systems such as Co-core Cu-shell islands supported on Ru(0001) (Cu@Co/Ru(0001)), Co@Pt/Pt(111), Ni@Al/Ru(0001) and Au@Pt/Ru(0001).

3.2 Electronic and geometric effects in adsorption processes

3.2.1 The d-band model

The influence of electronic and geometric effects on the adsorption properties of transition metals can be rationalized by the d-band model, which was first introduced by Hammer and Nørskov. In this model the coupling of the electronic states of an adsorbate with the d-band of the metal leads to the formation of bonding and antibonding adsorbate-metal d-states. While the coupling with a narrow d-band results in a distinct split-off of the bonding and antibonding states, the split-off is less pronounced for the coupling with a comparably broader d-band (see also Figure 3.5). For simplification, the d-band is characterized by its d-band center \( \varepsilon_d \), which is determined by the d-band filling and its width. Assuming a constant d-band filling the \( \varepsilon_d \) of a narrow d-band is thus higher in energy and closer to the Fermi level \( \varepsilon_F \) than the \( \varepsilon_d \) of a broader d-band (see also Figure 3.5). Hence, if the \( \varepsilon_d \) of a metal is high in energy (narrow d-band) there is a distinct split-off of the bonding and antibonding adsorbate-metal d-states and the antibonding states are likely to be above \( \varepsilon_F \). These antibonding states above \( \varepsilon_F \) are unoccupied which leads to a stabilized adsorption on the metal surface. On the other hand if the \( \varepsilon_d \) is located at lower energies (broad d-band), the antibonding adsorbate-metal d-states are likely to be below \( \varepsilon_F \) and get filled with electrons, which leads to a destabilized adsorption. Following this model, the energy level of the \( \varepsilon_d \) can be employed as a measure to describe the affinity of metals to bind adsorbates at the surface, where the adsorbates bind stronger to metals with an energetically high \( \varepsilon_d \) than to metals with
an energetically lower $\varepsilon_d^{[32]}$. Two main effects that determine the location of the $d$-band center of mixed metals, namely electronic strain and ligand effects, are briefly introduced in the following subsections.

### 3.2.2 Electronic strain effects

A guest metal A experiences strain if it is grown pseudomorphically on a metal substrate B which has a different lattice constant. In the case where the lattice constant of the guest metal A is larger (smaller) the metal A is under compressive (tensile) strain. This has a direct impact on the adsorption properties which are modified according to the $d$-band model $^{[26,32,79,81–86,99,100,136]}$. The modification of the adsorption strength of adsorbates at the metal surface can theoretically be described by the energetic shift $\delta \varepsilon_d$ of the $\varepsilon_d$. This is illustrated in Figure 3.5, where the red and green areas represent occupied metal $d$-states. Figure 3.5a shows the influence of compressive strain on $\varepsilon_d$, where the initial state is shown left. Compression of the metal lattice leads to a stronger overlap of the metal wave functions. As a result the $d$-band becomes broader (middle) $^{[32,136]}$. In order to maintain the filling of the $d$-band, $\varepsilon_d$ shifts down in energy by $\delta \varepsilon_d$. As described in Section 3.2.1 the downshift of $\varepsilon_d$ and the concomitant broadening of the $d$-band lead to a less pronounced split-off of the bonding and antibonding adsorbate-metal $d$-states which are illustrated in blue in Figure 3.5. The smaller amount of antibonding adsorbate-metal $d$-states above $\varepsilon_F$ finally results in a lower affinity to bind adsorbates $^{[26,32,136]}$. Accordingly, as illustrated in Figure 3.5b, for tensile strain the reduced overlap of the metal wave functions leads to an upshift of $\varepsilon_d$ by $\delta \varepsilon_d$ concomitant with a narrowing of the $d$-band. This results in a more distinct split-off of the adsorbate-metal $d$-states and thus to a higher affinity for adsorption $^{[26,32,136]}$. The effect of surface strain on the adsorption / electrocatalytic properties of bimetallic systems is addressed in Sections 6.3 and 6.4 for $\text{Pt}_{X-ML}/\text{Ru}(0001)$ and $\text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001)$ electrodes, respectively.

### 3.2.3 Electronic ligand effects

Electronic ligand effects result from electronic interactions between two different metals. Depending on their electron affinity the interaction of the two metals leads to a reduced / increased overlap of their wave functions $^{[32,136]}$. As described above, this leads to a narrowing / broadening of the $d$-band and thus to an upshift / downshift of $\varepsilon_d$. The adsorption properties of the individual transition metals are then modified according to the $d$-band model $^{[32,79,81–86,99,100,136]}$. **Vertical electronic ligand effects** describe the
3 General concepts

Figure 3.5: Energetic modifications of the transition metal $d$-band due to (a) compressive strain and (b) tensile strain. The adsorbate-metal $d$-states resulting from adsorption of a molecule on a metal with respective $d$-bands are shown schematically in blue. $\varepsilon_d$ denotes the $d$-band center, $\varepsilon_F$ the Fermi level and $\delta\varepsilon_d$ the shift of $\varepsilon_d$ due to the respective strain as described in the main text.

electronic modification of a surface metal A by a subsurface metal B. It was shown that the influence of this effect decreases with increasing film thickness of metal A $^{[79,84,85]}$. Lateral electronic ligand effects are present at surfaces consisting of two different metals A and B, i.e., in an alloy or a surface alloy $^{[82,87]}$. Here, the electronic modifications are determined by the surface composition, i.e., by the type and amount of next nearest neighbor atoms. The impact of vertical ligand effects on adsorption/electrocatalytic properties is discussed for Pt$_{X}$-ML/Ru(0001) electrodes in Section 6.4, while the role of both electronic effects is discussed for Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes in Section 6.3.

3.2.4 Ensemble effects

The adsorption of a molecule often demands for surface sites with specific geometry, e.g., ensembles with a defined number of atoms $^{[24,29,137]}$. A high abundance of such ensembles with beneficial adsorption geometries on an electrode surface may thus lead to high reaction rates for catalytic reactions. For instance, the formation of CO$_2$ via adsorbed CO during the methanol oxidation on Pt(111) was claimed to require at least three adjacent Pt atoms $^{[138-140]}$. The presence of two different metals in the surface of bimetallic systems further complicate a discrimination of geometric ensemble effects and lateral electronic ligand effects, since changing the chemical composition of an ensemble might not only affect the electronic properties of the atoms in the ensemble, but also the preferential adsorption site of adsorbates at the ensemble. Ensemble effects are discussed in more detail for the CO electro-oxidation on Pt$_x$Ru$_{1-x}$/Ru(0001) surfaces in Section 6.3.
3.3 Binding energy as descriptor for the (electro-)catalytic activity

(Electro-)catalytic reactions on metal surfaces involve the adsorption, dissociation, diffusion, recombination and desorption of reaction species. High reaction rates are achieved if all these processes are fast. In general, this is, however, not the case, since the overall reactivity strongly depends on the binding energies of the adsorbates. For example, if the adsorbate binding energies are too low, the dissociation or the adsorption of reactants on metal surfaces is hampered. On the other hand, if the species bind too strong on the metal surface, the sites are blocked for other surface processes. A high reactivity is thus provided by metal surfaces which contain adsorption sites that bind adsorbates neither too strong nor too weak, which is commonly known as the Sabatier principle\(^\text{[141]}\).

In other words, there exists an ideal intermediate binding energy of reaction species on metal surfaces which leads to a maximum in activity for the respective reaction. Accordingly, if the reactivity for a specific reaction that follows the Sabatier relation is mapped for the transition metals through the periodic table of elements, one obtains a volcano-like dependence between the activity and the binding energy of reaction species due to the steadily increasing binding energy on the elements\(^\text{[11,63,142–146]}\). Based on this simplified relation the binding energy of a specific reaction species is often used as a single descriptor to classify the activity of catalyst materials\(^\text{[143]}\).

A volcano-like dependence of the reactivity on the binding energy is illustrated exemplary for the HER on different (bi)metallic systems in Figure 3.6. Here the rate of the HER is given by the exchange current density \(j_0\), which is defined as the current density in the electrochemical equilibrium\(^\text{[147,148]}\). The \(j_0\) is plotted as a function of the free energy of the adsorbed hydrogen (\(H_{ad}\)) intermediate on the metal surface (\(\Delta G_{H_{ad}}\)) which is linearly correlated with the hydrogen binding energy\(^\text{[143]}\). Accordingly, Figure 3.6 demonstrates that under equilibrium conditions the rate for the HER should be maximum if the free energy of \(H_{ad}\) on the catalyst surface reaches \(\Delta G_{H_{ad}} = 0\text{ eV}\), i.e., if the reaction is thermo-neutral\(^\text{[143,144]}\). The (bi)metallic systems with \(\Delta G_{H_{ad}} > 0\text{ eV}\) (right branch of the volcano) in Figure 3.6 bind hydrogen too weakly which results in reduced activities. (Bi)metallic systems with \(\Delta G_{H_{ad}} < 0\text{ eV}\) (left branch) exhibit also reduced performances because they bind hydrogen too strong. Among the monometallic systems polycrystalline Pt is the most active material for the HER. It is situated at the left branch of the volcano close to the maximum activity. To further improve the HER activity it would thus be necessary to slightly lower the binding energy of hydrogen on
the Pt surface or alternatively to find another (bi)metallic system which binds hydrogen less strongly. Similar volcano-shaped relations are reported for a large number of reactions, such as the CO electro-oxidation\textsuperscript{[149,150]}, the ORR\textsuperscript{[151,152]} or the MOR\textsuperscript{[153]}.

![Volcano plot for the hydrogen evolution reaction (HER) on different (bi)metallic transition metals under electrochemical equilibrium conditions. The highest activity ($\log(j_0)$) is obtained at the apex of the volcano-shaped curve where the free energy of H adsorption on the metal is $\Delta G_{H_{ad}} = 0 \text{ eV}$. For $\Delta G_{H_{ad}} < 0 \text{ eV} (\Delta G_{H_{ad}} > 0 \text{ eV})$ the hydrogen bond on the metal surface is too strong (weak) resulting in lower activities for the HER according to the Sabatier principle.](image)

**Figure 3.6:** Volcano plot for the hydrogen evolution reaction (HER) on different (bi)metallic transition metals under electrochemical equilibrium conditions. The highest activity ($\log(j_0)$) is obtained at the apex of the volcano-shaped curve where the free energy of H adsorption on the metal is $\Delta G_{H_{ad}} = 0 \text{ eV}$. For $\Delta G_{H_{ad}} < 0 \text{ eV} (\Delta G_{H_{ad}} > 0 \text{ eV})$ the hydrogen bond on the metal surface is too strong (weak) resulting in lower activities for the HER according to the Sabatier principle. (Reprinted by permission from Springer Nature Customer Service Center GmbH: Springer Nature, Nature Materials, “Computational high-throughput screening of electrocatalytic materials for hydrogen evolution”, J. Greeley et al. © 2006\textsuperscript{[144]}).

### 3.4 Bimolecular reactions on electrode surfaces

The most commonly discussed reaction mechanisms for (electro-)catalytic reactions are the Langmuir-Hinshelwood (L-H) mechanism and the Eley-Rideal (E-R) mechanism. Both mechanisms are described in detail in References \textsuperscript{[148,154]} and are illustrated schematically in Figure 3.7.

**Langmuir-Hinshelwood mechanism**

The L-H mechanism is illustrated schematically in Figure 3.7a. Two types of molecules (A and B) diffuse towards the electrode surface, where they both adsorb. The molecules may then diffuse on the surface or remain at the adsorption site. As soon as an adsorbed
3.4 Bimolecular reactions on electrode surfaces

molecule A is adjacent to an adsorbed molecule B, they react to a molecule P. Subsequently, P desorbs from the electrode surface. For this reaction mechanism it is thus crucial that free surface sites are accessible for both reaction partners and that the distance between these sites is smaller than the molecules mean free paths of diffusion on the catalyst surface.

**Eley-Rideal mechanism**

The E-R mechanism is shown in Figure 3.7b. Here only one molecule (here A) adsorbs on the electrode surface after diffusion from the electrolyte solution towards the electrode. Subsequently, molecule B diffuses towards the electrode, hits molecule A and forms an adsorption complex. The product P is formed and finally desorbs from the electrode surface. Thus, in contrast to the L-H mechanism only one reaction partner is adsorbed on the surface, while the other reaction partner does not require free surface sites.

Figure 3.7: Schematic illustrations of (a) the Langmuir-Hinshelwood (L-H) mechanism and (b) the Eley-Rideal (E-R) mechanism.
4 Structure-activity relationships of Pt based electrodes

For an unambiguous correlation between the surface structure of a (2D) model electrode and its electrocatalytic activity it is mandatory i) to be aware of the commonly accepted mechanism of the electrocatalytic reaction studied at this electrode, ii) to ascertain specific structural parameters which determine the activity for the reaction, iii) to systematically vary the abundance/amount of these specific structural parameters on the surface of nanostructured 2D model electrodes, iv) to structurally characterize the model electrodes both before and after the electrochemical treatment, v) to measure the reaction rates on the electrodes, and finally vi) to correlate the reaction rates with the abundance/amount of the specific structural parameters present at the electrode surface. This Chapter focuses on different electrocatalytic reactions relevant for this work and their mechanism on Pt. Furthermore, the activity of different electrode (surface) structures for these reactions are compared based on findings from previous studies. Prior, however, it is shown in Section 4.1 that cyclic voltammetry can be employed as a highly sensitive tool to determine the presence of specific nanostructures at an electrode surface. In Section 4.2 the HER mechanism on Pt is described as basis for the later discussion of particle size effects of Pt NCs in the HER. Section 4.3 introduces the mechanism of the CO electro-oxidation on Pt(111) and highlights the influence of Pt step sites and the presence of bimetallic PtRu sites on the reactivity of Pt electrodes. Finally, Section 4.4 presents the MOR mechanism on Pt and deals with the influence of the surface structure on the MOR activity for monometallic Pt and bimetallic PtRu electrodes.

4.1 Structural fingerprints in cyclic voltammograms

The shape of cyclic voltammograms (CVs) recorded on Pt electrodes is highly sensitive to the electrode surface orientation and local atomic scale nanostructures as described
in detail in Reference\textsuperscript{155}. This is shown exemplary in the following CVs for Pt(111) and stepped electrodes vicinal to Pt(111) which were all prepared by the so-called Clavilier method\textsuperscript{48}. Figure 4.1a shows the CV of a defect free Pt(111) single crystal in 0.5 M H\textsubscript{2}SO\textsubscript{4} reported by Clavilier et al.\textsuperscript{156}. Similar CVs of Pt(111) recorded in sulfuric acid can be found in the literature, including the first reports on well oriented Pt(111) electrodes by Clavilier et al.\textsuperscript{48,157,158}. The currents between 0.07 V and 0.33 V (highlighted blue in Figure 4.1a) are ascribed to hydrogen adsorption/desorption on Pt(111)\textsuperscript{158–162}. The features between 0.33 V and 0.58 V (highlighted red) result from sulfate adsorption/desorption\textsuperscript{158–162}, where the sharp spikes at 0.44 V are ascribed to a phase transition of the sulfate adlayer from a disordered phase at low potentials to an ordered phase at higher potentials\textsuperscript{160,163}. The small features around 0.70 V and 0.68 V result from sulfate desorption (adsorption) which is in competition to the adsorption (desorption) of hydroxyde\textsuperscript{164}.

Stepped electrodes vicinal to Pt(111), prepared by the Clavilier method\textsuperscript{48}, usually consist of 5 to 30 atoms wide (111) oriented terraces, which are interrupted by steps of a defined local orientation, i.e., along (110) or (100) orientations. Figures 4.1b and 4.1c demonstrate that the CV shape is sensitive on the defect density at the Pt(111) surface\textsuperscript{158}. The CV of Pt(111) is shown in the front of Figure 4.1b while CVs of stepped electrodes vicinal to Pt(111) with increasing density of step sites with local (110) orientation are displayed according to the green arrow. The actual surface orientation is given on the z-axis. With increasing amount of step sites a small peak appears at 0.12 V and grows in intensity\textsuperscript{158}. Furthermore, the peak at 0.44 V and the features around 0.70 V disappear. The peak at 0.12 V was ascribed to hydrogen adsorption/desorption at the step sites with local (110) orientation\textsuperscript{69,155,158,166–168}. Similar changes in the shape of CVs were observed, if the density of step sites with local (100) orientation increases, as depicted in Figure 4.1c\textsuperscript{165}. As a result of the differently oriented step sites a peak appears at 0.26 V\textsuperscript{165}, which was ascribed to hydrogen adsorption/desorption at steps with local (100) orientation\textsuperscript{165,168}.

More recently it was proposed that the additional peaks at 0.12 V and 0.26 V in the H\textsubscript{upd} region arise due to the displacement of hydrogen by an anion species (most likely O\textsubscript{ad} or OH\textsubscript{ad}) at the step sites\textsuperscript{169,170}. Note that regardless of the underlying adsorption process (hydrogen or anion adsorption), the appearance of these peaks in the H\textsubscript{upd} region reveals sensitively the presence of defect sites at the electrode surface.
4.2 Particle size effects in the hydrogen evolution reaction (HER)

4.2.1 Hydrogen evolution reaction on Pt

The mechanism of the HER on metal surfaces, which was first introduced by Parsons\cite{Parsons63} and Gerischer\cite{Gerischer71}, is presented in the equations 4.1-4.3 employing Pt as catalyst material. The reaction proceeds via a two-step mechanism, where in the first step a proton is discharged and adsorbs in form of atomic hydrogen on the Pt surface according to the Volmer step in equation 4.1. Subsequently, molecular hydrogen is formed either in
an E-R mechanism (Heyrovsky step, equation 4.2) or in a L-H mechanism (Tafel step, equation 4.3).

\[
\begin{align*}
Pt^* + H^+ + e^- & \rightleftharpoons Pt - H_{ad} \quad (Volmer) \quad (4.1) \\
Pt - H_{ad} + H^+ + e^- & \rightleftharpoons Pt^* + H_2 \quad (Heyrovsky) \quad (4.2) \\
2 Pt - H_{ad} & \rightleftharpoons 2 Pt^* + H_2 \quad (Tafel) \quad (4.3)
\end{align*}
\]

As discussed in Section 3.3 and illustrated in Figure 3.6, Pt is the most active monometallic catalyst material for the HER, however, even higher activities should be achieved if the binding strength of H$_{ad}$ on a (bi)metallic system was slightly reduced towards $\Delta G_{H_{ad}} = 0$ eV$^{[143,144]}$. Accordingly, enhanced HER rates were reported for bimetallic systems such as Bismuth-Platinum surface alloys which exhibit free energies for hydrogen adsorption close to $\Delta G_{H_{ad}} = 0$ eV$^{[144]}$.

For monometallic Pt catalysts it was shown that among the Miller low-index Pt(hkl) single crystals, Pt(110) exhibits the highest activity for the HER, followed by Pt(100) and the least active Pt(111)$^{[172,173]}$.

### 4.2.2 Particle size effects

It was shown previously that a variation of the Pt NP size has an influence on the activity for electrocatalytic reactions such as the ORR$^{[174–176]}$, the CO electro-oxidation$^{[176,177]}$ or the HOR$^{[178]}$. While decreasing the size of the NPs was found to reduce the activity for the ORR$^{[174–176]}$ and the HOR$^{[178]}$ it leads to enhanced reaction rates for the CO electro-oxidation$^{[176,177]}$. A size dependent electrocatalytic activity might be rationalized by an increasing amount of highly active surface sites with decreasing NP size as the equilibrium shape of NPs strongly depends on the NP size$^{[33]}$. For NPs which approach NC size, i.e., approximately 2 nm and smaller, another explanation for a size dependent activity might be that the so-called non-scalable regime is reached$^{[34–36]}$. In this regime the physicochemical properties of the NCs do not scale with the NC size any more, but fluctuate randomly with each atom that is removed from or added to the NC$^{[34–36]}$. Accordingly, the electrocatalytic activity of a NC could also change in an unpredictable manner when the NC size decreases. A size effect can furthermore be rationalized by the $d$-band model, introduced in Section 3.2.1. With decreasing particle size the lattice constant of the atoms in the NCs becomes smaller resulting in a downshift of the $d$-band center (see Section 3.2.2). Thus, it is expected that the binding strength of adsorbates
4.2 Particle size effects in the hydrogen evolution reaction (HER)

on the Pt surface atoms decreases with decreasing Pt NC size which should affect its catalytic behavior.

For the HER it was already shown that compared to state-of-the-art Pt NP catalysts a distinctly enhanced activity – as represented by the mass-specific reaction rate – can be achieved by reducing the Pt particle size to a few nanometer\(^{[59,60]}\) or to single atoms\(^{[61,62]}\). Employing a so-called single atom catalyst (SAC), where the catalyst consists of single Pt atoms, Ye et al. achieved, for instance, a 46 times higher Pt mass-specific activity compared to commercial Pt NPs\(^{[62]}\). The optimum Pt particle size for the HER could, however, not be identified so far although several studies attempted to get this information by comparing the HER activity of NPs/NCs with different sizes\(^{[64–67,179–181]}\). For the HER on Pt NPs, Tan et al. suggested from theoretical investigations a volcano-like relation between the mass-specific HER activity and Pt NP size, where a maximum in activity was proposed for NP sizes around 2.2 nm\(^{[64]}\). In the size regime above 2 nm a volcano-like relation could, however, not be identified experimentally. Instead, it was found that the Pt mass-specific activity increases monotonically with decreasing particle size\(^{[65–67]}\). In the NC size regime below 2 nm a volcano-like relation was claimed by Tsunoyama et al.\(^{[179]}\) and Neuberger et al.\(^{[181]}\). Tsunoyama et al. investigated the HER on four different Pt NCs consisting of 3, 15, 30 and 45 atoms, respectively and proposed an optimum in activity for Pt NCs consisting of 30 atoms (Pt\(_{30}\))\(^{[179]}\). However, the activity of Pt\(_{45}\) NCs was almost identical to that of Pt\(_{30}\) in their study, indicating rather a monotonic increase in activity with increasing NC size. Neuberger et al. compared the activity of Pt\(_1\), Pt\(_{10}\) and Pt\(_{13}\) NCs with that of a Pt NP with a diameter of 230 nm\(^{[181]}\). They found a volcano-like dependence with a maximum in activity for Pt\(_{13}\) NCs\(^{[181]}\). In this case, the lack of NCs larger than Pt\(_{13}\) inhibits, however, a quantitative identification of the optimum Pt NC size for the HER. The presence of a volcano-like relation in the NC size regime is thus still unclear and the identification of the optimum NC size for the HER is missing. Thus, further experimental studies are required, which focus on the HER on Pt NCs with different sizes below 2 nm supported on a chemically inert material. This is subject of the study presented in Section 6.1.
4.3 Pt steps and bimetallic PtRu sites in the CO electro-oxidation

The CO electro-oxidation is a two electron process with a standard equilibrium potential of $E^o = 0.1$ V vs. SHE\cite n{182}. Focusing on Pt(111) the CO electro-oxidation mechanism is described in Section 4.3.1, followed by the comparison of two different experimental methods to study the CO electro-oxidation, namely the 'bulk CO electro-oxidation' and the 'CO stripping' method in Section 4.3.2. Section 4.3.3 presents previous findings on the role of Pt step and Pt terrace sites in the CO electro-oxidation together with mechanistic implications. These Sections serve as basis to discuss the results presented in Section 6.2, where new insights into the role of Pt step sites for the CO electro-oxidation are obtained by a highly controllable new method, i.e., by performing the CO electro-oxidation on 2D core-shell model electrodes. Finally, in Section 4.3.4 the so-called bifunctional mechanism is introduced, describing the influence of bimetallic PtRu sites in the CO electro-oxidation. This is relevant for Section 6.3 which focuses on electronic and geometric effects beyond the bifunctional mechanism and on their impact for the reactivity of PtRu electrodes in the CO electro-oxidation.

4.3.1 CO electro-oxidation on Pt(111)

The CO electro-oxidation on Pt is an extensively studied electrocatalytic reaction and an overview can be obtained from References\cite n{17,183}. On Pt surfaces the reaction proceeds via a L-H mechanism with the formation of two electrons, as illustrated in the reaction equations 4.4 to 4.7, which were proposed by Gilman et al.\cite n{184}.

\begin{align}
Pt^* + CO_{(aq.)} & \rightleftharpoons Pt - CO_{ad} \quad (4.4) \\
Pt^* + H_2O_{(aq.)} & \rightleftharpoons Pt - OH_{ad} + H^+_{(aq.)} + e^- \quad (4.5) \\
Pt - CO_{ad} + Pt - OH_{ad} & \rightleftharpoons Pt - COOH_{ad} + Pt^* \quad (4.6) \\
Pt - COOH_{ad} & \rightleftharpoons Pt^* + CO_2_{(aq.)} + H^+_{(aq.)} + e^- \quad (4.7)
\end{align}

In a first step CO adsorbs at a free Pt site, which is denoted as Pt$^*$ (equation 4.4). An oxygen species, which is necessary to oxidize the adsorbed CO (CO$_{ad}$), is provided by water splitting at another Pt$^*$ site (equation 4.5). The CO$_{ad}$ and the oxygen species may then be either adsorbed at adjacent Pt$^*$ sites or diffuse along the surface until
both molecules reach adjacent Pt sites, where they form a carboxyl intermediate (equation 4.6) and react to CO₂ (equation 4.7). The adsorbed oxygen species might be either O_ad or OH_ad. Experimentally, the active oxygen species during the CO electro-oxidation was not determined so far, however, density functional theory (DFT) studies of the CO electro-oxidation on Pt(111) imply that it is the hydroxide species \[^{185,186}\]. Thus, in the present thesis only OH_ad will be considered for any mechanistic descriptions. According to the equations 4.4 and 4.5 the CO_ad and the H₂O_ad / OH_ad species are competing for free Pt sites. At low electrode potentials in acidic solution, the surface is blocked for water splitting by strongly binding CO_ad species and furthermore by anions from the electrolyte solution\[^{187}\]. Therefore, the CO oxidation is inhibited at potentials below 0.60 V\[^{16}\]. Around 0.60 V the onset potential for Pt-OH_ad formation in acidic solution is reached\[^{185}\]. The OH_ad species may then displace CO_ad or anion species at the Pt surface and the CO oxidation sets in at 0.60 V\[^{16}\]. From theoretical studies it was suggested that a COOH_ad species appears as an intermediate species during the reaction on Pt(111)\[^{186,188}\]. Furthermore, in an experimental attentuated total reflection (ATR)-Fourier-transform infrared spectroscopy (FTIR) study the observation of an absorption band between 1300 - 1500 cm\(^{-1}\) was attributed to the presence of this carboxyl species\[^{189}\]. Despite these studies, the presence of the COOH_ad during the CO electro-oxidation is still under debate. Theoretical calculations suggested that the coupling of CO_ad and OH_ad according to reaction 4.6 might be rate determining for the CO electro-oxidation as soon as the OH_ad concentration on the surface is sufficiently high to start the oxidation reaction\[^{186,190}\].

4.3.2 Bulk CO electro-oxidation and CO stripping

Common methods to study the CO electro-oxidation are (i) CO stripping, where a pre-adsorbed CO adlayer is oxidized in an electrolyte solution which is free of CO and (ii) bulk CO electro-oxidation, where the supporting electrolyte is saturated with CO. On Pt(111) the continuous CO supply from the electrolyte solution for the latter method leads to a densely packed CO adlayer on the surface with a p(2 x 2)-3 CO structure and a saturation coverage of \( \theta_{CO} = 0.75 \) ML\[^{16,191}\]. In CO stripping experiments the absence of CO in solution results in a less dense adlayer with a \((\sqrt{19} x \sqrt{19})R23.4^\circ -13 \) CO structure and a saturation coverage of \( \theta_{CO} = 0.68 \) ML\[^{16,191}\]. If CO is introduced at a constant potential below 0.60 V, a dense CO adlayer forms at the Pt(111) surface, where the density of the CO adlayer depends on the potential, the partial pressure of CO in the solution and the dwell time at the respective potential\[^{192}\]. Introducing CO at 0.05 V
for 5 min, for instance, leads to a saturated CO adlayer where the CO molecules feel repulsive interactions, resulting in a weakening of their binding strength to Pt(111)\cite{17,192}. However, if parts of the CO adlayer are oxidized, the remaining adlayer relaxes and stronger Pt-CO\textsubscript{ad} bonds are formed\cite{17}. As a result, in the first potentiodynamic cycle of CO oxidation experiments one observes a pre-oxidation peak prior to the main oxidation peak, where in the pre-oxidation peak weakly bound CO\textsubscript{ad} molecules are oxidized from the densely packed saturated CO adlayer, followed by the oxidation of more strongly bound CO\textsubscript{ad} in the main peak\cite{16,193,194}. The absence of the pre-oxidation peak in the subsequent polarization cycles might be explained by a dwell time at low potentials which is not sufficient to form a saturated CO adlayer. In order to avoid misinterpretations arising from varying saturation coverages it is thus convenient to compare the second polarization cycles of the CO electro-oxidation on different electrodes instead of the first cycles.

In CO stripping experiments on Pt(111) the main CO oxidation peak is located at around 0.80 V\cite{195-197}, while it is at ca. 0.94 V\cite{16} in the bulk CO electro-oxidation. The higher CO overpotential for the bulk CO electro-oxidation is rationalized by the denser CO adlayer that hampers water splitting on Pt(111). The potentiodynamic curves for CO stripping and bulk CO electro-oxidation on Pt(111) are shown and discussed in detail in the Sections 5.5.1, 6.2 and 6.3.

### 4.3.3 Step sites and terrace sites

The role of Pt step sites in the CO electro-oxidation on Pt(111) is heavily debated. While some groups proposed that CO\textsubscript{ad} molecules are mobile at the surface and that the reaction takes place solely at step sites\cite{68,69,71,198}, there are other groups suggesting that at high potentials also the terrace sites are active\cite{197} or that the CO\textsubscript{ad} molecules are immobile at the surface and Pt terrace sites are the active centers rather than steps\cite{72,73}. To highlight this discrepancy about the role of Pt step sites in the CO electro-oxidation, two contradictory examples are briefly discussed in the following including the role of CO\textsubscript{ad}.

As depicted in Figure 4.2a, CO\textsubscript{ad} stripping experiments on Pt(111) and stepped electrodes vicinal to Pt(111) demonstrated that an increasing Pt step density leads to a reduced overpotential for the CO\textsubscript{ad} oxidation, which is equivalent to an increase in activity\cite{68}. This observation was explained by the preferential adsorption / formation of OH species at step sites\cite{68} which should, according to a FTIR study, occur rather at the step trough than at the step edge\cite{199}. The mechanism derived from these observations is
4.3 Pt steps and bimetallic PtRu sites in the CO electro-oxidation

illustrated in Figure 4.2b. CO\textsubscript{ad} molecules adsorbed on the terrace sites adjacent to the step trough are oxidized by OH\textsubscript{ad} molecules which are adsorbed at the latter site\textsuperscript{[71]}. Subsequently, new OH\textsubscript{ad} molecules occupy the step trough and CO\textsubscript{ad} molecules diffuse from the terrace towards the step, where they get oxidized\textsuperscript{[71]}. This process proceeds until all CO\textsubscript{ad} molecules have diffused towards the step site. No reaction occurs at the terrace sites\textsuperscript{[68,199]}. According to this proposed mechanism the CO electro-oxidation demands for a high mobility of CO\textsubscript{ad} molecules on the (111) terraces. Indeed, a fast CO\textsubscript{ad} diffusion on Pt was verified in a time-resolved infrared absorption spectroscopy (IRAS) study by a broadening and a red shift of the IR band which corresponds to CO\textsubscript{ad} molecules adsorbed on terrace sites during the reaction\textsuperscript{[198]}. More recently, based on CO stripping experiments on stepped electrodes vicinal to Pt(111), which are shown in Figure 4.2c, Farias \textit{et al.} proposed that CO\textsubscript{ad} molecules adsorbed on terrace sites are immobile\textsuperscript{[72,73]}. In their experiments the potential was first swept to an upper potential limit where the CO adlayer is only partially oxidized. Afterwards, the potential was stepped to 0.10 V, followed by another sweep to a slightly higher upper potential limit. This process was repeated until all pre-adsorbed CO\textsubscript{ad} was oxidized. If the mobility of all CO\textsubscript{ad} molecules on the surface was high, one would expect diffusion of CO\textsubscript{ad} molecules towards the most active sites, resulting in oxidation peaks at similar potentials for each potential sweep\textsuperscript{[72]}. However, as shown in Figure 4.2c, Farias \textit{et al.} observed a hierarchical oxidation process with (i) a pre-oxidation peak related to weakly adsorbed CO\textsubscript{ad} in the first sweep, (ii) the oxidation of CO\textsubscript{ad} from terrace sites in the subsequent sweeps and (iii) the oxidation of CO\textsubscript{ad} adsorbed at step sites in the final sweep\textsuperscript{[72]}. The assignment of the three different peaks to the respective surface sites is based on the presence and shape of the H\textsuperscript{upd} region (see Reference\textsuperscript{[72]} for more details). From these observations they concluded that terrace sites are more active surface domains than step sites and that CO species adsorbed at step sites are only oxidized if the terrace sites are free of CO\textsubscript{ad}\textsuperscript{[72]}. Furthermore, they proposed that diffusion of CO\textsubscript{ad} from less active sites towards more active sites should be absent\textsuperscript{[72]}. This might be rationalized by increasing adsorption energies going from the weakly adsorbed CO\textsubscript{ad} species to CO adsorbed at terrace sites and CO adsorbed at step sites.
A possible reaction mechanism derived from these CO stripping experiments is depicted in Figure 4.2d. In a first step, an OH\textsubscript{ad} molecule adsorbs at a defect site and forces the CO\textsubscript{ad} molecule, which was bond to this site, towards the terrace site\textsuperscript{200}. The CO molecule feels repulsive interactions from adjacent CO\textsubscript{ad} molecules, becomes weakly bound and is oxidized by the OH\textsubscript{ad} molecule\textsuperscript{200}. Subsequently, the OH\textsubscript{ad} species is replaced by another OH\textsubscript{ad}. Then the next CO\textsubscript{ad} molecule adsorbed at the domain boundary of the CO\textsubscript{ad} and OH\textsubscript{ad} domains gets oxidized. This process continues until all
terrace sites are free of CO\textsubscript{ad}. Finally, the CO species adsorbed at step sites are oxidized. These two contradictory examples demonstrate that further information on the role of Pt step sites in the CO electro-oxidation is necessary which is provided in Section 6.2.

4.3.4 Bifunctional mechanism

As described in Section 4.3.1, the strong binding energy of CO\textsubscript{ad} on Pt hampers the formation of OH\textsubscript{ad} at potentials below 0.60 V. It was shown previously for several bimetallic combinations, such as Pt-Re\textsuperscript{[15]}, Pt-Sn\textsuperscript{[15]}, Pt-Mo\textsuperscript{[15,201]}, Pt-Au\textsuperscript{[202]}, and Pt-Ru\textsuperscript{[78,203,204]} that introducing a guest metal into the Pt surface can reduce the potential necessary to oxidize carbon-containing species like CO. Among these bimetallic combinations, PtRu is the most studied system due to its relevance in fuel cell technology\textsuperscript{[15]}. It was proposed that the oxophilic Ru sites provide OH\textsubscript{ad} species at lower potentials than Pt sites, which enables the oxidation of CO adsorbed at the Pt sites at lower potentials via a L-H type mechanism\textsuperscript{[78]}. This so-called bifunctional mechanism was first proposed by Watanabe and Motoo\textsuperscript{[78]}. Accordingly, the reaction equations 4.5 and 4.6 change to

\begin{equation}
Ru^* + H_2O\textsubscript{(aq.)} \rightleftharpoons Ru - OH\textsubscript{ad} + H^+\textsubscript{(aq.)} + e^- \tag{4.8}
\end{equation}

\begin{equation}
Pt - CO\textsubscript{ad} + Ru - OH\textsubscript{ad} \rightleftharpoons Pt - COOH\textsubscript{ad} + Ru^* \tag{4.9}
\end{equation}

The bifunctional mechanism suggests that a high abundance of adjacent Pt and Ru atoms at an electrode surface leads to high CO oxidation rates. Indeed, for the CO oxidation on sputtered and annealed PtRu bulk alloys a maximum in activity was found for a 1:1 ratio of Pt and Ru in both the bulk and the surface of the alloys\textsuperscript{[203,204]}. Performing the bulk CO electro-oxidation on Ru(0001) electrodes modified with monolayer high Pt islands (Pt\textsubscript{isl}/Ru(0001)), Hoster \textit{et al.}\textsuperscript{[205]} observed dramatically increasing reaction rates compared to Ru(0001) in a potential region between 0.55 V and 1.05 V. The enhanced activity was ascribed to a high abundance of adjacent Pt step sites (Pt\textsubscript{step}) and Ru terrace sites (Ru\textsubscript{terrace}) in agreement with the bifunctional mechanism\textsuperscript{[205]}. However, a further study, where I contributed as co-author\textsuperscript{[58]}, demonstrated by combined UHV-STM and CO electro-oxidation measurements that the activity of Pt\textsubscript{isl}/Ru(0001) in this potential region is independent of the number of adjacent Pt\textsubscript{step}, Ru\textsubscript{terrace} sites and that enhanced activities result from a potential induced restructuring of the electrode surface\textsuperscript{[58,206]}. This is illustrated in Figure 4.3a, where a Pt\textsubscript{isl}/Ru(0001) electrode which was cycled to an upper potential limit of 1.05 V exhibits a higher activity in the poten-
tial range between 0.55 V and 0.90 V than a Pt$_{isl}$/Ru(0001) electrode with an identical Pt coverage, which was cycled only to 0.90 V. Comparison of STM images recorded before the CO electro-oxidation (see Figure 4.3b) and after the reaction with an upper potential limit of 1.05 V (see Figure 4.3c) revealed a step flow corrosion of the Ru areas, concomitant with the formation of monolayer deep holes in the former Pt islands and 3D Pt cluster formation$^{[58,206]}$. As a result, the enhanced activities were ascribed to the presence of sites with undefined structure, which were formed upon cycling to 1.05 V.

Furthermore, it was observed that Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys are more active than Pt$_{isl}$/Ru(0001) electrodes with similar amount of Pt surface atoms, as illustrated in Figure 4.3a$^{[58,205,206]}$. These results indicate that for Pt modified Ru(0001) electrodes
in-plane adjacent Pt and Ru atoms in the surface layer may significantly enhance the activity for the CO electro-oxidation, whereas Pt\textsubscript{step}Ru\textsubscript{terrace} sites are less active.

The influence of varying amounts of in-plane PtRu sites at the surface of Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) electrodes on their activity for the bulk CO electro-oxidation was not investigated prior to this thesis. This, as well as the assets and limitations of the bifunctional mechanism, are therefore addressed in Section 6.3.

### 4.4 Methanol oxidation reaction on Pt

The MOR on Pt is a multistep reaction which was reviewed in various References\[8,12,207]\. The reaction from MeOH to CO\textsubscript{2} has a standard equilibrium potential of $E^\circ = 0.02$ V vs. SHE and includes the transfer of six electrons in total. A scheme of the MOR on Pt is illustrated in Figure 4.4, revealing the complexity of this electrocatalytic reaction.

In a first step MeOH adsorbs at the Pt surface (step (1)). Theoretical studies proposed that MeOH adsorption is thermodynamically favored in the presence of adsorbed water species\[208,209]\. Furthermore, experimentally it was demonstrated that adsorbed hydrogen species hamper the MeOH adsorption, since MeOH is not able to displace H\textsubscript{ad} from Pt\[210,211]\. Subsequent to the adsorption of MeOH, its oxidation follows a sequence of C-H and O-H bond making and breaking processes\[209,210]\. While under UHV conditions the breaking of the O-H bond in MeOH was reported to be the first dehydrogenation step\[212,213]\, in electrochemical environment the dehydrogenation process was shown to begin with C-H bond breaking\[209,214]\. For the subsequent formation of CO\textsubscript{2} it is commonly accepted that there are two reaction pathways, namely i) an indirect pathway through an adsorbed CO molecule (2) and ii) a direct pathway involving formic acid (HCOOH\textsubscript{ad}) or formaldehyde (HCHO\textsubscript{ad}) (3). The latter two species are formed in a sequence of reactions involving the formation of two and four electrons, respectively\[12,215,216]\. Compared to CO\textsubscript{ad}, the molecules formed in the direct pathway are less strongly bonded and thus may desorb from the electrode surface without further reaction (4). This would lead to performance losses of the electrode due to the lower amount of electrons transferred. However, these species may also react to CO\textsubscript{2} directly (5) or via formation of CO\textsubscript{ad} (6), following the indirect pathway. The presence of formic acid during the MOR was observed by in-situ FTIR\[217]\ and mass spectrometry\[218,219]\ measurements. In the mass spectrometry measurements formic acid was detected in form of methylformate ($m/z = 60$) which is formed in electrolyte solution by reaction of formic acid and MeOH\[218]\. Formaldehyde could not be detected by mass
spectrometry so far due to the overlapping fragment masses of formaldehyde, MeOH and CO. However, besides in-situ FTIR\cite{217} measurements also colorimetric\cite{220} and fluorescence\cite{221} experiments indicated the presence of this species during the MOR. The direct pathway through the reactions $3$ and ($5$) was evidenced by Cuesta et al. who observed the formation of CO$_2$ during the MOR on a Pt(111) electrode which was blocked for CO$_{ad}$ formation by adsorbed cyanide\cite{139}. Finally, the adsorbed CO$_2$ desorbs from the electrode surface into the electrolyte solution ($7$), as evidenced by in-situ FTIR\cite{217} and mass spectrometry\cite{218,219} measurements. The last reaction step, i.e., the formation of CO$_2$ was suggested to be the rate determining step (rds) of the MOR at potentials between 0.40 V and 0.70 V\cite{210,222}. It is, however, under debate, whether the rate limiting elementary step proceeds via i) the reaction of CO$_{ad}$ and OH$_{ad}$\cite{210,214} or ii) the dehydrogenation of COOH$_{ad}$ or HCOO$_{ad}$\cite{209} towards CO$_2$. Below 0.40 V and above 0.70 V the adsorption of MeOH was suggested to be rate determining\cite{210}.

The MOR activity of Pt electrodes was shown to depend sensitively on the electrode surface structure\cite{223-225}. Among the low Miller index Pt(hkl) single crystals the lowest MOR activity was reported for Pt(111), while it increases with decreasing coordination number of Pt atoms at the surface, i.e., via Pt(111) < Pt(100) < Pt(110) in sulfuric acid solution\cite{223,226,227}. Furthermore, it was shown for stepped electrodes vicinal to Pt(111) that increasing the amount of steps with local (110) orientation enhances the MOR performance\cite{228}. Focusing on the MOR selectivity, a small CO$_2$ yield was observed during the reaction on Pt(111), while the formation of formic acid and / or formaldehyde was favored\cite{217,229,230}. On Pt NPs, on the other hand, the CO$_2$ yield was reported to constitute around 75\%\cite{219}.

![Figure 4.4: Schematic illustration of important reaction steps during the methanol oxidation reaction (MOR) labeled with numbers. Adsorbed and solvated species are labeled with an 'ad' and 'aq' subscript, respectively. See text for more details.](image-url)
4.4 Methanol oxidation reaction on Pt

Similar to the CO electro-oxidation, bimetallic PtRu systems exhibit higher activities for the MOR than bare Pt electrodes\[^{15}\]. Again this was ascribed to a bifunctional mechanism where the carbon containing species adsorb preferentially on Pt sites, while oxygen species adsorbed at adjacent Ru sites oxidize these species at low potentials\[^{231-233}\].

Higher MOR activities than for Pt were, however, also observed for Ru-core Pt-shell catalysts, where bimetallic PtRu sites are not present at the surface. In this case the higher activity cannot be rationalized by a bifunctional mechanism, but should result from electronic modifications of the Pt surface atoms due to the presence of the Ru(0001) substrate, \textit{i.e.}, from vertical ligand and compressive strain effects as discussed in Section 3.2.3. To investigate the inherent influence of the latter effects Pt films supported on a Ru(0001) single crystal (Pt\(_{X\text{-}\text{ML}}\)/Ru(0001)) constitute a suitable 2D model electrode. For Pt\(_{X\text{-}\text{ML}}\)/Ru(0001) samples with varying Pt film thickness, Schlapka \textit{et al.} demonstrated in a combined DFT and CO-TPD study, that the binding energy of CO on the Pt surface atoms is reduced compared to the respective binding energy on a Pt(111) single crystal (see Figure 4.5)\[^{79}\]. They showed that vertical electronic interactions between Pt and Ru in combination with compressive strain effects are responsible for this distinctly lower CO\(_{\text{ad}}\) binding energy on the Pt surface atoms\[^{79}\] (see also see Section 3.2.1). With increasing film thickness the CO\(_{\text{ad}}\) binding energy increases due to decreasing vertical Pt-Ru interactions\[^{79}\]. Finally, for films with a thickness larger than 3-4 ML the binding energy is still moderately reduced compared to Pt(111), solely due to compressive strain\[^{79,84}\]. The compression of the Pt surface layer arises from the larger lattice constant of Pt, which grows pseudomorphically on Ru(0001). Similar observations were obtained for the adsorption of oxygen\[^{85}\], hydrogen\[^{86}\] and water\[^{99}\] on Pt\(_{X\text{-}\text{ML}}\)/Ru(0001) surfaces with varying film thicknesses. Since the binding energy of these molecules on the metal electrode are relevant for the electrocatalytic activity of the electrode, a varying Pt film thickness might thus also affect the activity of Pt\(_{X\text{-}\text{ML}}\)/Ru(0001) electrodes for the MOR.

Prior to this thesis the MeOH oxidation was studied under UHV conditions on oxygen covered Pt\(_{X\text{-}\text{ML}}\)/Ru(0001) samples with Pt film thicknesses between 3 ML and 15 ML\[^{213}\]. In this work Gazdzicki \textit{et al.} proposed from combined FTIR and TPD measurements that the reaction pathway of the MeOH oxidation on Pt\(_{X\text{-}\text{ML}}\)/Ru(0001) and Pt(111) is very similar. This was based on their findings that the reaction temperature in the TPD measurements as well as the product yield distribution did not change with varying Pt film thickness\[^{213}\]. An electrocatalytic study of the MOR on Pt\(_{X\text{-}\text{ML}}\)/Ru(0001) samples was not conducted prior to this thesis. Thus, in Section 6.4 a study focusing on
the MOR activity and selectivity towards CO\(_2\) formation of Pt\(_{X-ML}\)/Ru(0001) electrodes with varying Pt film thickness is presented.

**Figure 4.5:** (a) Binding energy of CO at atop sites on Pt\(_{X-ML}\)/Ru(0001) as a function of the Pt film thickness. For \(x_{Pt} \geq 3 - 4\) ML the binding energy varies only little as indicated by the solid line (b) Desorption temperature of CO from Pt\(_{X-ML}\)/Ru(0001), determined from combined TPD and IRAS measurements, as a function of the Pt film thickness. The dotted lines in a) and b) represent the respective values for Pt(111). Reprinted Figure with permission from A.Schlapka et al., *Physical Review Letters*, **Vol. 91** (1), pp.016101-1 - 016101-4 (2003) © 2003 by the American Physical Society [79].
5 Experimental part

This Chapter provides a detailed overview of the experimental set-up and methods employed in the present work. All experiments were performed in a combined UHV-STM–electrochemical (EC) set-up. For this set-up I was strongly involved in the buildup and startup of the coupling between UHV and EC system. Details on the set-up can be found in Reference [53], where I contributed as co-author. In Section 5.1 the main UHV chamber equipped with a STM is presented. Section 5.2 focuses on the preparation of the nanostructured single crystals employed in this work, their structural characterization with STM and the STM data evaluation. A load-lock chamber attached to the main UHV chamber, which can be equipped with an EC flow cell, is described in Section 5.3. Section 5.4 focuses on the EC flow cell set-up, its operation and the implementation of electrocatalytic measurements relevant for the present work. Finally, a quadrupol mass spectrometer (QMS), set-up which is connected to the EC flow cell in a DEMS configuration and the calibration of this DEMS, set-up are described in Section 5.5.

5.1 Main UHV system

All model electrodes investigated in this work were prepared and structurally characterized in an UHV chamber which is depicted in Figure 5.1 and described in detail in Reference [234]. A base pressure of $p_0 \approx 1 \cdot 10^{-10}$ mbar in the chamber is maintained by a scroll pump (Varian SH-110), which generates a pre-vacuum of $p \approx 1 \cdot 10^{-2}$ mbar, a small turbomolecular pre-pump (Pfeiffer Vacuum TMU 071P, 60 L$s^{-1}$), a main turbomolecular pump (Varian TV301, 280 L$s^{-1}$) and an ion getter pump (Leybold-Heraeus IZ 270). The pressure within the chamber is measured by an ionization gauge (Granville-Phillips 350 Ionization Gauge, 1). A QMS (Pfeiffer QMA 120, 2) serves for residual gas analysis and leak detection. For the preparation of nanostructured single crystals the main chamber is equipped with a sputter gun (SPECS IQE 11/35, 3), an electron beam evaporator (Omicron EFM-3, 4), a Knudsen cell (Tectra WKC-3, 5), dosing valves for different gases (Ar, O$_2$, Ethylene) and a manipulator (6). The latter provides means
for sample heating via electron bombardment and enables to align the single crystals towards the respective preparation and characterization tools. The heart of the main chamber is a home-built pocket-size STM, which is used for structural characterization of the as-prepared electrodes. The STM is shown in the inset in Figure 5.1, together with a sample carousel which is attached to the STM. The latter serves for the storage of additional single crystals. A mechanical hand (VACGEN ZMH225, 7) and a wobble-stick (VACGEN ZWS07PG, 8) enable the lateral and vertical movement of the electrodes inside the chamber. Attached to the main chamber is a load-lock chamber (9), which allows for loading and unloading of samples, as well as for electrochemical characterization of the model electrodes. More details on the load-lock chamber are provided in Section 5.3.

Figure 5.1: UHV main chamber used in the present work. The chamber is equipped with an ionization gauge (1), a QMS (2), a sputter gun (3), an electron beam evaporator (4), a Knudsen cell (5), a manipulator (6), a mechanical hand (7), and a wobble-stick (8). A load-lock chamber (9) is attached to the main chamber at the backside. The inset shows the STM which is used for structural characterization together with a sample carousel attached to the STM.
5.2 Electrode preparation and structural characterization

This Section provides information about the electrode preparation procedures, the structural characterization and the data acquisition / evaluation of the nanostructured single crystal model electrodes discussed in Chapter 6. Depending on the model system either a Ru(0001) or a Pt(111) single crystal (MaTeck GmbH) served as substrate. The single crystals are both hat shaped (surface diameter, \(d = 10 \text{ nm}\)) and are fixed in a Tantalum sample holder. Nanostructuring of the single crystal surfaces was performed in the main UHV chamber where Pt and Au were deposited by physical vapor deposition (PVD) from the electron beam evaporator (4 in Figure 5.1) and the Knudsen cell (5 in Figure 5.1), respectively. STM images were recorded with an in-house programmed software. Surface coverages of Pt and Au on the respective single crystals were determined from at least five large scale STM images (at least 100 nm x 100 nm) with another in-house programmed software as described in more detail in Reference [235]. The accuracy of the coverage is \(\pm 0.02 \text{ ML}\).

5.2.1 Ru(0001) and Pt-gr/Ru(0001)

A clean Ru(0001) surface was obtained by first sputtering with Ar\(^+\)-ions for 30 minutes (3 \(\mu\)A sputter current) at room temperature, followed by a flash annealing step to 1600 K and a second Ar\(^+\)-sputter sequence (20 min, 3 \(\mu\)A, RT) in order to remove surface contaminants from the topmost surface layers. Subsequently, seven repeated cycles of flash annealing to 1600 K, followed by the dosing of 10 Langmuir (\(p_{O_2} = 1.34 \cdot 10^{-6} \text{ mbar}, t = 10 \text{ s}\)) of oxygen were conducted. The flash annealing leads to diffusion of carbon impurities from the crystal bulk towards the surface. The carbon at the surface gets oxidized to CO or CO\(_2\) by the adsorbed oxygen during the subsequent flash annealing step and then desorbs from the surface. Finally, three flash annealing steps to 1600 K were performed to remove residual oxygen and CO / CO\(_2\) from the surface. A representative STM image of a clean Ru(0001) surface prepared by this procedure is depicted in Figure 5.2a, revealing terraces of 50 nm - 200 nm width, separated by monoatomically high, almost straight steps. Furthermore, a high-resolution image of Ru(0001) is depicted in the inset of Figure 5.2a.

A Ru(0001) supported graphene layer (gr/Ru(0001)) was prepared by chemical vapor deposition (CVD) of ethylene on Ru(0001) at elevated sample temperatures to ensure
the formation of large graphene domains with a low defect density\textsuperscript{[116,236]}. The preparation parameters were adopted from Lorenz\textsuperscript{[116]} and refined to improve the quality of the graphene layer. Accordingly, ethylene was dosed for 90 minutes at $p_{C_2H_4} = 6.5 \times 10^{-9}$ mbar and a sample temperature of $T = 1118$ K. Subsequently, the sample was kept for additional 10 minutes at $T = 1118$ K without exposure to ethylene. As shown in the representative STM image of an as prepared gr/Ru(0001) surface in Figure 5.2b, this refinement led to a defect free graphene layer which extends over several hundred nanometers. Furthermore, it stretches over the monoatomic high Ru steps, which adopt to the graphene Moiré structure as shown in the inset in Figure 5.2b.

![Figure 5.2: Representative STM images of (a) clean Ru(0001) (500 nm x 500 nm, $I_T = 0.45$ nA, $U_T = 1.5$ V; Inset: 5 nm x 5 nm, $I_T = 4.5$ nA, $U_T = -16$ mV), (b) gr/Ru(0001) (150 nm x 150 nm, $I_T = 0.20$ nA, $U_T = -1.6$ V; Inset: 60 nm x 60 nm, $I_T = 0.8$ nA, $U_T = 0.9$ V), (c) Pt-gr/Ru(0001) (50 nm x 50 nm, $I_T = 0.01$ nA, $U_T = -1.3$ V) and (d) Pt$_{0.19\text{ ML}}$/Ru(0001) (100 nm x 100 nm, $I_T = 2.00$ nA, $U_T = 0.40$ V).](image)

Pt NCs with a narrow size distribution were obtained by PVD of Pt on a clean gr/Ru(0001) substrate, based on previous studies on the nucleation and growth of Pt-gr/Ru(0001)\textsuperscript{[113,114,116,120,122]}. Deposition of Pt at room temperature resulted in the for-
5.2 Electrode preparation and structural characterization

formation of Pt NCs with heights smaller than 3Pt MLs. The size of the NCs was varied by changing the evaporation duration at constant evaporation rate (see below). Larger Pt NCs were prepared by Pt deposition at room temperature and subsequent annealing of the sample to temperatures between $T = 673 \text{ K}$ and $T = 873 \text{ K}$. For more details on the NC size distributions, NC density and the average NC sizes see Section 6.1. A representative STM image of a Pt-gr/Ru(0001) surface is shown in Figure 5.2c, showing Pt NCs of similar sizes and their preferential nucleation at $\alpha$-sites (see also Figure 3.2b). Since the exact amount of Pt cannot be determined from the NC distribution, for each Pt-gr/Ru(0001) electrode the Pt coverage was determined by a reference sample. Here, directly after the preparation of Pt-gr/Ru(0001), Pt was deposited on a clean Ru(0001) single crystal for 10 minutes under exactly the same deposition parameters. The evaporation rate for the specific preparation sequence was then determined from STM images of the Pt/Ru(0001) reference sample. With this rate the exact Pt amount on the Pt-gr/Ru(0001) surface was determined, considering the respective evaporation duration. A representative STM image of a Pt/Ru(0001) reference sample with a Pt coverage of $\theta_{Pt} = 0.19 \text{ ML}$ is depicted in Figure 5.2d. The sample temperature during Pt deposition was ca. 340 K, resulting in large dendritically shaped Pt islands. Overall, the rates determined by this procedure varied between 0.019 ML min$^{-1}$ and 0.031 ML min$^{-1}$.

The height distributions of the Pt NCs were obtained for each Pt-gr/Ru(0001) electrode by evaluation of the apparent height of 300 to 1290 NCs. The Pt NC density was obtained by evaluation of 1350 to 2240 fcc-Moiré adsorption sites for each Pt-gr/Ru(0001) electrode. The evaluation procedures are described in detail in References [237,238].

5.2.2 $\text{PtxRu}_{1-x}/\text{Ru(0001)}$ and $\text{Ptx-ML/Ru(0001)}$

$\text{PtxRu}_{1-x}/\text{Ru(0001)}$: For the preparation of a $\text{PtxRu}_{1-x}/\text{Ru(0001)}$ surface alloy, first a specific amount of Pt in the submonolayer region was deposited on clean Ru(0001) at temperatures between 300 K - 600 K. This led to the formation of dendritic Pt islands on Ru(0001) ($\text{Pt}_{x-\text{ML}}/\text{Ru(0001)}$), from which the Pt coverage was determined by STM imaging. Subsequently, the sample was flash annealed to 1320 K to form the desired $\text{PtxRu}_{1-x}/\text{Ru(0001)}$ surface alloy. STM images of a $\text{Pt}_{x-\text{ML}}/\text{Ru(0001)}$ surface with $\theta_{Pt} = 0.82 \text{ ML}$ and the respective $\text{PtxRu}_{1-x}/\text{Ru(0001)}$ surface alloy with a Pt content $x_{Pt} = 0.82$ are depicted in Figure 5.3a and 5.3b, respectively. The $\text{Pt}_{0.82-\text{ML}}/\text{Ru(0001)}$ surface in Figure 5.3a reveals areas where Ru(0001) is exposed between dendritic shaped Pt islands. Due to the high Pt coverage also, bilayer islands were formed. For the $\text{Pt}_{0.82}\text{Ru}_{0.18}/\text{Ru(0001)}$ surface alloy in Figure 5.3b the topmost surface layer consists of
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a mixed Pt$_{0.82}$Ru$_{0.18}$ alloy, since the Pt atoms do not segregate into the bulk under these conditions\cite{87}. The former areas with Ru(0001) exposed to the surface turned into hexagonal shaped holes, again with a surface consisting of Pt$_{0.8}$Ru$_{0.2}$. A high-resolution STM image of a Pt$_{0.82}$Ru$_{0.18}$/ Ru(0001) surface is shown in the inset in Figure 5.3b, where the dark and bright spots are attributed to Pt and Ru atoms, respectively, demonstrating a random intermixing of the Pt and Ru atoms in the surface layer, as described in Reference\cite{87}. Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys with Pt contents of $x_{Pt} = 0.12, 0.24, 0.30, 0.48, 0.50, 0.58, 0.61, 0.82$ and $0.83$ were prepared accordingly by varying the evaporation duration at a constant evaporation rate of 0.03 ML min$^{-1}$. These surface alloys were employed to investigate the role of Pt$_n$Ru$_m$ ensembles in the CO electro-oxidation, as described in Section 6.3.

![Figure 5.3](image)

Figure 5.3: (a) Representative STM image of Pt$_{0.82}$-ML/Ru(0001) (200 nm x 200 nm, $I_T = 1.0$ nA, $U_T = 1.2$ V). (b) Representative STM image of Pt$_{0.82}$Ru$_{0.18}$/Ru(0001) (220 nm x 220 nm, $I_T = 0.9$ nA, $U_T = 0.2$ V). The inset shows a high resolution STM image of Pt$_{0.80}$Ru$_{0.20}$/Ru(0001) (Hoster et al., PCCP Vol. 10, pp. 3812-3823 – Reproduced by permission of the PCCP Owner Societies\cite{87}), 7 nm x 7 nm). (c) Representative STM image of Pt$_{5.53}$-ML/Ru(0001) (300 nm x 300 nm, $I_T = 1.0$ nA, $U_T = 1.5$ V).

Pt$_x$-ML/Ru(0001): Pseudomorphically grown multilayer thick Pt films on Ru(0001) (Pt$_x$-ML/Ru(0001)) were prepared by PVD of Pt on clean Ru(0001) at a sample temperature between 650 K and 680 K and a constant evaporation rate ($F = 0.03$ ML min$^{-1}$). After evaporation, the sample was kept at 650 K - 680 K for additional 10 minutes to improve the film quality and to reduce the amount of 3D islands. The Pt film thickness was varied by changing the evaporation duration $t_{Evap}$. A representative STM image of a Pt$_{5.53}$-ML/Ru(0001) electrode is shown in Figure 5.3c with local Pt film thicknesses of five and six Pt monolayers. In general, two to four different Pt layers were exposed to the surface of the different Pt$_x$-ML/Ru(0001) electrodes while pronounced 3D growth was not observed. The exact film thickness was obtained by first determining the Pt surface
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layer thickness distribution via STM imaging. Then, this distribution was adjusted to the overall Pt amount on the surface which was estimated with the knowledge of $F$ and $t_{Evap}$. Accordingly, in Section 6.4 five different Pt$_{X\text{-ML}}$/Ru(0001) electrodes with Pt film thicknesses between 1.1 ML and 5.5 ML were prepared and employed to study the influence of the Pt film thickness on the activity for the MOR.

5.2.3 Pt(111) and Pt/Pt(111)

A clean Pt(111) single crystal surface was obtained by Ar$^+$-sputtering for 10 minutes (3 $\mu$A, RT) followed by a heating step to 1050 K with a heating rate of 4 K s$^{-1}$ and a cooling rate of 2 K s$^{-1}$. The heating step leads to the segregation of carbon impurities to the topmost surface layer. In a next heating step the crystal was again heated to 1050 K (4 K s$^{-1}$, 2 K s$^{-1}$). During the cool down, at a sample temperature of 910 K, 10 Langmuir of O$_2$ were dosed in order to oxidize the carbon species at the surface to CO or CO$_2$. Finally, in a last heating step to 1000 K (4 K s$^{-1}$, 2 K s$^{-1}$) the CO/CO$_2$ molecules and residual oxygen desorb from the Pt(111) surface. The heating/cooling rates had to be strictly maintained to avoid Pt island formation and to obtain mono-atomically high, straight steps and terraces with a width of 50 nm - 200 nm, as shown in a representative STM image of an as prepared Pt(111) electrode in Figure 5.4a. The inset in Figure 5.4a shows a high resolution STM image of Pt(111) with a hexagonal arrangement of the surface atoms.

![Figure 5.4](image)

**Figure 5.4:** (a) Representative STM image of a clean Pt(111) surface (300 nm x 300 nm, $I_T = 2.8$ nA, $U_T = 1.2$ V). The inset shows a high-resolution STM image of the Pt(111) surface (6 nm x 6 nm, $I_T = 18$ nA, $U_T = 0.06$ V; the bright stripes are attributed to oscillations which, most likely, arise from electronic coupling with the grid). (b) Representative STM image of Pt/Pt(111) with $\theta_{Pt} = 0.20$ ML (220 nm x 220 nm, $I_T = 2.2$ nA, $U_T = 0.8$ V).

In order to increase the Pt step density on the Pt(111) surface, a preparation procedure
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from Michely et al.\cite{239} was adapted and modified. First, 0.20 ML of Pt were deposited at room temperature \((F = 0.017 \text{ ML min}^{-1}, t = 12 \text{ min})\) on Pt(111). Afterwards, the sample was annealed to 570 K for 1 min. An STM image of the resulting Pt/Pt(111) model surface is shown in Figure 5.4b, demonstrating a higher structuring of the former Pt steps due to the nucleation of Pt atoms at the step sites. Furthermore, hexagonal shaped homoepitaxially grown Pt islands were observed in accordance with previous results\cite{239–241}.

The Pt step densities were determined for Pt(111) and Pt/Pt(111) with an in-house programmed software. For this purpose the step edge sites present at a terrace were marked, as shown exemplary in the screenshot in Figure 5.5a which displays the evaluation of the STM image in Figure 5.4b. The number of Pt atoms forming the marked step sites were calculated as highlighted green in Figure 5.5b. For a single STM image the number of step atoms for each terrace was summed up to obtain the overall number of Pt step atoms in this image. Additionally, the total amount of Pt atoms present in the full STM image was determined as highlighted blue in Figure 5.5b. The Pt step density was then obtained by dividing the sum of Pt step atoms by the total amount of Pt atoms in the STM image. This procedure was conducted for five to seven different STM images for each electrode and the step density was averaged. The respective values obtained by this method and a more detailed structural characterization of Pt(111) and Pt/Pt(111) are given in Section 6.2.

Figure 5.5: Screenshots of the Pt step density evaluation with an in-house programmed software. (a) STM image of Pt/Pt(111) shown in Figure 5.4b with marked step sites at a terrace. (b) Number of Pt atoms forming the step sites (highlighted green) and the total amount of Pt atoms in the full STM image (highlighted blue).
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5.2.4 Au modification of ascending Pt steps

First attempts to modify the ascending Pt steps with a Au film were performed by deposition of Au on a clean Pt(111) electrode at room temperature with an evaporation temperature in the Knudsen cell of \( T_{\text{Evap}} = 1230 \text{ K} \). The evaporation temperature is well below the melting point of Au \( (T_m = 1337 \text{ K}) \) ensuring a low evaporation rate of \( F = 0.002 \text{ ML min}^{-1} \) and thus a higher probability for Au atoms to attach at the Pt step sites due to the large mean free path of diffusion (see Section 3.1.1). A representative STM image of a Au modified Pt(111) electrode is shown in Figure 5.6a. Dendrite-like Au structures located at the ascending Pt steps and areas with undecorated step sites in between were observed, which is ascribed to the low sample temperature during Au deposition in agreement with previous studies \([242-244]\). Additionally, as indicated by a blue arrow, Au island formation was observed on large terraces.

In order to completely modify the ascending Pt steps with a narrow Au stripe and to prevent Au island formation, Au was deposited at an elevated sample temperature of \( T_{\text{sample}} = 570 \text{ K} \) and kept at 570 K for 1 min after deposition (see Reference \([245]\) for more details). This temperature is sufficiently low to prevent surface alloy formation, which sets in at \( T_{\text{alloy}} \geq 750 \text{ K} \) \([246]\). Additionally, a lower amount of Au was deposited at a constant evaporation rate \( (F = 0.002 \text{ ML min}^{-1}) \) by reducing the evaporation duration. A representative STM image of a Au/Pt(111) electrode with a Au coverage of \( \theta_{\text{Au}} = 0.05 \pm 0.02 \text{ ML} \) is depicted in Figure 5.6b, revealing the full modification of the ascending Pt step with a narrow Au film of 1 nm to 5 nm width.

For the modification of the Pt steps of the Pt/Pt(111) sample the Au coverage was increased by increasing the evaporation duration, such that all Pt islands and Pt steps were decorated with a 1 nm to 5 nm wide Au stripe forming 2D Pt-core Au-shell structures. This was achieved with a Au coverage of \( \theta_{\text{Au}} = 0.08 \pm 0.02 \text{ ML} \). A representative STM image of the resulting structures on the surface of a Au/Pt/Pt(111) electrode is shown in Figure 5.6c. The width of the Au modification was determined with an in-house programmed software, using line profiles for 8-10 STM images as described in more detail in Reference \([245]\).
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Figure 5.6: Representative STM images of (a) Au/Pt(111) with $\theta_{Au} = 0.21$ ML deposited at room temperature (100 nm x 100 nm, $I_T = 1.4$ nA, $U_T = 1.2$ V), (b) Au/Pt(111) with $\theta_{Au} = 0.05$ ML deposited at $T_{Sample} = 570$ K (100 nm x 100 nm, $I_T = 1.8$ nA, $U_T = 1.1$ V) and (c) Au/Pt/Pt(111) with $\theta_{Pt} = 0.20$ ML and $\theta_{Au} = 0.08$ ML (100 nm x 100 nm, $I_T = 1.4$ nA, $U_T = 0.9$ V) where Au was deposited at $T_{Sample} = 570$ K. The as measured STM images are displayed in the respective upper part. The lower part shows the images with optimized contrast to visualize the chemical contrast between Pt (dark) and Au (bright).
5.3 Load-lock chamber

After the structural characterization of the model electrodes in the main UHV chamber, the electrodes were transferred into a load-lock UHV chamber, which is attached to the main chamber, separated with a gate valve. The load-lock chamber is depicted in Figure 5.7a and schematically illustrated in Figure 5.7b, where all important components are labeled with numbers. A pressure of $p_0 = 5 \cdot 10^{-8}$ mbar is maintained in the load-lock chamber by a turbomolecular pump (Pfeiffer TMU 071P, 1), which is attached to a scroll pre-pump (Varian SH-110, 2). To introduce the model electrodes into the load-lock chamber, the gate valve (3) between main chamber and load-lock chamber has to be opened first. A transfer rod (4) with a ceramic sample holder mounted at its front part is then introduced into the main chamber to pick up the electrode.

![Figure 5.7: (a) Picture and (b) schematic illustration of the UHV load-lock chamber. The illustration in b) shows the arrangement of the EC flow cell in the load-lock chamber during EC investigations. See main text for details.](image)

After retracting the transfer rod to the load-lock chamber and closing the gate valve 3, valve 5 has to be closed. Subsequently, N$_2$ (5.0 N) is introduced into the chamber through a venting valve (6) to avoid adsorption of contaminants like O$_2$ or hydrocarbons from ambient air on the model electrodes. As soon as the chamber is flooded with N$_2$, gate valve 7 is opened and the EC flow cell (8) is introduced from down below towards the electrode. The flow cell is guided with two steel rods (9), which are mounted to the load-lock chamber and two axle bearings, which are mounted at the EC flow cell (see
also Section 5.4). When the EC flow cell is in contact with the electrode, a copper rod (10) presses the electrode against the flow cell to seal the system. The copper rod serves additionally as electrical contact for the model working electrodes.

5.4 Electrochemical (EC) flow cell

A picture of the entire EC flow cell and its mounting system is depicted in Figure 5.8a. The core of the flow cell consists of a Kel-F™ body (1). The Kel-F™ body is mounted on a stainless steel tube, which is attached to a metal plate with two axle bearings (2), required for the vertical motion of the flow cell in the load-lock chamber (see Section 5.3). The bottom of the stainless steel tube (3) is connected to a QMS via a flexible hose as described in Section 5.5. The whole cell and all connectors are vented with N₂ (5.0 N) through tubes (4) or plastic bags (not shown here) to prevent oxygen traces creeping through the connectors in the EC system. A top view picture of the flow cell is shown in Figure 5.8b. Additionally, the picture of a self-made cross-section model of the flow cell as well as a schematic side-view sketch of the cell are shown in Figure 5.8c and Figure 5.8d, respectively. The most important components are labeled, where identical parts are labeled with the same numbers in the individual pictures/figures.

After introducing the EC flow cell into the load-lock chamber, as described in Section 5.3, the Kel-F™ body (1) is pressed against the electrode surface (5) via an O-ring made of perfluoroelastomer (FPM, Arcuss GmbH, 6). The O-ring has an inner diameter of $d = 0.70 \text{ cm}$, which becomes $d = 0.60 \text{ cm}$ upon pressing the electrode on the cell body. The O-ring seals a compartment (7) between electrode and Kel-F™ body. The electrolyte is introduced through an inlet capillary (8) and flows through the cell, as indicated by arrows in Figure 5.8c and Figure 5.8d. After wetting the electrode surface, the electrolyte solution leaves the first compartment either (i) through a glass frit (9) towards a Au wire, which serves as counter electrode (10), or (ii) towards a second compartment (11), where the electrolyte passes a gas permeable membrane (12), which is supported on a stainless steel frit. Volatile species which are carried with the electrolyte can diffuse through the membrane 12 and are detected on-line in a QMS, which is connected to the EC flow cell as described in Section 5.5. Finally, the electrolyte leaves the Kel-F™ body through an outlet capillary (13).

A three-electrode system was employed for the EC measurements, where the Au wire (10) serves as counter electrode. A reversible hydrogen electrode (RHE) serves as reference electrode and is connected to the cell at the end of the outlet capillary, outside of
the Kel-F\textsuperscript{TM} body. The potential was controlled by a Solartron potentiostat (Modulab ECS, model Pstat 1MS/s 2087A) and a Pine potentiostat (AFCBP1 Bipotentiostat) for the Ru(0001) based and the Pt(111) based electrodes, respectively. The electrodes were primarily investigated by cyclic voltammetry, both in supporting electrolyte and in a reactive medium. Internal resistances of the flow cell were compensated by a capacitor (330 $\mu$F), which was connected between counter electrode and reference electrode. All potentials in this work are referred to the RHE scale and the measurements were carried out at room temperature. The supporting electrolyte was in all cases 0.5 M H$_2$SO$_4$, which was introduced to the flow cell system via capillaries that are connected to a supply bottle. If not stated differently, for all electrodes the currents are normalized to the geometric surface area $A_{geom} = 0.28$ cm$^2$, which is defined by the inner diameter of the O-ring ($d = 0.60$ cm). For the Au modified Pt electrodes in Section 6.2 the currents are normalized to the bare Pt surface area, which is calculated from the $A_{geom}$ of the clean Pt surface minus the Au covered area. The electrochemical surface area (ECSA) of the Pt NCs in Section 6.1 was determined by employing hard sphere models as described in detail in Section 6.1.6.

5.4.1 Purification of the flow cell system

A clean EC flow cell set-up is crucial to obtain reliable and reproducible CVs. Thus, prior to each EC investigation on a model electrode, the system was tested with a polycrystalline Pt (Pt-poly) foil. The cleanliness of the flow cell system was checked by test measurements on the Pt-poly foil as described in the following. First, the potential was cycled between 0.05 V and 1.50 V for 30 min. This led to the removal of oxygen traces from the system and to the cleaning of the system, where the latter occurs at potentials above 0.80 V. As soon as the shape of the CV remained stable with consecutive cycling, the potential was cycled three times between 0.05 V and 1.40 V. The resulting CVs of Pt-poly are depicted as black curves in Figure 5.9a and Figure 5.9b, with the typical oxygen adsorption/desorption features at potentials above 0.80 V, a double layer region between 0.40 V and 0.80 V and the H$_{upd}$ adsorption/desorption region below 0.40 V\cite{155,247}. After cycling between 0.05 V and 1.40 V, the potential was kept at 0.50 V in the double layer region for 5 min. At this potential, possible impurities present in the flow cell system could adsorb on the Pt-poly surface due to the absence of competitive adsorption processes. Finally, to test the presence of impurities, in a next step the potential was cycled between 0.05 V and 0.80 V, where removal of impurities from the surface is unlikely. The respective CV measured in the presence of impurities is shown.
as red curve in Figure 5.9a. Compared to the previous cycles to 1.40 V the peak currents and therefore the charge in the H$_{upd}$ region ($E < 0.40$ V) are lowered. Since the charge in this region is considered as a fingerprint for the electrochemical active surface area of Pt$^{155,247,248}$, the lower charge is a strong evidence for the presence of adsorbed impurities at the Pt-poly surface.
A clean flow cell system, where the peak current densities in the positive-going scan deviate by less than 5 $\mu$A, is obtained if the following protocol is strictly maintained:

- Store the empty electrolyte supply bottles in a saturated pottassium hydroxide (KOH) solution over night
- Rinse the supply bottle with purified water (demineralized)
- Boil the supply bottle in purified water, take care that the bottle is completely immersed
- Rinse the supply bottle with ultra-pure water (Milli-Q, 18 M\( \Omega \)-cm)
- Rinse the supply bottle twice with 0.5 M H\(_2\)SO\(_4\) freshly prepared from Milli-Q water and concentrated H\(_2\)SO\(_4\) (suprapure, Merck)
- Fill the supply bottle with 0.5 M H\(_2\)SO\(_4\)
- Mount the supply bottle to the EC system
- Saturate the 0.5 M H\(_2\)SO\(_4\) with 6.0 N N\(_2\) (5.0 N N\(_2\) is not sufficient!)
- Boil the Pt-poly foil together with an O-ring in Milli-Q water
- Mount O-ring and Pt-poly foil on the EC flow cell
- Rinse the whole EC flow cell with 0.5 M H\(_2\)SO\(_4\) and remove possible gas bubbles
- Perform potentiodynamic cycles between 0.05 V and 1.50 V for 30 min to clean the system

Following this procedure, the cleanliness of the system is guaranteed as depicted in Figure 5.9b, which reveals that the currents/charge in the H\(_{\text{upd}}\) region is maintained when the potential is cycled between 0.05 V and 0.80 V (red curve).
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Figure 5.9: CVs of a polycrystalline Pt foil (Pt-poly) recorded in the EC flow cell (a) containing impurities and (b) in the absence of impurities. The CVs are measured in 0.5 M H2SO4 in a potential range between 0.05 V and 1.40 V (black curves) to clean the system and between 0.05 V and 0.80 V (red curves) to detect possible impurities. For more details the reader is referred to the main text.

5.4.2 Electrocatalytic measurement implementation

Prior to each electrocatalytic measurement, CVs of the model electrodes were recorded in N2 saturated 0.5 M H2SO4 supporting electrolyte. Comparison of the CVs of Ru(0001) and Pt(111) in 0.5 M H2SO4 with the respective CVs previously reported provided information about the electrode quality and the reliability of the EC data. CVs of the nanostructured model electrodes in 0.5 M H2SO4 allowed for a surface characterization with respect to adsorbate coverages and adsorption properties. Subsequent to the CV measurements in supporting electrolyte the electrocatalytic reaction of interest was performed on the respective model electrode. In detail the electrocatalytic reactions were: (i) the HER, (ii) the bulk CO electro-oxidation, (iii) the COad stripping and (iv) the MOR. The implementation of each reaction is described in the following.

Hydrogen evolution reaction (HER): Directly after recording CVs in 0.5 M H2SO4 supporting electrolyte to a lower potential limit of 0.07 V, the lower potential limit was reduced to potentials where H2 is evolved without any modification of the electrolyte solution. In the present work the HER was performed on Pt-gr/Ru(0001) electrodes with an applied lower potential limit of 0.01 V (see Section 6.1).

Bulk CO electro-oxidation: The potential was kept at 0.10 V and the N2 gas flow was stopped. Instead, the 0.5 M H2SO4 supporting electrolyte was saturated with CO. The EC flow cell set-up was rinsed with the CO saturated electrolyte for 15 min. Subsequently, the polarization curves were recorded, starting at 0.10 V with the negative-going
scan. Usually, two complete polarization cycles were recorded. In some cases three full polarization cycles were measured to ensure that the second polarization cycle reflects a steady-state situation, meaning that the second and third cycle are essentially identical. The bulk CO electro-oxidation was investigated on Au modified Pt(111) electrodes and on Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes (see Sections 6.2 and 6.3, respectively).

**CO$_{ad}$ stripping:** For the oxidation of a CO adlayer the potential was first kept at 0.10 V. At this potential CO was introduced to the 0.5 M H$_2$SO$_4$ electrolyte solution and the EC flow cell set-up was rinsed with the CO saturated electrolyte for 5 min. In order to completely remove CO from the EC flow cell system, the cell was then rinsed for 45 min with a N$_2$ saturated 0.5 M H$_2$SO$_4$ solution by switching the electrolyte supply towards a second supply bottle that contained the N$_2$ saturated electrolyte. Starting at 0.10 V, the potential was first cycled in the negative-going scan direction. CO$_{ad}$ stripping experiments were conducted on Pt(111) to calibrate the DEMS system as described in Section 5.5.1.

**Methanol oxidation reaction (MOR):** A second supply bottle containing 0.2 M CH$_3$OH (EMSURE®, Merck) dissolved in 0.5 M H$_2$SO$_4$ was connected to the EC system. After recording CVs in supporting electrolyte the potential was kept at 0.40 V. Subsequently, the electrolyte supply was switched to the second supply bottle and the set-up was rinsed with the MeOH containing electrolyte for 15 min at a flow rate of approximately 20 µL s$^{-1}$. Finally, the polarization curves were recorded, starting at 0.40 V in the negative-going scan direction. The MOR was performed on Pt$_x$-ML/Ru(0001) electrodes with multilayer thick Pt films (see Section 6.4).

### 5.5 Differential electrochemical mass spectrometer (DEMS)

A picture of a UHV chamber employed for DEMS measurements (UHV$_{DEMS}$) as well as a schematic illustration of the set-up are shown in Figure 5.10a and Figure 5.10b, respectively. The UHV$_{DEMS}$ chamber is differentially pumped by two turbomolecular pumps of different size (1: Pfeiffer-Vacuum HiPace 80; 2: Pfeiffer-Vacuum HiPace 300). A rotary vane pump (Pfeiffer-Vacuum DUO 10 M, 3) and a zeolite trap (4) serve as pre-pump system for the turbomolecular pumps, which are both separated by a valve (5 and 6) from the pre-pump system. The pressure in the UHV$_{DEMS}$ chamber is measured with an ionization gauge (Pfeiffer-Vacuum IKR 270, 7). The chamber is equipped with a QMS providing (i) two yttritised Iridium filaments (8) for the ionization of volatile
species, (ii) a quadrupole (9) for mass selection of ions and (iii) an off-axis secondary electron multiplier (SEM) (10) for ion detection. A valve (11) separates the UHV\textsubscript{DEMS} chamber from the flexible hose which is attached at the stainless steel tube holding the EC flow cell (see Section 5.4). Another valve (12) separates the volume between EC flow cell and the pre-pump system, while a third valve (13) can be used to vent the volume between EC flow cell and the valves 11 and 12. Prior to the on-line mass detection of volatile species that diffuse through the membrane in the EC flow cell (see Section 5.4), the volume between flow cell and the valves 11-13 has to be evacuated. This is achieved by closing the valves 5, 6, 11, and 13 and subsequent opening of valve 12 towards the pre-pump system. Subsequently, valve 12 is closed again and the valves 5 and 6 are opened. In order to introduce the volatile species to the UHV\textsubscript{DEMS} chamber, first the filament 8 has to be switched off to avoid damage of the filament. Then, valve 11 can be opened carefully such that the pressure in the chamber does not exceed $p_0 = 5 \cdot 10^{-4}$ mbar. When the pressure reaches $p_0 = 3 \cdot 10^{-5}$ mbar the filament can be switched on to start the ion detection.

The on-line ion detection of volatile species was conducted during the MOR on Pt\textsubscript{x,ML}/Ru(0001) electrodes with varying Pt film thicknesses as discussed in more detail in Section 6.4.

![Figure 5.10](image)

**Figure 5.10:** (a) Picture of the UHV chamber employed for DEMS measurements and (b) schematic illustration of the DEMS set-up. See main text for details.

### 5.5.1 DEMS calibration

Prior to the initial operation of the DEMS set-up it had to be calibrated. For this purpose CO\textsubscript{ad} stripping experiments as well as potential step measurements in CO containing
5.5 Differential electrochemical mass spectrometer (DEMS)

Electrolyte were conducted on a Pt(111) single crystal. The Faradaic current trace of the CO$_{\text{ad}}$ stripping experiment is shown in Figure 5.11a, where the red and blue curves represent the first positive-going scan and the full second scan, respectively. The absence of any reduction/oxidation features below 0.67 V in the first scan is ascribed to a poisoning of the Pt(111) surface by adsorbed CO$^{195,196}$. The CO$_{\text{ad}}$ oxidation starts at 0.67 V, resulting in a peak with a maximum at 0.80 V, which is in perfect agreement with previously reported results$^{195–197,249}$. The second scan shows the typical adsorption/desorption features for hydrogen (0.07 V to 0.33 V) and (bi)sulfate (0.33 V to 0.50 V)$^{17,155,158,160–162,164}$, revealing the absence of CO in the flow cell system$^{195,196}$. Figure 5.11b shows the mass ion current of $m/z = 44$ which was detected simultaneously in the QMS. The black dotted curve belongs to the as-measured response during the first potentiodynamic scan. The maximum of this peak is shifted by $\Delta V = 0.02$ V towards 0.82 V compared to the Faradaic peak in Figure 5.11a. Since the $m/z = 44$ signal belongs to CO$_2^+$ and furthermore CO$_2$ is the sole product formed during the oxidation of a CO$_{\text{ad}}$ monolayer, $\Delta V$ reflects the time delay between formation of the reaction product on the electrode in the EC flow cell and the detection of the product in the QMS. Knowing the sweep rate ($v = 20$ mV s$^{-1}$), the time delay $t_D$ can be calculated by

$$t_D = \Delta V \cdot v^{-1}. \tag{5.1}$$

For the present DEMS set-up the time delay is in the range of one second or below, which is significantly faster compared to other DEMS set-ups for single crystal investigations reported previously$^{250}$. In order to synchronize the Faradaic current signal and the as-measured mass ion current signal, the potential scale of the latter has to be shifted according to $t_D$ as displayed by the time delay corrected mass ion current trace in Figure 5.11b (red curve). The blue curve in Figure 5.11b shows the respective response for the second scan, evidencing the absence of CO$_2$ in the system.

For a quantitative analysis of the DEMS data it is necessary to determine the DEMS set-up specific calibration constant $K^*$ which is proportional to the collection efficiency $N$, i.e., the ratio of the amount of detected species in the QMS with respect to the amount of species produced in the EC flow cell$^{251–253}$. Since $N$ may vary for each experiment, e.g., due to different flow rates, $K^*$ should be determined for every experiment if possible. Additionally, $K^*$ is a mass specific constant and has to be determined separately for each molecule, i.e., for each ion mass, which is possible by the following equation
where \( n \) is the number of electrons exchanged during an electro-catalytic reaction, \( Q_{QMS} \) is the integrated mass ion charge and \( Q_F \) is the integrated Faradaic charge. Instead of \( Q_{QMS} \) and \( Q_F \) one might use employ the respective currents \((I_{QMS}, I_F)\) at a specific potential which is, however, less accurate. For CO\(_2\) \((m/z = 44)\), \( K^* \) is usually determined from CO\(_{ad}\) stripping experiments where \( Q_{QMS} \) and \( Q_F \) are obtained by integrating the Faradaic CO oxidation peak and the mass ion current peak associated with \( m/z = 44 \), respectively. The number of electrons exchanged for this reaction is \( n = 2 \), according to equations 4.4 - 4.7.

\[
K^* = \frac{n \cdot Q_{QMS}}{Q_F}
\]  

Figure 5.11: (a) Polarization curve of the oxidation of one CO\(_{ad}\) monolayer from Pt(111) (red curve) and the subsequent second cycle (blue curve) in 0.5 M H\(_2\)SO\(_4\). (b) As measured (black dotted curve) and time-delay corrected (red solid curve) mass spectrometric cyclic voltammogram (MSCV) of \( m/z = 44 \) corresponding to the first cycle in a) and MSCV of the second cycle (blue solid curve). (c) Faradaic current trace of a potential step from 0.10 V to 1.10 V in CO saturated 0.5 M H\(_2\)SO\(_4\) as well as (d) the simultaneously recorded mass ion current response for \( m/z = 44 \) as a function of time.

\( K^* \) can also be determined from \( Q_{QMS} \) and \( Q_F \) obtained from a potential step measurement in CO saturated supporting electrolyte. The Faradaic current response of a potential step from 0.10 V to 1.10 V in CO saturated 0.5 M H\(_2\)SO\(_4\) as well as the simul-
5.5 Differential electrochemical mass spectrometer (DEMS)

taneously recorded, time-delay corrected mass ion current response for \( m/z = 44 \) are shown in Figure 5.11c and Figure 5.11d, respectively. In both signals no currents were observed at 0.10 V due to the absence of CO oxidation. The CO oxidation initiated when the potential was stepped to 1.10 V, resulting in a sharp spike, followed by a small decay of the Faradaic current, in agreement with previous findings\cite{200}. When the potential was stepped back to 0.10 V the current drops again close to zero. Except for the initial spike, the mass ion current response of \( m/z = 44 \) in Figure 5.11d has a similar shape as the Faradaic current trace in Figure 5.11c. \( Q_F \) and \( Q_{QMS} \) were obtained by integrating both curves and \( K^* \) was determined.

From CO stripping and potential step measurements, depending on the electrolyte flow rate, values between \( K^* = 2.5 \cdot 10^{-5} - 3.5 \cdot 10^{-5} \) were obtained with an average value of \( K^* = (2.9 \pm 0.4) \cdot 10^{-5} \). This averaged \( K^* \) was employed in Section 6.4 to determine the current density \( j_{CO_2} \) during the MOR on Pt\(_{X\cdot\text{ML}}\)/Ru(0001) electrodes which is solely related to CO\(_2\) formation via

\[
j_{CO_2} = \frac{n \cdot j_{QMS}}{K^*} \tag{5.3}
\]

For this purpose the mass spectrometric currents of \( m/z = 44 \) were normalized to \( A_{geom} = 0.28 \text{ cm}^2 \) to obtain the corresponding ion current density \( j_{QMS} \). The number of electrons exchanged during CO\(_2\) formation in the MOR is \( n = 6 \). The resulting potential dependent \( j_{CO_2} \) traces in Section 6.4 were smoothed by a 10 point moving average smoothing.
6 Results and Discussion

This Chapter provides all publications listing me as first author which were published during the period of my thesis. The style and numbering of the Figures and References have been adapted to the layout of this thesis. The Experimental Sections of the original publications are merged to avoid duplication and are presented in more detail in Chapter 5. Additional publications where I contributed as co-author are References\cite{53} and\cite{58}.

6.1 Pt nanocluster size effects in the hydrogen evolution reaction: Approaching the theoretical maximum activity

The content of this Section is published in Physical Chemistry Chemical Physics and is reproduced from Reference\cite{254} with permission from the PCCP Owner Societies (Royal Society of Chemistry). My contribution to this work are the measurement of all experimental results and the full data evaluation. The Figures were prepared from me together with Sylvain Brimaud. Furthermore, I was strongly involved in the creative process of the publication.

6.1.1 Abstract

Hydrogen production from electrocatalytic water splitting in electrolysers is a key process to store excess electric energy produced from intermittent renewable energy sources. For PEM electrolysers, carbon supported Pt particles exhibit the highest rates for the HER, however, high Pt costs limit a wide spread use of this technology. Employing a graphene layer grown on a Ru(0001) single crystal as template for Pt NC growth, we studied the dependence of the HER activity on the NC size for a significant amount of different NC sizes. We provide clear quantitative experimental evidence for a volcano-like relation
between HER activity and NC size which was missing so far. For Pt NCs with very low sizes below 2 nm we found stunningly improved exchange HER current densities. The highest exchange current density was observed for Pt NCs with an average size of ca. 38 atoms. These Pt\textsubscript{38} NCs do not only surpass the Pt-mass-specific activity of commercial Pt electrode materials by well above three orders of magnitude. They are additionally located close to the maximum exchange current density for the HER predicted by theory for transition metal surfaces. The present work provides a strong stimulus for future research towards technically feasible Pt NC catalysts with cluster sizes in the range of few tens of Pt atoms.

### 6.1.2 Introduction

The generation of molecular hydrogen by electrochemical water electrolysis, \textit{e.g.}, in a PEM electrolyzer, is a cornerstone for the chemical storage of electric energy produced from intermittent renewable sources\textsuperscript{[4,255–257]}. Key problems for the commercialization of this technology are, however, the high costs and limited abundance of Pt, which is employed as catalyst material in PEM electrolyzers in form of carbon supported Pt particles, since Pt is by far the most efficient monometallic catalyst for the hydrogen evolution reaction (HER) in acid electrolyte\textsuperscript{[11,13,143]}. One approach to lower the amount of Pt involves a better utilization of the electrocatalytic material, by increasing the dispersion, \textit{i.e.}, by reducing the Pt particle size. This approach is, however, not straightforward, since it is well known that for decreasing particle sizes the catalytic properties of NPs may change\textsuperscript{[258,259]}, \textit{e.g.}, due to changes in the electronic properties\textsuperscript{[30,31]} or due to changes in the equilibrium shapes of the particles with decreasing particle size\textsuperscript{[33,260]}.
Furthermore, for particle sizes of typically 100 atoms and below (nanoclusters ‘NCs’), the so-called non-scalable regime is reached, where the physicochemical properties do not follow a continuous trend with decreasing particle size, but change drastically with each atom removed\cite{34}.

For a number of electrocatalytic reactions such as the HOR\cite{178} or the ORR\cite{175} it was suggested that the activity depends in a "volcano-like" way on the particle size, where the activity is defined as the mass-specific reaction rate. For the above catalysts and reactions, the optimum particle size was around 3.0-3.5 nm\cite{15} and 2.0 nm, respectively\cite{175}. For the HER, systematic studies of particle size effects are scarce. In an early study Bagotzky et al. demonstrated that for pyrographite supported Pt nanoparticles with sizes above 10 nm the HER activity decreases continuously with increasing particle size\cite{65}. Comparing three Pt/glassy carbon catalysts with mean particle sizes of 3.8 nm, 4.7 nm and 5.3 nm, Takasu et al. reported a slow decrease in the Pt-mass-specific rate with increasing particle size\cite{66}. Comparable findings were reported also by Durst et al. for Pt particles between 2.6 and about 10 nm\cite{67}. Hence, in the size range above 2-3 nm, the mass-specific HER rates were found to increase with decreasing particle size. A complete account of the main results of previous HER studies, focusing on Pt particle size effects and the related experimental conditions / parameters, is given in Table 6.2 in the Appendix. Based on calculations of the $H_{\text{ad}}$ binding energy on different sites on a Pt$_{55}$ cluster and micro-kinetic simulations for particles with different sizes, Tan et al. derived a volcano-like relation for the HER, again with a maximum in the mass-specific activity at around 2.2 nm\cite{64}. Note that this calculation does not account for changes in the local electronic properties with increasing particle size, as they were reported and discussed earlier\cite{261}. The results of the theoretical study by Tan et al. are not in contrast to the experimental findings presented above, as the latter did not cover the range of very small Pt particles below 2-3 nm.

This was topic of a number of recent studies, which explored particle size effects in the HER activity for Pt NCs with sizes between 2 nm and individual Pt atoms (single atom catalysts - SAC). Studying the HER activity of mass selected Pt NCs on TiO$_2$, Neuberger et al. compared Pt$_1$, Pt$_{10}$ and Pt$_{13}$ NCs with 230 nm NPs, and found that the Pt$_{13}$ NCs were most active\cite{181}. Covering mass selected Pt NCs between Pt$_3$ and Pt$_{45}$, supported on SrTiO$_3$(100), Tsunoyama et al. found a steady-increase of the mass-specific HER rate with increasing NC size. Although the activity varied only little between the Pt$_{30}$ and Pt$_{45}$ NCs, these authors claimed a maximum for Pt$_{30}$ NCs\cite{179}. Zhou et al., observed monotonically increasing HER rates for particle sizes up to 8 nm, followed by a constant...
Normalizing their HER currents to the respective particle mass, one obtains a monotonic increase of the mass-specific activity with increasing NC size in the range between 0.5 nm and 1.5 nm. For particles with sizes between 3.0 nm and 20.2 nm, the mass-specific activity steadily decreases with increasing particle size. Thus, a maximum in mass-specific activity should be obtained for particle sizes somewhere between 1.5 nm and 3.0 nm. Cheng et al. investigated the HER performance of Pt NCs, which were prepared on N-doped graphene, by atomic layer deposition (ALD). Compared to a Pt/C catalyst with a mean Pt particle size of 5.0 nm, they reported a much higher Pt-mass-specific HER rate for the ALD-prepared catalysts, which they ascribed to a higher HER activity of the small NCs and single Pt atoms in those catalysts.

Finally, SACs have attracted a lot of interest over the past few years, since based on the high utilization of the active Pt metal high Pt-mass-specific HER rates can be expected. Extensive overviews are given in. Zhang et al. reported for a SAC supported on a porous carbon matrix an increase of the Pt-mass-specific HER rate by a factor of about 13.5 compared to that obtained on a commercial Pt/C catalyst. Recently, Ye et al. reported a 46 times higher Pt-mass-specific activity for a Pt SAC supported on aniline-stacked graphene compared to commercial Pt/C. In many cases, however, a quantitative determination of the HER activity of these SACs was not possible, as they contained a mixture of single metal atoms and small clusters.

Overall, the above mentioned studies demonstrated that reducing the particle size below 2-3 nm may result in dramatically enhanced mass-specific activities for the HER. The role of particle size effects in the HER and the existence of a volcano shaped size-dependence of the HER activity are, however, still unresolved on a quantitative scale. This is mainly due to a lack of systematic quantitative data in the range of particle sizes below 2-3 nm.

This is topic of the present study, where we systematically investigated the HER on Pt NCs with mean sizes between Pt$_{25}$ and Pt$_{110}$. We employed a combined Surface Science/electrochemical approach involving UHV-STM and an electrochemical flow cell set-up. Structurally and chemically well-defined model electrodes consisting of arrays of Pt NCs with a specific size and a narrow size distribution were grown under UHV conditions on an (electro)chemically inert substrate which consists of a defect free graphene layer supported on a Ru(0001) single crystal (gr/Ru(0001)). It has been demonstrated earlier that such gr/metal templates allow for the growth of NC arrays with a rather narrow NC size distribution, with the mean NC size depending on the growth conditions. These NC-gr/metal systems are stable against sin-
6.1 Pt NC size effects in the HER

tering at room temperature. Furthermore, the gr/metal template is chemically inert to (electro-)chemical reactions under present reaction conditions. Thus, it was considered to not affect the catalytic properties of the supported Pt NCs as it might occur with other templates\cite{266,267}. Thus, these NC-gr/metal samples are promising model systems for studies of particle size effects, as had been demonstrated recently in gas phase catalysis\cite{266–268}.

The structural characteristics of the gr/Ru(0001) supported Pt NCs were derived from direct imaging \textit{via} UHV-STM. We then characterized the electrochemical properties and the HER performance in an electrochemical flow cell set-up attached to the UHV system\cite{53}. The Pt-mass-specific HER rates as well as the exchange current density were derived, where the latter was normalized to the active experimentally determined surface area of the Pt NCs. Both parameters were used to derive cluster size effects on the activity of the Pt NCs. The resulting activities are compared with those of systems in the same size range and of commercial carbon supported Pt catalysts.

6.1.3 Results

**Structural characteristics – Control of the Pt NC size**

The Pt NCs were grown on gr/Ru(0001) and structurally characterized by STM imaging under UHV conditions, following procedures that are described in Section 5.2.1 and in previous References\cite{53,120}. Representative STM images of the well-ordered defect-free graphene film on Ru(0001) are depicted at different magnifications in Figure 6.2a. They illustrate a Moiré pattern with a regular buckling of the graphene layer on the Ru(0001) substrate, which originates from the lattice mismatch between the graphene layer and the substrate\cite{123}. The high resolution STM image of the gr/Ru(0001) surface in Figure 6.2a exhibits three regions with different geometric/electronic properties ($\alpha, \beta$ and $\gamma$) on the surface, where the $\alpha$-site (fcc-site) represents the preferential Pt NC nucleation center\cite{51,113,114,120}. The quality of the graphene layer was also controlled by electrochemical measurements in supporting electrolyte (see Appendix, Figure 6.5). Since the characteristic redox features of bare Ru(0001) are virtually absent in the voltammetric traces, we verified by electrochemical measurements that the Ru(0001) surface was almost fully covered by a continuous graphene film.

The nucleation and growth behavior of Pt NCs deposited on gr/Ru(0001) \textit{via} physical vapor deposition was already described previously, including both experimental and computational approaches\cite{51,113,114,120}. Based on these insights we prepared a set of six
different electrodes, each with Pt NCs of a different average size and with a narrow size distribution. As illustrated in Figure 6.2b and elaborated in more detail in the Appendix (Table 6.3), this was achieved by varying the amount of Pt deposited and for some electrodes by annealing the sample subsequent to the Pt deposition. As a result we obtained a set with increasing Pt NC sizes from electrode 1 to 6 (Table 6.1).
6.1 Pt NC size effects in the HER

Figure 6.2: Structural characterization of the gr/Ru(0001)-supported Pt NCs. (a) Representative 100 nm x 100 nm STM image (left) showing an as-prepared graphene layer on Ru(0001), a 10 nm x 10 nm high resolution STM image (right) illustrating the three different adsorption regions on the graphene monolayer (α: fcc, β: hcp and γ: top). (b) Pt coverage (blue) and sintering temperature (orange) for each of the electrodes. The error bars of $\theta_{Pt}$ indicate the approximate absolute uncertainty of the coverage determination from STM images (see Section 5.2.1). (c) Representative 50 nm x 50 nm STM images of electrodes 1, 3 and 5 (from left to right) illustrating the influence of increasing Pt coverage and of the sintering temperature (here 673 K) on the Pt NC size. (d) Plots of the NC height distribution (in units of Pt layers) of the different electrodes (a set of STM images for each electrode and full details of the statistical analysis are given in the Appendix). (e) Graphical representations of the Pt NC models employed for the size and surface area evaluation.

Representative STM images of the electrodes 1, 3 and 5 are depicted in Figure 6.2c (additional STM images for all six electrodes are given in the Appendix, Figure 6.6).

To minimize the influence of tip effects in the evaluation, we evaluated the heights
of the NCs\cite{121}, which are given in multiples of a Pt(111) monolayer (ML$_{Pt}$, 1 ML$_{Pt}$ = 0.226 nm). The height distributions shown in Figure 6.2d were derived from a quantitative statistical analysis of the NC heights from the STM images (for details see the Appendix).

The data confirm narrow NC height distributions and increasing NC heights from electrode 1 to 6. This underlines the ability of gr/Ru(0001) to stabilize very small Pt NCs at room temperature in agreement with previous studies\cite{51,117,120}. To correlate the electrocatalytic activity of the Pt NCs and their respective size we determined for each electrode the average number of Pt atoms per NC ($S_{av}$). This was obtained by dividing the total number of Pt atoms per cm$^2$ by the number of NCs per cm$^2$ (see Table 6.3, Appendix). The number of Pt atoms is accessible from the overall Pt coverage, which was determined from reference experiments (see Table 6.3 and Section 5.2.1).

### Table 6.1: Structural characteristics and electrocatalytic properties of the Pt-gr/Ru(0001) electrodes and of Pt-poly. Average number of Pt atoms per NC ($S_{av}$), average diameter of the NC ($d_{av}$), electrochemical surface area ($ECSA_{Pt}$), maximum current density at 0.01V ($j_{max}$) and mass current density at 0.01V ($j_{mass}$) for each electrode. The uncertainty values of $S_{av}$ are standard deviations, determined from the height distributions shown in Figure 6.2d. Note that regardless of the uncertainties, the average size increases steadily from Electrode 1 to 6, which is evident from the height distributions in Figure 6.2d. The uncertainty values of $|j_{max}|$ and $|j_{mass}|$ are approximate absolute uncertainties, based on the accuracy of the potentiostat and the propagation error from the Pt coverage.

| Electrode | $S_{av}$ (atoms) | $d_{av}$ (nm) | $ECSA_{Pt}$ (cm$^2$/Pt) | $|j_{max}|$ at 0.01 V (mA cm$^2$/Pt) | $|j_{mass}|$ at 0.01 V (A mg$^{-1}$Pt) |
|-----------|------------------|--------------|-------------------------|-------------------------------|-------------------------------|
| 1         | 25 ± 13          | 1.13         | 0.00963                 | 0.06 ± 0.02                   | 0.14 ± 0.02                   |
| 2         | 33 ± 10          | 1.24         | 0.02325                 | 0.90 ± 0.02                   | 1.77 ± 0.02                   |
| 3         | 38 ± 8           | 1.30         | 0.03664                 | 3.39 ± 0.02                   | 5.27 ± 0.02                   |
| 4         | 49 ± 9           | 1.41         | 0.03893                 | 2.28 ± 0.02                   | 3.76 ± 0.02                   |
| 5         | 99 ± 40          | 1.79         | 0.02842                 | 0.62 ± 0.02                   | 0.89 ± 0.02                   |
| 6         | 110 ± 39         | 1.85         | 0.00605                 | 0.42 ± 0.02                   | 0.11 ± 0.02                   |
| Pt-poly   | -                | -            | 0.87385                 | 0.20 ± 0.02                   | -                             |

The $S_{av}$ values resulting for each electrode are summarized in Table 6.1 and range from $S_{av} = 25$ (Pt$_{25}$) for electrode 1 to $S_{av} = 110$ (Pt$_{110}$) for electrode 6. For comparison with literature data the respective average diameter of the NCs was determined by calculating the diameter of a hemispherical particle consisting of the respective average number of atoms. The values are given in Table 6.1. To determine the electrochemically
active Pt surface area \((ECSA_{Pt})\) we did not follow the typical procedure \(\text{via } H_{\text{upd}}\), since this may be affected by variations in the hydrogen adsorption energy on these small particles compared to extended surfaces. Instead, we calculated the \(ECSA_{Pt}\) from cluster models of the NCs. Based on the height distributions, we designed Pt cluster models with different heights, whose size was adjusted such that the total Pt coverage and the Pt NC density were reproduced for every single electrode. The cluster models were created in such a way that the contribution of the thermodynamically most stable (111) facets of Pt \[^{33}\] is maximized (see Figure 6.2e). Details of the fit procedure are given in the Appendix. The \(ECSA_{Pt}\) values resulting for the different electrodes are listed in Table 6.1. The reliability of this approach is further illustrated by the fact that the mean NC sizes calculated from the cluster models agree very well with the \(S_{ac}\) values derived from the total amount of Pt deposited and the NC density determined by STM.

**HER on size-controlled Pt NCs**

For the electrocatalytic measurements the electrodes were transferred from the UHV system to an electrochemical flow-cell set-up under controlled conditions (for details see Section 5.3 and Reference \[^{53}\]). A first important finding is that the electrocatalytic activity of the pristine gr/Ru(0001) template for the HER is negligible in the potential range investigated (see Figure 6.5a, Appendix). Furthermore, the Ru(0001) supported graphene layer stays fully intact during the electrocatalytic treatment. This was evidenced by STM imaging after the electrochemical measurements (see Figure 6.5, Appendix) and by the fact that the CVs did not change during repeated cycling in the potential range investigated. Therefore, we can unequivocally attribute any HER activity measured on the Pt-gr/Ru(0001) electrodes to the Pt NCs.

Polarization curves recorded on the six different Pt-gr/Ru(0001) electrodes are depicted in Figure 6.3a. All currents are normalized to the respective \(ECSA_{Pt}\) determined from the cluster models (see Table 6.1). For each electrode we recorded three polarization curves, where only the first cycle is shown in Figure 6.3a. Subsequent cycles revealed a consecutive slight deactivation (Figure 6.8), which implies that some of the clusters were either dissolved or underwent a ripening during the HER. A more detailed description of the stability as well as of the reproducibility of the measurements is provided in Figure 6.9 and Figure 6.10 in the Appendix.

In addition to the Pt-gr/Ru(0001) electrodes, we included a polarization curve for a bulk polycrystalline Pt (Pt-poly) electrode measured in the same flow-cell set-up under the same experimental conditions as a reference. Different from the NC samples, for the
Results and Discussion

Pt-poly electrode the currents are normalized to the ECSA determined from the H$_{\text{upd}}$ charge\cite{248} (see Table 6.1). On bulk Pt-poly the HER is initiated at $E = 0.07$ V. This potential is very close to values reported previously under similar experimental conditions ($E = 0.06$ V) and is typical for H$_2$-free electrolytes\cite{269}. For the Pt-gr/Ru(0001) electrodes, except for the electrode with Pt$_{25}$ NCs, the onset potential for the HER, is located at around $E = 0.10$ V, i.e., it is shifted by ca. 0.04 V towards more positive potentials compared to Pt-poly. More important, for Pt NCs with sizes between 33 and 110 atoms the ECSA$_{Pt}$ normalised maximum current density $j_{\text{max}}$ at the lowest applied potential ($E = 0.01$ V) is clearly above the $j_{\text{max}}$ of Pt-poly. Furthermore, $j_{\text{max}}$ is affected by the NC size, with a maximum of $|j_{\text{max}}| = 3.39 \pm 0.02$ mA cm$^{-2}$ Pt obtained for Pt$_{38}$ NCs (see Table 6.1).

For smaller NCs (Pt$_{33}$ and Pt$_{25}$), $|j_{\text{max}}|$ continuously decreases with decreasing NC size, while for larger NCs (Pt$_{49}$ - Pt$_{110}$), $|j_{\text{max}}|$ decreases as the NC size increases. The smallest (Pt$_{25}$) and largest (Pt$_{110}$) Pt NCs exhibit $|j_{\text{max}}|$ values well below that of Pt$_{38}$. Furthermore, the $|j_{\text{max}}|$ value of Pt$_{110}$ is very close to that of bulk Pt-poly. The observed NC size effect also appears if the as-measured currents at 0.01 V are normalized to the mass of Pt deposited on each electrode ($j_{\text{mass}}$, see Figure 6.3b). In the range between Pt$_{38}$, Pt$_{49}$, Pt$_{99}$ and Pt$_{110}$, $|j_{\text{mass}}|$ decreases continuously with increasing Pt NC size, resulting in mass-specific HER currents of $5.27 \pm 0.02$ A mg$^{-1}$ Pt and $0.11 \pm 0.02$ A mg$^{-1}$ Pt at 0.01 V for Pt$_{38}$ and Pt$_{110}$, respectively. At lower loadings, in the range between Pt$_{25}$, Pt$_{33}$ and Pt$_{38}$, $|j_{\text{mass}}|$ increases continuously with increasing amount of Pt deposited (see Figure 6.3b). Overall, the above data clearly demonstrate the existence of a particle size effect in the HER in the size range investigated.

For a convenient comparison of these activities with those reported in the literature and from a technical and economic point of view the rates are normalized to the mass of the noble metal (‘Pt-mass-specific rates / currents’) when describing the activity of the active material. A normalization to the area of the electrode (‘current density’) is standard in the electrochemistry literature, while from a catalysis science perspective a normalization to the number of Pt surface atoms (turnover frequency (TOF)) would be most informative. Regardless of the normalization procedure, our data always show a clear maximum, although on a quantitative scale the effects are different. For instance, the change in Pt-mass-specific HER activity from Pt$_{25}$ to Pt$_{38}$ by a factor of ca. 40 is clearly different from the change in the ECSA$_{Pt}$ normalized current, which increased by factor of ca. 60, when going from Pt$_{25}$ to Pt$_{38}$.

As listed in Table 6.2, for different commercial Pt/C catalysts, Pt-mass-specific HER
current values of ca. 0.032 A mg\(_{-1}\)\(\text{Pt} \) at -0.10 V (20 wt.% Pt/C Vulcan XC-72R E-Tek) and of ca. 0.27 A mg\(_{-1}\)\(\text{Pt} \) at -0.05 V (Vulcan XC-72R) were reported by Cheng et al.\(^{[61]}\) and by Ham et al.\(^{[59]}\). Based on the exchange current density, Durst et al. determined a Pt-mass-specific activity of ca. 100 A mg\(_{-1}\)\(\text{Pt} \) at a \(\text{H}_2\) pressure of 100 kPa and 313 K for a Pt/C catalyst (5 wt.%) consisting of Pt NPs with a size of 2.6 nm \(^{[67]}\). The highest Pt-mass-specific HER rates determined at standard conditions so far were, to the best of our knowledge, reported for i) a catalyst consisting of individual Pt atoms and small Pt clusters supported on nitrogen-doped graphene nanosheets (ca. 10.1 A mg\(_{-1}\)\(\text{Pt} \) at -0.05 V) \(^{[61]}\) and ii) a Pt SAC supported on aniline-stacked graphene with mass-specific current of 22.4 A mg\(_{-1}\)\(\text{Pt} \) at -0.05 V \(^{[62]}\), which roughly corresponds to 0.44 A mg\(_{-1}\)\(\text{Pt} \) at 0.01 V.

Thus, our results (5.27 A mg\(_{-1}\)\(\text{Pt} \) at 0.01 V) indicate that compared to commercial Pt/C catalysts\(^{[59,61]}\) the Pt loading could be dramatically reduced when employing Pt\(_{38}\) NCs, as their Pt-mass-specific HER rate at 0.01 V exceeds those of the former catalysts by at least three orders of magnitude. Even compared to the novel Pt based catalysts described above the mass-specific activity of Pt\(_{38}\) NCs it is higher by one order of magnitude (see also Table 6.2).

From a Tafel analysis of the current densities determined on the our Pt-poly electrode (see Figure 6.11, Appendix) we determined a Tafel slope of 36 ± 3 mV dec\(^{-1}\), which is in good agreement with the slope of 30 mV dec\(^{-1}\) reported in literature\(^{[270]}\). The Tafel slopes of the Pt-gr/Ru(0001) electrodes are in the same range, with values between 34 ± 3 mV dec\(^{-1}\) and 38 ± 3 mV dec\(^{-1}\) (see Table 6.4), suggesting that there is no change in the rate determining step when lowering the Pt NC size down to \(S_{av} = 25\) atoms. Note that similar HER Tafel slopes were also reported previously on low-index Pt single crystal electrodes\(^{[271,272]}\) and on carbon supported Pt NP catalysts\(^{[273,274]}\). Classically, the exchange current density (\(j_0\)) is employed to quantify the reactivity of different (bulk) electrode materials\(^{[11]}\), since it reflects the intrinsic rate of the electron transfer in this reaction on the respective electrode\(^{[275]}\). The \(j_0\) values determined here from the Tafel analysis are plotted as a function of the average NC size (\(S_{av}\)) in Figure 6.3b. Also here we obtain a volcano-shaped curve with a maximum of 10.1 ± 0.1 mA cm\(^{-2}\) for Pt\(_{38}\) (normalized to the ECSA\(\text{Pt} \)). For mean NC sizes below (above) Pt\(_{38}\), \(j_0\) decreases with decreasing (increasing) Pt NC size. The value of \(j_0\) for Pt\(_{110}\) is identical to that of Pt-poly (\(j_0 = 1.0 ± 0.1\) mA cm\(^{-2}\)). Previously reported \(j_0\) values for the HER on Pt electrodes, including supported nanoparticle catalysts and single crystal electrodes, vary in the range of ca. 0.8 mA cm\(^{-2}\) to ca. 2.1 mA cm\(^{-2}\)\(^{[59,172,271,272,274,276]}\), in good agreement with the value that we obtained on Pt-poly.
In summary, we have identified a volcano-shaped dependence of the activity ($|j_{max}|$, $|j_{mass}|$ and $j_0$) on the averaged Pt NC size for mean NC sizes below 110 atoms. A maximum in the ($ECSA_{Pt}$ normalized) exchange current density of $j_0 = 10.1 \pm 0.1 \text{ mA cm}^{-2}_{Pt}$ was determined for Pt$_{38}$ NCs, which exceeds previously reported $j_0$ values obtained for the Pt electrodes mentioned above by about one order of magnitude.

Figure 6.3: (a) HER polarization curves of the different Pt NC electrodes and of a bulk polycrystalline Pt (Pt-poly) electrode for comparison, as indicated in the Figure (10 mV s$^{-1}$, N$_2$-saturated 0.5 M H$_2$SO$_4$) and (b) plot of the exchange current densities $j_0$ for the HER as determined from a Tafel analysis (black squares) and of the mass-specific activity $j_{mass}$ (red circles) as a function of the average number of Pt atoms per NC $S_{av}$ (the black dotted line represents $j_0$ for a bulk Pt-poly electrode). The error bars are based on the accuracy of the linear regression in the Tafel analysis (see Figure 6.11).

6.1.4 Discussion

To begin with we compare our data with the volcano-shaped ORR activity curve by Shao et al.$^{[175]}$, the HOR activity curve derived by Sun et al.$^{[178]}$ and the HER activity predicted by Tan et al.$^{[64]}$, all of which exhibited a typical volcano shaped size. Figure 6.4 shows the Pt–mass-specific activity as a function of the particle size reported in these studies, where the maximum mass-specific activities are normalized to the same value.
6.1 Pt NC size effects in the HER

Since in this figure we are specifically interested in the position of a possible activity maximum, we focused on studies that reported a maximum in the Pt-mass-specific rate. Other studies which reported a steady decline of the Pt-mass-specific activity with increasing particle size are not included[277]. For all three electrocatalytic reactions the predicted maximum activity is located in the NP size range of 2.2 - 3.5 nm. For comparison our experimental data is also included in Figure 6.4, indicating that there is indeed an optimum particle size for Pt in the HER, but at significantly lower particle size compared to the ORR and the HOR. Furthermore, it is much lower than that predicted in the theoretical study by Tan et al.[64]. Comparing with experimental HER studies, this activity trend differs from the data reported by Durst et al.[67], who reported a steady decline in the Pt-mass-specific activity for particle sizes between 2.1 and 8.7 nm. It seems to agree with the claims of Tsunoyama et al. and Neuberger et al., who proposed i) a subtle maximum for Pt$_{30}$ NCs and ii) a maximum for Pt NCs with sizes at or above Pt$_{13}$, respectively[179,181]. The latter data suffered, however, i) from a large error bar in the activity of the Pt$_{30}$ NCs, which would leave them also compatible with a continuous increase in activity with increasing cluster size up to Pt$_{45}$[179], and ii) from the fact that besides Pt-bulk no larger Pt NCs (> Pt$_{13}$) were tested which inhibits the identification of the optimum cluster size[181]. Considering this, our data provide the first clear experimental and unambiguous identification of an optimum Pt particle size for the HER.

Figure 6.4: Overview of literature data, where the Pt-mass-specific rates for different electrocatalytic reactions are plotted as a function of the Pt NC/NP size, together with the experimental data obtained in the present work. Black: experimental HOR study[178]. Green: experimental ORR study[175]. Red: theoretical HER study[64]. Blue: experimental HER data from present work. Markers indicate actual data points and lines are shown to guide the eye.
Volcano-type activity plots are well known from the literature for various reactions, including the HER, both from experiment and from theory\textsuperscript{[11,143,145]}. These plots refer, however, to a correlation between activity (exchange current density) and the binding energy of a reactant (adsorbate) on a homogeneous, single-crystalline substrate, which is considered as descriptor for the catalytic activity. In good agreement with the so-called Sabatier principle\textsuperscript{[141]}, the maximum activity should be obtained for a specific binding energy of the given reactant. For the HER it has been proposed previously that this optimum situation is reached for a standard free adsorption enthalpy of atomic hydrogen on the material of $\Delta G_{H^*} = 0$ eV\textsuperscript{[63]}. More recently, Nørskov and co-workers employed the adsorption energy of $H_{\text{ad}}$ ($\Delta E_{H^*}$) as a descriptor to rationalize the reactivity of electrode materials with computational methods and arrived at the same conclusion (for a given temperature $\Delta E_{H^*}$ and $\Delta G_{H^*}$ are linearly correlated)\textsuperscript{[143]}.

In the present case, the situation is distinctly different. First, in addition to the exchange current density, we decided to employ the Pt-mass-normalized HER current as measure for the activity, since the mass-normalized current allows for a better comparison with application oriented studies. Most important, however, the x-axis relates to the variation in particle size instead of the binding energy in the above representation. As a result, the situation is significantly more complex than in the above case. This is discussed in the following, where we assume that the general relation between $H_{\text{ad}}$ binding energy (descriptor) and HER activity is also valid for ultrasmall particles.

When discussing the relation between particle size and binding energy we first have to consider that the NPs/NCs feature a number of different adsorption sites with different binding energies to an adsorbate. On a qualitative scale this reflects the well-known trend that adsorbates tend to bind more strongly on under-coordinated sites such as edge and corner sites than on highly coordinated sites such as smooth facet sites\textsuperscript{[278]}. Quantitatively, this was demonstrated for hydrogen adsorption on Pt NCs, \textit{e.g.}, in a previous DFT study on a Pt\textsubscript{24} NC\textsuperscript{[279]}. The authors could show that $\Delta E_{H^*}$ varies strongly on the different adsorption sites considered. With increasing particle size the relative amount of the different sites will vary significantly, \textit{i.e.}, the relative amount of under-coordinated edge and corner sites will decrease, while that of highly coordinated facet sites will increase. Undercoordinated sites are frequently considered as active sites in a reaction. This is only true, however, if the optimum activity in the volcano plot requires a higher binding energy. Only in that case a higher fraction of undercoordinated sites is beneficial for the reaction, while they contribute only little in the opposite case. Nørskov \textit{et al.} derived in a theoretical study that an electrode material with a slightly lower $\Delta E_{H^*}$-
than Pt (lower by ca. 0.10 eV) should be at the top of a volcano-shaped curve\textsuperscript{[143]}. This claim was confirmed by Sheng \textit{et al.}, who showed experimentally, from pH-dependent measurements, that the reactivity of bulk single crystalline Pt electrodes for the HER increases with decreasing $\Delta E_{H^*}$ and that $\Delta E_{H^*}$ can be employed as sole reaction descriptor for the HER\textsuperscript{[280]}. Therefore, we suggest that bulk-like under-coordinated sites do not contribute to a higher HER activity.

Second, one would expect that the binding energy on similar types of adsorption sites changes with increasing size, in particular for very small particles and for NCs. In a theoretical study on cluster size effects in the binding energy of H\textsubscript{ad} ($\Delta E_{H^*}$), Okamoto \textit{et al.} calculated the $\Delta E_{H^*}$ values for different sites on a series of Pt NCs, including Pt\textsubscript{13}, Pt\textsubscript{38}, Pt\textsubscript{55} and Pt\textsubscript{147}\textsuperscript{[261]}. They reported that for the largest cluster the binding energies in the central, homogeneous part of the facets, \textit{e.g.}, (111) facets, had almost reached the values of bulk Pt(111) or Pt(100). On the other hand, significant differences were observed for the smaller clusters. Interestingly, depending on the adsorption site the binding energies were smaller or higher than on the smooth bulk surfaces\textsuperscript{[261]}.

Third, also interactions between support and the active metal (‘metal-support interactions’), which are well known both from heterogeneous catalysis\textsuperscript{[281–284]} and electrocatalysis\textsuperscript{[284–286]}, have to be considered. Zhou \textit{et al.} reported a much higher overpotential for the HER on Pt nanoparticles deposited on a Pb ultramicroelectrode than for a similar Pt/Bi system, which they explained by strongly different metal-support interactions\textsuperscript{[180]}. Tsunoyama et al. suggested for Pt NCs supported on a SrTiO\textsubscript{3} semiconductor that an overlap of the electronic bands of the semiconducting substrate with the Pt NCs results in changes of the H\textsubscript{ad} binding energy and thus of the HER rate\textsuperscript{[179]}. For the present case effects from metal NC-gr/Ru(0001) interactions were considered to be negligible in previous gas phase catalysis studies\textsuperscript{[266–268]}. Nevertheless, considering the much higher stability of these Pt NCs compared to Pt NCs on graphite we think that metal-support interactions have to be considered in the present case\textsuperscript{[51,122]}.

Summarizing these points we suggest that i) the maximum in the exchange current density is due to electronic size effects, which modify the Pt-H binding energy of given sites, and that ii) undercoordinated Pt atoms do not act as active sites, since they exhibit a generally higher Pt-H binding energy, while theoretically the maximum activity is expected for sites with lower binding energy. Note, however, that the overall activity of the NCs is an average activity of NCs with different sizes (see height distribution in Figure 6.2d), and of all sites present at the surface of these NCs. Accordingly, the Pt\textsubscript{38} NC should exhibit an optimum fraction of sites highly active for the HER.
Considering the vast number of different adsorption sites on a single Pt NC, the presence of Pt NCs with different size at each of the Pt-gr/Ru(0001) electrode surfaces (see Figure 6.2d) and the lack of detailed calculations of the particle size and site dependence of the hydrogen adsorption energy on Pt NCs it is not possible to provide a more detailed explanation for the observed optimum in HER activity for Pt$_{38}$ NCs. This would require extensive theoretical studies which are well beyond the scope of the present work.

A second, equally important result of this study is that the exchange current density of the Pt$_{38}$ NCs is close to the maximum exchange current density proposed from previous experimentally$^{[11,280]}$ and theoretically$^{[143,144]}$ derived volcano-shaped correlations between HER activity and H$_{ad}$ binding energy on transition metals. The maximum exchange current density, which is accessible according to these models, is around one order of magnitude higher than that of bulk Pt electrodes$^{[11,143–145]}$. Note that the absolute value of $j_0$ for bulk Pt electrodes in the volcano-shaped curves is located at around 1-2 mA cm$^{-2}$$^{[11,143–145]}$ which is in perfect agreement with experimentally determined values ($j_0 \approx 1$ mA cm$^{-2}$) for the HER on bulk Pt electrodes and Pt NP catalysts$^{[59,172,271,272,274,276]}$. This demonstrates that from the volcano-shaped curves it is also possible to predict absolute values for the exchange current density of metal catalysts. Hence, with an exchange current density of $j_0 = 10.1 \pm 0.1$ mA cm$_{Pt}^{-2}$ our Pt$_{38}$ NCs electrode should be close to the maximum of the volcano. As a result, for an electrode loaded with Pt$_{38}$ NCs, the Pt loading can be massively reduced compared to current state-of-the-art Pt/C catalysts to achieve a similar H$_2$ production rate. This is even more obvious from the Pt-mass-specific activity of the Pt$_{38}$ NCs ($j_{mass} = 5.27 \pm 0.02$ A mg$_{Pt}^{-1}$), which is at least by three orders of magnitude higher than that of commercial Pt/C catalysts.

Finally, note that for the development of technical Pt NC catalysts it is inevitable to develop suitable high surface area support materials which stabilize the Pt NCs against sintering or dissolution without affecting their high activity, similar to the role of the gr/Ru(0001) support in the present work. This is precondition for the long-term stability of such catalysts under electrocatalytic reaction conditions, and thus for their technical application. Furthermore, beyond such a fundamental study, suitable preparation procedures with cost-effective methods are required for both the high surface area support materials and the Pt NCs before considering their implementation as electrode material in a technical electrolyzer.
6.1 Pt NC size effects in the HER

6.1.5 Conclusions

Electrodes consisting of Pt NCs supported on electrochemically inert gr/Ru(0001) substrates were prepared under UHV conditions to yield Pt NCs with different, well-defined sizes and narrow size distributions. With these electrodes we have clearly demonstrated the presence of a pronounced volcano-like relation between HER activity and Pt NC size in the size regime below 110 atoms. While in previous theoretical and experimental studies a volcano-like relation was solely proposed, the present study provides clear experimental evidence for such a relation, since a significant amount of Pt NC sizes above and below the optimum NC size was investigated.

We observed the volcano-like relation for both the Pt-mass-specific activity, which is more relevant for practical application, and the \( \text{ECSA}_{\text{Pt}} \) normalized exchange current density. Note that this relation is fundamentally different from the well-known volcano type relation between activity and binding energy, as it includes effects from i) different sites on the NC, ii) electronic size effects and iii) metal–support interactions. The observation of a maximum in the Pt-mass-specific activity is in principal agreement with findings for other electrocatalytic reactions, while a maximum in the exchange current density was not reported so far. This occurs for a mean average NC size of ca. 38 atoms, with an exchange current density of \( j_0 = 10.1 \pm 0.1 \text{mAcm}^{-2} \text{Pt}^{-1} \). It is about one order of magnitude higher than that of classical Pt electrode materials and approaches the maximum activity proposed by theory. Highly important for practical applications, for the same HER rate the Pt loading of Pt catalysts could be reduced by at least three orders of magnitude when using NCs with an average size of ca. 38 atoms compared to state-of-the-art commercial Pt/C catalysts. The striking results presented in the present work are a stimulus for future research aiming at the design and preparation of technical Pt NC catalysts with cluster sizes in the range of few tens of Pt atoms.

6.1.6 Appendix

Overview on previous experimental HER studies on Pt NCs
### Table 6.2: Summary of the results of previous experimental HER studies on Pt NCs, with focus on NC sizes ranging from single atom catalysts (SACs) to 2 nm. SAC studies are only listed when included in the NC study.

<table>
<thead>
<tr>
<th>Particle size effect</th>
<th>Particle size</th>
<th>Most active</th>
<th>Support</th>
<th>Mass activity</th>
<th>$j_0$</th>
<th>Theory</th>
<th>Stability</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23 nm - 10.12 nm</td>
<td>(0.46 nm - 3.04 nm)</td>
<td>Bi, Pb</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Deactivation after 1st cycle</td>
<td>[180]</td>
</tr>
<tr>
<td>Pt₁, Pt₁₀, Pt₁₃, 230 nm</td>
<td>Pt₁₃</td>
<td>TiO₂ / Ti</td>
<td>229 A mg⁻¹⁻¹Pt @ -0.60 V</td>
<td>N/A</td>
<td>N/A</td>
<td>SA: Agglomeration</td>
<td>[181]</td>
<td></td>
</tr>
<tr>
<td>Pt₃, Pt₁₅, Pt₃₀, Pt₄₅</td>
<td>Pt₃₀ / Pt₄₅</td>
<td>SrTiO₃(100)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>NC: Dissolution Agglomeration</td>
<td>[179]</td>
</tr>
<tr>
<td>3.8 nm, 4.7 nm, 5.3 nm</td>
<td>3.8 nm</td>
<td>Glassy carbon</td>
<td>N/A</td>
<td>0.9 mA cm⁻²</td>
<td>N/A</td>
<td>N/A</td>
<td>Own work</td>
<td>[66]</td>
</tr>
<tr>
<td>2.1 nm, 3.3 nm, 4.4 nm, 8.7 nm</td>
<td>2.1 nm</td>
<td>N/A</td>
<td>100 A mg⁻¹⁻¹Pt (j₀, mass)</td>
<td>135 mA cm⁻²</td>
<td>N/A</td>
<td>N/A</td>
<td>Own work</td>
<td>[67]</td>
</tr>
<tr>
<td>Pt₂₅, Pt₃₃, Pt₃₈, Pt₄₉, Pt₉₉, Pt₁₁₀</td>
<td>Pt₃₈</td>
<td>gr/Ru(0001)</td>
<td>5.27 A mg⁻¹⁻¹Pt @ 0.01 V</td>
<td>10.1 mA cm⁻²</td>
<td>N/A</td>
<td>Slight deactivation after 3 cycles</td>
<td>Own work</td>
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</table>

<table>
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<tr>
<th>Pt-mass-specific activity</th>
<th>Catalyst</th>
<th>Support</th>
<th>Mass activity</th>
<th>$j_0$</th>
<th>Theory</th>
<th>Stability</th>
<th>Ref</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Pt NP</td>
<td>Vulcan XC-72</td>
<td>0.27 A mg⁻¹⁻¹Pt @ -0.05 V</td>
<td>N/A</td>
<td>Yes</td>
<td>Deactivation @ 0.04 V</td>
<td>[61]</td>
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<tr>
<td></td>
<td>Pt NP (20 wt%)</td>
<td>Vulcan XC-72R</td>
<td>0.03 A mg⁻¹⁻¹Pt @ -0.10 V</td>
<td>1.5 mA cm⁻²</td>
<td>N/A</td>
<td>N/A</td>
<td>[59]</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Support</td>
<td>Mass activity</td>
<td>$j_0$</td>
<td>Theory</td>
<td>Stability</td>
<td>Ref</td>
<td></td>
</tr>
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<td></td>
</tr>
<tr>
<td>Pt NP (7.5 wt%)</td>
<td>W$_2$C</td>
<td>0.07 A mg$^{-1}$Pt @ -0.10 V</td>
<td>2.1 mA cm$^{-2}$</td>
<td>N/A</td>
<td>N/A</td>
<td>[59]</td>
<td></td>
</tr>
<tr>
<td>ALD-50-Pt</td>
<td>N-doped graphene</td>
<td>10.1 A mg$^{-1}$Pt @ -0.05 V</td>
<td>N/A</td>
<td>Yes</td>
<td>Stable @ 0.04 V</td>
<td>[61]</td>
<td></td>
</tr>
<tr>
<td>SAC</td>
<td>Single walled CNT</td>
<td>N/A</td>
<td>1.94 mA cm$^{-2}$</td>
<td>Yes</td>
<td>Stable after 5000 cycles</td>
<td>[265]</td>
<td></td>
</tr>
<tr>
<td>SAC</td>
<td>CoP-Nanotubes on Ni foam</td>
<td>70 A g$_{Pt}^{-1}$ @ -0.05 V</td>
<td>N/A</td>
<td>N/A</td>
<td>Stable after 5000 cycles</td>
<td>[287]</td>
<td></td>
</tr>
<tr>
<td>SAC</td>
<td>Aniline-stacked graphene</td>
<td>22.4 A mg$^{-1}$Pt @ -0.05 V</td>
<td>4.56 mA cm$^{-2}$</td>
<td>Yes</td>
<td>Stable after 2000 cycles</td>
<td>[82]</td>
<td></td>
</tr>
<tr>
<td>3.5 nm</td>
<td>DNA</td>
<td>1.33 A mg$^{-1}$Pt @ -0.045 V</td>
<td>N/A</td>
<td>N/A</td>
<td>1000 min @ -0.035 V</td>
<td>[60]</td>
<td></td>
</tr>
<tr>
<td>SAC</td>
<td>PyPOP@G</td>
<td>0.37 A mg$^{-1}$Pt @ -0.05 V</td>
<td>N/A</td>
<td>N/A</td>
<td>Stable after 1250 cycles</td>
<td>[288]</td>
<td></td>
</tr>
<tr>
<td>Pt$_3$Ni$_2$</td>
<td>Carbon</td>
<td>3.25 A mg$^{-1}$Pt @ -0.07 V</td>
<td>N/A</td>
<td>Yes</td>
<td>N/A</td>
<td>[289]</td>
<td></td>
</tr>
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</table>
6 Results and Discussion

Electrochemical properties and stability of gr/Ru(0001)

The CVs for bare Ru(0001) and gr/Ru(0001) electrodes in supporting electrolyte are compared in Figure 6.5. The CV of Ru(0001) exhibits characteristic current features for surface oxidation and reduction processes which were already described in detail in Reference [58]. This contains a broad oxidation peak in the positive-going scan initiated at 0.45 V and two reduction peaks centered at 0.52 V and 0.32 V. The CV of the gr/Ru(0001) electrode shows an almost complete suppression of these potential-induced surface oxidation/reduction current features, indicating a successful coverage of the Ru(0001) by the graphene layer. Nonetheless, we note a tiny reduction peak at 0.32 V, which might be attributed to the reduction of surface Ru oxide of non-covered Ru(0001). The coulometric charge under this peak equals 2 \( \mu \text{C cm}^{-2} \) whereas the charge of the peak at 0.32 V on the bare Ru(0001) electrode is 131 \( \mu \text{C cm}^{-2} \). This indicates that ca. 98.5% of the Ru(0001) single crystal is covered by the graphene layer, which can be rated as defect free. On both Ru(0001) and gr/Ru(0001), the hydrogen evolution reaction is initiated at ca. 0.10 V. At -0.02 V, the current density for the HER is about 10 \( \mu \text{A cm}^{-2} \) for both electrodes, which is far below the current densities measured for the Pt-gr/Ru(0001) electrodes being in the mA cm\(^{-2}\) range. Thus, the contribution from the gr/Ru(0001) substrate is considered as negligible.

Figure 6.5b shows an STM image recorded after electrochemical measurements. The periodic buckling of the Moiré is still clearly visible and no defects were observed in the...
6.1 Pt NC size effects in the HER

There is no restructuring of graphene in the potential range where the HER is performed on the Pt-gr/Ru(0001) electrodes.

Size control of Pt NCs on gr/Ru(0001)

The nucleation and growth behavior of Pt NCs on gr/Ru(0001) was already studied extensively in previous studies \[51,113,114,120\]. Based on these studies we tuned the size of the Pt NCs as described in the following. For NCs with sizes below 1 nm we deposited Pt on gr/Ru(0001) with a constant evaporation rate \(0.03 \text{ML min}^{-1}\) at room temperature. The size of the Pt NCs was increased by increasing the Pt coverage \(\theta_{\text{Pt}}\), i.e., by increasing the evaporation duration. Accordingly, the Pt coverage was varied from \(\theta_{\text{Pt}} = 0.02 \text{ML}\) to \(\theta_{\text{Pt}} = 0.12 \text{ML}\) for electrode 1 to 3 (see Figure 6.6b in the main text and Table 6.3). For even larger Pt NCs we first deposited Pt with a coverage of \(\theta_{\text{Pt}} = 0.12 \text{ML}\) on gr/Ru(0001) at room temperature. Subsequently, the samples were annealed to a specific temperature \(T_{\text{sint}}\), which led to ripening of the Pt NCs \[117\]. Accordingly, we annealed the electrodes 4 to 6 to temperatures between \(T_{\text{sint}} = 473 \text{K}\) to \(T_{\text{sint}} = 873 \text{K}\) subsequent to the Pt deposition at room temperature (see Figure 6.2b and Table 6.3).

As depicted in Figure 6.6, which presents representative STM images and corresponding NC height distributions of the different electrodes, we obtained by the above described preparation procedure, six electrodes with increasing Pt NC size from electrode 1 to 6. For the electrodes 1 to 5 the NC height distributions are very narrow compared to commercial Pt/C catalyst materials thanks to the gr/Ru(0001) template (The broader height distribution of electrode 6 is discussed below). The most abundant Pt NC height \(h_{\text{max}}\) for electrode 1 is \(h_{\text{max}} = 1 - 2 \text{ML}_{\text{Pt}}\), while it is \(h_{\text{max}} = 3 \text{ML}_{\text{Pt}}\) for electrode 3 (see also Table 6.3). Post-annealing of the electrodes 4-6 led to a continuous increase of \(h_{\text{max}}\). The so-called filling factor \(FF\), which is defined as the ratio of the number of Pt NCs to the overall amount of existing fcc-Moiré adsorption sites \[117,120\] was determined by statistical analysis of the Pt NCs in a total area containing 1350 to 2240 fcc-Moiré sites and the resulting values are given in Table 6.3. Since the distance between two adsorption sites for the Pt NCs on the gr/Ru(0001) substrate is 3 nm, there are one hundred adsorption site within a 30 nm x 30 nm unit cell. Thus, the NC density can be calculated by dividing the \(FF\) value by the respective area in this unit cell (779.4 nm\(^2\)). The values of the respective NC densities are given in Table 6.3. Increasing the Pt coverage from \(\theta_{\text{Pt}} = 0.02 \text{ML}\) to \(\theta_{\text{Pt}} = 0.12 \text{ML}\) led to an increase of the \(FF / \text{NC density}\) for the electrodes 1-3. As expected, the \(FF / \text{NC density}\) then decreased for the electrodes 4 to 6 with increasing annealing temperature due a ripening process.
A closer inspection of the STM image of electrode 6 in Figure 6.6 reveals two different kinds of nanostructures on the surface: bright NCs with heights in the range of 2-12 ML\textsubscript{Pt} and monolayer high Pt islands (less bright) exceeding the size of a single Moiré adsorption site. For a better characterization of these islands a zoom in of such an island is depicted in Figure 6.7a. In this image the corrugation of the graphene sheet as well as two bright spots on top of the 1 ML high Pt-island are observed where the latter exhibit the same distance as two $\gamma$-regions of the corrugated graphene sheet.

Table 6.3: Structural characteristics and electrocatalytic properties of the Pt-gr/Ru(0001) electrodes. Pt coverage ($\theta_{Pt}$), annealing temperature ($T_{sint}$), filling factor ($FF$) cluster density ($\rho_{Cluster}$), most abundant cluster height ($h_{max}$), and average number of Pt atoms per cluster ($S_{av}$) for each electrode.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$\theta_{Pt}$ / ML</th>
<th>$T_{sint}$/ K</th>
<th>$FF$ / %</th>
<th>$\rho_{Cluster}$/ \texttimes 10^{12} \text{ cm}^{-2}</th>
<th>$h_{max}$/ ML\textsubscript{Pt}</th>
<th>$S_{av}$/ atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.02</td>
<td>298</td>
<td>14.4</td>
<td>1.85</td>
<td>1 - 2</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>0.06</td>
<td>298</td>
<td>27.0</td>
<td>3.47</td>
<td>2 - 3</td>
<td>33</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>298</td>
<td>37.2</td>
<td>4.77</td>
<td>3</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>0.12</td>
<td>473</td>
<td>32.1</td>
<td>4.12</td>
<td>4</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>0.11</td>
<td>673</td>
<td>12.7</td>
<td>1.63</td>
<td>4 - 5</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>0.12</td>
<td>873</td>
<td>3.19</td>
<td>0.41</td>
<td>2 - 12</td>
<td>110</td>
</tr>
</tbody>
</table>

A height profile along the blue line in Figure 6.7a is depicted in Figure 6.7b. The island width along the blue line is around $d = 6$ nm and the height from the lowest part of the island (at $d = 8.9$ nm) to the lowest point of the graphene corrugation was determined to be $h = 2.26$ Å which is equal to the height of one monolayer of Pt. Furthermore, the corrugation on top of the island presents the same periodicity ($d = 3$ nm) and height ($h = 0.36$ Å) as the Ru(0001) supported graphene layer. Similar observations for Pt-gr/Ru(0001) electrodes which were annealed to temperatures above $T = 800$ K were reported by Huang et al. who rationalized this observation by an intercalation of Pt between the graphene layer and the Ru(0001) substrate\cite{290}.
6.1 Pt NC size effects in the HER

Figure 6.6: (a) - (f): STM images (50 nm x 50 nm) of the six different Pt-gr/Ru(0001) with a coverage of (a) $\theta_{Pt} = 0.02$ ML ($I_T = 0.089$ nA, $U_T = 1.75$ V), (b) $\theta_{Pt} = 0.06$ ML ($I_T = 0.013$ nA, $U_T = 2.3$ V) and (c) $\theta_{Pt} = 0.12$ ML ($I_T = 0.013$ nA, $U_T = -1.3$ V) and subsequent annealing to (d) $T_{sint} = 473\,\text{K}$ ($\theta_{Pt} = 0.12$ ML) ($I_T = 0.028$ nA, $U_T = 0.7$ V), (e) $T_{sint} = 673\,\text{K}$ ($\theta_{Pt} = 0.10$ ML) ($I_T = 0.013$ nA , $U_T = 2.3$ V) and $T_{sint} = 873\,\text{K}$ ($\theta_{Pt} = 0.12$ ML) ($I_T = 0.631$ nA, $U_T = 1.5$ V). (g) - (l): Respective height distributions. The heights are given in multiples of one monolayer height of Pt (ML$_{Pt}$). In each height profile the respective $\theta_{Pt}$, the annealing temperature $T_{sint}$, the average number of atoms per Pt NC (SAV) and hard sphere models of the most abundant Pt NCs are shown. (l): The inset shows the same height distribution without $h_{\text{max}} = 1\,\text{ML}_{Pt}$. 

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Therefore, we conclude that also the 1 ML high islands for our electrode 6 are intercalated between the graphene layer and Ru(0001). Since these graphene-covered 1 ML high Pt islands are presumed to be inactive for adsorption (as it is the case for graphene-covered Ru(0001), Figure 6.5), they were excluded for the statistical analysis of the NC height distribution and the determination of the ECSA. The trend in the normalized electrode activity for the HER (see Figure 6.3) support the correctness of this assumption.

Figure 6.7: (a) Zoom in of a STM image from a monolayer high Pt-island of electrode 6 which was annealed to 873 K (15 nm x 15 nm). (b) Height profile along the blue line in a). The black horizontal bars indicate the presence of the same corrugation on top of the Pt-island as it appears for the Ru(0001) supported graphene sheet.

**Electrochemical Surface Area (ECSA)**

The electrochemical surface area (ECSA) is defined as the active area of the electrode surface which is exposed to the electrolyte and contributes to the electrocatalytic reaction. The methodology employed to determine the ECSA for the gr/Ru(0001) support and bulk polycrystalline Pt electrodes, serving as reference sample, is described in the following. Furthermore, the evaluation of the ECSA for the Pt NCs, which includes the development of a hard sphere model, is described below.

**ECSA of gr/Ru(0001) and polycrystalline Pt** The preparation of gr/Ru(0001) under UHV conditions provides a surface with terraces of widths up to 500 nm and, besides the small graphene corrugation, the surface can be assumed to be flat. In this case, the geometrical area \( A_{geom} \) can be assimilated to the ECSA. \( A_{geom} \) is determined by the inner diameter of the O-ring of the electrochemical flow cell onto which the electrode prepared under UHV conditions is pressed. The diameter of the pressed O-ring
is \( d = 6.0 \text{ mm} \) and therefore \( \text{ECSA}_{\text{gr/Ru}(0001)} = 0.28 \text{ cm}^2 \). Bulk polycrystalline Pt (Pt-poly) served as a reference electrode for the properties of bulk Pt towards the HER. Its \( \text{ECSA} \) was determined with the method described by Biegler et al.\[248\] by a coulometric analysis of the \( \text{H}_{\text{upd}} \) region from cyclic voltammograms in supporting electrolyte. As a result an \( \text{ECSA}_{\text{Pt-poly}} = 0.874 \pm 0.027 \text{ cm}^2 \) was determined.

**ECSA of Pt NCs** For the Pt NCs the latter method to determine \( \text{ECSA}_{\text{Pt}} \) via the \( \text{H}_{\text{upd}} \) region is not applicable, since the \( \text{H}_{\text{upd}} \) region is not present due to the early onset of the HER. Therefore, the \( \text{ECSA}_{\text{Pt}} \) of the Pt-gr/Ru(0001) electrodes were determined by the design of hard sphere models of the Pt NCs for which the atom composition and surface dispersion are well-known. For the design of the hard sphere models the following procedure was performed separately for each of the six Pt-gr/Ru(0001) electrodes.

At first, the amount of Pt (\( \theta_{\text{Pt}} \)) which was deposited on gr/Ru(0001) was used to determine the total number of Pt atoms (\( N_{\text{Pt,theo}} \)) within a 30 nm x 30 nm Moiré unit cell:

\[
N_{\text{Pt,theo}} = \theta_{\text{Pt}} \cdot A_{30 \times 30} \cdot \rho_{\text{Pt}}
\]

where \( A_{30 \times 30} = 779.4 \text{ nm}^2 \) is the surface area of the Moiré unit cell and \( \rho_{\text{Pt}} = 1.51 \cdot 10^{15} \text{ atoms cm}^{-2} \) is the atom density of the close-packed (111) surface on the Ru(0001) substrate. The term \( (A_{30 \times 30} \cdot \rho_{\text{Pt}}) \) is equivalent to a full monolayer coverage inside the Moiré unit cell. Since \( \theta_{\text{Pt}} \) represents the fraction of the area covered with Pt, \( N_{\text{Pt,theo}} \) equals the number of Pt atoms which are actually available to form clusters inside the Moiré unit cell. The 30 nm x 30 nm unit cell contains exactly one hundred adsorption sites.[128]

The hard sphere models are designed in a way that the total number of atoms used to design the NCs (\( N_{\text{Pt,model}} \)) within a Moiré unit cell is equal to \( N_{\text{Pt,theo}} \). \( N_{\text{Pt,model}} \) itself is given by:

\[
N_{\text{Pt,model}} = \sum_{i \text{ML}_{\text{Pt}}} N_{i \text{ML}_{\text{Pt}}} \cdot N_{i \text{ML}_{\text{Pt}},30 \times 30}
\]
Results and Discussion

\begin{equation}
N_{i \text{ML}_{\text{Pt}}, 30 \times 30} = n_{i \text{ML}_{\text{Pt}}} \cdot FF
\end{equation}

where \(n_{i \text{ML}_{\text{Pt}}}\) is the fraction of a NC with a height of \(i\) ML from the total amount of NCs on the Pt-gr/Ru(0001) sample. \(n_{i \text{ML}_{\text{Pt}}}\) is obtained from the respective height distribution of each sample. Since within a Moiré unit cell there are exactly one hundred adsorption sites, the multiplication with the respective \(FF\) directly provides \(N_{i \text{ML}_{\text{Pt}}, 30 \times 30}\). The hard sphere models were then designed such that \(N_{\text{Pt}, \text{model}} = N_{\text{Pt}, \text{theo}}\) is true for all six Pt-gr/Ru(0001) electrodes. Two main criteria for the design have been that i) the NCs consist of as many fcc-sites as possible, since this is the thermodynamically most favorable facet for Pt, and ii) the surface dispersion \(d_{OF}\) decreases with increasing NC size. Based on these hard sphere models the total number of Pt surface atoms \((N_{\text{Pt-surf}})\) at a Pt-gr/Ru(0001) electrode was then derived by

\begin{equation}
N_{\text{Pt-surf}} = \sum_{i \text{ML}_{\text{Pt}}} N_{\text{OF}, i \text{ML}_{\text{Pt}}} \cdot N_{i \text{ML}_{\text{Pt}}, 30 \times 30}
\end{equation}

, where \(N_{\text{OF}, i \text{ML}_{\text{Pt}}}\) is the number of surface atoms of a hard sphere model with \(i\) ML Pt height. The ECSA of a Pt-gr/Ru(0001) sample is finally given by

\begin{equation}
\text{ECSA}_{\text{Pt-Cluster}} = \frac{N_{\text{Pt-surf}}}{A_{30 \times 30} \cdot \rho_{\text{Pt}}} \cdot A_{\text{geom}}
\end{equation}

The ratio between \(N_{\text{Pt-surf}}\) and \((A_{30 \times 30} \cdot \rho_{\text{Pt}})\) gives the percentage of Pt surface atoms on the substrate. The product of this percentage with \(A_{\text{geom}}\) which is the geometrical area of the sample finally leads to \(\text{ECSA}_{\text{Pt-Cluster}}\). The ECSA for all six Pt-gr/Ru(0001) electrodes are listed in Table 6.1.

Pt NC stability

The first three HER polarization cycles of each of the six different Pt-gr/Ru(0001) electrodes are depicted in Figure 6.8. Regardless of the average Pt NC size the activity for the HER decreases with consecutive cycling. The extent of this deactivation varies, however, with NC size. While all electrodes except the one with Pt\(_{49}\) NCs reveal only a slight deactivation the electrode with Pt\(_{49}\) NCs exhibits a strong deactivation in the
6.1 Pt NC size effects in the HER

second cycle which we tentatively explain by the formation of a H₂ bubble in the EC flow cell during the first cycle leading to a reduced electrode surface area.

The slight decrease of all other electrodes might be explained by dissolution or ripening of the Pt NCs resulting in a lower Pt surface area and thus in lower HER currents. STM images recorded after the HER are shown in Figure 6.9a and 6.9b demonstrating the existence of NCs also during / after the HER. The respective height distributions are shown in Figure 6.9c and 6.9d in comparison with the height distributions before the HER. After the HER the distribution is broadened and also shifted to higher NCs. This might be explained by a ripening of the NCs during the HER, however, also molecules on top of the NCs which were adsorbed in the electrochemical environment might be a reason for this larger apparent heights.

Figure 6.8: First three potentiodynamic HER cycles (0.01 V - 0.90 V, 0.5 M H₂SO₄, 10 mV s⁻¹), on the Pt-gr/Ru(0001) electrodes with a) Pt₂₅ NCs, b) Pt₃₃ NCs, c) Pt₃₈ NCs, d) Pt₄₉ NCs, e) Pt₉₉ NCs and f) Pt₄₁₀ NCs.
Figure 6.9: Representative STM images of the Pt-gr/Ru(0001) electrodes with a) Pt$_{38}$ NCs and b) Pt$_{99}$ NCs recorded after the HER on these electrodes. The respective height distributions before the HER (blue) and after the HER (red) are illustrated in c) (Pt$_{38}$) and d) (Pt$_{99}$).
6.1 Pt NC size effects in the HER

Reproducibility

Figure 6.10: Potentiodynamic HER curves of two different Pt-gr/Ru(0001) electrodes with Pt\textsubscript{38} NCs recorded on different measurement days (10 mV s\textsuperscript{-1}, 0.5 M H\textsubscript{2}SO\textsubscript{4}). The lower potential limits are 0.00 V and 0.01 V, respectively.

Tafel analysis

Tafel plots of each Pt-gr/Ru(0001) electrode and of Pt-poly are shown in Figure 6.11. The Tafel slopes vary in the range between 34 mV dec\textsuperscript{-1} and 38 mV dec\textsuperscript{-1} for the different electrodes. For the most active electrode with Pt\textsubscript{38} NCs the Tafel slope is 34 mV dec\textsuperscript{-1} (see also Table 6.4). The exchange current densities which are plotted in Figure 6.3b are also given in Table 6.4.

Figure 6.11: Tafel plots of the Pt NCs and Pt-poly: Overpotential $\eta$ for the HER as a function of the logarithm of the experimentally measured current density related to the HER.
### Table 6.4: Tafel analysis of the Pt-gr/Ru(0001) electrodes and of Pt-poly. Average number of Pt atoms per cluster ($S_{av}$), Tafel slope ($b$) and exchange current density ($j_0$) for each electrode.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$S_{av}$ / atoms</th>
<th>$b$ / mV dec$^{-1}$</th>
<th>$j_0$ / mA cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>$37 \pm 3$</td>
<td>$0.1 \pm 0.1$</td>
</tr>
<tr>
<td>2</td>
<td>33</td>
<td>$38 \pm 3$</td>
<td>$2.0 \pm 0.1$</td>
</tr>
<tr>
<td>3</td>
<td>38</td>
<td>$34 \pm 3$</td>
<td>$10.1 \pm 0.1$</td>
</tr>
<tr>
<td>4</td>
<td>49</td>
<td>$35 \pm 3$</td>
<td>$6.2 \pm 0.1$</td>
</tr>
<tr>
<td>5</td>
<td>99</td>
<td>$36 \pm 3$</td>
<td>$1.5 \pm 0.1$</td>
</tr>
<tr>
<td>6</td>
<td>110</td>
<td>$34 \pm 3$</td>
<td>$1.0 \pm 0.1$</td>
</tr>
<tr>
<td>Pt-poly</td>
<td></td>
<td>$36 \pm 3$</td>
<td>$1.0 \pm 0.1$</td>
</tr>
</tbody>
</table>
6.2 Selective modification and probing of the electrocatalytic activity of step sites

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![Graphical abstract](image)

**Figure 6.12**: Graphical abstract.

All experiments of this work besides the TPD measurements were planned by me. The preparation procedure of the Au modified Pt samples was elaborated by Valeria Chesnyak in her Bachelor Thesis \[245\] under my supervision. All experimental results of this work besides the TPD results were measured by me. The CO-TPD spectra were recorded by Mario Löw in his Bachelor Thesis \[292\]. I performed the full data evaluation and prepared all Figures. Furthermore, I was strongly involved in the creative process of the publication. The experimental procedure for the CO-TPD measurements is briefly described in the Appendix in Section 6.2.5.

### 6.2.1 Abstract

Employing Pt(111) supported 2D Pt-core Au-shell model catalysts, we demonstrate that 2D core-shell surfaces prepared under ultrahigh vacuum (UHV) conditions constitute excellent model systems to determine the activity of step sites in electrocatalysis, especially because UHV-scanning tunneling microscopy (STM) enables to control the quality of narrow step modifications with high accuracy on such systems. As verified with STM, cyclic voltammetry (CV) and temperature programmed desorption (TPD)
measurements, this approach allows us i) to increase the step density by homoepitaxial growth of monolayer high islands on the respective single crystal and ii) to modify the step sites for adsorption of reactants by selective deposition of a guest metal. Herein, STM imaging in combination with electrochemical characterization provides a direct control to ascertain a selective modification of the entire steps. Comparing the electrocatalytic activity of 2D core-shell systems with and without the shell enables us to identify the activity of step sites for electrocatalytic reactions, as demonstrated for the bulk CO electro-oxidation.

6.2.2 Introduction

The precise identification of the active surface sites in catalytic and electrocatalytic reactions is of utmost importance for the rational design of new catalyst materials with improved performance. For monometallic catalysts increased activities are often associated with surface defect sites with low coordination surface atoms such as in steps and kinks. The improved activity is explained by the different electronic and chemical properties of these sites compared to sites formed by surface atoms with higher coordination, as they appear on close-packed terraces\(^\text{[18–22]}\). Experimentally, the most common approach to derive information on the electrocatalytic properties of step sites involves model studies, where the (electro-)catalytic activity of low-index single crystal electrode surfaces is compared to that of stepped surfaces vicinal to those orientations\(^\text{[22,68,72]}\). Additional information was gained by selective modification of the steps with a guest metal, which does not influence the chemical or catalytic properties of these surfaces\(^\text{[18]}\). Focusing on electrocatalytic reactions, which are particularly relevant in future energy storage and conversion processes, step modification was primarily achieved via underpotential metal deposition\(^\text{[70,293–295]}\). The structural properties of the resulting step modified vicinal surfaces were usually characterized only by cyclic voltammetry.

Main problems in these studies are on the one hand the often ill-defined local step structures and – for high step densities, where step induced electronic or chemical effects may possibly interfere with each other – the fact that the step density is generally concluded from the macroscopic misorientation of the surfaces compared to the respective close-packed surfaces rather than by direct imaging. For a better controlled approach, in particular in the range of low step/defect densities, we followed a different procedure, where we created surfaces with well-defined step densities by formation of monolayer islands via physical vapor deposition under UHV conditions on a smooth substrate of the same material. By proper choice of the deposition parameter (deposition rate, surface
6.2 Pt step sites in the CO electro-oxidation

temperature, amount of deposit), this approach allows for creation of surfaces with well-defined island sizes and densities, which can be characterized by STM and other surface science tools. The resulting step edges can be modified by post-deposition of a second metal under conditions, where the surface mobility is sufficiently high that nucleation of additional islands is inhibited\cite{75,105}. In that case, the post-deposited metal condenses at the ascending steps, which results in the desired step modification.

These structures can be considered as 2D core-shell model catalysts, where the monoatomically high island structures are selectively modified at their perimeter by narrow stripes of a guest metal. These rather complex 2D core-shell structures, which are only accessible by preparation under UHV conditions\cite{18,74,75} have not been employed so far for electrochemical/-catalytic studies. With the recent progress in combining surface science tools and electrochemical techniques, the investigation of the electrochemical/-catalytic properties of highly complex but well-defined nanostructured mono- and bimetallic surfaces has, however, become feasible\cite{50,52–55,205}. Here we report results of a study where we investigated the impact of Pt steps on the bulk CO electro-oxidation on Pt(111) surfaces by comparing this reaction on a bare Pt(111) electrode with a low step density, on a Pt(111) electrode modified by monolayer high Pt islands with an increased step density (Pt/Pt(111)), and finally on the above surfaces with the step edges modified by a narrow stripe of Au. For the Au modified Pt/Pt(111) electrode this results in a 2D Pt-core Au-shell model catalyst.

To demonstrate the high potential of this approach for investigating the role of step sites in electrocatalytic reactions, we employed the CO electro-oxidation as model reaction, since it is known to be structure sensitive and mechanistically reasonably well understood on simple Pt metal electrodes\cite{17,23,68,69,72,73,199,296,297}. There is agreement that CO molecules adsorbed on a Pt surface are electro-oxidized to CO$_2$ via a Langmuir-Hinshelwood mechanism by reaction with OH$_{\text{ad}}$ species, which are formed by dissociation of water at an adjacent Pt site\cite{184}. From studies investigating the oxidation of a CO monolayer pre-adsorbed on Pt(111) and on stepped surfaces vicinal to Pt(111) (‘CO$_{\text{ad}}$ stripping’) it was suggested that the reaction takes place only at step sites\cite{68,69,71}. More recently, on the other hand, it was proposed that the reaction takes place mainly at terrace sites\cite{72,73}. Overall, these controversial proposals demonstrate that the role of Pt steps in the CO electro-oxidation is still unclear.
6.2.3 Results and Discussion

A representative STM image of an as-prepared clean Pt(111) electrode surface with a Pt step density (fraction of step sites) of approximately $0.8 \pm 0.1\%$ and terrace widths of 50 nm to 200 nm is shown in Figure 6.13a. Deposition of 0.20 ML Pt at room temperature and subsequent annealing to 570 K lead to the formation of compact, hexagonally shaped Pt monolayer islands on Pt(111) (Pt/Pt(111)) with a small fraction of second layer islands on top, as shown in Figure 6.13b and the inset therein, (see also Table 6.5). This results in a 3-fold increase of the total number of Pt step sites to $2.6 \pm 0.1\%$ (see Table 6.5), including the step sites along second layer islands. The latter is justified by the similar electronic nature of first and second layer Pt island edges. The separation between different islands (distance between island edges) is above 3 nm for 90% of the Pt islands, indicating that step–step interactions can be neglected.

Au deposition on the as-prepared Pt(111) and on the Pt/Pt(111) surface at $T = 570 \text{K}$ leads to the formation of 1-5 nm wide stripes of a pseudomorphically grown monolayer high Au film attached to the ascending Pt step and island edges. This is clearly resolved in the STM images due to the chemical contrast between both metals (see Figures 6.13c ($\theta_{\text{Au}} = 0.05 \pm 0.02 \text{ML}$) and 6.13d ($\theta_{\text{Au}} = 0.08 \pm 0.02 \text{ML}$), respectively). The varying widths of the Au stripes at the former Pt step/island edge sites provide further support to this assignment. Images with enhanced contrast, resolving the Au modifications at the Pt step edge and the island edges, are depicted in the inset in Figure 6.13c as well as in Figure 6.13e and 6.13f, respectively. The rim of the islands in Figure 6.13e and Figure 6.13f appears brighter, indicating that the island edges are fully modified by a thin monolayer high Au stripe, which is attached at the ascending Pt step edge. Comparison with the non-modified Pt monolayer island in the inset in Figure 6.13b, where such bright stripe is not observed, demonstrates that this is not due to electronic effects, but reflects the Au decoration. The difference in apparent height at the island edges is illustrated also by representative line scans of the images shown in Figure 6.13, which are given in Figure 6.17 in the Appendix, and is evident also in additional STM images of Au/Pt/Pt(111) in Figure 6.18 in the Appendix. The island densities and the fraction of 2\textsuperscript{nd} layer Pt islands in the Au/Pt/Pt(111) and Pt/Pt(111) surfaces vary little (see Table 6.5), which can be rationalized by small differences in the deposition conditions. This also indicates that nucleation of Au islands between the Pt islands is negligible under these deposition conditions, which is further supported by the absence of island formation upon Au deposition on a pristine Pt(111) surface.

The stability of these model electrodes in an electrochemical environment, under the
6.2 Pt step sites in the CO electro-oxidation

Table 6.5: Structural properties determined before and after bulk CO electro-oxidation. $\rho_{isl}$: Pt island density. $\rho_{steps}$: Pt step density. $r(2^{nd})$: ratio of bilayer Pt islands with respect to the overall amount of Pt islands.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Before EC</th>
<th>After EC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\rho_{isl}$</td>
<td>$\rho_{steps}$</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>-</td>
<td>0.8 ± 0.1</td>
</tr>
<tr>
<td>Pt/Pt(111)</td>
<td>4.4 ± 0.7</td>
<td>2.6 ± 0.1</td>
</tr>
<tr>
<td>Au/Pt(111)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Au/Pt/Pt(111)</td>
<td>2.7 ± 0.7</td>
<td>-</td>
</tr>
</tbody>
</table>

conditions used in this study, was explored by a combination of ex situ STM imaging, characterizing the electrodes under UHV conditions before and after the electrochemical measurements, and the electrochemical measurements. STM images recorded on the samples after bulk CO electro-oxidation are depicted in Figure 6.13g-j. They demonstrate that the reaction does not cause any significant macroscopic restructuring or roughening of the surface such as the formation of islands or holes and that the density of Pt islands and Pt step sites remained approximately identical (Figure 6.13a-d, Table 6.5). This fully agrees with previous observations for the CO electro-oxidation on Pt(111)\textsuperscript{[23]}. Line profiles of the apparent height in STM images recorded after the CO electro-oxidation (Figure 6.17, Appendix) reveal a higher noise level in the STM images compared to those of the as-prepared surfaces. Since the noise is much less than the height of a Pt or Au monolayer step, it is attributed to electrolyte residues remaining on the surface upon emersion of the electrodes from the electrochemical cell, as observed previously\textsuperscript{[162]}. Due to the larger noise level caused by the electrolyte residues, resolution of a chemical contrast is not possible any more after the electrochemical measurements on these electrodes for such small structures. Nevertheless, the complete modification of the Pt steps by a continuous, narrow Au stripe can be verified by a combination of STM and electrochemical measurements. STM measurements performed on Au/Pt(111) electrodes with wider Au stripes, i.e., with increased Au coverage ($\theta_{Au} = 0.30$ ML – Figure 6.20), can clearly resolve the chemical contrast between Pt and Au after cyclic voltammetry measurements in pure and CO containing electrolyte (Figure 6.20). In addition, these images reveal a much lower noise on the Au covered areas (less residue adsorption),
in perfect agreement with expectations for a chemically inert surfaces such as Au covered Pt. These findings provide already strong evidence that the Pt step/island edges are fully modified by the Au stripes during/after the CO electro-oxidation also for the Au/Pt(111) electrodes with narrow Au stripes. Final proof for this comes from the electrochemical/CO electro-oxidation measurements, which will be discussed below. In addition, this topic is discussed extensively in the Appendix.

**Figure 6.13:** Representative STM images (100 nm x 100 nm) of (a) Pt(111), (b) Pt/Pt(111), (c) Au/Pt(111) and (d) Au/Pt/Pt(111) electrode surfaces recorded before bulk CO electro-oxidation together with a side view sketch of each electrode below the respective STM image. The inset in b) shows an enlarged STM image with enhanced contrast of the Pt island marked in b). The inset in c) shows the Au modified Pt step edge with enhanced contrast. (e) and (f): Enlarged STM images with enhanced contrast of 2D core-shell islands (the island shown in f) is marked in d). Bottom images: (g) - (j): Representative STM images (100 nm x 100 nm) of the four electrodes recorded after bulk CO electro-oxidation. Additional STM images of Pt/Pt(111) and Au/Pt/Pt(111) surfaces recorded before the CO electro-oxidation are presented in Figure 6.18 in the Appendix.

To gain additional insight into the presence of defects on the as-prepared surfaces we performed CO-TPD and cyclic voltammetry (CV) measurements in 0.5 M H$_2$SO$_4$. These provide information also about the influence of steps on the CO adsorption/desorption behavior (TPD) and on the competitive adsorption of hydrogen and hydroxide (CV), respectively.

CO-TPD spectra recorded from CO$_{ad}$ saturated Pt(111), Pt/Pt(111) and Au/Pt/Pt(111) surfaces are presented in Figure 6.21 in the Appendix. TPD spectra of sub-monolayer
6.2 Pt step sites in the CO electro-oxidation

CO\textsubscript{ad} covered surfaces, where desorption from defect sites is relatively more pronounced, are depicted in Figure 6.14a. With focus on the latter spectra, CO desorption from Pt(111) closely resembles results reported previously\cite{298}, with a single desorption peak in the range 400-500 K (peak temperature 466 K) and a very weak high-temperature shoulder in the range 500-530 K. The latter is attributed to desorption from strongly adsorbing defects such as step sites\cite{299}. For CO desorption from Pt/Pt(111), the higher number of step sites compared to Pt(111) leads to a pronounced increase in the intensity of the high-temperature shoulder in the range 500-530 K, as expected for an increased number of such sites with higher adsorption energy. This causes a decrease in the peak height at 466 K compared to Pt(111) at the approximately constant overall CO\textsubscript{ad} coverage\cite{299}. For Au/Pt/Pt(111) the high-temperature shoulder is absent. Apparently, the stabilized adsorption at the Pt steps, on the low-coordination Pt step atoms, is inhibited by the Au stripes attached to the ascending steps. This result agrees with a previous report, where Au deposited at the step sites of a Pt(335) surface was shown to significantly reduce the intensity of the high-temperature shoulder related to CO desorption from Pt step sites\cite{300}.

![Figure 6.14: (a) CO TPD spectra recorded from sub-monolayer CO\textsubscript{ad} covered Pt(111), Pt/Pt(111) and Au/Pt/Pt(111) surfaces (nominal exposure $\varepsilon_\text{CO} = 0.2$ L). (b) CVs recorded on Pt(111), Pt/Pt(111), Au/Pt(111) and Au/Pt/Pt(111) in 0.5 M H\textsubscript{2}SO\textsubscript{4} at 50 mV s\textsuperscript{-1}. Peaks A, B, and C see text.](image-url)
The CV recorded on Pt(111) in Figure 6.14b exhibits the typical reversible reduction / oxidation features for underpotential deposition / desorption of hydrogen (0.07 V to 0.33 V) and sulfate desorption / adsorption (0.33 V to 0.58 V), which were described in detail previously\cite{17,155,158,196}. The spikes at 0.44 V originate from an order-disorder phase transition in the adsorbed sulfate layer\cite{160,163}, while the small features around 0.68 V and 0.65 V were ascribed to competitive OH adsorption and sulfate desorption\cite{164}. Note that for Pt(111) the potential regions for H\textsubscript{upd} and for OH adsorption and desorption do not overlap\cite{301}.

In general, the H\textsubscript{upd} region of Pt(111) is considered as fingerprint to determine the quality of the electrode surface structure\cite{155,165-167}. The appearance of additional peaks at 0.12 V (peak A), 0.26 V (peak B) and 0.31 V (peak C) in this potential region of Pt/Pt(111) was ascribed to H adsorption on defect sites (steps and kinks) with different adsorption properties (adsorption strength) than on the terrace sites of the Pt(111) surface\cite{155,165-167}. Here peaks A and B were ascribed to H adsorption on step sites with different local structure, including step sites with local (110) structure\cite{158,166} (peak A) and step sites with local (100) structure\cite{165} (peak B). A peak at 0.31 V was, to the best of our knowledge, so far only observed on electrochemically roughened Pt(111)\cite{167} but not on stepped surfaces vicinal to Pt(111). We tentatively assume that this peak is related to the presence of kink sites (for details see Section 6.2.5, Appendix). It was also speculated that on defect sites the adsorption / desorption of H\textsubscript{upd} and OH are no longer separated, but may overlap or even overcross\cite{169,170,302}. From a quantitative evaluation we find that the peaks A-C include about 3 % of the coulometric charge (see Section 6.2.5, Appendix) for Pt/Pt(111), which agrees well with the fraction of step sites determined by STM for this surface. A faint peak B is also observed in the H\textsubscript{upd} region of Pt(111); its intensity is, however, close to the signal-to-noise ratio. On the Au modified surfaces the peaks A - C are absent and the CVs look essentially identical to the CV of Pt(111). Hence, the Pt defect sites are selectively blocked by Au for H\textsubscript{upd} and OH adsorption. The site blocking should show up also in the total charge transfer, but because of the low Au coverage (approximately 0.05 - 0.08 ML) this decay is below the detection limit. For higher Au coverages this loss in adsorption sites is clearly visible – see Figure 6.22, Appendix). Here it is important to note that repeated potential cycling of the Au modified electrodes in this potential range does not cause any change in the shape of the voltammograms, further supporting our STM based claim that these electrode surfaces are stable under electrochemical conditions.

Overall, the combined results obtained from the STM, TPD and CV measurements
consistently demonstrate that adsorption on Pt step edge atoms results in a stronger binding of H$_{\text{upd}}$ (or of OH$_{\text{ad}}$) and CO$_{\text{ad}}$, in good agreement with previous observations and claims\cite{299,303}. Furthermore, they demonstrate that upon decoration of the ascending step/island edges with a narrow, monolayer high Au stripe, adsorption on these sites is no more distinguishable from that on terrace sites. Obviously, these strongly binding defect sites do not exist any more.

Next we focus on the CO bulk electro-oxidation on the same electrodes. The j–E traces recorded during potentiodynamic bulk CO electro-oxidation on these electrodes are shown in Figure 6.15. The shape of the Pt(111) trace in Figure 6.15a is very similar to that of j-E traces reported previously for the same electrolyte\cite{16,17,297,304}. In the positive-going scan, starting from a CO$_{\text{ad}}$ covered surface\cite{305}, measurable reaction currents appear at about 0.55 V. They increase with potential and then change into an almost vertical current increase at 0.95 ± 0.01 V, which has been termed as ‘ignition potential’\cite{16}. Here we define the ignition potential $E_{\text{ign}}$ as that potential where the current density corresponds to 0.3 mA cm$^{-2}$. Above the ignition potential, the j-E trace in Figure 6.15a passes through a maximum, followed by an almost constant current density up to the upper potential limit, in the range 1.0 to 1.1 V. In the negative-going scan, the oxidation rate initially follows the same trace and then slightly increases between 1.00 V and 0.93 V. Below 0.93 V the rate decreases rapidly, until at around 0.80 V the reaction is completely inhibited. This reaction behavior results in a distinct hysteresis between the positive- and negative-going scan.
Figure 6.15: High potential region (> 0.70 V) of the second potential cycle during bulk CO electro-oxidation in CO saturated 0.5 M H₂SO₄ solution (0.07 V to 1.10 V, 10 mV s⁻¹) recorded on (a) Pt(111), (b) Pt/Pt(111), (c) Au/Pt(111) and (d) Au/Pt/Pt(111). The arrows indicate the scan direction. ΔE_Hyst displays the difference between E_{ign} and the potential in the negative-going scan at \( j = 0.3 \text{ mA cm}^{-2} \). The faint red bars indicate the experimental error range of the potential where the current density is \( j = 0.3 \text{ mA cm}^{-2} \). The break in the positive-going scan in d) is an artifact of the measurement, which was also observed in other measurements on Au/Pt(111). These artifacts are ascribed to a switch of the current range which, however, does not affect the hysteresis width at \( j = 0.3 \text{ mA cm}^{-2} \).
Going to the bulk CO electro-oxidation traces for the modified Pt(111) electrodes in Figure 6.15b-6.15d, they largely resemble that obtained for Pt(111) in their characteristic features. Differences appear, however, in details. First of all, the sharp current spikes following the ignition of the reaction are differently pronounced. Second, the steepness of the increasing current at the ignition potential varies somewhat. Third, the potential of the current decay in the negative-going scan varies such that the hysteresis width $\Delta E_{\text{Hyst}}$ in the traces of the Au modified electrodes is by about 20 mV smaller than on the pure Pt electrodes, both for Pt(111) and for Pt/Pt(111). On the basis of the overall similarity of the traces, we assume that similar surface processes occur on all electrodes. The differences in the onset potential and in the ignition potential between the different current traces, by $\pm 10$ mV (see marked range in Figure 6.15), reflect subtle shifts in the measured potential between different experiments. Shifts in this range were observed also in other experiments on the same type of electrode, i.e., on Pt(111), on Pt/Pt(111) and on Au/Pt(111). However, these shifts do not affect the width of the hysteresis. Similarly, also the slightly different currents in the potential range between 1.0 and 1.1 V are related to slight variations in the experimental conditions, in this case mainly to the thickness of the flowing electrolyte layer, which is affected by the force that presses the electrode on the flow cell. The similarity in ignition potentials means that neither the 3-fold increase in Pt step density (Pt/Pt(111) vs. Pt(111)) nor the presence of Au lead to a measurable change of the CO oxidation onset behavior. Assuming that at low potentials all Pt step and terrace sites on the different electrodes are saturated with adsorbed CO, similar to Pt(111), and that OH$_{\text{ad}}$ formation is considered as potential limiting for the initiation of CO$_{\text{ad}}$ oxidation in the range of the onset potential and slightly above, OH$_{\text{ad}}$ formation must be at least equally facile on Pt terrace sites as on step sites for comparably high CO$_{\text{ad}}$ coverage.

In the negative-going scan the reaction ceases already at higher potentials on the Au modified Pt electrodes compared to the Au-free Pt electrodes. Thus, while we had observed a distinct hysteresis between the positive- and negative-going scan for all electrodes, independent of the Pt step density, it is 30% smaller for the Au modified Pt surfaces than for the Au-free surfaces (see Figure 6.15). Although the difference in the hysteresis is only around 20 mV, it is clearly outside the error range, considering that we are dealing here with potential differences rather than with absolute potential values. Final proof for our claim that the Au modified electrode surfaces are stable under electrochemical conditions (see above) comes from an additional CO oxidation measurement.
on a Au/Pt(111) electrode with a broader Au stripe ($\theta_{\text{Au}} = 0.30$ ML). Also in this case we observed a hysteresis width of 40 mV, which did not change during repeated potential cycling (see Figure 6.20e). Considering that for this electrode STM images had clearly demonstrated that the Au modification of the step/island edges remains intact during CO electro-oxidation (see Figure 6.20e), the hysteresis width of 40 mV can be considered as typical for electrodes with intact, completely Au modified island/step edges. Therefore, the observation of a narrow, 40 mV hysteresis width also for the Au/Pt(111) and Au/Pt/Pt(111) electrodes over several potential cycles is definite proof that also for these electrodes the Au decoration remained intact during CO electro-oxidation. Otherwise, if the Au decoration were (locally) removed from the Pt step/island edge, the hysteresis of the Au modified surface would increase with increasing cycle number to the value typical for the pristine Pt electrodes (60 mV).

Possible reasons for the narrower hysteresis of the Au modified Pt electrodes, which we attribute to an earlier decay of the reaction current in the negative-going scan, shall be discussed in the following, using the schematic illustration in Figure 6.16. Here we would like to note that in this discussion we did not consider effects caused by sulfate adsorption (see Section 6.2.5 in the Appendix). Starting from the positive potential limit (1), the surface is essentially covered with a (dilute) OH adlayer\cite{297,306–309}, which allows for high reaction rates of adsorbed CO molecules at both Pt terrace and step sites. We would like to note, however, that we had demonstrated recently that also under these conditions the CO oxidation rate is not purely mass transport limited, but must be affected also by kinetic limitations imposed, e.g., by the presence of surface oxides\cite{310}. On the Au modified Pt electrodes we expect that terrace and former step sites are rather similar in their CO oxidation properties. This is rationalized by the fact that these sites exhibit an identical coordination of the Pt surface atoms and differences arise only from electronic ligand effects\cite{136}. Decreasing the potential reduces the rate for OH$_{\text{ad}}$ formation\cite{185,311}. At the same time, the CO oxidation rate increases slightly in the potential range from 1.00 V to ca. 0.93 V. This can most easily be explained by a reaction model where the adsorbed OH slightly reduces the CO adsorption rate and where this effect decreases with decreasing potential, hence with decreasing OH$_{\text{ad}}$ coverage. Below 0.93 V the amount of OH$_{\text{ad}}$ at the surface is not sufficient to oxidize all CO$_{\text{ad}}$, leading to a reduction in the CO oxidation rate (2a) and to an accumulation of CO$_{\text{ad}}$ species. Considering that OH$_{\text{ad}}$ formation is favored on step sites\cite{185,311,312} and that this was proposed to suppress the re-population of these sites by CO$_{\text{ad}}$\cite{312}, CO$_{\text{ad}}$ accumulation will start on the terrace sites (2b). Because of the facile CO$_{\text{ad}}$ surface diffusion under these conditions, in the
limits of low adsorbate coverage, we expect that this accumulation of CO$_{\text{ad}}$ will initially occur only on larger terraces while CO molecules adsorbed close to a Pt step site will react with OH species adsorbed on the step sites. On the Au modified electrodes Pt step sites are absent and surface poisoning due to CO$_{\text{ad}}$ accumulation will set in at higher potentials than on the pure Pt surfaces, due to the lack of OH$_{\text{ad}}$ species at the Pt-Au interface sites. Vice versa, on the bare Pt electrodes the ongoing formation of OH$_{\text{ad}}$ at low coordination step sites enables high CO oxidation rates between 0.93 V and 0.80 V. Thus, in the negative-going scan, under the condition of low CO$_{\text{ad}}$ coverages, the Pt steps are more active in the CO electro-oxidation than the Pt$_{\text{core}}$-Au$_{\text{shell}}$ interface sites, the Pt terrace sites, or the Au step sites. Note that these statements refer to an average value of differently structured step sites, while the properties of individual local step nanostructures cannot be discerned. In principle, on the basis of these arguments one would expect also a slight increase in hysteresis when going from the Pt(111) to the Pt/Pt(111) electrode, since the 3-fold higher density of step sites should result in a 3-fold higher OH$_{\text{ad}}$ formation rate at identical potential. Most likely, this difference is too small to be resolved. This interpretation is supported by the fact that for Pt/Pt(111) electrodes, which after electrochemical restructuring contained an even higher density of defect sites, we observed a hysteresis of 80 mV (see Figure 6.23, Appendix). Finally, for potentials below 0.80 V both types of electrodes are fully covered by CO$_{\text{ad}}$ again (3)$^{[192]}$.

**Figure 6.16:** Schematic illustration of the negative-going scan during bulk CO electro-oxidation on bare Pt electrodes (solid line) and Au modified Pt electrodes (dashed line). The frames illustrate the surface states at different potentials on the respective electrodes, labeled accordingly at the j-E traces and the frames.

As a result, Pt steps enhance the CO oxidation rate only in the negative-going scan, in the range of the hysteresis, where the reactivity is limited by the OH$_{\text{ad}}$ formation rate on a surface largely free of CO$_{\text{ad}}$, while in the positive-going scan the onset of the CO
oxidation reaction is limited by OH$_{\text{ad}}$ formation (and subsequent reaction with CO$_{\text{ad}}$) on a CO$_{\text{ad}}$ saturated surface. Note that in previous CO stripping experiments in CO-free electrolyte Pt step sites were concluded to be more active than terrace sites, based on the shift of the onset potential to lower potentials with increasing step density$^{[68,69,183,199]}$. We assume that this discrepancy is caused by the different CO pressure in the electrolyte, resulting in lower CO$_{\text{ad}}$ coverages in those measurements. This is less efficient for site blocking and thus OH$_{\text{ad}}$ formation is more facile. In that case, step effects are possible also in the positive-going scan. Furthermore, it was shown in bulk CO electro-oxidation measurements under enforced electrolyte transport that the $E_{\text{ign}}^{[68,297]}$ and the $\Delta E_{\text{Hyst}}^{[297]}$ decrease with increasing step density on stepped single crystals vicinal to Pt(111). The only exception from this trend was a $\{331\}$ surface, where according to those authors the step density is so high that the step effects interfere, resulting in a different reaction behavior. We think that the discrepancy to the present data, which were recorded on surfaces with a well-characterized step morphology, are mainly due to the much smaller average terrace widths in the latter studies$^{[68,297]}$, with mean terrace widths of 2-19 atoms. Furthermore, these are average values with a spread over an unknown range$^{[313]}$. In the meantime it has been shown that steps affect the electronic properties over at least 2 sites$^{[297,314]}$, and therefore narrow terraces are dominated by electronic properties that are distinctly different from what would be expected for individual step sites or wider terraces on a Pt(111) surface. In that sense, even for a terrace of 10 sites in width, 40% would show modified adsorption properties. Variations in the properties of step sites were demonstrated, e.g., for terraces up to 7-8 atoms on vicinal Pt(111) surfaces$^{[315,316]}$, which is in the range of many if not most studies on stepped surfaces vicinal to Pt(111). The combination of UHV preparation and STM characterization allows for an excellently controlled preparation and characterization of surfaces with well-defined step densities in ranges where step–step interactions can be excluded. This enables a systematic determination of the role of step sites in electrocatalytic reactions.

6.2.4 Conclusions

Combining UHV-based sample preparation, structural characterization by STM and electrochemical characterization / measurements we have explored the electrocatalytic activity of step sites using a new class of nanostructured materials, bimetallic 2D core-shell structures, which are only accessible via this route. In CO bulk electro-oxidation measurements on pure and Au modified Pt(111) electrodes with different step density, performed under controlled electrolyte transport, we show that neither the presence of
step sites nor their modification for the adsorption of reactants by a narrow stripe of monolayer high Au have a measurable influence on the onset of the bulk CO oxidation reaction in the positive-going scan, which is dominated by site blocking effects caused by the densely packed CO adlayer. In the negative-going scan, however, under conditions of low CO\textsubscript{ad} coverages, the Au modified surfaces deactivate at higher potentials than the pure Pt surfaces, leading to a narrowing of the hysteresis between positive- and negative-going scan on the Au modified surfaces compared to that obtained on pure Pt surfaces, both for flat Pt(111) and for Pt/Pt(111) electrode surfaces. This is explained by the lack of under-coordinated Pt step sites on the Au modified electrodes, which are more active in providing OH\textsubscript{ad} for the reaction under these conditions. Under these conditions Pt step sites are more active for CO electro-oxidation than Pt\textsubscript{core}Au\textsubscript{shell} interface sites, Pt terrace sites or Au step sites, allowing CO oxidation at potentials where on the Au modified surfaces the reaction is inhibited by CO\textsubscript{ad} blocking.

In total, the approach presented here for determining the role of step sites in an electrocatalytic reaction constitutes a route combining the potential for directed nanostructuring with an excellent control over the type and quantity of the respective nanostructures, and electrocatalytic reaction studies on these surfaces, without requiring further cleaning procedures that might affect the resulting structures. It should be applicable for various kinds of electrocatalytic reactions and also for gas phase catalytic model studies\cite{18}, as long as the model surfaces are experimentally accessible and sufficiently stable under reaction conditions.

### 6.2.5 Appendix

#### Line profiles

Figure 6.17 shows apparent height profiles in STM images recorded before and after the CO electro-oxidation. The profiles are along the red line marked in the respective STM image. The STM images are identical with those shown in Figure 6.13. The apparent height of both the Pt steps (Figure 6.17a) and the Pt islands (Figure 6.17b) is 2.26 Å. For Au monolayers on Pt(111) the apparent height is 2.40 Å as determined from Au islands grown on a Pt(111) surface with a submonolayer coverage. The height of a Pt monolayer and a Au monolayer are displayed schematically in the height profiles in Figure 6.17 by blue and yellow rectangles, respectively. When comparing the height profiles of the STM images recorded before (Figure 6.17a - d) and after (Figure 6.17g - j) the CO electro-oxidation, one finds a more pronounced noise in the images recorded after
the CO electro-oxidation. We suggest that the larger noise and the different apparent height arise from adsorbates remaining on the surface upon from emersion from the electrolyte.

**Figure 6.17**: STM images shown in Figure 6.13 and height profiles along the red lines in the STM image. The blue and yellow rectangles illustrate a monolayer high Pt and Au step/island, respectively.

**Additional STM images**

Additional STM images of the Pt/Pt(111) and Au/Pt/Pt(111) electrodes recorded before the CO electro-oxidation are presented in Figure 6.18. The island density, the number of bilayer islands and the step density listed in Table 6.5 were obtained from statistical evaluation of the images in Figure 6.18, in Figure 6.13 and from additional images. The STM images of Au/Pt/Pt(111) in Figure 6.18a and 6.18b are displayed with enhanced contrast to visualize the Au rim at the Pt island edges.
6.2 Pt step sites in the CO electro-oxidation

Figure 6.18: (a) and (b): Additional STM images of Pt/Pt(111). (a): 200 nm x 200 nm, (b): 220 nm x 220 nm. (c) and (d): Additional STM images of Au/Pt/Pt(111). (c): 80 nm x 80 nm, (d): 100 nm x 100 nm.

Electrode surface stability

For Au/Pt(111) and Au/Pt/Pt(111) electrodes with 1 nm - 5 nm narrow stripes of Au at the Pt steps it was not possible to elucidate if the Au films are stable during the bulk CO electro-oxidation, since a chemical contrast was not accessible from STM images recorded after the electrocatalytic reaction. In addition, some surface spots of Au/Pt(111) exhibited bilayer structures at step sites after the CO electro-oxidation which could not be assigned (see Figure 6.19).

In order to determine the origin of these bilayer islands we prepared Au/Pt(111) electrodes with higher Au coverage ($\theta_{\text{Au}} = 0.30$ ML), as shown in representative STM images in Figure 6.20a and 6.20d. The stability of the $\text{Au}_{0.30-\text{ML}}$/Pt(111) electrode shown in Figure 6.20a was probed by cyclic voltammetry in 0.5 M H$_2$SO$_4$ supporting electrolyte (see Figure 6.20b). Starting at 0.85 V, the upper potential limit was successively increased in steps of 0.05 V up to 1.10 V. The latter was also the upper potential limit during the bulk CO electro-oxidation. Regardless of the upper potential limit the CVs look essentially identical indicating that in 0.5 M H$_2$SO$_4$ the Au films located at the ascending Pt steps remain intact up to 1.10 V. This is evidenced by STM images of $\text{Au}_{0.30-\text{ML}}$/Pt(111)
6 Results and Discussion

Figure 6.19: STM image of Au$_{0.07}$-ML/Pt(111) recorded after the bulk CO electro-oxidation (100 nm x 100 nm, $I_T = 5.0$ nA, $U_T = 0.4$ V).

recorded after the electrochemical treatment (see Figure 6.20c).

The stability of the Au$_{0.30}$-ML/Pt(111) electrode during bulk CO electro-oxidation was probed by measuring three potential cycles in CO saturated 0.5 M H$_2$SO$_4$ (see Figure 6.20e). With consecutive cycling the absolute current density in the potential regime above the ignition potential increases. STM images recorded after the CO electro-oxidation demonstrate the formation of second layer islands on top of the Au films of Au$_{0.30}$-ML/Pt(111). As shown in the representative STM image in Figure 6.20f these second layer islands are solely formed on top of the Au film. Height profiles of the bilayer structures showed that they have an apparent height equivalent to a Au monolayer. Note that despite the formation of second layer Au islands, the ascending Pt steps remain completely modified by a Au film (see Figure 6.20f). We suggest that this is also the case for small Au coverages as in Figure 6.19. Since bilayer Au islands were only observed in the presence of CO in the electrolyte solution we suggest that CO might trigger to some extent the detachment of Au atoms from the Au step edge, followed by re-adsorption of Au atoms on top of the monolayer high Au film. A similar behavior was observed previously for the CO adsorption on Pt nanoparticles which are fully encapsulated by a Au film[317]. In the latter study the presence of CO leads to the diffusion of Pt towards the surface due to the thermodynamically favored Pt–CO bond[317]. Thus, we believe that Au atoms at the perimeter of the Au stripes can be forced into the next layer, with the strong Pt–CO bond providing the driving force. This process is however rather slow, and is likely to be inhibited for Au atoms in contact with the Pt steps. The Au adatoms that are forced into the second layer may diffuse on the Au monolayer areas.
and possibly nucleate 2nd layer islands. However, from the present data it is not possible to derive an exact mechanism. In that case, the increasing absolute current density observed in the high potential region might be explained by the increase in Pt terrace sites accessible for CO electro-oxidation. The results shown in Figure 6.20 indicate that the bilayer structures observed for Au$_{0.07}$-ML/Pt(111) in Figure 6.18 are ascribed to Au bilayers.

Finally, the CO oxidation traces shown in Figure 6.20e show a hysteresis with a width typical for Au modified Pt(111) electrodes, which is stable also during repeated cycles. This demonstrates that Au removal from the steps is either inhibited or hindered to an extent that the Pt steps are still Au modified. If this were not the case, we would expect that the hysteresis of the Au modified surface increases with increasing cycle number to the value typical for step containing Pt(111) surfaces. The same observation is found for smaller Au coverages, equivalent to narrower Au decorations. Hence, in combination, these findings (from STM and electrochemical measurements) clearly demonstrate that the Au modification at the Pt steps remains stable upon CO electro-oxidation.

**CO TPD**

CO TPD measurements on Pt(111), Pt/Pt(111) and Au/Pt/Pt(111) were performed in a separate UHV chamber which is described in more detail in Reference[130]. The surfaces were prepared as described in Sections 5.2.3 and 5.2.4. Au was deposited with an evaporation rate of 0.006 ML min$^{-1}$ for $t = 14$ min, resulting in a Au coverage of 0.08±0.02 ML. For the TPD measurements, the samples were cooled with liquid N$_2$ to 100 K. Subsequently, either 10 L or 0.2 L of CO were dosed to obtain saturation or sub-monolayer CO coverages, respectively. CO TPD spectra were obtained by heating the sample with a heating rate of 4 K s$^{-1}$ to 650 K for Pt(111) and to 620 K for Pt/Pt(111) and Au/Pt/Pt(111). A lower final temperature was used for the latter samples to avoid temperature induced surface restructuring or alloy formation. CO desorption ($m/z = 28$) was recorded by a quadrupole mass spectrometer (Pfeiffer Vacuum, Prisma 200). The CO$_{ad}$ coverage on the sample surfaces was obtained from integration of the TPD spectra between the onset temperature for desorption and 600 K, after a linear background subtraction, and normalization of the saturation coverage $\theta_{CO} = 0.68$ ML.

CO TPD spectra of CO saturated Pt(111), Pt/Pt(111) and Au/Pt/Pt(111) surfaces are depicted in Figure 6.21. The small peak around 110 K is attributed to CO desorption from the sample holder. CO desorption from Pt(111) starts at 305 K, followed by an asymmetric peak with a peak maximum at around 400 K. This is in good agreement with
Figure 6.20: (a) STM image of Au\textsubscript{0.30-ML}/Pt(111) before EC (100 nm x 100 nm, \(I_T = 4.5\) nA, \(U_T = 4.5\) V). (b) CVs of the Au\textsubscript{0.30-ML}/Pt(111) shown in a) in 0.5 M H\textsubscript{2}SO\textsubscript{4} with increasing upper potential limits (0.05 V to 0.85 V - 1.10 V, 50 mV s\(^{-1}\)). (c) STM image of Au\textsubscript{0.30-ML}/Pt(111) after potential cycling in supporting electrolyte up to 1.10 V (100 nm x 100 nm, \(I_T = 5.0\) nA, \(U_T = 0.01\) V). (d) STM image of Au\textsubscript{0.30-ML}/Pt(111) before EC (300 nm x 300 nm, \(I_T = 4.5\) nA, \(U_T = 4.5\) V). (e) Three consecutive potential cycles during bulk CO electro-oxidation on the Au\textsubscript{0.30-ML}/Pt(111) electrode shown in d) in CO saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} (0.07 V to 1.10 V, 10 mV s\(^{-1}\)). (f) STM image of Au\textsubscript{0.30-ML}/Pt(111) after bulk CO electro-oxidation (100 nm x 100 nm, \(I_T = 5.0\) nA, \(U_T = 0.01\) V).

previous results and corresponds to a saturation coverage of \(\theta_{CO} = 0.68\) ML\textsuperscript{[298,318–320]}. The CO desorption spectrum of Pt/Pt(111) has an almost identical shape as the one of Pt(111), besides the appearance of a small shoulder at 510 K for Pt/Pt(111), which is attributed to CO desorption from Pt steps\textsuperscript{[299]}. This peak is not present in the CO desorption spectrum of Au/Pt/Pt(111), demonstrating that the Pt steps are no more activated for CO adsorption in the presence of the narrow Au stripe at the ascending step edges. Furthermore, compared to the bare Pt electrodes, CO desorption starts at lower temperatures (280 K) for Au/Pt/Pt(111) and the absolute peak height decreases. Nevertheless, the integrated peak intensity varies only by 2% for the three different surfaces indicating that changes in the CO saturation coverage on the three surfaces are below the detection level. It was shown previously that Pt(111) supported Au films are not available for CO adsorption under these conditions\textsuperscript{[300,321]}. Thus, an identical CO saturation coverage for Au/Pt/Pt(111) and Pt/Pt(111) may at least partly be rational-
6.2 Pt step sites in the CO electro-oxidation

This would also explain the earlier onset of desorption observed for Au/Pt/Pt(111), since a higher coverage CO adlayer leads to increased repulsive CO–CO interactions, which facilitate the desorption of CO molecules at lower temperature. A higher density CO adlayer on the Pt terrace sites could result from a so-called spillover effect, where the Au film acts as additional channel for CO adsorption onto the Pt terraces, leading to higher saturation coverages on the Pt terrace sites than one would obtain for adsorption on the bare substrate. Based on CO TPD measurements on AuPt/Pt(111) surface alloys, where surface Au and Pt atoms tend to a phase separation, it was already proposed previously that CO molecules that reach Au adsorption sites at the surface may migrate along the surface until they find a Pt adsorption site. Such kind of spillover effect was also reported for CO adsorption on Pt modified Ru(0001) surfaces.

Figure 6.21: CO TPD spectra of a saturated CO adlayer from Pt(111) (solid green line), Pt/Pt(111) (black dotted line) and Au/Pt/Pt(111) (blue dashed line) with a nominal exposure of $\varepsilon_{CO} = 10$ Langmuir (L).

**Peak C in the CV of Pt/Pt(111)**

So far a peak at 0.31 V (peak C) was reported for electrochemically roughened Pt(111). In previous studies, a small shoulder at 0.31 V appeared also in the CVs of Pt(100) and Pt(23,1,1) single crystals. For Pt(100) this peak is related to the hydrogen adsorption / desorption on wide (100) terraces. As the Pt islands on Pt/Pt(111) grow homoepitaxial, such wide (100) terraces should, however, not be present on the surface of Pt/Pt(111). In CVs of shape-selected Pt NPs with cubic or octahedral shape a shoulder was observed at potentials between 0.30 V and 0.37 V.
Since these NPs have sizes between 8 nm and 12 nm and the number of wide terraces is low, the shoulder should be ascribed to \( \text{H}_{\text{upd}} \) on low-coordination Pt sites. Support for this assumption is the previously observed decrease of the shoulder in the CV of Pt(100) with increasing temperature\[^{[327]}\], since an annealing process should favor larger terraces rather than new defect sites. Thus, we suggest that peak C in Figure 6.14b originates from H/OH adsorption/desorption on low-coordination sites such as kink sites, which have so far not been studied systematically.

\textbf{\( \text{H}_{\text{upd}} \) charges}

The overall coulometric charges (\( Q_{\text{H}_{\text{upd}}} \)) associated with \( \text{H}_{\text{upd}} \) are listed for all electrodes investigated in Table 6.6. The \( Q_{\text{H}_{\text{upd}}} \) of Pt(111) is in perfect agreement with previously reported values, it corresponds to a \( \theta_{\text{H}_{\text{ad}}} \) coverage of \( \theta_{\text{H}_{\text{ad}}} = 0.66 \text{ ML} \[^{[17]}\]. The Au modified electrodes exhibit similar \( Q_{\text{H}_{\text{upd}}} \) values as observed for Pt(111). For Pt/Pt(111) the larger \( Q_{\text{H}_{\text{upd}}} \) is partly caused by the additional small peaks A to C, related to Pt defect sites. The total charge density of the peaks A to C is ca. 5 \( \mu \text{C cm}^{-2} \), which corresponds to a contribution of these peaks of approximately 3%. This value is in good agreement with the step density determined from STM imaging.

\begin{table}[h]
\centering
\caption{Coulometric charges (\( Q_{\text{H}_{\text{upd}}} \)) associated with \( \text{H}_{\text{upd}} \)}
\begin{tabular}{|c|c|}
\hline
\textbf{Electrode} & \textbf{\( Q_{\text{H}_{\text{upd}}} \) / \( \mu \text{C cm}^{-2} \)} \\
\hline
Pt(111) & 159 \\
Pt/Pt(111) & 179 \\
Au/Pt(111) & 165 \\
Au/Pt/Pt(111) & 161 \\
\hline
\end{tabular}
\end{table}

\textbf{Monolayer high Au film on Pt(111)}

A representative STM image of an almost closed monolayer high Au film supported on Pt(111) (Au\(_{1\text{-ML}}\)/Pt(111)) is shown in Figure 6.22a. In this case there is no formation of second layer Au islands and the fraction of holes in the Au film is less than 4%. The CV of Au\(_{1\text{-ML}}\)/Pt(111) in 0.5 M H\(_2\)SO\(_4\) supporting electrolyte, which is shown in Figure 6.22b together with the CV of Pt(111), is in perfect agreement with previously reported CVs for a Au\(_{1\text{-ML}}\)/Pt(111) electrode\[^{[294]}\]. Compared to Pt(111) the \( \text{H}_{\text{upd}} \) region between 0.07 V and 0.33 V almost vanishes for Au\(_{1\text{-ML}}\)/Pt(111). Furthermore, between 0.33 V and 0.58 V, where sulfate adsorption/desorption is observed on Pt(111), there are...
solely currents arising from charging of the double layer in the CV of Au₁-ML/Pt(111). At potentials above 0.58 V small features are observed, which are related to anion adsorption/desorption as reported for Au(111)\textsuperscript{[330,331]}.

Figure 6.22: (a) Representative STM image of Au₁-ML/Pt(111) (100 nm x 100 nm, \( I_T = 1.4 \) nA, \( U_T = 1.2 \) V). (b) CVs of Pt(111) (green dotted curve) and Au₁-ML/Pt(111) (orange solid curve) in 0.5 M H₂SO₄ (0.07 V to 0.85 V, 50 mV s⁻¹).

**Sulfate species in the CO electro-oxidation**

Even though sulfate does not participate in the CO electro-oxidation, its presence may alter the electrode activity due to competitive adsorption with the reactants (here primarily OH\textsubscript{ad}, since CO binds stronger than sulfate). This has been demonstrated in previous studies, where the hysteresis width in the bulk CO electro-oxidation on Pt(111) was shown to decrease in the presence of strongly binding anions in the electrolyte solution\textsuperscript{[304,308,332]}. In sulfuric acid the competitive adsorption between OH\textsubscript{ad} and sulfate starts with the initiation of the CO electro-oxidation\textsuperscript{[304]}. As a result, the OH\textsubscript{ad} coverage may decrease resulting in lower CO oxidation rates\textsuperscript{[304]}. However, the almost identical shapes of the CVs in Figure 6.14b demonstrate that the influence of sulfate should be identical for all electrodes investigated regardless of the step density or the Au modification of steps.

**Electrochemically restructured Pt/Pt(111)**

Figure 6.23a shows CVs in 0.5 M H₂SO₄ supporting electrolyte recorded on an as-prepared Pt/Pt(111) electrode and a Pt/Pt(111) electrode where the surface was exposed to potentials above 1.10 V for several seconds. A potential induced restructuring of the latter
electrode is obvious from the presence of distinct peaks in the H\textsubscript{upd} region, which are ascribed to competitive adsorption / desorption of H / OH at defect sites\textsuperscript{[158,163,169]}. STM imaging of this restructured Pt/Pt(111) electrode after CO electro-oxidation revealed the formation of small clusters adjacent to small holes in the surface as shown in the inset in Figure 6.23b. The CV and STM measurements thus indicate the formation of defect rich Pt clusters at the surface. The bulk CO electro-oxidation on the restructured Pt/Pt(111) electrode is shown in Figure 6.23b. Compared to the polarization curves of Pt/Pt(111) shown in Figure 6.15, we find a further broadening of the hysteresis width to 80 mV, which we relate to the high amount of defect sites at the surface.

**Figure 6.23:** (a) CVs of intact Pt/Pt(111) (black dotted curve) and electrochemically restructured Pt/Pt(111) (orange solid curve) in 0.5 M H\textsubscript{2}SO\textsubscript{4} (50 mV s\textsuperscript{-1}, 0.05 V - 0.85 V). (b) High-potential region (0.70 V - 1.1 V) of the bulk CO electro-oxidation on the restructured Pt/Pt(111) electrode in CO saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} (10 mV s\textsuperscript{-1}, 0.05 V - 1.10 V). The inset shows an STM image (100 nm x 100 nm, I\textsubscript{T} = 2.5 nA, U\textsubscript{T} = 0.4 V) recorded after the CO electro-oxidation. \(\Delta E_{Hyst}\) displays the difference between \(E_{ign}\) and the potential in the negative-going scan at \(j = 0.3\) mA cm\textsuperscript{-2}. The faint red bars indicate the experimental accuracy of the potential.
6.3 Atomic scale insights on the electronic and geometric effects in the electro-oxidation of CO on Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys

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My contribution to this work are the planing of the experiments and the measurement of all experimental results. I performed the full data evaluation and prepared all Figures. I was also strongly involved in the creative process of the publication.

6.3.1 Abstract

The enhanced activity of various bimetallic catalysts / electrodes in electrocatalytic reactions is usually ascribed to a bifunctional mechanism. This seems to neglect other effects arising from electronic modifications and further geometric effects, which are known to strongly affect the interaction of these surfaces with adsorbed species. In this work we elucidate the role of electronic and geometric effects on the activity of structurally well-defined PtRu electrodes in the bulk CO oxidation reaction, using model electrodes prepared and structurally characterized on an atomic scale by scanning tunneling microscopy under UHV conditions. Samples include Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys with varying Pt content consisting of a Ru(0001) substrate and a Pt$_x$Ru$_{1-x}$ alloy surface layer as well as a Ru(0001) electrode covered by a pseudomorphic Pt monolayer (x = 1), and Pt(111) for comparison. Comparing the structural / chemical properties and the relative
abundance of specific Pt$_n$Ru$_m$ ensembles on the electrode surfaces with the respective bulk CO electro-oxidation activity enabled us to identify Pt$_1$Ru$_3$ ensembles as the most active ensembles under the present conditions. The importance of electronic and geometric ensemble effects are discussed. The results demonstrate that the reactivity of bimetallic surfaces is much more complex than described by the classical bifunctional mechanism, which is proposed as a general feature.

### 6.3.2 Introduction

Bimetallic electrocatalysts have attracted enormous attention in the last decades because of their improved electrocatalytic properties compared to monometallic systems, which are reflected by enhanced catalytic activities, selectivities and stabilities\textsuperscript{[205,333–336]}. The systematic improvement of the electrocatalytic performance of bimetallic electrocatalysts requires a detailed understanding of the influence of specific nanostructures present at the catalyst surface on the catalytic properties. Deriving such kind of structure-activity relationship is, however, rather complicated, if not impossible, for real catalysts due to their mostly ill-defined surface structure with high defect densities and due to the lack of methods suitable to probe the lateral distribution of elements in the surface layer/surface region. This is different for bimetallic single crystal model surfaces, where the nature and abundance of local structures can be probed on an atomic scale, e.g., by scanning tunneling microscopy (STM)\textsuperscript{[87,337–339]}. In the present work we report results of a combined \textit{ex situ} STM and electrochemical model study on the electrocatalytic oxidation of CO on bimetallic single-crystalline PtRu model electrodes. In addition to exploring Pt monolayer covered Ru(0001) surfaces (Pt$_{1-\text{ML}}$/Ru(0001)), we particularly focus on the influence of different Pt contents ($x_{\text{Pt}}$) in Pt$_x$Ru$_{1-x}$/Ru(0001) monolayer surface alloys on the reaction. We also aim at deriving a more detailed picture of the bifunctional mechanism that had been proposed for this reaction\textsuperscript{[78]}, and to identify possible effects beyond the present mechanistic picture. As will be outlined in more detail later, the bifunctional mechanism largely argued with geometric effects, while electronic effects beyond the elemental differences were neglected. Later on, Smotkin and coworkers emphasized, however, that electronic effects may be sufficient to rationalize the enhanced reactivity of PtRu alloys for the CO oxidation, as they found from DFT calculations that introducing Ru into a Pt cluster modifies the electron density of both elements\textsuperscript{[27,340]}, and this was soon followed by other groups\textsuperscript{[28]}. The bimetallic combination PtRu is a prominent anode catalyst material in fuel cells due to its higher performance for the electro-oxidation of methanol (MeOH) and CO com-
6.3 CO electro-oxidation on Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001)

pared to bare Pt which is the most active monometallic catalyst for these reactions\textsuperscript{[12,15]}. Here the CO electro-oxidation is of special interest, since CO is also a strongly binding reaction intermediate in the electrocatalytic MeOH oxidation reaction, which acts as a catalyst poison on the Pt sites\textsuperscript{[16,17]}, reducing the performance of a fuel cell system.

Focusing on the reaction mechanism on monometallic Pt, the electro-oxidation of CO was proposed by Gilman \textit{et al.} to follow a L-H mechanism, where CO\textsubscript{ad} and an oxygen containing species (OH\textsubscript{ad} or O\textsubscript{ad}) have to be co-adsorbed in direct vicinity on the electrode surface to form CO\textsubscript{2}, which then desorbs from the metal surface\textsuperscript{[184]}. Experimental evidence for the nature of the oxygen species is, as to the best of our knowledge, still missing. Calculations indicate, however, that OH\textsubscript{ad} is the active oxygen species\textsuperscript{[185,186]}. The reaction scheme presented below illustrates the resulting L-H mechanism, where \textit{*s}\textsubscript{1} and \textit{*s}\textsubscript{2} denote two different, adjacent free adsorption sites on the Pt surface.

\begin{equation}
CO + *s\textsubscript{1} \rightleftharpoons CO\textsubscript{s}\textsubscript{1} \quad (6.6)
\end{equation}

\begin{equation}
H\textsubscript{2}O + *s\textsubscript{2} \rightleftharpoons OH\textsubscript{s}\textsubscript{2} + H^+ + e^- \quad (6.7)
\end{equation}

\begin{equation}
CO\textsubscript{s}\textsubscript{1} + OH\textsubscript{s}\textsubscript{2} \rightarrow CO\textsubscript{2} + H^+ + e^- + *s\textsubscript{1} + *s\textsubscript{2} \quad (6.8)
\end{equation}

\begin{equation}
CO + H\textsubscript{2}O \rightarrow CO\textsubscript{2} + 2H^+ + 2e^- \quad (6.9)
\end{equation}

Both, the adsorption of CO in reaction 6.6 and the adsorption of OH in reaction 6.7 require a free adsorption site, which results in a competition between these two reactions for adsorption sites on the Pt electrode and thus to a decline of the reaction rate if one of the adspecies largely covers the surface (‘site blocking’). At too low potentials the reaction is furthermore inhibited since the electrochemical formation of OH\textsubscript{ad}, by dissociation of water, requires a minimum potential, which on Pt(111) was reported to be around 0.6V\textsuperscript{[185]}. The latter can be lowered significantly by introducing Ru into the surface of pure Pt electrodes, which leads to an enhanced electrode activity\textsuperscript{[14,15,78,203,204]}. The enhanced activity of PtRu electrodes for CO electro-oxidation was commonly explained \textit{via} the bifunctional mechanism, which is a special type of the L-H mechanism\textsuperscript{[78,231]}. The bifunctional mechanism assumes that the carbon-containing species adsorb preferentially on Pt sites, while the oxophilic Ru atoms provide OH\textsubscript{ad} at lower electrode potentials compared to Pt and thus facilitate the oxidation of the carbon-containing species\textsuperscript{[78,203,204,231,232]}. According to this model, the highest activity for the CO oxidation should be achieved if the number of adjacent PtRu sites is maximum and indeed, the highest reaction rates were observed for sputtered PtRu bulk alloys with a 1:1 ratio.
6 Results and Discussion

of Pt and Ru\textsuperscript{[203]}. The current understanding of the bifunctional mechanism was derived from experiments on complex particle catalysts or structurally less well-defined polycrystalline PtRu materials\textsuperscript{[78,203,204,231,232]}. A more detailed understanding of the structure-activity relationship on an atomic scale can be obtained from PtRu single crystal studies. Experimental studies on different PtRu surfaces/electrodes performed under UHV conditions\textsuperscript{[79,80,82,84,87,88,130]} and in an electrochemical environment\textsuperscript{[86,89,205,341]} as well as DFT based computational studies\textsuperscript{[28,81,85,153]} revealed that modifications in the electronic properties of the individual metals, which are commonly summarized as electronic ligand\textsuperscript{[24,25]} and strain\textsuperscript{[26]} effects, and possibly also geometric ensemble effects\textsuperscript{[29]}, severely affect the adsorption properties and the catalytic activities on these surfaces. We would expect that such kind of modifications should also affect the CO oxidation reaction on PtRu surfaces, leading to a more complicated or even different picture of the bifunctional mechanism than used so far. This was illustrated for the ORR, where the high activity of some surface alloys was shown to be related to a high activity of Pt\textsubscript{2}Ru sites, due to the electronic effects mentioned above\textsuperscript{[89]}. Focusing on the CO electro-oxidation, previous studies of this reaction on Pt modified Ru(0001) electrodes indicated that Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) electrodes are more active than monolayer high Pt island modified Ru(0001) (Pt\textsubscript{isl}/Ru(0001)) electrodes\textsuperscript{[58,205,206]}. In those studies we compared the reaction behavior of surface alloys with Pt monolayer island modified Ru(0001) electrodes\textsuperscript{[58,205,206]}, whereas the influence of the surface composition in the surface alloys was hardly considered. This is topic of the present work, where we derive structure-activity relationships for Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) surface alloys with varying compositions on the atomic scale.

The experimental set-up, the sample preparation and the electrocatalytic measurement implementation are described in detail in Chapter 5. In the following, we present results of electrochemical flow-cell measurements of the electrochemical properties and subsequently of the bulk CO electro-oxidation characteristics. In Section 6.3.4 we relate the activity of the surface alloys to their respective structural and chemical properties, which were already extensively investigated in previous studies\textsuperscript{[79,82,84,85,87,88,130]}. Here we also assess the role of the relative coverages of OH\textsubscript{ad} and CO\textsubscript{ad} species on the Pt\textsubscript{1-ML}/Ru(0001) and Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) electrode surfaces. Furthermore, we discuss the role and influence of geometric ensemble/electronic ligand and strain effects in this reaction, and how they affect the picture of the bifunctional mechanism. Finally, the main results and conclusions are summarized in Section 6.3.5.
6.3 CO electro-oxidation on Pt$_x$Ru$_{1-x}$/Ru(0001)

6.3.3 Results

First we present STM images of the model electrodes prepared under UHV conditions, i.e., Ru(0001), Pt(111), Pt$_{1\text{-ML}}$/Ru(0001) and Pt$_x$Ru$_{1-x}$/Ru(0001), and describe the structural and electronic properties of the electrode surfaces, based also on previous experimental studies on these model electrodes\cite{87,88}. Then we focus on the electrochemical properties of the model electrodes in supporting electrolyte, as evidenced by their cyclic voltammograms in supporting electrolyte, and finally we present results of bulk CO electro-oxidation measurements on these electrodes. In total, this aims at identifying correlations between the structural/electronic properties of the model electrodes and their respective electrochemical and electrocatalytic properties.

Structural characterization

Representative large-scale STM images (200 nm x 200 nm) of the different electrodes are depicted in the top row of Figure 6.25. Sideview sketches of the respective electrodes are shown in the bottom row. Both, the Ru(0001) and Pt(111) single crystal surfaces in Figure 6.25a and 6.25b, respectively, exhibit almost straight steps of monoatomic height, with the terrace width varying between 50 nm and 200 nm. These structures are a clear indication for chemically clean and structurally perfect single crystal surfaces. For the Pt$_{1\text{-ML}}$/Ru(0001) surface (Figure 6.25c), we obtained about 5% bilayer Pt areas and 5% holes in the Pt film, despite optimized experimental conditions (see Section 5.2.2). Hence, about 5% of the Ru(0001) substrate are exposed to the electrolyte for this surface. Finally, an STM image of a Pt$_{0.82}$Ru$_{0.18}$/Ru(0001) surface alloy, representative for all surface alloys investigated, is depicted in Figure 6.25d. A detailed description of the structural properties of the surface alloys can be found in Reference\cite{87}. In total, we prepared nine different Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys with Pt contents between $x_{Pt} = 0.12$ and $x_{Pt} = 0.83$.

Since the structural, chemical and electronic properties of the Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys were described in detail elsewhere\cite{80,82,87,88,130,341}, we here summarize only the most important aspects relevant for this work. Focusing on the structural properties, the following aspects have to be highlighted: (i) alloy formation is restricted to the topmost atomic surface layer under these preparation conditions, (ii) diffusion of small amounts of Pt surface atoms into the deeper regions of the crystal is possible only for Pt contents above $x_{Pt} > 0.80$ under the present conditions and (iii) the Pt and Ru atoms are randomly distributed in the surface layer\cite{87,88}. These properties were primarily derived
6 Results and Discussion

Figure 6.25: Representative STM images (200 nm x 200 nm) of the as-prepared electrodes before the electrochemical /-catalytic investigations (top row) and the corresponding side-view sketches of the electrode surfaces (bottom row). (a) Ru(0001) \( (I_T = 0.45 \text{nA}, U_T = 1.5 \text{V}) \), (b) Pt(111) \( (I_T = 4.0 \text{nA}, U_T = 0.9 \text{V}) \), (c) Pt_{1-ML}/Ru(0001) \( (I_T = 0.18 \text{nA}, U_T = 1.6 \text{V}) \) and (d) Pt_{0.82}Ru_{0.18}/Ru(0001) \( (I_T = 1.8 \text{nA}, U_T = 0.8 \text{V}) \). The latter is representative for all surface alloys investigated with various Pt surface contents.

from atomically resolved STM images of Pt_{x}Ru_{1-x}/Ru(0001) surface alloys with chemical contrast and subsequent statistical evaluation of the Pt content in the surface\[^{[87]}\].

The relative abundance \( r \) of the most relevant compact Pt\(_n\)Ru\(_m\) ensembles such as Pt\(_n\)Ru\(_{2-n}\) dimers (Figure 6.26a), Pt\(_n\)Ru\(_{3-n}\) trimers (Figure 6.26b) and Pt\(_n\)Ru\(_{4-n}\) tetrayers (Figure 6.26c) in the surface layer as a function of the Pt content \( x_{Pt} \) is depicted in Figure 6.26. The results in Figure 6.26 were adapted from Reference\[^{[87]}\] and reflect a perfect random distribution of the atoms in the surface layer. The different ensembles considered are schematically illustrated by a hard sphere model next to their distribution maximum in Figure 6.26a-c. These relative abundances will be compared later (Section 6.3.3) with the electrochemical /-catalytic properties of Pt\(_x\)Ru\(_{1-x}\)/Ru(0001) electrodes with different \( x_{Pt} \), in order to obtain information on the nature of the (most) active ensemble for the bulk CO electro-oxidation reaction.

**Electrochemical properties**

The electrochemical properties of the electrodes introduced above were investigated by cyclic voltammetry in 0.5 M H\(_2\)SO\(_4\) supporting electrolyte. The characteristics of the CV of the Ru(0001) surface, depicted in Figure 6.27a (black solid line), are very similar to those reported previously\[^{[58,206,342–344]}\]. The CV shows a distinct broad oxidation peak at 0.64 V in the positive-going scan direction and two reduction peaks centered at
Figure 6.26: Relative abundance $r$ of compact $\text{Pt}_n\text{Ru}_m$ atomic ensembles in the surface layer of $\text{Pt}_x\text{Ru}_{1-x}/\text{Ru}(0001)$ surface alloys, plotted as a function of the Pt content $x_{\text{Pt}}$, for (a) dimers ($\text{Pt}_n\text{Ru}_{2-n}$), (b) trimers ($\text{Pt}_n\text{Ru}_{3-n}$) and (c) tetramers ($\text{Pt}_n\text{Ru}_{4-n}$). The solid orange curve and the dashed blue curve represent the relative abundance of bare Ru ensembles and bare Pt ensembles, respectively, while the other curves represent the relative abundance of mixed ensembles. For each compact atomic ensemble a hard sphere model is depicted at the maximum of the respective distribution curve. The bright orange spheres represent Ru atoms and the dark blue spheres represent Pt atoms. Results are adapted from Reference [87].

0.50 V and 0.30 V in the negative-going scan direction. These peaks were attributed to the adsorption (0.64 V) and desorption (0.50 V and 0.30 V) of OH species on and from the Ru(0001) surface, respectively [58,206,342–344]. In the negative-going scan direction the HER sets in at a potential of 0.08 V. Different from similar CVs recorded in HClO$_4$ based electrolyte [345,346], we cannot identify currents related to hydrogen adsorption. This result agrees well with previous findings for polycrystalline Ru [347], for Ru(0001) [58,342] and for Ru(1010) [348] single crystal electrodes, where the absence of an H$_{\text{upd}}$ region on Ru(0001) was attributed to blocking of surface sites by (bi)sulfate species adsorbed on the Ru(0001) surface [58,342].
Figure 6.27: Cyclic voltammograms (CVs) measured at 10 mV s\(^{-1}\) in 0.5 M H\(_2\)SO\(_4\) of (a) Ru(0001) (-0.02 V - 0.90 V, black solid trace) and Pt\(_{0.12}\)Ru\(_{0.88}\)/Ru(0001) (0.05 V - 0.90 V, red dashed trace), (b) Pt\(_{0.24}\)Ru\(_{0.76}\)/Ru(0001) (0.05 V - 0.85 V, blue dotted trace), Pt\(_{1-}\)ML/Ru(0001) (0.05 V - 0.85 V, orange dashed trace) and Pt(111) (0.05 V - 0.85 V, black solid trace). The inset in b) shows the H\(_{\text{upd}}\) region of Pt\(_{0.12}\)Ru\(_{0.88}\)/Ru(0001) (red), Pt\(_{0.24}\)Ru\(_{0.76}\)/Ru(0001) (blue), Pt\(_{0.48}\)Ru\(_{0.52}\)/Ru(0001) (green), Pt\(_{0.58}\)Ru\(_{0.42}\)/Ru(0001) (grey) and Pt\(_{0.83}\)Ru\(_{0.17}\)/Ru(0001) (brown). The arrow indicates the trend with increasing Pt surface content \(x_{Pt}\).

The CV of the Pt\(_{0.12}\)Ru\(_{0.88}\)/Ru(0001) surface alloy is shown in Figure 6.27a (red dashed line) for comparison. It resembles to some extent the CV of the bare Ru(0001) electrode. The main difference is the shift of the HER onset potential to more positive potentials (0.15 V) in the negative-going scan. Looking at details in the positive-going scan, the onset of the oxidation peak is shifted to 0.25 V and the current increases continuously with increasing potential, until a broad peak maximum is reached at 0.67 V. This results in a shift of the maximum by 30 mV to higher potentials compared to bare Ru(0001). In the negative-going scan direction, the two reduction peaks become broader and shift to more positive potentials, with maxima at 0.52 V and 0.36 V, respectively. Despite of the presence of Pt atoms in the surface layer the CV of Pt\(_{0.12}\)Ru\(_{0.88}\)/Ru(0001) (Figure 6.27a)
does not show any indication for a H\textsubscript{upd} region. In total, the little changes in the current features compared to Ru(0001) indicate that the surface electrochemistry is still dominated by Ru. Nevertheless, the small amounts of Pt in the surface significantly modify the OH adsorption and desorption properties of the surface.

Significant changes in the CV of Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) surface alloys occur once the Pt content reaches $x_{Pt} = 0.24$ or higher. This is shown for the CV of a Pt\textsubscript{0.24}Ru\textsubscript{0.76}/Ru(0001) surface in Figure 6.27b (blue dotted line, representative for surface alloys with $x_{Pt} \geq 0.24$), together with the CVs of a Pt(111) (black solid line) and a Pt\textsubscript{1-ML}/Ru(0001) electrode (orange dashed line). CVs of the other surface alloys with higher Pt contents are shown in the Appendix in Figure 6.30. In the CVs of the surface alloys with $x_{Pt} \geq 0.24$, we do not find the distinct oxidation peak in the positive-going scan direction (Figure 6.27). Instead, a rather continuous (and small) increase of the current density is observed, which varies only slightly with increasing $x_{Pt}$ (see Fig. S1). Second, the two reduction peaks which are clearly resolved between 0.28 V and 0.64 V on Ru(0001) and which, though less prominent, are also visible on Pt\textsubscript{0.12}Ru\textsubscript{0.88}/Ru(0001), merge into a broad feature for $x_{Pt} = 0.24$ and $x_{Pt} = 0.30$. For $x_{Pt} > 0.30$ they cannot be discerned from the low currents related to double layer charging (see Figure 6.30). Finally, for surface alloys with $x_{Pt} \geq 0.24$ we also find H\textsubscript{upd} features in the CVs at potentials between 0.05 V and 0.25 V. The H\textsubscript{upd} region is magnified in the inset in Figure 6.27b, with an arrow indicating the increase of the current density with increasing $x_{Pt}$. Further, the onset of the H\textsubscript{upd} region shifts to more positive potentials with increasing $x_{Pt}$. The largest adsorption feature is obtained for $x_{Pt} = 0.83$. Overall, with increasing Pt surface content, the H\textsubscript{upd} region resembles more and more that observed for the Pt monolayer modified Ru(0001) electrode (see Figure 6.27b).

The CV of the Pt\textsubscript{1-ML}/Ru(0001) electrode is characterized by a broad H\textsubscript{upd} region, which is similar in size compared to the Pt\textsubscript{0.83}Ru\textsubscript{0.17}/Ru(0001) surface alloy. Furthermore, the CV of Pt\textsubscript{1-ML}/Ru(0001) does not exhibit sharp redox peaks similar to the surface alloys with $x_{Pt} > 0.30$ ML.

The CV of a Pt(111) single crystal electrode in Figure 6.27b shows the typical redox features of hydrogen adsorption/desorption at 0.07 V–0.33 V, which overlap with (bi)sulfate adsorption/desorption present in the potential range from 0.33 V to 0.58 V\textsuperscript{155,157,195}. The coulometric charge in the H\textsubscript{upd} region (between 0.07 V and 0.33 V) on Pt(111) is $159 \pm 7 \text{ mC cm}^{-2}$, while on Pt\textsubscript{1-ML}/Ru(0001) the charge is $55 \pm 4 \text{ mC cm}^{-2}$. This charge can be related to the hydrogen coverage. Accordingly, the H\textsubscript{ad} coverage decreases from 0.66 ML on Pt(111) to 0.21 ML on Pt\textsubscript{1-ML}/Ru(0001), assuming that the
total theoretical charge for the formation of one monolayer of adsorbed hydrogen (one hydrogen per surface Pt atom) on Pt(111) and Pt_{1-ML}/Ru(0001) are 240 mC cm\(^{-2}\)\[^{[172]}\] and 260 mC cm\(^{-2}\)\[^{[342]}\], respectively. The total charge per H monolayer is larger for Pt_{1-ML}/Ru(0001) than for Pt(111), since the Pt adlayer is compressed by 2.5\% (Pt-Pt distance) compared to the Pt(111) surface. This results from the fact that the Pt monolayer is pseudomorphically grown on the Ru(0001) substrate. The experimentally observed lower H\(_{\text{upd}}\) charge on Pt_{1-ML}/Ru(0001) compared to Pt(111) must be due to a lower H\(_{\text{ad}}\) coverage, caused by lowered adsorption energies of adsorbates on the Pt surface layer of Pt_{1-ML}/Ru(0001). As had been previously discussed in detail, this lowering of the adsorption energy results from vertical electronic interactions and compressive lateral strain\[^{[79,80,84–86]}\] (see also Section 6.3.4).

Finally, we would like to note that these CVs recorded in sulfuric acid solution differ distinctly from those obtained in perchloric acid solution, in particular in the H\(_{\text{upd}}\) region\[^{[89,341]}\]. In the present work, in H\(_2\)SO\(_4\) based electrolyte, we find clear features related to H adsorption / desorption only on the Pt modified surfaces for \(x_{\text{Pt}} \geq 0.24\), which increase with increasing \(x_{\text{Pt}}\) (no H\(_{\text{upd}}\) on bare Ru(0001) and Pt_{0.12Ru_{0.88}}(0001)). In 0.1 M HClO\(_4\) electrolyte, in contrast, the H\(_{\text{upd}}\) region is largest for bare Ru(0001)\[^{[345,346,349]}\] and decreases with increasing \(x_{\text{Pt}}\[^{[341]}\]. A more detailed discussion of these differences is, however, outside the scope of this paper, and would require also further experimental and / or theoretical work.

**Bulk CO electro-oxidation**

The bulk CO electro-oxidation was investigated on nine Pt\(_x\)Ru\(_{1-x}\)/(0001) surface alloys with different Pt contents. For better visibility we only show the polarization curves of the Pt\(_x\)Ru\(_{1-x}\)/(0001) electrodes with \(x_{\text{Pt}} = 0.30\), \(x_{\text{Pt}} = 0.61\) and \(x_{\text{Pt}} = 0.82\) in Figure 6.28, together with the polarization curves of Pt_{1-ML}/Ru(0001) and Pt(111). For all electrodes the second polarization cycle is presented. The full polarization curves of the first and the second cycle of all electrodes investigated are shown in the Appendix in Figure 6.31.

The characteristics of the polarization curve for the bulk CO electro-oxidation on Pt(111) are in perfect agreement with literature data\[^{[16,53,297,350]}\]. CO oxidation starts at around 0.60 V (see inset a) in Figure 6.28 and the so-called ignition region with its almost vertical current increase is reached at around 0.94 V. Here the CO oxidation current density increases steeply, passing through a maximum of 1.42 mA cm\(^{-2}\). It then decreases equally steeply, passes through a second peak and finally decays to an approximately
6.3 CO electro-oxidation on Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001)

![Graph showing polarization curves](image)

**Figure 6.28:** Polarization curves (0.02 V - 0.90 V, 10 mV s\(^{-1}\)) recorded on three Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) electrodes with Pt contents of \(x_{Pt} = 0.30\) (blue dotted line), \(x_{Pt} = 0.61\) (magenta dashed line) and \(x_{Pt} = 0.82\) (green solid line), respectively, as well as polarization curves recorded on Pt\textsubscript{1-ML}/Ru(0001) (red dash-dotted line) and on Pt(111) (0.07 V - 1.10 V, 10 mV s\(^{-1}\), black short-dashed line) in CO saturated 0.5 M H\textsubscript{2}SO\textsubscript{4}. The small arrows indicate the scan direction, while the large arrow indicates the increase of the Pt content \(x_{Pt}\). The inset a) shows a magnified presentation of the positive-going scans of the respective electrodes in the potential range around the onset for bulk CO electro-oxidation. The inset b) shows the width of the hysteresis (\(\Delta E_{Hyst}(x_{Pt})\)) between positive-going scan and negative-going scan at a current density of \(j = 350 \mu\text{Acm}^{-2}\) of all Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) electrodes with Pt contents between \(x_{Pt} = 0.12\) and \(x_{Pt} = 0.83\), of Pt\textsubscript{1-ML}/Ru(0001) and of Pt(111) as a function of \(x_{Pt}\).

The sharp peak in the ignition region was ascribed to the simultaneous oxidation of the CO adlayer on the Pt(111) surface (CO stripping) and of CO from solution\(^{309,351}\). In the negative-going scan direction, the CO oxidation current density follows the same constant value, increasing only slightly before it starts to decay at 0.91 V and almost disappears (< 0.01 mA cm\(^{-2}\)) at ca. 0.79 V. Hence, in the negative-going scan the CO oxidation reaction proceeds at potentials well below the ignition region. As a result, the polarization curve exhibits a hysteresis between the positive-going and the negative-going scan, which has been explained by the presence of different surface states at the beginning of each scan direction\(^{307,352}\). Below the so-called inhibition potential at around 0.60 V, where the current density is close to zero in the negative-going scan, the surface is again fully poisoned by CO\textsubscript{ad}\(^{305}\). Ru(0001) is known to be little active for bulk CO electro-oxidation\(^{58,353}\). The related polarization curve is shown in the Appendix in Figure 6.32. While the onset potential for CO oxidation on Ru(0001) is rather low, at around 0.55 V compared to 0.60 V for Pt(111), the maximum current density measured on Ru(0001) is much lower than on Pt(111). With only 0.01 mA cm\(^{-2}\) at around 0.90 V it is approximately two orders of magnitude...
smaller than that measured on all Pt modified Ru(0001) electrodes and almost a factor of 40 lower than for Pt(111) at 1.10 V. Therefore, Ru(0001) can be considered as inactive for the bulk CO electro-oxidation.

As illustrated in Figure 6.28, the Pt modified Ru(0001) electrodes show a lower onset potential than Pt(111). Furthermore, they require distinctly lower potentials to reach a certain current density for CO electro-oxidation in the whole potential range compared to Pt(111). Focusing on the positive-going scan direction, the onset for CO oxidation is located between 0.46 V and 0.53 V for the Pt modified Ru(0001) electrodes, as illustrated in the inset a) in Figure 6.28.

Starting from the onset potential, the polarization curves of all Pt modified Ru(0001) electrodes increase about exponentially with increasing potential, until they saturate at current densities in the range of 1.0 mA cm\(^{-2}\) to 1.2 mA cm\(^{-2}\). This regime, where the current is likely limited by transport effects, is reached at potentials close to 0.90 V. The small variations of the transport limited current densities between the Pt modified Ru(0001) electrodes are ascribed to slightly varying thicknesses of the electrolyte diffusion layer, and thus to varying diffusion rates, due to different pressings of the electrodes on the electrochemical cell (for more details see Reference \[53\]). Interestingly, the current densities in the transport limited potential regime are significantly higher for the Pt\(_{X}\)ML/Ru(0001) electrodes than for Pt(111). Hence, on Pt(111) the reaction in this potential regime cannot be purely mass transport limited, but must be affected by kinetic limitations. Most likely, these are related to a lowering of the rate due to the presence of surface oxides under these conditions.

For the Pt\(_{x}\)Ru\(_{1-x}\)/Ru(0001) surface alloys and Pt\(_{1}\)ML/Ru(0001), the upper potential limit was fixed to 0.90 V. Applying higher potentials results in a dramatic decrease of the absolute activity with increasing number of potential cycles, as demonstrated for Pt\(_{0.30}\)Ru\(_{0.70}\)/Ru(0001) in the Appendix in Figure 6.33. We tentatively attribute this deactivation to a potential induced restructuring of the surface, similar to observations for Pt island modified Ru(0001) electrodes\[^{[58,206]}\]. So far, however, we were not able to resolve structural changes of the surface alloys by \textit{ex situ} STM under UHV conditions after potential cycling, which could be made responsible for this deactivation.

Similar to the situation for Pt(111), a hysteresis is observed for all Pt modified Ru(0001) electrodes, resulting in higher CO oxidation rates in the negative-going scan compared to the respective positive-going scan at potentials below the ignition potential. Finally, the reaction is inhibited at potentials between 0.50 V and 0.54 V in the negative-going scan direction for all Pt modified Ru(0001) electrodes. The width of the hystere-
6.3 CO electro-oxidation on Pt$_x$Ru$_{1-x}$/Ru(0001)

sis $\Delta E_{Hyst}(x_{Pt})$ was determined for all electrodes investigated at a current density of $j = 0.35$ mA cm$^{-2}$, where the influence of diffusion controlled current densities is negligible. The variation of $\Delta E_{Hyst}(x_{Pt})$ with increasing $x_{Pt}$ is illustrated in the inset b) in Figure 6.28. It decreases with increasing Pt content $x_{Pt}$ in the surface layer of the Pt modified Ru(0001) electrodes. In addition, the hysteresis is more pronounced for Pt(111) than for Pt$_{1-ML}$/Ru(0001). Possible effects of the different structural properties of the electrode surfaces on the observed change in the hysteresis width will be discussed in Section 6.3.4.

Focusing first on the potential range below the inhibition potential in the negative-going scan, we observed a number of overlapping reduction peaks with small current densities on the Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys with $x_{Pt} \leq 0.50$, which are centered at 0.14 V, 0.22 V, 0.40 V and 0.48 V, respectively. This is shown in the Appendix in Figure 6.34. These features are ascribed to the displacement of adsorbed O/OH species on the surface by CO$_{ad}$, similar to previous observations for Ru(0001) in HClO$_4$ based electrolyte$^{346}$. The observed displacement charge is maximum for Pt$_{0.12}$Ru$_{0.88}$/Ru(0001) and decreases with increasing $x_{Pt}$, until it completely vanishes for $x_{Pt} > 0.50$. Also for Pt$_{1-ML}$/Ru(0001) and Pt(111) these reduction features were not observed.

For better comparison of the bulk CO electro-oxidation activity of the different electrodes, the positive-going scans are displayed in Figure 6.29. Here we used the second positive-going scan, which reflects a steady-state voltammogram. The first positive-going scan may exhibit a pre-oxidation region, which is known to result from the formation of a more densely packed CO$_{ad}$ adlayer upon CO adsorption at low potentials$^{17,193}$. Scans of six Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes with different Pt contents, ranging from $x_{Pt} = 0.12$ to $x_{Pt} = 0.82$, are presented in that Figure, while the curves of the remaining three Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes, which closely resemble the curves of $x_{Pt} = 0.48$, $x_{Pt} = 0.61$ and $x_{Pt} = 0.82$, are shown in the Appendix. The potential range displayed starts at 0.40 V.

Figure 6.29 demonstrates that for all Pt modified Ru(0001) electrodes and for Pt(111) the current densities are negligible at potentials below 0.60 V ($j < 0.01$ mA cm$^{-2}$). The potential where significant, exponentially increasing currents ($j > 0.01$ mA cm$^{-2}$) are resolved, is lowest for the Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys, higher for the Pt$_{1-ML}$/Ru(0001) electrode, and highest for Pt(111). Among the Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys it is lowest for the Pt$_{0.30}$Ru$_{0.70}$/Ru(0001) electrode. For $x_{Pt} > 0.30$ and also for $x_{Pt} < 0.30$ this potential increases again. This trend in activity is illustrated by comparing the activities at 0.75 V, indicated by the downwards pointing arrow and the vertical
6 Results and Discussion

Figure 6.29: Second positive-going scans of the polarization curves recorded in CO saturated 0.5 M H₂SO₄ on PtₓRu₁₋ₓ/Ru(0001) surface alloys (0.02 V - 0.90 V, 10 mV s⁻¹) with Pt contents between \( x_{Pt} = 0.12 \) and \( x_{Pt} = 0.82 \), on Pt₁-ML/Ru(0001) (0.02 V - 0.90 V, 10 mV s⁻¹) and on Pt(111) (0.07 V - 1.10 V, 10 mV s⁻¹). For better readability and understanding, only the potential range between 0.40 V and 1.03 V is shown and all electrodes are labeled. The horizontal dashed line indicates a current density of \( j = 350 \mu \text{A cm}^{-2} \). The inset shows the potential shifts (\( \Delta E_{350}(x_{Pt}) \)) between the potential \( E_{350}(x_{Pt}) \) where the PtₓRu₁₋ₓ/Ru(0001) electrodes and Pt₁-ML/Ru(0001) have \( j = 350 \mu \text{A cm}^{-2} \) and the respective potential of Pt(111) (\( E_{350}(\text{Pt}(111)) \)), plotted as a function of the Pt content in the surface (\( x_{Pt} \)). For comparison the relative abundance of PtRu₂ trimers (blue curve) and PtRu₃ tetramers (orange curve) from Figure 6.26b and 6.26c are also plotted as a function of \( x_{Pt} \) in the inset. The star (*) indicates polarization curves of surface alloys with similar Pt contents and thus only one representative curve is shown in the main Figure.

dotted line in Figure 6.29. At this potential, the highest CO oxidation rate is observed on Pt₀.₃₀Ru₀.₇₀/Ru(0001), with a current density of around 0.70 mA cm⁻², followed by 0.34 mA cm⁻² for Pt₀.₄₈Ru₀.₅₂/Ru(0001), 0.24 mA cm⁻² (Pt₀.₆₁Ru₀.₃₉/Ru(0001)), 0.21 mA cm⁻² (Pt₀.₂₄Ru₀.₇₆/Ru(0001)), 0.14 mA cm⁻² (Pt₀.₁₂Ru₀.₈₈/Ru(0001)) and 0.08 mA cm⁻² for Pt₀.₈₂Ru₀.₁₈/Ru(0001). The lowest oxidation currents are obtained for Pt₁-ML/Ru(0001) (0.04 mA cm⁻²) and finally for Pt(111) (0.01 mA cm⁻²). Obviously, PtRu sites in the surface layer play a crucial role for enhancing the bulk CO electro-oxidation activity of these electrodes.

For a more detailed discussion of the influence of \( x_{Pt} \) on the CO electro-oxidation activity of the Pt modified Ru(0001) electrodes we extracted the potentials at which each electrode exhibits a current density of \( j = 350 \mu \text{A cm}^{-2} \) (\( E_{350}(x_{Pt}) \)), as indicated by the horizontal dashed line in Figure 6.29. From the difference between \( E_{350}(x_{Pt}) \) and \( E_{350}(\text{Pt}(111)) \), we obtain a shift in potential (\( \Delta E_{350}(x_{Pt}) = |E_{350}(x_{Pt}) - E_{350}(\text{Pt}(111))| \)) with respect to the potential where pure Pt(111) exhibits the same CO oxidation rate.
\[ \Delta E_{350}(x_{Pt}) \] can therefore be considered as a direct measure of the overpotential required for this current density value and thus of the electrode activity, always relative to Pt(111). The resulting values are plotted as a function of \( x_{Pt} \) in the inset in Figure 6.29. Clearly, this plot shows a volcano-like dependence of the activity on \( x_{Pt} \). The lowest activity is obtained for Pt\(_{1-ML}/\text{Ru}(0001)\), for which \( E_{350}(1-ML) \) is shifted by 0.08 V to lower potentials compared to Pt(111). The maximum of \( \Delta E_{350}(x_{Pt}) \), corresponding to the highest CO electro-oxidation activity, is located at \( x_{Pt} = 0.30 \), with a potential shift of 0.22 V. Hence, Pt\(_{0.30}\)Ru\(_{0.70}/\text{Ru}(0001)\) is the most active electrode among those investigated. Surface alloys with larger and smaller Pt contents show lower activities. A similar trend in activity has been observed also for the first positive-going potential cycle and for the second negative-going cycle, as shown in the Appendix in Figure 6.35 and Figure 6.36, respectively.

The trend in activity shown in Figure 6.29 implies that the rate of the bulk CO electro-oxidation on Pt\(_x\)Ru\(_{1-x}/\text{Ru}(0001)\) is mainly driven by catalytic sites, (i) which are more active than monometallic Pt ensembles on a Ru(0001) substrate, since Pt\(_{1-ML}/\text{Ru}(0001)\), consisting only of pure Pt ensembles, is rather inactive compared to the surface alloys, and (ii) whose relative abundance depends on \( x_{Pt} \). Consequences of these findings shall be discussed in more detail in the following Section, using also our knowledge about the abundance of Pt and Ru surface atoms and mixed Pt\(_n\)Ru\(_m\) ensembles for different Pt surface contents \( x_{Pt} \), which was summarized in Figure 6.26.

### 6.3.4 Discussion

Our results demonstrate that compared to monometallic Ru(0001) and Pt(111) the electrochemical properties of the Pt modified Ru(0001) electrodes as well as their electrocatalytic activity for the bulk CO electro-oxidation are strongly modified. According to the classical bifunctional mechanism\(^{[78]}\), the activity of a bimetallic AB surface can be enhanced compared to the respective monometallic surfaces if one of the surface species, e.g., atom A, stabilizes one reactant or facilitates its formation, while the other reactant adsorbs on a neighboring atom of the other type (here B). Specifically for bimetallic PtRu surfaces it was proposed that OH\(_{ad}\) species are formed more easily on ‘Ru sites’ than on ‘Pt sites’, while CO can adsorb on ‘Pt sites’. In this very simplified picture CO\(_{ad}\) is located atop of a Pt atom, while OH\(_{ad}\) is adsorbed atop on a Ru atom. Accordingly, the highest activity for the reaction should be obtained for alloys with a 1:1 surface ratio of Pt and Ru (assuming a random distribution of the atoms), which was supported experimentally by Gasteiger et al.\(^{[203,204]}\). This picture is, however, strongly simplified.
First it assumes that the (electro-)chemical properties of the Pt and Ru surface atoms are similar to those they have in a monometallic Pt surface or Ru surface, respectively. Hence, it does not consider the severe electronic modifications of the surface atoms that will arise from electronic effects such as ligand effects\cite{24,25,32,137} and strain effects\cite{26,32}, which have been discussed extensively before (see also Section 6.3.2).

Focusing on Pt\textsubscript{X-ML}/Ru(0001) surfaces, the influence of strain and vertical ligand effects is illustrated best by comparing the CO oxidation activity of Pt(111) and Pt\textsubscript{1-ML}/Ru(0001). Considering that for Pt(111) and Pt\textsubscript{1-ML}/Ru(0001) both surfaces present only one type of surface atoms, the higher activity of the latter surface, as indicated by the lower potential necessary to obtain $j = 350 \mu$A cm$^{-2}$, can be rationalized by (i) a vertical ligand effect, which is caused by the different electronic structure of the respective substrates, Pt(111) and Ru(0001), and (ii) a compressive lattice strain effect, which results from the smaller in-plane lattice constant in the latter surface\cite{24,26,79,81,83,136}. Note that the bimetallic PtRu step sites located at the edges of the small holes in the Pt film should not significantly affect the electrode activity, since it was shown previously for monolayer high Pt island modified Ru(0001) electrodes, that varying the amount of such sites at constant Pt coverage does not change the reaction rate\cite{58,206}.

For the surface of the bimetallic Pt\textsubscript{1-ML}/Ru(0001) electrode, the ligand and strain effects lead, according to the $d$-band model, to a down-shift of the $d$-band center towards lower energies, with a concomitant lowering of the binding energy of adsorbates on the surface\cite{32}. This was demonstrated in detailed experimental and theoretical studies on the adsorption of CO\cite{28,79,80,82,84,130}, oxygen\cite{85}, hydroxyde\cite{28} and hydrogen\cite{86,354} on Pt covered Ru(0001) surfaces. A lowering of the binding energy of Had due to these effects is also the reason for the observed lower H\textsubscript{upd} coverage on Pt\textsubscript{1-ML}/Ru(0001) compared to Pt(111)\cite{86}. The influence of ligand and strain effects is very different, however, for CO\textsubscript{ad} and OH\textsubscript{ad}. While the adsorption energy of OH\textsubscript{ad} is lowered only by a negligible amount on Pt\textsubscript{1-ML}/Ru(0001) ($E_B(OH_{ad}) = -2.31$ eV) compared to Pt(111) ($E_B(OH_{ad}) = -2.27$ eV), the CO\textsubscript{ad} binding energy is significantly lower on Pt\textsubscript{1-ML}/Ru(0001) ($E_B(CO_{ad}) = -1.08$ eV) than on Pt(111) ($E_B(CO_{ad}) = -1.75$ eV)\cite{28}. Koper \textit{et al.} derived from DFT based calculations that CO\textsubscript{ad} and OH\textsubscript{ad} are both adsorbed on atop sites on a pseudomorphic Pt film on Ru(0001)\cite{28}. There is, however, no experimental information available on the adsorption site of OH\textsubscript{ad} or O\textsubscript{ad} on these Pt\textsubscript{1-ML}/Ru(0001) surfaces.

Based on these results, the higher activity of Pt\textsubscript{1-ML}/Ru(0001) for the CO electro-
6.3 CO electro-oxidation on Pt$_x$Ru$_{1-x}$/Ru(0001)

oxidation compared to Pt(111) must primarily arise from the difference in $E_B(CO_{ad})$ on Pt$_{1-ML}$/Ru(0001). Most simply, this can be explained by a lower tendency for CO$_{ad}$ poisoning of the Pt$_{1-ML}$/Ru(0001) surface than of Pt(111): the lowering of $E_B(CO_{ad})$ leads to a lower CO$_{ad}$ saturation coverage on Pt$_{1-ML}$/Ru(0001) compared to Pt(111). Indeed, from a high-pressure STM study it was reported that at ambient pressure and at room temperature the CO$_{ad}$ saturation coverage on Pt(111) is $\theta_{CO} = 0.68$ ML$^{355}$. For Pt$_{1-ML}$/Ru(0001) there are no data for CO adsorption at ambient pressure; however, a near-ambient pressure XPS study on a near surface alloy with similar properties like Pt$_{1-ML}$/Ru(0001) determined a CO coverage of $\theta_{CO} = 0.30$ ML at 0.055 mbar$^{356}$. Assuming that the trend for CO adsorption on these surfaces at the solid-liquid interface is similar, we argue that at low potentials a less dense CO$_{ad}$ adlayer on Pt$_{1-ML}$/Ru(0001) results in a lower tendency to inhibit the formation of OH$_{ad}$ via water dissociation on Pt$_{1-ML}$/Ru(0001) compared to Pt(111). In that case, bulk CO electro-oxidation on Pt(111) is limited by the high CO adsorption energy and the resulting high CO$_{ad}$ coverage rather than by an intrinsic lack of OH$_{ad}$ formation. This is in accordance with previous findings of higher onset potentials for bulk CO oxidation than for the oxidation of a pre-adsorbed CO adlayer (‘COad stripping’) on Pt$^{309,351}$. Furthermore, due to the lower binding energies for both OH$_{ad}$ and CO$_{ad}$ on the Pt$_{1-ML}$/Ru(0001) electrode the activation barrier for CO$_2$ formation should, according to the Brønsted-Evans-Polanyi principle$^{357}$, be lower than on Pt(111).

The situation changes again for the reaction on Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys. For these surfaces we observe that all electrodes, independent of the surface Pt content $x_{Pt}$, show a higher activity for CO oxidation than Pt$_{1-ML}$/Ru(0001), with the highest activity for the surface alloy with $x_{Pt} = 0.30$. Assuming that the vertical ligand effect is rather similar for Pt$_{1-ML}$/Ru(0001) and the Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes (in all cases the bulk consists of pure Ru(0001)) and focusing on electronic properties, this difference in activity can result from two effects that cannot be separated experimentally: from i) lateral variations in the strain effect and from ii) lateral ligand effects, due to different interactions between neighboring Pt–Pt, Pt–Ru, and Ru–Ru surface atoms$^{24}$. More specific, the compressive strain increases locally upon incorporation of Pt atoms into the Ru(0001) surface layer, leading to a local down-shift of the $d$-band center and thus to a smaller binding energy of adsorbates on the Ru sites. Vice versa, the incorporation of Ru atoms into a Pt monolayer film on Ru(0001) slightly releases the lattice strain in the topmost surface layer, leading to an upshift of the $d$-band center on the Pt sites adjacent to Ru surface atoms and thus to a stronger bonding of adsorbates on
these sites than on Pt$_{1-ML}$/Ru(0001)$^{[26,82,358]}$. On the other hand, the stronger bond between Pt and Ru in the surface layer compared to Pt–Pt should result in a lowering of the adsorption strength of adsorbed species on these Pt surface atoms compared to adsorption on Pt$_{1-ML}$/Ru(0001), due to lateral ligand effects. Likewise, we would expect an opposite trend for adsorption on Ru surface atoms (stronger Ru–Ru interactions than Pt–Ru interactions). Rauscher et al. showed in a combined STM / TPD / IRAS study on the CO adsorption properties on Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys, that with decreasing $x_{Pt}$ (increasing amount of Ru) the CO$_{ad}$ is increasingly stabilized on both, the Pt and the Ru atoms at the surface$^{[82]}$. Based on that the authors concluded that the influence of compressive lattice strain release dominates over the lateral electronic ligand effects for Pt$_x$Ru$_{1-x}$/Ru(0001)$^{[82]}$. Here it had been shown by FTIR measurements that CO adsorbs preferentially in an on top configuration on both Pt atoms and Ru atoms, with Ru surface atoms being populated first, underlining that adsorption on these sites is energetically most favorable$^{[82]}$. It should be noted that these data refer to adsorption at the solid gas interface, in the absence of an electrolyte.

Unfortunately, there is no comparable experimental data on the adsorption / formation of OH via water dissociation on these surfaces. From DFT calculations, Ru$_3$ threefold hollow sites were determined as the most favorable adsorption sites for OH adsorption$^{[341]}$. Other atop-Ru and bridge-Ru$_2$ configurations as well as the OH adsorption on mixed Pt$_n$Ru$_m$ ensembles were found to be less favorable$^{[341]}$. Here the atop-Ru and bridge-Ru$_2$ configurations were identified as the most favorable adsorption sites for OH$_{ad}$ on a PtRu$_2$ trimer ensemble$^{[341]}$.

In total, the results described above indicate that the adsorption of OH$_{ad}$ and CO$_{ad}$ is directly affected by the chemical and electronic nature of atomic ensembles on the surface and thus by the chemical composition of these ensembles. From previous studies on the CO oxidation at the solid-gas interface it was already shown that the two reactants adsorbed on the surface may prefer other or even different types of adsorption geometries, e.g., with CO adsorbing in an ‘on top’ configuration, while OH (or O) prefers to adsorb on a three-fold hollow site. For Pt(111), both CO$^{[359]}$ and OH$^{[360]}$ are assumed to preferentially adsorb in on top configurations, on a single Pt atom, at least at moderate coverages. For adsorbed oxygen, in contrast, threefold-hollow sites on a Pt$_3$ ensemble are considered as preferable adsorption site$^{[361,362]}$. Hence, in this case the ‘site’ is not equivalent to a single surface atom. Moving to co-adsorbed species, the situation becomes more complex. CO oxidation on Pt(111) at the solid-gas interface seems to start with CO adsorbed on an on top site and O adsorbed on the next-nearest threefold
hollow site, about 3.2 Å apart\textsuperscript{[363]}. For Ru(0001), the situation is likely to be comparable\textsuperscript{[364]}. Thus, on both metal surfaces at least 4 atoms arranged in a compact 4-atom ensemble (‘tetramer’) are necessary to perform the CO oxidation on metal surfaces, and therefore the chemical composition of such tetramers should drive the reaction. For the Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) surface alloys this suggests that the adsorption behavior of CO\textsubscript{ad} and OH\textsubscript{ad} as well as the CO oxidation rate is largely determined by Pt\textsubscript{n}Ru\textsubscript{4-n} tetramers which thus represent the critical ensemble for this reaction. Here we define the critical ensemble as the ensemble of surface atoms which largely determines the adsorption and reaction behavior of the co-adsorbed reactants. This does not exclude that smaller modifications are possible also by surface atoms adjacent to that ensemble. Already in earlier literature geometric ensemble effects were considered to play an important role in catalytic reactions on bimetallic catalysts\textsuperscript{[24,137]}. Here it was assumed that a minimum ensemble of n surface atoms of a given type is required to support the respective reaction. Given the previous discussion, we would like to modify this definition in the sense that on inhomogeneous surfaces such as bimetallic surfaces the reactivity of a given ’site’ is mainly determined by the chemical composition (or structure) of this ensemble of atoms.

Experimentally, this can be tested by comparing the abundance of the surface ensembles with different elemental composition, as illustrated in Figure 6.26, with the trend of the activity in Figure 6.29. In good agreement with our above arguments, Pt\textsubscript{n}Ru\textsubscript{2-n} dimers can be excluded as critical ensemble based on our experimental finding that the highest activity was obtained for the surface with \(x_{Pt} = 0.30\) rather than at \(x_{Pt} = 0.00\), \(x_{Pt} = 0.50\) or \(x_{Pt} = 1.00\), where the abundance of Ru\textsubscript{2} dimers, bimetallic PtRu dimers or Pt\textsubscript{2} dimers is highest (see Figure 6.26a). The closest agreement between the experimentally observed trend in CO oxidation activity and the relative abundance of specific bimetallic ensembles is obtained for PtRu\textsubscript{2} trimers (Figure 6.26b) and PtRu\textsubscript{3} tetramers (Figure 6.26c) as illustrated in the inset in Figure 6.29. Both show a maximum at around \(x_{Pt} = 0.25 - 0.30\), and their abundance decreases rapidly for lower \(x_{Pt}\) values, while for higher Pt contents it decreases more slowly. Considering again our above arguments that the binding properties of co-adsorbed OH\textsubscript{ad} and CO\textsubscript{ad} species are determined by the chemical/electronic properties of at least the 4 atoms in a compact tetramer, the experimental results indicate that the CO electro-oxidation activity of the bimetallic Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) surface alloys is dominated by PtRu\textsubscript{3} ensembles, which seem to represent the most active ensemble.

Correlation between adsorption or binding energies and the catalytic activity of different surfaces for a specific catalytic reaction have mostly been discussed based on the
Sabatier principle, which states that there is an optimum interaction of reactants to the catalyst surface for each catalytic reaction and that for stronger or weaker interactions the overall reaction rate decreases\textsuperscript{[365]}. For example for the electroreduction of $O_2$ (ORR) on metal surfaces, which is a complex multistep reaction, it could be demonstrated that the decisive parameter for the ORR activity is the oxygen binding energy, which for the optimum catalyst should be slightly lower than on Pt\textsuperscript{[151]}. In a number of recent studies on the ORR on bimetallic surfaces\textsuperscript{[89,366,367]}, including also Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys\textsuperscript{[89]}, we could demonstrate that the trend in ORR activity with surface composition can be properly described by the abundance of different A$_x$B$_{3-x}$ sites, and for Pt$_x$Ru$_{1-x}$/Ru(0001) the ORR rate was found to be dominated by the Pt$_2$Ru ensembles\textsuperscript{[89]}. Hence, although the reaction may proceed via a complex multistep mechanism, the reactivities of the different Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys was reasonably well described by the abundance of Pt$_2$Ru sites. Accordingly, the CO oxidation activity may well be correlated to the abundance of PtRu$_3$ tetramers, as indicated experimentally.

So far, however, we did not discuss possible reasons for the observation that under present reaction conditions the CO electro-oxidation activity of the Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes increases with increasing abundance of PtRu$_3$ tetramers. According to the Sabatier principle, the PtRu$_3$ tetramers seem to provide adsorption sites for adjacent CO$_{ad}$ and OH$_{ad}$ species whose binding energies are beneficial for the reaction to CO$_2$. Here we suggest that the CO species adsorb atop on the Pt atom of PtRu$_3$ while OH$_{ad}$ is located in the threefold hollow site of the Ru$_3$ trimer. This is based on the results of the adsorption studies described above, which reported CO adsorption\textsuperscript{[82]} and OH adsorption\textsuperscript{[341]} to be most favorable on these sites on Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys. In both cases the adsorption properties will be significantly affected by compressive lattice strain effects and/or lateral ligand effects, in addition to the vertical ligand effects which are present for all Pt modified Ru(0001) electrodes.

Further information on details of the reaction process can be obtained from the pronounced hysteresis, which had been observed for the potentiodynamic bulk CO electro-oxidation on all surfaces investigated. This hysteresis is generally explained by the different states of the surface in the low-potential regime and in the high-potential regime. At low potentials the reaction is inhibited by a densely packed CO adlayer, while at high potentials the reaction is facile due to the presence of adsorbed OH and surface oxides. In analogy to Heterogeneous Catalysis, these two states may also be termed as ‘low-rate branch’ (at high CO partial pressures and/or low potentials) and ‘high-rate branch’ (at high $O_2$ partial pressures and/or high potentials)\textsuperscript{[368]}. As expected, the
hysteresis shifts with surface composition and hence with adsorption energies. Interestingly, however, not only the potential range of the hysteresis shifts, but also its width, which increases with decreasing Pt content from 0.03 V for Pt$_{1}$ML/Ru(0001) to 0.14 V for Pt$_{0.12}$Ru$_{0.88}$/Ru(0001) (Figure 6.28, inset). While in the positive-going scan the onset of the CO oxidation reaction and the subsequent increase of the oxidation rate, including the potential for reaching 350 $\mu$A cm$^{-2}$, are likely to be determined mainly by the efficiency of the CO$_{ad}$ induced site blocking (inhibition of OH$_{ad}$ formation), the decay of the oxidation rate in the negative-going scan is most simply governed by the ability for the surface to supply the OH$_{ad}$ species required for the reaction (for exceptions see below). Once the OH$_{ad}$ formation rate decreases below the OH$_{ad}$ removal rate, by reaction with CO$_{ad}$, CO$_{ad}$ species can accumulate on the surface and increasingly poison this for further OH$_{ad}$ formation. Interestingly, this decay occurs rather slowly on the Pt modified surfaces, extending over almost 200 mV, which is very different to the much steeper decay (over ~50 mV) on Pt(111). In this picture one can most easily correlate the potential for the decay in CO$_{ad}$ oxidation rate in the negative-going scan with the ability of the surface to generate OH$_{ad}$ species, which in turn is related to the OH$_{ad}$ binding energy. Hence, one would expect Ru-rich surfaces to exhibit the lowest potential for the decay in the CO$_{ad}$ oxidation rate.

Experimentally, we found similar trends for the increase / decrease in the CO oxidation rate in the positive-going and negative-going scan. With decreasing Pt surface content we observe a down-shift of the potential at which the increase / decay of the CO oxidation rate occurs. The down-shift stops, however, at $x_{Pt} = 0.30$, and for further decreasing Pt contents it reverts into an up-shift. We tentatively explain this by a too high stability of the OH$_{ad}$ species on the Ru-rich surfaces, specifically on the Ru$_4$ sites. We suggest that on the Ru$_4$ sites not the formation of OH$_{ad}$ species is rate limiting, but their reaction with CO$_{ad}$. In that case the reaction on Ru$_4$ sites may either be shifted to higher potentials, or these sites are essentially inactive and the reaction rate is determined by the decreasing amount of (remaining) active Pt$_n$Ru$_{4-n}$ tetramer sites with $n \geq 1$ for surface alloys with $x_{Pt} < 0.30$. This may equally apply in the negative-going and positive-going scan. Under these conditions, CO$_{ad}$ and OH$_{ad}$ may even coexist on the Ru$_4$ ensembles and react only slowly with each other, different from the behavior of Pt-rich surfaces. This suggestion fits well to observations for CO oxidation on the Ru(0001) electrode surface, which is known to be poorly active for CO oxidation (see Figure 6.32 and References. [$^{58,353}$]). In the same way, OH$_{ad}$ formation may occur on Ru$_4$ ensembles in the positive-going scan, without, however, causing an immediate start of the reaction. This in turn would
6 Results and Discussion

result in an upshift of the steep increase of the reaction rate for $x_{Pt} < 0.30$, as observed experimentally.

In contrast to the formation of a maximum in the down-shift discussed above, the width of the hysteresis increases steadily with decreasing Pt surface content. For surface compositions down to $x_{Pt} = 0.30$ this is due to the more pronounced shifts in the negative-going scan as compared to those in the positive-going scan. At lower Pt contents this is opposite, and the increasing width of the hysteresis is dominated by the more pronounced shift in the positive-going scan. For higher Pt contents we assume that the effects of the increasing OH$_{ad}$ bonding strength with decreasing $x_{Pt}$ should be more pronounced in the negative-going scan, while in the positive-going scan also surface site blocking by CO$_{ad}$ plays a role, leading to less pronounced shifts, as observed experimentally. For low Pt contents, we have no good explanation for the further increasing width of the hysteresis at present.

Finally, we would like to comment on the distinctly different onset behavior in the positive-going scan observed for all Pt surface modified Ru(0001) electrodes compared to Pt(111). Bulk CO oxidation on Pt(111) is known to show an almost vertical increase of the reaction rate at a critical potential of about 0.94 V$^{[350]}$. The Pt surface modified Ru(0001) electrodes, on the other hand, exhibit an almost exponential increase of the oxidation current, which extends over almost 200 mV. Since for both, Pt$_{1-ML}$/Ru(0001) and Pt(111) the surface consists solely of Pt atoms, the different onset behavior on the former surface is likely due to the weaker binding energy of adsorbates compared to Pt(111), and the same argument holds true also for the surface alloys. We suggest that for Pt(111) the site blocking by adsorbed CO$_{ad}$ inhibits OH$_{ad}$ formation up to the ignition potential, where the reaction rate shoots up almost vertically. Hence, CO$_{ad}$ inhibition dominates the onset behavior for this electrode. For the Pt modified Ru(0001) electrodes site blocking effects play only a minor role, due to the weaker CO$_{ad}$ binding. In these cases, specifically for Pt$_n$Ru$_{4-n}$ tetramers with $n \geq 1$, the onset behavior is dominated by the intrinsic tendency for OH$_{ad}$ formation rather than by site blocking, where the former is a potential dependent process$^{[185]}$, and thus should exhibit an approximately exponential rate increase, in good agreement with our experimental observations. Although we cannot exclude that the reaction between CO$_{ad}$ and OH$_{ad}$ is rate limiting on these sites, we find this less likely based on the exponential potential dependence of the rate. In contrast, for Ru-rich surfaces, specifically for Ru$_4$ tetramers, we propose that the reaction between CO$_{ad}$ and OH$_{ad}$ is rate limiting.
6.3.5 Conclusions

Aiming at a better understanding of electrocatalytic reactions on bimetallic surfaces we have investigated the electro-oxidation of bulk CO on different Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes with increasing Pt contents $x_{Pt}$ under enforced electrolyte transport conditions in sulfuric acid in a combined UHV-STM–EC flow cell set-up. The electrochemical/-catalytic properties were compared with the corresponding properties of Pt(111), Ru(0001) and a monolayer high Pt film supported on Ru(0001) (Pt$_{1-ML}$/Ru(0001)) to derive structure-activity relationships. Correlating the electrochemical properties of these electrodes and their electrocatalytic activity for the bulk CO electro-oxidation with their structural characteristics, on an atomic scale, we arrived at the following conclusions:

1. All Pt surface modified Ru(0001) electrodes exhibit a higher activity for bulk CO oxidation than Pt(111) and Ru(0001). For the Pt monolayer modified Ru(0001) this is ascribed to a lowering of the CO$_{ad}$ adsorption strength on Pt$_{1-ML}$/Ru(0001) compared to Pt(111) due to a downshift of the $d$-band center induced by compressive lattice strain and vertical ligand effect. In contrast, the differences in the OH$_{ad}$ adsorption energy on the Pt terminated surfaces are much smaller. The higher activity of Pt$_{1-ML}$/Ru(0001) over Pt(111) indicates that vertical ligand effect and compressive lattice strain significantly enhance the CO oxidation rate without the need of bifunctional sites on the surface.

2. The activity for bulk CO oxidation is further enhanced for bimetallic Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys with a maximum activity observed for $x_{Pt}= 0.30$. On these surfaces the electronic properties of the Pt and Ru surface atoms are further modified compared to Pt$_{1-ML}$/Ru(0001) by lateral ligand effects and local modifications of the strain, due to unlike neighbors. Based on the statistically determined relative abundance of bimetallic ensembles and correlation with the experimentally observed activity trends, we suggest that Pt$_n$Ru$_{4-n}$ tetramers dominate the activity for CO oxidation and thus represent the critical ensemble. Among these tetramers the most active ensemble for the bulk CO electro-oxidation was determined to consist of a single Pt atom adjacent to three Ru atoms (Pt$_1$Ru$_3$). On these ensembles CO$_{ad}$ is adsorbed atop on the Pt atom directly adjacent to a Ru$_3$ trimer, where the latter is the most favored adsorption site for OH on Pt$_x$Ru$_{1-x}$/Ru(0001) surfaces.

3. The identification of compact Pt$_1$Ru$_3$ tetramers as the most active ensemble for the bulk CO oxidation implies that the presence of Ru surface atoms indeed improves
the oxidation of CO$_{\text{ad}}$ adsorbed on Pt. The situation is, however, more complex than in the picture of the classical bifunctional mechanism, where a single Ru atom adjacent to a Pt atom is believed to be the most active promoter for the CO oxidation, and where the severe electronic modifications of the surface atoms induced by the neighboring atoms are neglected. Therefore, it is not sufficient to strive for adjacent Pt and Ru surface atoms on the surface, but more important to strive for optimized electronic and geometric properties of the surface sites. In the present case, these are obtained for Pt$_1$Ru$_3$ tetramers.

4. For all Pt surface modified Ru(0001) electrodes we find a distinctly different onset behavior in the positive-going scan compared to Pt(111). While on Pt(111) the reaction suddenly takes off at a critical potential of about 0.94 V, with an almost vertical increase of the reaction rate, the Pt surface modified Ru(0001) electrodes exhibit an almost exponential increase of the oxidation current, which extends over almost 200 mV. We tentatively conclude that for the Pt modified Ru(0001) electrodes with $x_{Pt} \geq 0.30$ this is most likely dominated by the intrinsic tendency of the surface for OH$_{\text{ad}}$ formation, with site blocking effects playing only a minor role, whereas the latter are dominant for Pt(111). For Ru-rich electrodes, whose reaction behavior is increasingly dominated by Ru$_4$ tetramers, reaction between CO$_{\text{ad}}$ and OH$_{\text{ad}}$ is proposed to be rate limiting.

5. The pronounced hysteresis observed for bulk CO oxidation between positive-going and negative-going scan on all Pt modified Ru(0001) electrodes is related to different states of the surface in the low-potential and high-potential regimes, similar to earlier proposals for Pt(111). In both scan directions the increase / decrease of the CO oxidation rate shifts to lower potential with decreasing $x_{Pt}$, reaching a minimum value at around $x_{Pt} = 0.30$. Further decrease of the Pt surface content results in an up-shift again. The formation of the minimum was tentatively ascribed to a change in the limiting step responsible for the decay of the activity, from OH$_{\text{ad}}$ formation for $x_{Pt} \geq 0.30$ to reaction of OH$_{\text{ad}}$ with CO$_{\text{ad}}$ for lower values of $x_{Pt}$. This change is largely controlled by the high OH$_{\text{ad}}$ bond strength on Ru-rich ensembles (Ru$_4$). A similar change in the limiting reaction step with $x_{Pt}$ is proposed also for the increase in CO oxidation rate in the positive-going scan. Such behavior would be compatible also with the observation of a continuously increasing width of the hysteresis, at least in the range $x_{Pt} \geq 0.30$, since the effects of the increasing OH$_{\text{ad}}$ bonding strength should be more pronounced in the negative-going scan, while in
the positive-going scan also surface site blocking by CO$_{\text{ad}}$ may play a role.

6. Finally, the significantly higher CO oxidation rates obtained on the Pt surface modified Ru(0001) electrodes at potentials around 0.90 V compared to the rates obtained at around 1.10 V on Pt(111) indicate that in contrast to earlier assignments the CO oxidation rate on Pt(111) under these conditions is significantly affected by kinetic limitations.

Overall, the results of the present work demonstrate that the activity of bimetallic surfaces is more complex than described by the classical bifunctional mechanism, with each ‘reaction site’ being comprised of an ensemble of adjacent surface atoms and with the activity of each ‘reaction site’ being determined by its chemical composition and structure. We postulate that this ‘active ensemble’ approach is of general validity for the description not only of bimetallic catalysts/surfaces, but of inhomogeneous catalysts in general.
6.3.6 Appendix

Cyclic voltammograms of Pt modified Ru(0001) electrodes

The cyclic voltammograms of the nine Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes investigated with Pt contents between $x_{Pt} = 0.12$ and $x_{Pt} = 0.83$ and of Pt$_{1-ML}$/Ru(0001) in 0.5 M H$_2$SO$_4$ supporting electrolyte are shown in Figure 6.30. The CVs of Pt$_{0.12}$Ru$_{0.88}$/Ru(0001) and Pt$_{0.24}$Ru$_{0.76}$/Ru(0001) are discussed in Section 6.3.3. The CV of Pt$_{0.30}$Ru$_{0.70}$/Ru(0001) exhibits the same features as the Pt$_{0.24}$Ru$_{0.76}$/Ru(0001) surface alloy with no distinct oxidation peaks in the anodic scan direction and a broad reduction peak in the cathodic scan as well as a small H$\text{upd}$ feature. With further increasing the Pt content above $x_{Pt} \geq 0.48$ the broad reduction peak vanishes and cannot be discerned from the currents related to double layer charging. The current densities related to H$\text{upd}$ increase with increasing $x_{Pt}$ and become largest for Pt$_{0.83}$Ru$_{0.17}$/Ru(0001). Additionally, the onset of the H$\text{upd}$ region shifts to higher potentials with increasing $x_{Pt}$ indicating an increasing H$\text{upd}$ adsorption strength on the Pt modified Ru(0001) surfaces with increasing $x_{Pt}$. When the Pt content is above $x_{Pt} > 0.30$ the CVs of the Pt$_{x}$Ru$_{1-x}$/Ru(0001) electrodes resemble the CV of Pt$_{1-ML}$/Ru(0001) which exhibits a H$\text{upd}$ region that is slightly smaller compared to Pt$_{0.83}$Ru$_{0.17}$/Ru(0001) but still larger than for all other surface alloys investigated. The highest current densities related to the HER measured at the lower potential limit of 0.05 V are -31 $\mu$A cm$^{-2}$ for $x_{Pt} = 0.12$, -36 $\mu$A cm$^{-2}$ for $x_{Pt} = 0.24$, -75 $\mu$A cm$^{-2}$ for $x_{Pt} = 0.30$ (50 mV s$^{-1}$) and between -45 $\mu$A cm$^{-2}$ and -53 $\mu$A cm$^{-2}$ for the surface alloys with $x_{Pt} \geq 0.48$ and Pt$_{1-ML}$/Ru(0001). On Pt$_{0.30}$Ru$_{0.70}$/Ru(0001) the HER currents are significantly higher since the CV was measured with 50 mV s$^{-1}$ while all other CVs were measured with 10 mV s$^{-1}$.

Bulk CO oxidation on Pt modified Ru(0001) electrodes

The first (dotted line) and the second (solid line) polarization cycles of the nine Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes investigated with Pt contents between $x_{Pt} = 0.12$ and $x_{Pt} = 0.83$ and of Pt$_{1-ML}$/Ru(0001) in CO saturated 0.5 M H$_2$SO$_4$ are shown in Figure 6.31. For Pt$_{0.12}$Ru$_{0.88}$/Ru(0001) and Pt$_{0.30}$Ru$_{0.70}$/Ru(0001) a steady-state was reached already after the second polarization cycle displayed by the overlapping first and second cycles. For all other electrodes a pre-oxidation region is observed in the first positive-going scan direction which is ascribed to the formation of a dense CO$_\text{ad}$ adlayer on the electrode surfaces prior to the first potential cycle when the EC flow cell is rinsed with CO saturated sulfuric acid for 15 minutes. For some electrodes the third
potential cycle was measured (not shown here) to ensure that the second cycle corresponds to the steady-state polarization curve. The Pt$_{0.24}$Ru$_{0.76}$/Ru(0001) electrode was measured in a different potential range (0.12 V to 0.85 V instead of -0.02 V to 0.90 V). The different potential limits for this electrode should, however, not affect the trends in activity or hysteresis width discussed, since the mass transport limited plateau is already reached around 0.85 V and the electrode is poisoned by CO$_{ad}$ at potentials below 0.50 V in the positive-going scan direction. The low potential region in the negative-going scan direction is discussed in Section 6.3.6.

**Bulk CO electro-oxidation on Ru(0001)**

The polarization curve for the bulk CO oxidation on Ru(0001) is shown in Figure 6.32. In the positive-going scan direction, no current features are observed until 0.55 V due to blocking of the surface by CO$_{ad}$. This onset potential is lower compared to the onset potential for CO oxidation on Pt(111) (0.60 V) due to the oxophilic character of Ru(0001) which provides OH$_{ad}$ species at lower potentials than Pt. In the potential range investigated, a maximum current density of ca. 0.01 mA cm$^{-2}$ is reached at around 0.90 V which is by two orders of magnitude lower than on Pt modified Ru(0001) electrodes. Thus, Ru(0001) is basically inactive for the bulk CO electro-oxidation. In the negative-going scan direction below 0.60 V a number of overlapping reduction peaks are observed on Ru(0001), which are attributed to the reduction of surface Ru-OH$_{ad}$ and the displacement by CO$_{ad}$\[346\]. The shape of the polarization curve in Figure 6.32 is thus in good agreement with previously reported polarization curves on Ru(0001) in 0.5 M H$_2$SO$_4$\[58] and in 0.1 M HClO$_4$\[346\]. For more detailed information the reader is referred to References \[58,346\].

**Deactivation of Pt$_x$Ru$_{1-x}$/Ru(0001) for the bulk CO oxidation**

Consecutive polarization cycles of the bulk CO oxidation on a Pt$_{0.30}$Ru$_{0.70}$/Ru(0001) surface alloy with different upper potential limits are displayed in Figure 6.33. The blue dotted curve shows the bulk CO oxidation on the initially prepared electrode surface in the potential range between -0.02 V and 0.90 V as it is displayed in Figure 6.28 and Figure 6.29 and discussed above. After three cycles with an upper potential limit of 0.90 V the upper potential limit was increased to 1.05 V and another three cycles were recorded (orange dashed curves). Subsequently, the upper potential was increased to 1.25 V and again three cycles were recorded (red dash-dotted curves). Finally, for the 10$^{th}$ cycle the applied upper potential limit was set again to 0.90 V (green solid curve).
When the upper potential limit was increased to 1.05 V, the positive-going scan of the 4th cycle first followed the 1st polarization cycle. In the negative-going scan direction and in the following scans, however, distinct changes compared to the 1st cycle were observed which result in a lower overall activity after the 6th polarization cycle. Further increasing the upper potential limit to 1.25 V led to additional dramatic changes of the potential dependent current response and a strong deactivation of the electrode for the bulk CO oxidation with increasing number of cycles was observed. Finally, the electrode was irreversibly deactivated as displayed by the 10th cycle in Figure 6.33 which exhibits a higher onset potential (0.54 V) for the bulk CO oxidation compared to the 1st cycle (0.50 V) and a fourfold decrease of the maximum current density (0.2 mA cm\(^{-2}\) instead of 1.1 mA cm\(^{-2}\)) although the potential limits are the same for the 1st and the 10th polarization cycle. A change in activity with increasing upper potential limit was also observed for the bulk CO oxidation on Pt island modified Ru(0001) electrodes in a previous study where STM imaging after the CO oxidation revealed that such a change in activity should be ascribed to a restructuring of the electrode surface\(^{[58,206]}\). So far, we were not able to atomically resolve the surface of the Pt\(_x\)Ru\(_{1-x}\)/Ru(0001) electrodes after CO oxidation in order to see such a surface restructuring. Nevertheless, we assume that the observed deactivation of the surface alloys in Figure 6.33 are rationalized by a potential induced restructuring of the electrode surfaces. This assumption is also in line with observed changes in the CV of Pt\(_{0.30}\)Ru\(_{0.70}\)/Ru(0001) in supporting electrolyte after applying high potentials as shown in the inset in Figure 6.33. The CV of the intact surface (blue dotted line) is already described in the main text and in Figure 6.30. The orange dashed curve shows the CV of the same electrode after the applied potential was above 1.00 V for less than two seconds. Subsequently, the potential was again kept above 1.00 V for less than two seconds and then the CV displayed as green solid curve was recorded. Comparing the first CV (blue dotted curve) and the second CV (orange dashed curve) reveals that after applying potentials above 1.00 V the oxidation currents above 0.25 V as well as the H\(_{\text{upd}}\) region become larger and that the broad reduction peak separates into two reduction peaks for the second CV. Further exposure to high potentials (green solid curve) results in a distinct oxidation peak and two reduction peaks which are all at similar positions as the observed redox features on Ru(0001) (see Figure 6.32a). Additionally, the H\(_{\text{upd}}\) region is further broadened compared to the CVs recorded prior to the second high potential step. These observations indicate that there are major changes in the electrochemical ad-/desorption properties of the surface alloys if they are exposed to potentials above 1.00 V. The ad-/desorption properties
of an electrode surface are strongly related to the electrode surface structure and thus these observations indicate that there is a distinct potential induced restructuring of the surface alloys if the applied potential is above 1.00 V.

**Reduction features in the bulk CO oxidation on Pt modified Ru(0001)**

The polarization curves of the nine Pt$_x$Ru$_{1-x}$/Ru(0001) electrodes investigated with Pt contents between $x_{Pt} = 0.12$ and $x_{Pt} = 0.83$ and of Pt$_{1-ML}$/Ru(0001) in CO saturated 0.5 M H$_2$SO$_4$ are shown in Figure 6.34a. The current density range and the potential range is adjusted in order to display the reduction features in the negative-going scan below the inhibition potential ($< 0.55$ V). These reduction features are ascribed to the displacement of oxygen species from the surface by CO$_{ad}$. While the features are pronounced for Pt$_{0.12}$Ru$_{0.88}$/Ru(0001), they decrease with increasing $x_{Pt}$ and vanish for $x_{Pt} \geq 0.58$. The integrated charges of the reduction features ($Q_{Red}$) in the negative-going scan was determined for all electrodes and plotted as a function of $x_{Pt}$ in Figure 6.34b. The decreasing $Q_{Red}$ with increasing $x_{Pt}$ indicates that the amount of adsorbed oxygen species on the surface decreases with increasing $x_{Pt}$. For Pt$_{0.24}$Ru$_{0.76}$/Ru(0001) the double layer region seems not to be reached because the lower potential limit is different (0.12 V). This indicates that the charge for this electrode should be higher. A higher charge would fit well with an exponential decay of the charges with increasing $x_{Pt}$.

**Bulk CO oxidation – 1st positive-going / 2nd negative-going scan**

The first positive-going scans and the second negative-going scans of the polarization curves in CO saturated 0.5 M H$_2$SO$_4$ of Pt$_x$Ru$_{1-x}$/Ru(0001) surface alloys with Pt contents between $x_{Pt} = 0.12$ and $x_{Pt} = 0.83$, of Pt$_{1-ML}$/Ru(0001) and of Pt(111) are shown in Figure 6.35 and Figure 6.36, respectively. For a better illustration, only the potential range between 0.40 V and 1.03 V is displayed and the polarization curve of each electrode is labeled with a number that increases with increasing $x_{Pt}$. The horizontal dashed line indicates a current density of 350 $\mu$A cm$^{-2}$. The inset shows the shifts of the potential ($\Delta E_{350}(x_{Pt})$) of each Pt$_x$Ru$_{1-x}$/Ru(0001) electrode and Pt$_{1-ML}$/Ru(0001) with respect to Pt(111) as a function of $x_{Pt}$. $\Delta E_{350}(x_{Pt})$ shows also for the first positive-going scan and the second negative-going scan a similar volcano-like dependence on $x_{Pt}$ as it was observed for the second positive-going scan with a maximum around $x_{Pt} = 0.30$ (see Figure 6.29).
Figure 6.30: Cyclic voltammograms of the nine Pt$_{x}$Ru$_{1-x}$/Ru(0001) electrodes investigated with Pt contents ranging from $x_{Pt} = 0.12$ to $x_{Pt} = 0.83$ and of Pt$_{1-ML}$/Ru(0001) in 0.5 M H$_2$SO$_4$ supporting electrolyte (0.05 V to 0.85 V, 10 mV s$^{-1}$). The Pt content of each surface alloy is labeled at the respective CV. The Pt$_{0.30}$Ru$_{0.70}$/Ru(0001) electrode was measured with a sweep rate of 50 mV s$^{-1}$ (0.05 V to 0.90 V) which is why the measured current densities are approximately five times higher compared to the other electrodes.
6.3 CO electro-oxidation on $Pt_xRu_{1-x}$/Ru(0001)

Figure 6.31: Full traces of the first (dotted line) and second (solid line) polarization cycles of the bulk CO oxidation on the nine $Pt_xRu_{1-x}$/Ru(0001) electrodes investigated with Pt contents ranging from $x_{Pt} = 0.12$ to $x_{Pt} = 0.83$ and on $Pt_{1-ML}$/Ru(0001) in CO saturated 0.5 M $H_2SO_4$ (-0.02 V to 0.90 V, 10 mV s$^{-1}$). The Pt content of each surface alloy is labeled at the respective polarization curve. The $Pt_{0.24}Ru_{0.76}$/Ru(0001) electrode was measured in a different potential range (0.12 V to 0.85 V) which should, however, not affect the discussion in Section 6.3.4.
Figure 6.32: Polarization curve (-0.02 V to 0.90 V, 10 mV s\(^{-1}\)) of Ru(0001) in CO saturated 0.5 M H\(_2\)SO\(_4\).

Figure 6.33: Consecutive polarization cycles of the bulk CO oxidation on a Pt\(_{0.30}\)Ru\(_{0.70}\)/Ru(0001) surface alloy with increasing upper potentials (0.5 M H\(_2\)SO\(_4\) (CO sat.), 10 mV s\(^{-1}\)). Blue dotted curve: 1\(^{\text{st}}\) cycle of the intact electrode in the potential range between -0.02 V and 0.90 V. Orange dashed curves: 4\(^{\text{th}}\) and 6\(^{\text{th}}\) cycle with an upper potential limit of 1.05 V. Red dash-dotted curves: 7\(^{\text{th}}\) and 9\(^{\text{th}}\) cycle with an upper potential limit of 1.25 V. Green solid curve: 10\(^{\text{th}}\) cycle with the same potential limits as in the 1\(^{\text{st}}\) cycle (-0.02 V to 0.90 V). The arrows indicate the scan directions. The inset shows the CVs (0.05 V to 0.90 V, 50 mV s\(^{-1}\)) of Pt\(_{0.30}\)Ru\(_{0.70}\)/Ru(0001) in 0.5 M H\(_2\)SO\(_4\) supporting electrolyte for the initially prepared electrode (blue dotted curve), for the electrode after the applied potential was once above 1.00 V for less than 2 seconds (orange dashed curve) and after the applied potential was twice above 1.00 V, each time for less than 2 seconds (green solid curve).
6.3 CO electro-oxidation on $Pt_xRu_{1-x}/Ru(0001)$

**Figure 6.34:** (a) Low potential region (-0.05 V to 0.65 V) of the bulk CO oxidation on the nine investigated $Pt_xRu_{1-x}/Ru(0001)$ electrodes with Pt contents ranging from $x_{Pt} = 0.12$ to $x_{Pt} = 0.83$ and of Pt$1$-ML/Ru(0001) in CO saturated 0.5 M $H_2SO_4$ (-0.02 V to 0.90 V, 10 mV s$^{-1}$) in order to display the reduction features in the cathodic scan below the inhibition potential (< 0.55 V). For $Pt_{0.24}Ru_{0.76}$/Ru(0001) the applied potential was different (0.12 V to 0.85 V). (b) Integrated charges of the reduction features ($Q_{Red}$) of all electrodes shown in a) as a function of $x_{Pt}$. $Q_{Red}$ decreases with increasing $x_{Pt}$ indicating that the amount of adsorbed oxygen species on the surface decreases with increasing $x_{Pt}$.
Figure 6.35: First positive-going scans of the polarization curves in CO saturated 0.5M H₂SO₄ of PtₓRu₁₋ₓ/Ru(0001) surface alloys (-0.02 V to 0.90 V, 10 mVs⁻¹) with Pt contents between \(x_{Pt} = 0.12\) and \(x_{Pt} = 0.83\), of Pt₁-ML/Ru(0001) (-0.02 V to 0.90 V, 10 mVs⁻¹) and of Pt(111) (0.07 V to 1.10 V, 10 mVs⁻¹). For a better illustration, only the potential range between 0.40 V and 1.03 V is shown and the curve of each electrode is labeled with a number that increases with increasing \(x_{Pt}\). The inset shows the shifts of the potential \(\Delta E_{350}(x_{Pt})\) of each PtₓRu₁₋ₓ/Ru(0001) electrode and Pt₁-ML/Ru(0001) at which \(j = 350 \mu A cm^{-2}\) with respect to the respective potential of Pt(111) \(E_{350}(Pt(111))\) as a measure for the activity of the electrodes for the bulk CO oxidation, plotted as a function of \(x_{Pt}\).

Figure 6.36: Second negative-going scans of the polarization curves in CO saturated 0.5M H₂SO₄ of PtₓRu₁₋ₓ/Ru(0001) surface alloys (-0.02 V to 0.90 V, 10 mVs⁻¹) with Pt contents between \(x_{Pt} = 0.12\) and \(x_{Pt} = 0.83\), of Pt₁-ML/Ru(0001) (-0.02 V to 0.90 V, 10 mVs⁻¹) and of Pt(111) (0.07 V to 1.10 V, 10 mVs⁻¹). For a better illustration, only the potential range between 0.30 V and 1.03 V is shown and the curve of each electrode is labeled with a number that increases with increasing \(x_{Pt}\). The inset shows the shifts of the potential \(\Delta E_{350}(x_{Pt})\) of each PtₓRu₁₋ₓ/Ru(0001) electrode and Pt₁-ML/Ru(0001) at which \(j = 350 \mu A cm^{-2}\) with respect to the respective potential of Pt(111) \(E_{350}(Pt(111))\) as a measure for the activity of the electrodes for the bulk CO oxidation, plotted as a function of \(x_{Pt}\).
6.4 Electro-oxidation of methanol on Ru-core Pt-shell type model electrodes

The content of this Section is published in *Electrochimica Acta* and adapted in this thesis with permission from Reference[369] (Elsevier Science Publisher B.V.).

The experiments were planned by Albert K. Engstfeld and me. The experimental results of this work were measured by Fabian Argast and me. I performed the full data evaluation and prepared all Figures. Furthermore, I was strongly involved in the creative process of the publication.

6.4.1 Abstract

Ru-core Pt-shell nanoparticles show an enhanced electrocatalytic activity for the MOR compared to the respective monometallic or most bimetallic alloy systems. Due to their ill-defined structure, however, a simple interpretation of these findings is challenging. In the present work we present results of a systematic study on the influence of the Pt film thickness of structurally well-defined Pt$_{X}$ML/Ru(0001) model electrodes with varying Pt film thickness (1.1 – 5.5 MLs) on their MOR performance. The electrodes are prepared and structurally characterized by STM under UHV conditions. The electrochemical / -catalytic properties of the electrodes are evaluated in an electrochemical flow cell, which is attached to the UHV system and combined with a mass spectrometer in a DEMS set-up, allowing for on-line detection of volatile reaction products / intermediates. We demonstrate that the MOR activity of Pt$_{X}$ML/Ru(0001) increases with increasing Pt film thickness and that thicker Pt films (> 2.5 ML) are significantly more active.
than Pt(111) and thinner Pt films, whereas the selectivity for CO₂ formation remains essentially constant. We explain this trend in the activity via the Sabatier principle, where the higher activities of the Pt film electrodes with thicker Pt films compared to both Pt(111) and electrodes with thinner Pt films are due to a lower binding strength of adsorbed species than on Pt(111), due to vertical electronic ligand effects (Ru–Pt interactions) and compressive strain effects in the pseudomorphic films, and due to an increasing binding strength with increasing Pt film thickness, due to decreasing electronic ligand effects. In this picture the Pt₅.₅-ML/Ru(0001) electrode exhibits the best value of the binding strength and thus the highest rates, while for electrodes with lower/higher binding strength the rates are lower. Consequences of these findings for bimetallic PtRu nanoparticle catalysts are discussed.

6.4.2 Introduction

Bimetallic platinum-ruthenium (PtRu) NPs supported on carbon materials have been identified as highly active for the electrocatalytic MOR and represent the state-of-the-art anode catalyst in DMFCs[8,14,15,370,371]. The high activity of these catalysts was explained by the so-called bifunctional mechanism, where the oxygen species (OHₐd or Oₐd) necessary to oxidize the carbon containing reaction intermediates are formed on the oxophilic Ru surface sites at less positive potentials than on Pt. Subsequently, the oxygen species react with the carbon containing species adsorbed on a neighboring Pt surface atom[78,231]. This results in higher rates than observed for monometallic Pt electrodes / nanoparticles[203,232,233,372]. However, besides this bifunctional mechanism, additional effects have to be considered that enhance the reaction rates on supported PtRu catalysts. This was concluded for CO oxidation in the gas-phase[373] as well as for electrocatalytic reactions such as the ORR[89,374], the MOR[90–95] and the electro-oxidation of CO[92,95–98]. In these studies Ru-core Pt-shell NPs showed a higher activity than Pt NPs of similar shape for these electrocatalytic reactions, even though bifunctional PtRu sites are not present on the electrode surface. Therefore, the improved electrocatalytic activity of the Pt surface atoms was ascribed to electronic and/or geometric effects induced by the Ru-core[89,90]. It has also been shown in gas phase model studies that these effects strongly depend on the shell thickness[79,85]. MOR studies on Ru-core Pt-shell NPs with varying Pt-shell thicknesses have shown that the MOR activity increases with decreasing thickness of the Pt-shell[94,375]. However, due to the large number of defect sites as well as possible alloy formation, it is challenging to obtain isolated insights from such complex real catalyst materials about how the Ru-core
induced electronic / geometric effects influence the electrocatalytic MOR activity of the Pt surface atoms.

In order to reduce the structural complexity we have started to explore structure-activity correlations using structurally well-defined, single crystal model systems, where the model systems were prepared and characterized structurally by STM under UHV conditions \[53,205\]. For the subsequent electrochemical / electrocatalytic measurements the samples were transferred into an electrochemical flow cell set-up, without getting into contact with air. Here we report on a model study of the MOR on Ru(0001) electrodes which, using this approach were modified by ultrathin pseudomorphic Pt films of between 1.1 and 5.5 MLs thickness. These can be considered as structurally well-defined analogues to Ru-core Pt-shell catalyst systems. Before moving on to the presentation of the results, we briefly summarize previous findings on the electronic and chemical properties of such Pt\textsubscript{X-ML}/Ru(0001) surfaces. It has been demonstrated, both experimentally and theoretically, that the binding strength of simple adsorbates such as atomic species or small molecules on the Pt atoms of these surfaces is lower than on Pt(111) and that it increases with increasing thickness of the Pt film, up to about 4 layers thickness \[79,81,84–86,88,130,205,213,376,377\]. This was explained by a combination of electronic ligand effects \[24,25,32,137\], caused by the different electronic structure of the Ru(0001) substrate compared to Pt(111), and by strain effects \[26,32\], arising from the compressive strain in the pseudomorphic Pt layers on the smaller Ru(0001) substrate. Moreover, it is well known that according to the Sabatier principle subtle changes in the binding energy of reactants / reaction intermediates on the catalyst surface can have a significant impact on its (electro-)catalytic activity \[141,378\]. Furthermore, previous studies have shown that the MOR results in different products, including the partially oxidized reaction products formaldehyde and formic acid, and the fully oxidized product CO\textsubscript{2} \[12,211,218\]. On Pt(111), formaldehyde and formic acid were reported to represent the dominant reaction products at room temperature \[230,379\]. The experimental set-up as well as the sample preparation and the electrocatalytic measurement implementation are described in Chapter 5. In the following we will first summarize the structural properties of the Pt\textsubscript{X-ML}/Ru(0001) model electrodes and, for comparison, of a Pt(111) electrode (Section 6.4.3). This is followed by an account of their electrochemical properties, as derived from cyclic voltammetry measurements (Section 6.4.3), and DEMS measurements of the MOR activity and selectivity, as indicated by the CO\textsubscript{2} product formation (Section 6.4.3). The resulting structure-activity correlation, its effect on the selectivity, and its physical basis are discussed in Section 6.4.4, followed by the conclusions.
6.4.3 Results

Structural characterization

Representative STM images of a UHV prepared Pt(111) single crystal and of the Pt\textsubscript{X-ML}/Ru(0001) electrodes are presented in Figure 6.38a and Figures 6.38b-f, respectively. For Pt(111) this resolves wide terraces (50 nm - 100 nm width) separated by monoatomically high, straight steps. The images of the Pt\textsubscript{X-ML}/Ru(0001) electrodes, with Pt coverages of $\theta_{Pt} = 1.1$ ML (Figure 6.38b), $\theta_{Pt} = 1.4$ ML (Figure 6.38c), $\theta_{Pt} = 2.5$ ML (Figure 6.38d), $\theta_{Pt} = 4.2$ ML (Figure 6.38e) and $\theta_{Pt} = 5.5$ ML (Figure 6.38f), demonstrate the formation of smooth Pt films, including compact, large Pt islands which grow preferentially at step edges. In addition, compact hexagonally shaped islands are formed on the terraces, indicating a reasonably fast Pt adatom diffusion along the island edges under the present conditions. Slightly varying island shapes for different Pt\textsubscript{X-ML}/Ru(0001) electrodes are ascribed to minor deviations of the sample temperature during or after Pt deposition on Ru(0001). Overall, these surface morphologies agree well with previous findings for comparable Pt\textsubscript{X-ML}/Ru(0001) surfaces prepared under similar conditions\textsuperscript{[79,86,131]}. These surfaces reflect an almost perfect, kinetically limited layer-by-layer growth under present conditions. The resulting layer thickness distribution for the different surfaces, as determined by STM for all Pt\textsubscript{X-ML}/Ru(0001) electrodes shown in Figures 6.38b-f, is summarized in Table 6.7. It should be noted that the resulting films are pseudomorphic, \textit{i.e.}, they exhibit the structure of the underlying Ru(0001) substrate\textsuperscript{[79]}.

From the STM image of the Pt\textsubscript{1.1-ML}/Ru(0001) surface in Figure 6.38b it is evident that in this case the first Pt layer is not completely closed, leaving 6% of the Ru(0001) substrate accessible to the electrolyte (see Table 6.7). For slightly higher coverages, \textit{i.e.}, for Pt\textsubscript{1.4-ML}/Ru(0001), the amount of Pt free areas becomes negligible (1% of exposed Ru(0001)). Finally, for higher Pt coverages with $\theta_{Pt} \geq 2.5$ ML (Figure 6.38d-f) the Pt film is perfectly closed.

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6.4 MOR on Pt$_{x}$-ML/Ru(0001)

Figure 6.38: (a)-(f): STM images of (a) Pt(111) (300 nm x 300 nm, $I_T = 2.8$ nA, $U_T = 1.2$ V) and the Pt$_{x}$-ML/Ru(0001) electrodes (150 nm x 150 nm, $I_T = 0.3$ nA - 1.6 nA, $U_T = 0.8$ V - 1.5 V) with Pt amounts of (b) $\theta_{Pt} = 1.1$ ML, (c) $\theta_{Pt} = 1.4$ ML, (d) $\theta_{Pt} = 2.5$ ML, (e) $\theta_{Pt} = 4.2$ ML and (f) $\theta_{Pt} = 5.5$ ML. The thickness of Pt-(Ru-) layers exposed to the surface is labeled with the respective number of Pt layers at these sites. (g)-(l): Cyclic voltammograms (0.05 V - 0.85 V, 10 mVs$^{-1}$) of (g) Pt(111), (h) Pt$_{1.1}$-ML/Ru(0001), (i) Pt$_{1.4}$-ML/Ru(0001), (j) Pt$_{2.5}$-ML/Ru(0001), (k) Pt$_{4.2}$-ML/Ru(0001) and (l) Pt$_{5.5}$-ML/Ru(0001) in 0.5 M H$_2$SO$_4$. 

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6 Results and Discussion

Electrochemical characterization

CVs recorded on these electrodes in 0.5 M H$_2$SO$_4$ are depicted in Figure 6.38g-l. For the as prepared Pt(111) electrode (Figure 6.38g) this shows the typical current features for a Pt(111) single crystal as described in detail in the literature$^{[155,156,161,195]}$. In brief, the features between 0.08 V and 0.33 V are ascribed to H$_{\text{upd}}$, which overlap with the (bi)sulfate adsorption / desorption region between 0.33 V and 0.58 V. The small redox feature around 0.66 V - 0.67 V is ascribed to the adsorption / desorption of OH, which competes with (bi)sulfate adsorption / desorption$^{[164]}$. Furthermore, the pronounced negative current densities observed at potentials below 0.08 V are related to the HER on Pt(111).

The CVs of the Pt$_{X\text{-ML}}$/Ru(0001) electrodes show the following trends: For Pt$_{1.1\text{-ML}}$/Ru(0001) (Figure 6.38h) the redox features are significantly smaller compared to Pt(111). This results in (i) a distinctly smaller H$_{\text{upd}}$ region at potentials below 0.20 V, (ii) the absence of the large (bi)sulfate features observed for Pt(111) and (iii) the appearance of a broad redox feature at higher potentials with low current densities, with an onset potential at around 0.44 V in the positive-going scan. Assuming that the surface processes are comparable on Pt(111) and on the Pt$_{X\text{-ML}}$/Ru(0001) electrodes, we ascribe this broad feature to the adsorption / desorption of (bi)sulfate, which is shifted to higher potentials compared to Pt(111). The HER on Pt$_{1.1\text{-ML}}$/Ru(0001) is initiated at 0.09 V in the negative-going scan with similar current densities at 0.05 V as observed for Pt(111). In contrast to the CV of Pt(111), we find a peak in the negative-going scan for Pt$_{1.1\text{-ML}}$/Ru(0001) at 0.32 V, which is missing again in the CVs of Pt$_{X\text{-ML}}$/Ru(0001) electrodes with higher Pt coverages. A peak at this position is characteristic for the reduction of oxygenated Ru surface sites$^{[58,206,342]}$, in perfect agreement with the conclusion of an incomplete termination of the Ru(0001) surface by Pt derived from STM imaging (see above and Table 6.7). On Pt$_{1.4\text{-ML}}$/Ru(0001), which based on STM imaging still contains about 1% of accessible Ru(0001) substrate area, this reduction peak at 0.32 V can no longer be resolved in the CV (Figure 6.38i). We assume that the small amount of available Ru sites is below the detection limit of the current response. For larger Pt coverages ($\theta_{\text{Pt}} \geq 2.5 \text{ ML}$) the Ru reduction peak is not observed, indicating that the entire surface is covered by the Pt film, again in good agreement with STM imaging (see Table 6.7). Regardless of the Pt film thickness, HER currents are observed at potentials below $E < 0.10 \text{ V}$ on all Pt$_{X\text{-ML}}$/Ru(0001) electrodes, with similar magnitude as those obtained on Pt(111). Compared to the positive-going scan, this contribution of the HER leads to an asymmetry of the H$_{\text{upd}}$ region between the negative- and positive-going
6.4 MOR on Pt$_{X}$-ML/Ru(0001)

scan. This asymmetry is more pronounced for the Pt$_{X}$-ML/Ru(0001) electrodes than for Pt(111), due to the lower currents related to H$_{\text{upd}}$ but similar currents related to the HER on the bimetallic electrodes. At higher potentials we find a broad redox feature for all Pt modified electrodes, which shifts to slightly higher potentials with increasing Pt film thickness (onset potential ca. 0.44 V for Pt$_{1.1}$-ML/Ru(0001) and ca. 0.48 V for Pt$_{5.5}$-ML/Ru(0001)).

Figure 6.39: Hydrogen coverage $\theta_H$ (left y-axis) and integrated charge of the H$_{\text{upd}}$ region $Q$ (right y-axis) of the Pt$_{X}$-ML/Ru(0001) electrodes (orange squares) as a function of the Pt film thickness on Ru(0001) and the respective values of Pt(111) (dashed blue line).

In perfect agreement with previously reported cyclic voltammetry results obtained on similar Pt$_{X}$-ML/Ru(0001) electrodes in perchloric acid$^{[86]}$ we find that in sulfuric acid electrolyte the H$_{\text{upd}}$ onset shifts to higher potentials with increasing Pt film thickness. Quantitatively, this corresponds to a shift from 0.20 V for Pt$_{1.1}$-ML/Ru(0001) to 0.35 V for Pt$_{5.5}$-ML/Ru(0001). Also this agrees well with previous findings in HClO$_4$ by Hoster et al.$^{[86]}$. The latter result is explained by smaller adsorption energies of H$_{\text{ad}}$ on the Ru(0001) supported Pt films compared to Pt(111)$^{[86]}$. Lower H$_{\text{ad}}$ adsorption energies are also rationalized from the overall feature related to H$_{\text{upd}}$ in the CVs of the Pt$_{X}$-ML/Ru(0001) electrodes in Figure 6.38h-l (potential window between 0.07 V and 0.35 V). The integrated charges corresponding to the H$_{\text{upd}}$ region which reflects the hydrogen coverage $\theta_H$ on the Pt surfaces for all electrodes is illustrated in Figure 6.39. The charges were determined in the positive-going scan by integrating the charge between the lowest potential where positive currents were measured and the H$_{\text{upd}}$ onset potential. Here the contribution of the double-layer charging was subtracted. Contributions from currents related to the HOR from H$_2$ formed during the HER in the negative-going scan can be considered as insignificant, since at a scan rate of 10 mV s$^{-1}$ the transport of H$_2$ out of the cell is fast and hence H$_2$ is not available at potentials where HOR
would occur in the positive-going scan. The $H_{\text{upd}}$ charge of Pt(111) is $Q = 161 \mu \text{C cm}^{-2}$ corresponding to a hydrogen coverage of $\theta_H = 0.66 \text{ML}$ in agreement with previous findings\cite{172}. The highest hydrogen uptake on the Pt$_X$-ML/Ru(0001) electrodes is obtained for Pt$_{5.5}$-ML/Ru(0001) ($\theta_H = 0.38 \text{ML}$) while the hydrogen coverage decreases with decreasing Pt film thickness. Hence, the hydrogen uptake on the Pt$_X$-ML/Ru(0001) electrodes is significantly lower compared to Pt(111).

**Methanol oxidation reaction (MOR)**

The polarization curves for the MOR on the Pt$_X$-ML/Ru(0001) electrodes recorded in the potential range between 0.05 V and 0.85 V ($v = 10 \text{mVs}^{-1}$, 0.5 M H$_2$SO$_4 + 0.2$ M CH$_3$OH) are depicted in Figure 6.40a. For comparison, we also include a MOR polarization curve recorded on Pt(111) in the range between 0.07 V and 0.90 V under similar conditions. Such measurements on Pt(111) served also for testing the reproducibility of the measurements. For better visibility the positive- and negative-going scans are indicated by arrows, and we only show the potential window between 0.40 V and 0.85 V (0.90 V for Pt(111)), while the potential window between 0.05 V and 0.40 V is presented in the inset of Figure 6.40a (for a full scan of Pt(111) see Figure 6.41 in the Appendix). The upper potential limit was fixed at 0.85 V/0.90 V to avoid surface restructuring, which has been shown to occur at 0.90 V or 1.10 V for Pt modified Ru(0001)\cite{58,206} and Pt(111) electrodes\cite{380}, respectively, by combined (in situ) STM–electrochemistry measurements. The integrity of the surfaces has been verified by STM imaging after the electrocatalytic investigation (see Figure 6.42). On Pt(111) the MOR starts at around 0.45 V, then the current density increases approximately exponentially with increasing potential, until it saturates and reaches a plateau between 0.82 V and 0.90 V. This behavior agrees fully with previous results for the MOR on Pt(111) single crystals obtained in 0.5 M H$_2$SO$_4$\cite{223,227,381}. The result for Pt(111) can be used as a benchmark for the MOR activity of the Pt$_X$-ML/Ru(0001) electrodes.

For the Pt$_X$-ML/Ru(0001) electrodes the MOR equally starts at about 0.50 V (0.48 V-0.51 V, see Figure 6.40a). Then the current density increases in an about similar way as described for Pt(111), but more steeply for most of them. Comparing the different electrodes, the current densities increase with increasing Pt film thickness, which will be discussed below in more detail. For all samples, the curves do not show a maximum, i.e., the highest current density was obtained at the upper potential limit at 0.85 V. Therefore, the maxima in the current density curves must be at higher potentials, which we did not reach in these measurements in order to avoid any potential induced surface
Restructuring of the electrodes. In the following negative-going scan the current densities are initially smaller than in the positive-going current traces, but then decay less steeply, until they intersect between 0.75 V and 0.65 V. At lower potentials the current densities are slightly higher than in the positive-going scan direction, until they drop to zero somewhere between ca. 0.58 V for Pt$_{1.1}$ML/Ru(0001) and ca. 0.47 V for Pt$_{5.5}$ML/Ru(0001).

Continuous potential cycling leads to a slight loss in activity with increasing number of cycles, i.e., a loss of about 5% in current density at 0.85 V per cycle. This is shown exemplarily for the first six cycles on Pt$_{1.4}$ML/Ru(0001) in Figure 6.43 in the Appendix. Recalling that the surfaces are stable during the MOR measurements, as demonstrated by STM imaging (see Figure 6.42) and CV measurements (see Figure 6.38), we suggest that the deactivation process is related to the accumulation of adsorbed species on the surface. Since test experiments confirmed that accumulation of contaminants from the EC flow cell is negligible (see Figure 5.9, Section 5.4.1), the observed deactivation must originate from adsorbed species formed during the MOR such as CH$_x$O$_y$ or CO$_{ad}$ on specific sites, which cannot be removed by potentiodynamic oxidation in this potential range$^{[211,223,232]}$.

Focusing on the H$_{upd}$ region of the Pt$_{X}$ML/Ru(0001) electrodes during the MOR, depicted in the inset in Figure 6.40a, we find that for each electrode the charge (H$_{upd}$ coverage) is reduced by approximately 50% compared to the H$_{upd}$ charge obtained in the CVs of the respective electrodes in pure H$_2$SO$_4$ solution. Obviously the surface is partially blocked for hydrogen adsorption, either by MeOH or its dehydrogenation products, if MeOH is introduced at 0.40 V, where H$_{upd}$ is not present on the Pt surfaces, and the potential is then scanned to lower values (see Figure 6.38g-l). This agrees with previous results, indicating that H$_{upd}$ is not able to displace MeOH dehydrogenation products. On the other hand, MeOH is not able to displace H$_{ad}$ when introduced below 0.3 V$^{[210,211]}$. Interestingly, in contrast to the MOR activity, which decreases with increasing number of cycles, the H$_{upd}$ charge does not diminish further upon potential cycling (see Figure 6.44). Apparently, the number of sites blocked by adsorbed carbon containing species remains constant during cycling, while the nature of these species changes slowly with increasing number of cycles, towards species which are more effective in inhibiting the MOR. A blocking of the Pt surface at low potentials during the MOR is usually ascribed to the formation of adsorbed CO$^{[226,382]}$. For our electrodes, full poisoning by CO during the MOR can be ruled out, since there is still a considerable H$_{upd}$ uptake, while in CO stripping experiments (electro-oxidation of a pre-adsorbed CO adlayer in supporting electrolyte) the H$_{upd}$ region was found to be completely inhibited,
as shown exemplarily for Pt$_{5.5}$-ML/Ru(0001) in Figure 6.45 in the Appendix.

**Figure 6.40:** (a) Polarization curves of Pt$_{X}$-ML/Ru(0001) (0.05 V - 0.85 V) and Pt(111) (0.07 V - 0.90 V) in 0.5 M H$_2$SO$_4$ + 0.2 M CH$_3$OH ($v = 10$ mV s$^{-1}$). The scan direction is indicated by arrows and only the potential window between 0.40 V and 0.90 V is shown. The respective curves are labeled with the amount of Pt deposited on Ru(0001) in multiples of Pt MLs. The inset shows the H$_{\text{upd}}$ region in the potential window between 0.05 V and 0.40 V from the same polarization curves where the arrow indicates an increasing H$_{\text{upd}}$ region with increasing Pt coverage $\theta_{\text{Pt}}$ on Ru(0001). (b) Potential dependent faradaic current densities corresponding to CO$_2$ formation during the MOR, determined from the DEMS signal of CO$_2$ ($m/z = 44$) (see text for details). Only the positive going scans are shown. (c) Potential dependent CO$_2$ current efficiency (CCE) of Pt(111) (blue stars), Pt$_{1.1}$-ML/Ru(0001) (black squares), Pt$_{1.4}$-ML/Ru(0001) (green circles), Pt$_{2.5}$-ML/Ru(0001) (orange upwards pointing triangles), Pt$_{4.2}$-ML/Ru(0001) (red downwards pointing triangles) and Pt$_{5.5}$-ML/Ru(0001) (pink pentagons).
According to Figure 6.40a, the onset potentials for the MOR are almost identical (ca. 0.5 V) for all Pt$_{X\text{-ML}}$/Ru(0001) electrodes (within the experimental accuracy), while the absolute current densities increase with increasing Pt film thickness. At 0.85 V the MOR activity of the Pt$_{5.5\text{-ML}}$/Ru(0001) electrode is more than five times higher than that of Pt(111). Only the Pt$_{1.1\text{-ML}}$/Ru(0001) electrode is less active than Pt(111) over the entire potential range investigated, while the Pt$_{4.2\text{-ML}}$/Ru(0001) and Pt$_{5.5\text{-ML}}$/Ru(0001) electrodes exceed the activity of Pt(111) in the whole potential range. For the Pt$_{1.1\text{-ML}}$/Ru(0001) and Pt$_{2.5\text{-ML}}$/Ru(0001) electrodes the relative activity compared to Pt(111) depends on the potential, with a lower activity of the Pt modified Ru(0001) electrodes at potentials below 0.75 V and 0.73 V, respectively, while it exceeds the activity of Pt(111) above these potentials.

In order to gain more insight on the reaction products, we performed simultaneous DEMS measurements to detect characteristic masses of possible reactants, reaction intermediates and products, including CO$_2$ ($m/z = 44$), methanol ($m/z = 32$), formaldehyde ($m/z = 30$), formic acid ($m/z = 46$) and methyl formate ($m/z = 60$)\cite{218}. Due to experimental constraints, mainly due to the low active surface area of the single crystal electrodes we were, however, only able to detect CO$_2$.

Positive-going scans of the current densities $j_{\text{CO}_2}$ related to CO$_2$ formation, which were determined as described in the experimental part (Section 5.5.1), are plotted as a function of the applied electrode potential in Figure 6.40b. For Pt(111) the potential dependent $j_{\text{CO}_2}$ exhibits the same shape as the MOR polarization curve of Pt(111) in Figure 6.40a. The onset of CO$_2$ formation is at around 0.50 V, in agreement with previous findings\cite{230}. For Pt$_{1.1\text{-ML}}$/Ru(0001) no CO$_2$ product formation was detected, the amount of CO$_2$ formation is below the detection limit (see also above). For the Pt$_{X\text{-ML}}$/Ru(0001) electrodes with $\theta_{\text{Pt}} > 1.1$ ML the $j_{\text{CO}_2}$ increase with increasing potential and with increasing Pt film thickness, in a similar way as the MOR polarization curves in Figure 6.40a. The only exception is Pt$_{5.5\text{-ML}}$/Ru(0001), where the $j_{\text{CO}_2}$ seems to saturate at potentials above 0.75 V, leading to a plateau between 0.80 V and 0.85 V. For all Pt$_{X\text{-ML}}$/Ru(0001) electrodes, CO$_2$ formation starts at significantly higher potentials than the overall MOR reaction, which starts at ca. 0.50 V. This effect is most pronounced for the thin Pt film covered electrodes, while with increasing Pt film thickness the onset for CO$_2$ formation $E_{\text{Onset}(\text{CO}_2)}$ seems to shift to lower potentials, e.g., from ca. 0.72 V for Pt$_{1.1\text{-ML}}$/Ru(0001) to ca. 0.60 V for Pt$_{5.5\text{-ML}}$/Ru(0001). While the difference compared to Pt(111) is obvious, the latter shift may, however, be due to the small amounts of CO$_2$ formation on the Pt film surfaces.
The activity for CO$_2$ formation can be quantified by the CO$_2$ current efficiency (CCE), which describes the fraction of the total Faradaic charge (current) resulting from CO$_2$ formation. For comparison with previous DEMS data we first determined the averaged CCE for Pt(111) by integrating the Faradaic current densities and $j_{\text{CO}_2}$ from the onset of the MOR up to the upper potential limit, i.e., from 0.50 V to 0.90 V. This way we obtained a mean CCE of 10 ± 5% for Pt(111), indicating that on Pt(111) the complete oxidation of methanol to CO$_2$ accounts only for a minor fraction of the total current and that incomplete oxidation products (formic acid and formaldehyde) constitute the major part of reaction products on Pt(111), although they were not detected in our DEMS measurements. Qualitatively, this is in good agreement with previous findings for the MOR on Pt(111)\cite{230,379}. Wang and Baltruschat reported a mean CCE of 20 ± 2% for the MOR on Pt(111) in 0.5 M H$_2$SO$_4$ + 0.1 M CH$_3$OH electrolyte\cite{230}, and concluded that at higher potentials (> 0.6 V) the formation of formaldehyde and formic acid is favored. The difference to our data is at least partly explained by the higher electrolyte flow rate in our experiment (20 µL s$^{-1}$ compared to 10 µL s$^{-1}$ in their experiment), as it is well known that transport effects result in higher CCEs with decreasing electrolyte flow or increasing catalyst loading\cite{383–385}.

To gain information about the potential dependent CO$_2$ formation the CCE was determined for a number of different potentials (between 0.45 V and 0.85 V) for all electrodes investigated (see Figure 6.40c). This Figure shows that for Pt(111), the CCE decreases from ca. 30% at 0.55 V to ca. 10% at 0.85 V. In contrast to Pt(111), the CCEs of the Pt$_{X}$-ML/Ru(0001) electrodes are significantly lower at potentials below 0.70 V and slightly increase with increasing electrode potential. Between 0.80 V and 0.85 V there are almost no variations in the CCEs for all electrodes, with values between 6 ± 5% and 12 ± 5%. Hence, while the reaction rate for the MOR on Pt$_{X}$-ML/Ru(0001) strongly depends on the thickness of the Pt film deposited on Ru(0001) – resulting in an activity increase by a factor of ca. 8 at 0.85 V when the Pt film thickness increases from $\theta_{\text{Pt}} = 1.1$ ML to $\theta_{\text{Pt}} = 5.5$ ML – the selectivity for CO$_2$ formation in the MOR is almost invariant and CO$_2$ formation contributes only little to the total amount of products formed.

### 6.4.4 Discussion

In this section, we will focus on the influence of subsurface Ru(0001) on the catalytic properties of the surface Pt atoms in the MOR. The results reported above reveal a clear trend for an increasing MOR activity of the Pt$_{X}$-ML/Ru(0001) electrodes with increasing Pt film thickness, showing that the electrodes with thicker Pt films, in particular those
with $\theta_{\text{Pt}} = 4.2 \text{ML}$ and $\theta_{\text{Pt}} = 5.5 \text{ML}$, are significantly more active than Pt(111). While this observation does not provide direct information about the molecular mechanism of the MOR, it does provide insights on the influence of structural and electronic effects on the MOR activity. Considering that the Pt films are pseudomorphic to the Ru(0001) substrate and rather flat\cite{79,130}, the variation with increasing film thickness must result from varying electronic properties due to a decreasing influence of the underlying Ru(0001) substrate, \textit{i.e.}, due to (vertical) electronic ligand effects. On the other hand, the difference compared to Pt(111) can involve also electronic strain effects, due to the different lattice constants of Pt(111) and Ru(0001). In addition to affecting the activity for the MOR, these effects are also assumed to modify the hydrogen and (bi)sulfate adsorption behavior on the electrode surfaces. Here we note that it has been demonstrated in previous studies\cite{26,32,81} that the binding energy of adsorbates on a metal film B supported on a substrate metal A decreases compared to the binding energy on the respective bulk metal B with both i) an increasing electronic interaction between metal film B and the underlying substrate A relative to the corresponding interaction in bulk metal B, and ii) a smaller lattice constant (compressive strain) in the film relative to the lattice constant of the bulk metal B. Note that from STM imaging after the MOR we exclude any restructuring of the Pt\textsuperscript{X-ML}/Ru(0001) electrodes during the MOR.

Starting with the influence of hydrogen adsorption for the MOR it has been demonstrated that on Pt surfaces MeOH can hardly displace H\textsubscript{ad} at potentials below 0.30 V\cite{210,211}. However, since similar as for Pt(111) the MOR only starts at potentials significantly above the H\textsubscript{upd} desorption, site blocking effects by H\textsubscript{ad} cannot affect the MOR activity. Furthermore, specific adsorption of (bi)sulfate species on Pt surfaces was reported to strongly diminish the MOR activity of Pt(111) due to site blocking effects\cite{223,225}, which are more pronounced than for other anions such as ClO\textsubscript{4}\textsuperscript{−}\cite{225}. If the broad features at high potentials in the CVs of the Pt\textsubscript{X-ML}/Ru(0001) electrodes in Figure 6.38g-l are related to adsorption of (bi)sulfate species, these would be formed at potentials $E > 0.40 \text{ V}$, which may well affect the MOR performance. Assuming that the adsorption energy of (bi)sulfate on the Pt\textsubscript{X-ML}/Ru(0001) electrodes is also significantly lower than on Pt(111), but increases with increasing Pt film thickness, similar to the trend of other adsorbed small molecules such as CO\cite{79,130}, one would expect an increasing site blocking with increasing Pt film thickness, although in all cases it should be lower than on Pt(111). Experimentally, however, we observe an increase in MOR activity with increasing Pt film thickness. Hence, site blocking by adsorbed (bi-)sulfate species seems to be of minor importance for the observed activity trend on the Pt mod-
ified Ru(0001) electrodes, and other effects seem to overcompensate such kind of site blocking effects by adsorbed (bi-)sulfate species.

Next we concentrate on the increasing MOR activity with increasing Pt film thickness, and thus on the effect of the underlying Ru(0001) substrate, using the activity in the first potential cycle to exclude deactivation effects. Here we first want to note that for the Pt$_{1.1}$-ML/Ru(0001) electrode, which still contains ca. 6% of bare Ru(0001) (see Table 6.7), these Ru areas are considered to not contribute significantly to the activity of that electrode. It has been demonstrated in previous studies$^{[231,232,386]}$ and also confirmed in this work (see Figure 6.46 in the Appendix) that bare Ru(0001) is essentially inactive for the MOR. Furthermore, in Figure 6.47 in the Appendix we showed for a Pt$_{0.3}$-ML/Ru(0001) electrode that also Ru(0001) surfaces modified by monolayer high Pt islands are almost inactive for the MOR (only slightly more active than Ru(0001) at 0.85 V). Thus, we assume that the higher catalytic activity of the Pt$_{1.1}$-ML/Ru(0001) electrode compared to Ru(0001) electrodes modified with monolayer high Pt islands is primarily caused by the 20% of the surface covered by Pt bilayer structures. For the same reason, the higher activity of Pt$_{1.4}$-ML/Ru(0001) compared to Pt$_{1.1}$-ML/Ru(0001) is related to the larger fraction of Pt bilayer areas, which cover almost half of the active surface area, while the other part is covered by a little active Pt monolayer (see Table 6.7). For the remaining Pt film electrodes, which generally consist of contributions from areas with different thickness (see Table 6.7), the experimental data show a clear increase of the MOR activity with increasing Pt film thickness, at least up to 5 layers, as well as a beneficial effect of the presence of the underlying Ru(0001) substrate. The latter is evident from the fact that except for the monolayer film all Pt film covered Ru(0001) electrodes are more active than Pt(111) at 0.85 V. The higher activities of the Pt film modified Ru(0001) electrodes compared to Pt(111) and the increasing activity with increasing Pt film thickness must be due to the electronic modifications of the Pt surface layer due to the vertical electronic ligand and strain effects discussed above. The influence of compressive lattice strain effects should be identical for Pt film thicknesses up to $d_{Pt} = 8$ ML and should lead to a lowering of the binding energy compared to Pt(111)$^{[79,84]}$. The influence of the Ru(0001) substrate on the surface Pt layers (vertical ligand effect) is highest for the Pt monolayer film and decreases gradually with increasing Pt film thickness, until it essentially vanishes for three to four Pt layers, as demonstrated experimentally and in theory for CO, O and H adsorption on Pt$_X$-ML/Ru(0001)$^{[79,84–86,130]}$. We expect similar trends also for the adsorbed species involved in the MOR, including reactants, reaction intermediates and products/side products. In that case, the adsorbate binding on Pt(111) is obvi-
6.4 MOR on Pt\textsubscript{X-ML}/Ru(0001)

ously too strong, while on the Pt monolayer covered Ru(0001) electrode it is too weak. The significantly higher MOR activity of the Pt\textsubscript{5.5-ML}/Ru(0001) electrode compared to Pt\textsubscript{4.2-ML}/Ru(0001) is tentatively ascribed to a remaining vertical electronic influence of the Ru(0001) substrate on the Pt surface atoms for a Pt film with \(d_{Pt} = 4\) ML. This is the main contribution for the 4.2 ML Pt film (see Table 6.7), while for the 5.5 ML Pt film its contribution is negligible. In contrast, for thicker pseudomorphic films, in the range of 5-8 ML, we expect little contributions from electronic effects, and thus a rather similar local MOR activity. Here it should be noted that in previous studies a structural relaxation of Ru(0001) supported Pt films, which is visible by a distinct dislocation pattern in STM images\cite{79,84}, was observed only for Pt films with \(d_{Pt} \geq 8\) ML.

The fact that the highest activity is obtained for the Pt\textsubscript{5.5-ML}/Ru(0001) surface indicates that the binding strength of the adsorbed species on this surface reaches an optimum value, while on Pt(111) it is too high and on the thinner Pt films it is too low. This activity trend provides a direct illustration of the Sabatier principle, which states that there exists an optimum bond strength for adsorbates to maximize the reaction rate\cite{141}. The more beneficial binding energies present for Pt\textsubscript{5.5-ML}/Ru(0001) lead to a MOR activity, which at 0.85 V is by a factor of 5 higher than that of Pt(111), and the difference is even more pronounced compared to the Pt\textsubscript{1.1-ML}/Ru(0001) electrode. Note that we cannot decide from the present data whether the Pt\textsubscript{5.5-ML}/Ru(0001) electrode surface represents the optimum in activity, or whether a surface with a somewhat higher binding strength to adsorbates, in between those of the Pt\textsubscript{5.5-ML}/Ru(0001) and of the Pt(111) electrode, would be even more active.

While the present data clearly illustrate the validity of the Sabatier principle, they do not allow detailed conclusions on the reaction mechanism, including the identification of reaction intermediates and their role in the sequence of elementary reaction steps or of activation barriers for the individual reaction steps. Such information was provided from DFT for the MOR on Pt(111)\cite{186,209,214}. In the reaction scheme proposed by Sakong \textit{et al.}\cite{209}, the highest activation barriers for both reaction pathways possible for the MOR were found for the last dehydrogenation step, where HCOO\textsubscript{ad} or COOH\textsubscript{ad} react to CO\textsubscript{2}.

Next we want to briefly comment on the selectivity towards CO\textsubscript{2} formation of our model surfaces. From previous DEMS results it is known that on Pt(111) the CO\textsubscript{2} yields are rather low at room temperature, in the range of a few percent, leaving the partially oxidized reaction products formaldehyde and formic acid as main products\cite{230,379}. Note that in earlier studies the CO\textsubscript{2} yield was found to increase with lower electrolyte flow / higher catalyst loading\cite{383,384}, and in particular when going to higher tempera-
6 Results and Discussion

tures, where 100% CO\textsubscript{2} yield were reached at about 100 °C\textsuperscript{[387]}. Correspondingly, formation of the partial oxidation products formaldehyde and formic acid decreased\textsuperscript{[383,384]}. Our DEMS results show within the accuracy of our measurement rather similar CCE values between 6 ± 5% and 12 ± 5%. Hence, the electronic modification of the Pt surface layer has no major influence on the selectivity, accelerating both pathways in more or less the same way. Most simply, this may be explained by either a rate determining step which is before the two reaction pathways split up, or by a later rate determining step, which changes in a similar way with increasing Pt film thickness in both pathways. The latter would be compatible with the mechanistic proposal by Sakong et al.\textsuperscript{[209]}, where the last step to form CO\textsubscript{2} was determined as the rate determining step (C–H bond breaking in HCOO\textsubscript{ad} and O–H bond breaking in COOH\textsubscript{ad}) in both reaction pathways. In other cases, one would have a change in selectivity despite the correlation between binding energies and activation energies predicted by the universal Brønsted-Evans-Polanyi relation\textsuperscript{[357,378,388,389]}, since because of the exponential relation between rates and activation energies similar changes in the binding energies on a relative scale result in exponential changes in rates and hence in selectivities.

Finally, we would like to comment on the relevance of these results for the understanding of the MOR on technical PtRu catalysts. Obviously, the Pt\textsubscript{X-ML}/Ru(0001) electrodes investigated here represent 2D models for Ru-core Pt-shell NPs. Hence, the low MOR activity observed for Pt\textsubscript{1.1-ML}/Ru(0001) indicates that a NP consisting of a Ru-core encapsulated by a perfect monolayer Pt-shell should be less active for the MOR compared to a monometallic Pt NP, when neglecting structural effects; an increasing Pt-shell thickness should result in an increasing MOR rate, which exceeds the rates of Pt NPs of similar shape and size in the whole potential range if the film thickness is ≥ 4 ML. The opposite trend was, however, derived from potentiodynamic measurements on carbon supported Ru-core Pt-shell NPs by Chen et al.\textsuperscript{[375]} and Xie et al.\textsuperscript{[94]}. Comparing the current densities in the forward-going anodic peak maximum (0.90 - 0.95 V), they observed decreasing MOR activities with increasing shell thickness from ca. 1.5 ML - 3.6 ML\textsuperscript{[375]} and from ca. 2.9 ML - 5.4 ML\textsuperscript{[94]}, respectively. Chen et al. also found that their NPs with a shell thickness larger than 1.5 ML consisted of a Ru-core covered with a near surface alloy, where Ru atoms are larger at the surface\textsuperscript{[375]}. Xie et al. attributed the maximum in activity for Ru-core Pt-shell NPs with a 2.9 ML thick Pt-shell to a beneficial weakening of the adsorbate binding strengths induced by the Ru-core, although they could not exclude effects caused by the NP structure\textsuperscript{[94]}. Note that the above trends were evaluated at rather high potentials around 0.85 V (our data) or 0.90 - 0.95 V\textsuperscript{[94,375]},
while for technical applications stationary MOR currents at potentials $\leq 0.50 \text{ V}$ are of interest. Considering the smooth exponential decay of the current densities with decreasing potential (Figure 6.40), a similar trend in activities is expected also for lower potentials down to 0.5 V, where the currents are too low for a quantitative comparison. The only exception is Pt(111), where the decay is slower and which therefore is more active than the thin Pt film modified samples ($\leq 2.5 \text{ ML Pt}$) in the low potential regime ($\leq 0.7 \text{ V}$).

Based on our findings on well-defined smooth surfaces we suggest that the higher MOR activity of Ru-core Pt-shell NPs with lower Pt-shell thickness observed in the previous studies mentioned above is primarily caused by structural effects, e.g., by the large number of defect sites usually found in supported nanoparticle systems or by PtRu alloy formation, rather than representing an inherent shell thickness effect due to increasing interactions with the Ru core (vertical ligand effects).

Comparison of our data with PtRu alloy or surface alloy NP catalysts, in contrast, is hardly possible. For these materials also the formation of bimetallic neighborhoods in the surface layer (surface alloys) and also in deeper layers (alloys) has to be considered, in addition to the vertical ligand and strain effects discussed in this work. We have shown recently for a closely related electrocatalytic reaction, the continuous bulk CO electro-oxidation, that the formation of mixed neighborhoods or ensembles can considerably affect the reaction kinetics \cite{310}, and we expect similar effects also for the MOR. This is topic of a study which we just started.

### 6.4.5 Conclusions

Aiming at a better understanding of shell thickness effects in electrocatalytic reactions on bimetallic core-shell type catalysts we have systematically investigated the MOR in sulfuric acid solution on different $\text{Pt}_{X-\text{ML}}/\text{Ru(0001)}$ electrodes with increasing Pt film thickness between $\theta_{\text{Pt}} = 1.1 \text{ ML}$ and $\theta_{\text{Pt}} = 5.5 \text{ ML}$ in a combined UHV-STM–EC flow cell/DEMS set-up. Structurally well-defined electrodes were prepared and structurally characterized by STM under UHV conditions. The electrochemical/electrocatalytic properties were compared with the corresponding properties of Pt(111) to derive trends in the structure $\leftrightarrow$ activity relationship, leading to the following conclusions:

1. For all $\text{Pt}_{X-\text{ML}}/\text{Ru(0001)}$ electrodes we found a lower adsorption strength of $\text{H}_{\text{ad}}$ in sulfuric acid compared to Pt(111), whereas the $\text{H}_{\text{ad}}$ adsorption strength on $\text{Pt}_{X-\text{ML}}/\text{Ru(0001)}$ increases with increasing Pt film thickness. The former behav-
ior is attributed to electronic vertical ligand effects, induced by the underlying Ru(0001) substrate, in combination with electronic/geometric lattice strain effects, caused by the smaller lattice constant of the Ru substrate compared to Pt(111). The increase in $H_{ad}$ binding strength with increasing Pt film thickness, in contrast, must be solely due to decreasing vertical ligand effects, since the lattice of the pseudomorphic Pt films does not change in this coverage range.

2. The observation of a higher MOR activity of the Pt$_{X\text{-ML}}$/Ru(0001) electrodes compared to Pt(111), except for the monolayer Pt modified Ru(0001) electrode (Pt$_{1.1\text{-ML}}$/Ru(0001)), and the steady increase of the MOR activity with increasing Pt film thickness point to a correlation between binding strength of adsorbed reactants/reaction intermediates and MOR activity, as proposed by the Sabatier principle. In this case, the binding strength on Pt(111) is too high, while on the monolayer Pt covered Ru(0001) substrate ($d_{Pt} = 1$ ML) the binding strength is too low, due to (vertical) electronic ligand (Ru–Pt interactions) and compressive strain effects. The Pt$_{5.5\text{-ML}}$/Ru(0001) electrode shows the highest MOR activity over the entire potential regime accessible, i.e., it is closest to the optimum binding strength. From our measurements we cannot conclude, however, whether the optimum binding strength is actually reached for Pt$_{5.5\text{-ML}}$/Ru(0001) or if a slightly lower/higher value would further improve the activity.

3. Since bimetallic PtRu sites are not present at the Pt$_{X\text{-ML}}$/Ru(0001) electrode surface, the higher MOR activity compared to Pt(111) observed for $\theta_{Pt} > 1.1$ ML cannot be ascribed to a bifunctional effect, emphasizing the importance of the above mentioned electronic and geometric effects for the MOR on bimetallic PtRu electrodes.

4. In contrast to the MOR activity, the electronic modifications of the Pt surface layer do not significantly change the selectivity for CO$_2$ formation, indicating that the rate determining step is either before the split-up into different reaction pathways or that the change in the rate determining steps in the different reaction pathways is comparable for the different electrodes.

5. Comparing with realistic PtRu nanoparticle catalysts our findings on these Pt$_{X\text{-ML}}$/Ru(0001) 2D model systems predict that Ru-core Pt-shell type NPs can be more active for the MOR than monometallic Pt NPs, in agreement with previous reports. The effect should, however, be more pronounced for thicker Pt-shells.
This work impressively demonstrates the quality of insights on the influence of structural and electronic effects on the electrocatalytic reactivity that can be derived from systematic electrocatalytic model studies on structurally well-defined 2D model electrodes. Our results provide valuable insights for a rational catalyst design of more complex 3D catalysts with an improved electrocatalytic performance.

### 6.4.6 Appendix

**MOR on Pt(111)**

A polarization curve of the MOR on Pt(111) in the potential range between 0.07 V - 1.00 V (0.5 M H$_2$SO$_4$ + 0.2 M CH$_3$OH, 50 mV s$^{-1}$) is shown in Figure 6.41. After a small shoulder between 0.40 V and 0.50 V in the positive-going scan the MOR is initiated at 0.50 V and increases in rate until the maximum current density (220 $\mu$A cm$^{-2}$) is reached at 0.86 V. This is followed by a decrease of the current density in the potential range between 0.86 V - 1.00 V. In the negative-going scan the current densities are lower than in the positive-going scan for potentials between 0.72 V - 1.00 V and the maximum of the MOR current density is shifted to lower potentials (0.85 V) compared to the positive-going scan. The reduced activity in the negative-going scan indicates a poisoning of the Pt(111) surface by products/intermediates formed during the MOR. However, as shown in Figure 6.41, there is still a clear H$_{\text{upd}}$ region in the range below 0.30 V, indicating that the surface is not completely poisoned. Comparing the H$_{\text{upd}}$ charge in Figure 6.41 with that in the CV in pure 0.5 M H$_2$SO$_4$ supporting electrolyte (Figure 6.41a), the partial poisoning of the Pt(111) surface leads to a decrease of the H$_{\text{upd}}$ charge by 54%.

**Structural characterization of Pt$_{x-\text{ML}}$/Ru(0001) after the MOR**

Representative STM images of the Pt$_{x-\text{ML}}$/Ru(0001) electrodes with $x_{\text{Pt}} = 1.1$ ML (Figure 6.42a), $x_{\text{Pt}} = 1.4$ ML (Figure 6.42b), $x_{\text{Pt}} = 2.5$ ML (Figure 6.42c), $x_{\text{Pt}} = 4.2$ ML (Figure 6.42d) and $x_{\text{Pt}} = 5.5$ ML (Figure 6.42e and Figure 6.42f) recorded after the MOR on the respective electrodes are depicted in Figure 6.42. A comparison of these STM images with STM images of the respective electrodes obtained before the oxidation reaction (Figures 6.38b-f) demonstrates that the MOR does not induce any significant changes in the Pt film morphology in the potential range between 0.05 V and 0.85 V. This is also illustrated by a large scale STM image of the Pt$_{5.5-\text{ML}}$/Ru(0001) electrode in Figure 6.42f, which shows that the Pt islands keep their compact hexagonal-like shape and...
that there is no detectable restructuring of the closed Pt layers. This fact ensures that it is possible to use the Pt layer distributions determined by STM imaging before the MOR for the discussion of structure-activity relationships of the PtX-ML/Ru(0001) electrodes. The only difference of the PtX-ML/Ru(0001) surface structure observed by STM imaging before and after the MOR is the presence of small dots on the Pt areas after the MOR as can be seen in all STM images in Figure 6.42. The exact nature of these dots could not be determined by STM. However, the line profile in Figure 6.42f demonstrates that these dots do not originate from a Pt restructuring, since their apparent heights are not a multiple of a Pt monolayer. Therefore, we ascribe these small dots to adsorbates formed on Pt in the electrochemical environment, \( \text{i.e., adsorbed (bi)sulfate, O}_{\text{ad}} \text{ OH}_{\text{ad}}, \text{MeOH}_{\text{ad}} \) and/or MOR intermediates/products.

**MOR deactivation on PtX-ML/Ru(0001)**

The first six potential cycles of the MOR on Pt1.4-ML/Ru(0001) are shown in Figure 6.43a. For a better visibility only the positive-going scans are depicted in a potential window between 0.55 V and 0.85 V. With increasing number of cycles we find a decrease of the current densities. Since Figure 6.42 demonstrates that there is no restructuring of the PtX-ML/Ru(0001) in the potential window investigated, the deactivation between the 1\textsuperscript{st} and the 6\textsuperscript{th} cycle in Figure 6.43a must result from a slightly increasing poisoning of the surface with the number of MOR cycles on this electrode. Such a deactivation process with increasing number of cycles was also observed for the other PtX-ML/Ru(0001) electrodes investigated. To better visualize the changes in activity for each PtX-ML/Ru(0001)
electrode, we determined a weighted difference in current density $\Delta j_{0.85V}$ at 0.85 V

$$\Delta j_{0.85V} = \frac{j_{0.85V}(1^{st}) - j_{0.85V}(6^{th})}{j_{0.85V}(1^{st})}$$  \hspace{1cm} (6.10)$$

where $j_{0.85V}(1^{st})$ and $j_{0.85V}(6^{th})$ denote the current density of the 1\textsuperscript{st} and the 6\textsuperscript{th} cycle at 0.85 V, respectively. The resulting $\Delta j_{0.85V}$ values are plotted as a function of the Pt film thickness on Ru(0001) in Figure 6.43b. Since $\Delta j_{0.85V}$ is a measure of the relative deactivation, Figure 6.43b demonstrates that the overall activity loss between the 1st and the 6\textsuperscript{th} cycle is maximum for Pt$_{1.1-ML}$/Ru(0001) and decreases with increasing Pt film thickness. These trends indicate that an increasing Pt film thickness results in a lower blocking effect by MOR products/intermediates on the Pt$_{X-ML}$/Ru(0001) electrode surfaces.

Figure 6.44 shows the 1\textsuperscript{st}, 2\textsuperscript{nd} and 6\textsuperscript{th} cycle of a voltammogram in the H$_\text{upd}$ region recorded during the MOR on a Pt$_{5.5-ML}$/Ru(0001) electrode in a potential window between 0.05V and 0.85V. As illustrated, there are no changes of the H$_\text{upd}$ region during the MOR, demonstrating that the active surface area for hydrogen adsorption remains constant regardless of the decreasing activity with increasing amount of cycles (see Figure 6.43).

**CO stripping on Pt$_{5.5-ML}$/Ru(0001)**

The electro-oxidation of a pre-adsorbed CO$_\text{ad}$ monolayer on Pt$_{5.5-ML}$/Ru(0001) is shown in Figure 6.45. In the first cycle no currents are observed at potentials below 0.60 V, which is ascribed to a poisoning of the electrode surface by strongly bound CO$_\text{ad}$ molecules.\[16,305] The onset of CO$_\text{ad}$ oxidation is at around 0.60 V, with a peak maximum at 0.73 V. In the subsequent cycles no oxidation peak is observed at potentials above 0.60 V. Instead, a pronounced H$_\text{upd}$ region is resolved at potentials below 0.35 V, demonstrating that the surface is not blocked by CO$_\text{ad}$ any more.

**Cyclic voltammogram and MOR on Ru(0001)**

A cyclic voltammogram of a clean Ru(0001) single crystal in 0.5 M H$_2$SO$_4$ supporting electrolyte is depicted in Figure 6.46 (black solid line), exhibiting the typical redox features for Ru(0001) as described in detail elsewhere.\[58,206] Additionally, a polarization curve of the MOR on Ru(0001) in the same potential region is shown in Figure 6.46 (blue dotted line). We find essentially no changes of the potentiodynamic curve compared to the CV in pure supporting electrolyte, indicating that Ru(0001) is completely inactive.
for the MOR in the potential window investigated. This is in agreement with previous findings\cite{231,232,386}.

**MOR on Pt\textsubscript{0.3-ML}/Ru(0001)**

A representative STM image of a Ru(0001) surface with monolayer high Pt islands at a coverage of $\theta_{Pt} = 0.3$ (Pt\textsubscript{0.3-ML}/Ru(0001)) is shown in Figure 6.47a. The respective CV in pure 0.5 M H\textsubscript{2}SO\textsubscript{4} supporting electrolyte is presented in Figure 6.47b. It shows similar redox features as observed in CVs of bare Ru(0001)\cite{342,343}. The main differences compared to Ru(0001) are higher HER currents at potentials below 0.10 V and lower peak intensities of the redox features at higher potential. The polarization curve of the MOR on the Pt\textsubscript{0.3-ML}/Ru(0001) electrode is also shown in Figure 6.47b. Compared to the CV in pure supporting electrolyte there are no substantial changes at potentials below 0.65 V. Above 0.65 V only small oxidation currents (maximum current density $j = 20 \mu$A cm\textsuperscript{-2}) related to the MOR on Pt\textsubscript{0.3-ML}/Ru(0001) are observed, demonstrating that the Pt modified Pt\textsubscript{0.3-ML}/Ru(0001) electrode has a poor activity for the MOR. Figure 6.47c shows a representative STM image of Pt\textsubscript{0.3-ML}/Ru(0001) after the MOR demonstrating the stability of this electrode during the MOR.
Figure 6.42: (a)-(e): STM images (150 nm x 150 nm, $I_T = 2$ nA - 6.5 nA, $U_T = 0.3$ V - 0.6 V) of the Pt$_{X\text{ ML}}$/Ru(0001) electrodes with (a) $x_{Pt} = 1.1$ ML, (b) $x_{Pt} = 1.4$ ML, (c) $x_{Pt} = 2.5$ ML, (d) $x_{Pt} = 4.2$ ML and (e) $x_{Pt} = 5.5$ ML recorded after the MOR on these surfaces. (f): Large scale STM image (500 nm x 500 nm, $I_T = 6.3$ nA, $U_T = 0.7$ V) obtained on the same electrode as shown in (e). The Pt layers exposed at the surface are labeled with the Pt film thickness at the respective sites in all STM images. The inset in f) shows the apparent height profile along the blue line in e).
Figure 6.43: (a) Anodic scans of the first six potential cycles of the MOR on a Pt$_{1.4}$ML/Ru(0001) electrode in 0.5 M H$_2$SO$_4$ + 0.2 M CH$_3$OH (0.05 V - 0.85 V, 10 mV s$^{-1}$). For better visibility only the potential window of 0.55 V - 0.85 V is shown and the respective cycles are labeled. (b) Weighted difference in current density $\Delta j_{0.85V}$ at 0.85 V as a function of the Pt film thickness on Ru(0001) to demonstrate the variation of the deactivation with increasing Pt film thickness.
Figure 6.44: Voltammogram of the H\textsubscript{upd} region of a Pt\textsubscript{5.5-ML}/Ru(0001) electrode during the MOR in the potential range between 0.05 V and 0.85 V in 0.5 M H\textsubscript{2}SO\textsubscript{4} + 0.2 M CH\textsubscript{3}OH. The 1\textsuperscript{st}, 2\textsuperscript{nd} and 6\textsuperscript{th} cycle are illustrated (0.03 V - 0.35 V, 10 mV s\textsuperscript{-1}). There are no significant changes in the H\textsubscript{upd} region during the MOR.

Figure 6.45: Polarization curve of the oxidation of a CO adlayer adsorbed at 0.20 V on a Pt\textsubscript{5.5-ML}/Ru(0001) electrode (blue dotted curve) and the subsequent CV (black solid curve), both recorded in 0.5 M H\textsubscript{2}SO\textsubscript{4} (0.05 V - 0.90 V, 20 mV s\textsuperscript{-1}).
6 Results and Discussion

**Figure 6.46:** Cyclic voltammogram of a clean Ru(0001) single crystal in 0.5 M H₂SO₄ supporting electrolyte (black solid line) and polarization curve of the MOR (blue dotted line) on Ru(0001) in 0.5 M H₂SO₄ + 0.2 M CH₃OH (0.07 V - 0.90 V, 10 mV s⁻¹).

**Figure 6.47:** (a) STM image of a Pt_{0.3-ML}/Ru(0001) electrode recorded before the MOR. (b) CV of Pt_{0.3-ML}/Ru(0001) in 0.5 M H₂SO₄ supporting electrolyte (black solid curve) and the polarization curve of the MOR on this electrode in 0.5 M H₂SO₄ + 0.2 M CH₃OH (blue dashed curve). (c) STM image of the Pt_{0.3-ML}/Ru(0001) electrode recorded after the MOR.
7 Summary

This thesis focused on structure-activity relationships between structural parameters present for Pt and PtRu NPs and their influence on the activity of the NPs for fuel cell relevant electrocatalytic reactions. Preparation under UHV conditions enabled the design and preparation of 2D nanostructured model electrodes with respective structural parameters at the surface which in most cases are not accessible under laboratory conditions, e.g., by electro-deposition. The occurrence/amount of a nanostructure of interest was varied systematically. STM imaging under UHV conditions allowed for direct visual inspection of the surface quality and for a quantitative structural characterization of the nanostructured surfaces. Electrocatalytic reactions were performed on the model electrodes and an unambiguous structure-activity relationship was derived by comparing their reactivity with the amount of specific nanostructures on the respective surfaces. Furthermore, comparison of the experimental results obtained in this work with previously reported results from theoretical studies helped to gain new insights into the influence of electronic and geometric effects – which arise due to the presence of specific nanostructures or catalyst compositions – on the electrocatalytic activity of the model electrodes. In detail, the work succeeded in gaining deeper insights into i) the influence of the NC size, for Pt NCs with sizes below 2 nm, on their activity for the HER, ii) the role of Pt step sites in the CO electro-oxidation on Pt electrodes, iii) the impact of the Pt content in the surface of Ru NPs encapsulated by a monolayer thick Pt$_x$Ru$_{1-x}$ alloy on their performance for the CO electro-oxidation and iv) the influence of the Pt film thickness of Ru-core Pt-shell NPs on the MOR activity. The main findings from these investigations and their impact for the rational design of catalyst materials are highlighted in the following.

The influence of Pt NC size on the HER activity: The preparation of Pt NC arrays with NCs of uniform sizes below 2 nm was achieved under UHV conditions by employing a defect free graphene layer supported on a Ru(0001) single crystal as template for the NC growth. While nucleation and growth studies on such nanostructured
2D model surfaces already existed, electrocatalytic investigations on Pt-gr/Ru(0001) model surfaces were not reported prior to this thesis. Six Pt-gr/Ru(0001) samples were prepared, each with a different average Pt NC size. The chemically inert gr/Ru(0001) substrate was shown to have a negligible reactivity for the HER. In addition, it is stable during the electrocatalytic treatment, as evidenced by STM imaging after the HER. By performing the HER on the gr/Ru(0001) supported Pt NCs of different size, a distinct volcano-like relation between HER activity and Pt NC size was observed in the size range below 2 nm for both, the mass-specific HER activity and the surface-specific HER exchange current density. A maximum in HER activity was observed for Pt NCs with an average size of 38 atoms (Pt$_{38}$), whereas Pt NCs of larger and smaller size revealed lower average activities. Comparison with commercial carbon supported Pt NPs showed that the mass-specific HER activity of the Pt$_{38}$ NCs surpasses that of state-of-the-art Pt NP catalysts used in PEM electrolyzers by at least three orders of magnitude. Furthermore, the surface-specific HER exchange current density of the Pt$_{38}$ NCs is by about one order of magnitude higher than that of state-of-the-art NP catalysts, and is located close to the maximum HER activity accessible according to theory. These results could serve as starting point for the design of technically feasible Pt based catalysts with an excellent performance for the HER.

The role of Pt step sites in the CO electro-oxidation: The Pt step density of a Pt(111) single crystal was increased by homoepitaxial growth of hexagonal Pt islands under UHV conditions. Subsequently, the ascending Pt steps were modified with a narrow Au stripe, forming 2D Pt-core Au-shell nanostructures. This was the first electrocatalytic study on 2D core-shell structures. STM imaging under UHV conditions allowed for a quantitative analysis of the Pt step density. Furthermore, a homogeneous selective modification of all Pt step sites was achieved, as evidenced from direct visual inspection via STM imaging under UHV conditions in combination with electrochemical/-catalytic measurements. CO TPD and CV measurements on the pristine and Au modified Pt electrodes showed that it is possible to detect a 3-fold increased Pt step density of Pt/Pt(111) compared to Pt(111), although the step densities are in the range of a few percent. These measurements also demonstrate that the Au modification distinctly alters the Pt sites at the former Pt step for CO adsorption and competitive hydrogen adsorption/anion desorption. Performing the bulk CO electro-oxidation on the structurally different model electrodes showed that Pt step sites do not enhance the electrocatalytic reaction in the positive-going scan direction, i.e., in the case of an
Summary

initially high CO\text{ad} coverage at the electrode surface. On the other hand, in the negative-going scan direction, \textit{i.e.}, in the case of an initially low CO\text{ad} coverage at the surface, the presence of step sites leads to higher reaction rates over a broader potential range compared to the respective rate on Pt terrace sites. The stability of the nanostructured electrodes during the bulk CO electro-oxidation was verified by STM imaging after the reaction in combination with the electrochemical-/catalytic measurements. This ensured an accurate correlation between surface structure and activity. The presented approach to study the role of step sites in electrocatalysis via 2D core-shell structures prepared under UHV conditions should be applicable for other electrocatalytic reactions and also for gas phase catalysis employing suitable metal combinations which are stable under the given reaction conditions.

The influence of electronic and geometric effects in the CO electro-oxidation on PtRu electrodes: CO electro-oxidation studies on Pt island modified Ru(0001) and Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) electrodes were already reported previously. However, a systematic investigation of the influence of the Pt content \textit{x}_{Pt} on the reactivity of Pt\textsubscript{x}Ru\textsubscript{1-x}/Ru(0001) surface alloys was missing so far, which is addressed in the present work. The surface composition was varied between \textit{x}_{Pt} = 0 and \textit{x}_{Pt} = 1, where \textit{x}_{Pt} = 1 corresponds to a monolayer high Pt film on Ru(0001) (Pt\textsubscript{1-ML}/Ru(0001)). Comparing the activity of these Pt modified Ru(0001) electrodes for the CO electro-oxidation with that of Pt(111) and Ru(0001) demonstrated that all bimetallic electrodes are more active than the monometallic systems. For Pt\textsubscript{1-ML}/Ru(0001) the enhanced activity compared to Pt(111) results from combined vertical ligand and compressive strain effects induced by the Ru(0001) substrate. The latter effects lower the adsorption strength of CO\text{ad} on the Pt surface towards more beneficial values. For the surface alloys the adsorption properties are furthermore affected by the presence of Ru atoms in the surface. This leads to the presence of additional lateral ligand effects and local modifications of the strain and furthermore to the formation of ensemble sites with different chemical composition. The highest activity was observed for a surface alloy with \textit{x}_{Pt} = 0.30, which is in contradiction to the bifunctional mechanism where the highest activity would be expected at \textit{x}_{Pt} = 0.50, corresponding to a maximum amount of Pt\textsubscript{1}Ru\textsubscript{1} dimers. Instead, comparing the observed activity trends with the statistically determined relative abundance of bimetallic Pt\textsubscript{n}Ru\textsubscript{m} ensembles showed that Pt\textsubscript{1}Ru\textsubscript{3} tetramers should be the most active ensembles for this reaction. This was rationalized by preferential adsorption properties of the reactants on these tetramer ensembles arising from combined electronic
and ensemble effects. Here, CO$_{ad}$ adsorbs atop on Pt sites, while OH$_{ad}$ adsorbs at the threefold hollow site of an adjacent Ru$_3$ trimer. While the above mentioned adsorption sites were already shown previously by theoretical calculations to be favorable for the respective isolated reactants, further calculations on the co-adsorption of CO and OH on such tetramer ensembles might provide further validation. Since such calculations constitute a theoretical work by itself, they were not performed in this thesis. Differences in the shape of the CO oxidation polarization curves between the Pt modified Ru(0001) electrodes and Pt(111) were explained by different adsorption properties of specific ensembles on an atomic scale and by a different surface state of the Pt(111) surface. In total, these results illustrate the importance of electronic and geometric effects present for bimetallic PtRu electrodes for their CO electro-oxidation activity beyond the bifunctional mechanism.

The impact of the Pt film thickness on Ru(0001) for the MOR activity: Prior to this thesis the MOR on Pt$_{X-ML}$/Ru(0001) samples was only studied under UHV conditions, while electrochemical /-catalytic investigations were missing. Pt$_{X-ML}$/Ru(0001) model electrodes with film thicknesses between 1.1 ML and 5.5 ML were prepared and structurally characterized by STM under UHV conditions. CV measurements showed that the adsorption strength of hydrogen is lowered on the Pt$_{X-ML}$/Ru(0001) electrodes compared to Pt(111), which is ascribed to combined vertical ligand and compressive strain effects induced by Ru(0001) in agreement with previous studies. Furthermore, the adsorption strength of H$_{ad}$ increases with increasing Pt film thickness due to a reduced vertical ligand effect. All Pt$_{X-ML}$/Ru(0001) electrodes except for the Ru(0001) supported monolayer high Pt film revealed higher activities for the MOR than Pt(111). This is rationalized by the Sabatier principle. On Pt(111) the adsorbed reactants /reaction intermediates bind too strong, whereas they bind too weak to the Ru(0001) supported monolayer high Pt film. The intermediate binding strength on Pt$_{5.5-ML}$/Ru(0001) leads to the highest MOR rates among the electrodes investigated. Thicker Pt films might lead to even more beneficial adsorption strengths, which could, however, not be elucidated from the measurements performed in this study. The observed trends demonstrate that electronic and geometric effects may enhance the reactivity of PtRu electrodes, even for the absence of bimetallic PtRu sites at the surface. While the MOR activity steadily increases with increasing Pt film thickness, it was found that the selectivity for CO$_2$ formation is not affected by the film thickness. This indicates that either the rate determining steps of the two different reaction pathways present for the MOR change in a
similar fashion or that the rds is located before the split-up of the reaction mechanism into the two different pathways.

**Structure-activity relationships as stimulus for the rational design of Pt based NP electrocatalysts:** Note that besides the above discussed structural parameters a NP surface is also characterized by other structural elements which could affect the electrocatalytic activity of the NP. Nevertheless, the above presented results should serve as stimulus for the design of future catalyst materials with improved electrocatalytic activity which is achieved by striving for a high abundance of highly active structures. The observed size effect of Pt NCs for the HER indicates, for instance, that for a PEM electrolyzer catalyst material, which consists of carbon supported Pt NPs / NCs, a high abundance of NCs with an average size of 38 atoms might be favorable to form molecular hydrogen. Due to the high mass-specific activity of these Pt\(_{38}\) NCs this could allow to reduce the Pt catalyst loading and thus to reduce costs of the catalyst material.

Focusing on catalyst materials employed in DMFCs, the results of the CO electro-oxidation on Pt(111) supported 2D Pt-core Au-shell catalysts obtained in this thesis indicate that Pt step sites may increase the activity for the CO oxidation in the case of low CO concentrations in the system. However, CO is continuously formed during the MOR in DMFCs resulting in high CO concentrations. Since in the case of high CO concentrations the step sites do not enhance the activity for the CO electro-oxidation, the effect of Pt low-coordination step sites at the surface of Pt NPs on the performance of the NPs might thus be negligible.

More promising might be to improve bimetallic PtRu NP catalysts to obtain a higher CO tolerance in DMFCs. As shown in this thesis the latter approach does not necessarily demand for a high amount of adjacent Pt and Ru atoms as proposed by the classical bifunctional mechanism. Instead, it is important to strive for optimized electronic and geometric properties. Based on the findings of the CO electro-oxidation on Pt\(_x\)Ru\(_{1-x}\)/Ru(0001) surface alloys a high CO tolerance might be achieved by designing a catalyst which consists of a Ru NP surrounded by a monolayer thick shell of a Pt\(_x\)Ru\(_{1-x}\) alloy with a Pt content of \(x_{\text{Pt}} = 0.30\).

For the MOR it was already reported previously that Ru-core Pt-shell NPs exhibit higher activities and a higher durability compared to Pt NPs of similar shape and size. The findings for the MOR on Pt\(_x\)-ML/Ru(0001) from the present thesis show that the activity for the MOR might be further improved if the Pt shell thickness was increased to 5-6 MLs. While this should enhance the reactivity of the Ru-core Pt-shell NPs, the
selectivity for CO$_2$ formation cannot be varied with this attempt.

**Scientific value**

In total, this thesis demonstrates the enormous strength of employing nanostructured 2D model electrodes, which are prepared and structurally characterized by STM under UHV conditions, for electrocatalytic studies. This approach allows to determine unambiguous structure-activity relationships for electrocatalytic reactions. The fundamental electrocatalytic studies on nanostructured 2D single crystal model electrodes presented in this thesis help to understand the inherent influence of a specific structural parameter present for NPs on the catalyst reactivity as well as to localize and quantify electrocatalytic active sites at the surface. Furthermore, the possibility to directly compare the experimental results with theoretical studies, due to the low complexity of the electrodes, enables to determine the impact of electronic and geometric effects on the electrocatalytic activity. In some cases it is also possible to derive mechanistic insights on the nanoscale or even on the atomic scale. While this thesis provides an excerpt for possibilities to study electrocatalytic reactions with focus on a specific structural parameter, there are innumerable other options to derive structure-activity relationships due to the variety of nanostructures accessible by preparation under UHV conditions. The structure-activity relationships derived in this work contribute to a better fundamental understanding of electrocatalytic reactions on the nanoscale. If they are considered for the design of catalyst materials in fuel cell relevant systems, the structure-activity relationships should significantly help to improve the overall performance of those systems which is crucial in terms of cost reduction and their commercialization.
8 Zusammenfassung

**Zusammenfassung**


**Die Rolle von Pt Stufenplätzen in der CO Elektrooxidation:** Die Pt Stufen-dichte eines Pt(111) Einkristalls wurde durch homoepitaktisches Wachstum von Pt Inseln unter UHV-Bedingungen erhöht. Anschließend wurden die aufsteigenden Pt Stufen mit einem schmalen Au Streifen modifiziert, wodurch 2D Pt-Kern Au-Schalen Nanostrukturen geformt wurden. Dies war die erste elektrokatalytische Studie an 2D Kern-Schalen Strukturen. STM Messungen unter UHV-Bedingungen ermöglichten eine quantitative Analyse der Pt Stufendichte. Weiterhin wurde eine homogene selektive Modifizierung aller Pt Stufenplätze erreicht, was bewiesen wurde durch eine direkte visuelle Untersuchung durch STM Messungen unter UHV-Bedingungen in Kombination.
mit elektrochemischen /-katalytischen Messungen. CO-TPD und CV Messungen an den ursprünglichen und den Au modifizierten Pt Elektroden zeigte, dass es möglich ist eine dreifach erhöhte Pt Stufendichte für Pt/Pt(111) im Vergleich zu Pt(111) zu detektieren, obwohl die Stufendichten im Bereich weniger Prozenten liegt. Diese Messungen demonstrierten zudem, dass die Au Modifikation die Pt Plätze an den vorherigen Pt Stufen merklich für die CO Adsorption und die konkurrierende Wasserstoff Adsorption / Anion Desorption verändert. Die Durchführung der CO Elektrooxidation an den strukturell unterschiedlichen Modelelektroden zeigte, dass Pt Stufenplätze die elektrokatalytische Reaktion in der positiv verlaufenden Scan-Richtung, d.h. im Falle einer anfänglich hohen CO$_{ad}$ Bedeckung an der Elektrodenoberfläche, nicht erhöht. In der negativ verlaufenden Scan-Richtung, d.h. im Falle einer anfänglich niedrigen CO$_{ad}$ Bedeckung an der Oberfläche, führt die Gegenwart von Stufenplätzen hingegen zu höheren Reaktionsraten über einen breiteren Potentialbereich verglichen mit der entsprechenden Rate auf Pt Terrassen-Plätzen. Die Stabilität der nanostrukturierten Elektroden während der bulk CO Elektrooxidation wurde durch STM Messungen nach der Reaktion in Kombination mit elektrochemischen /-katalytischen Messungen verifiziert. Dies stellte eine akkurate Korrelation zwischen Oberflächenstruktur und Aktivität sicher. Der präsentierte Ansatz zur Untersuchung der Rolle von Stufenplätzen in der Elektrokatalyse über 2D Kern-Schalen Strukturen, welche unter UHV-Bedingungen präpariert werden, sollte für andere elektrokatalytische Reaktionen und auch für die Gasphasen-Katalyse anwendbar sein, sofern geeignete Metallkombinationen verwendet werden, die stabil unter den gegebenen Reaktionsbedingungen sind.

Der Einfluss von elektronischen und geometrischen Effekten in der CO Elektrooxidation auf PtRu Elektroden: CO Elektrooxidations-Studien auf Pt Insel modifizierten Ru(0001) und auf Pt$_x$Ru$_{1-x}$/Ru(0001) Elektroden wurden bereits zuvor durchgeführt. Eine systematische Untersuchung über den Einfluss des Pt Anteils $x_{pt}$ auf die Aktivität von Pt$_x$Ru$_{1-x}$/Ru(0001) Oberflächenlegierungen existierte bisher allerdings nicht, weshalb dies in der vorliegenden Arbeit untersucht wurde. Die Oberflächen-Zusammensetzung wurde zwischen $x_{pt} = 0$ und $x_{pt} = 1$ variiert, wobei $x_{pt} = 1$ einem Monolagen hohen Pt Film auf Ru(0001) (Pt$_{1-ML}$/Ru(0001)) entspricht. Der Vergleich der Aktivität dieser Pt modifizierten Ru(0001) Elektroden für die CO Elektrooxidation mit der von Pt(111) und Ru(0001) demonstrierte, dass alle bimetallischen Elektroden aktiver sind als die monometallischen Systeme. Die erhöhte Aktivität von Pt$_{1-ML}$/Ru(0001) verglichen mit Pt(111) resultiert von kombinierten vertikalen Liganden- und komprim-
ierenden Spannungseffekten, welche durch das Ru(0001) Substrat induziert werden. Die letztgenannten Effekte reduzieren die Adsorptionsstärke von CO$_{ad}$ auf der Pt Oberfläche in Richtung vorteilhafterer Werte. Für die Oberflächenlegierungen sind die Adsorptions-Eigenschaften zudem durch die Gegenwart von Ru Atomen in der Oberfläche beeinflusst. Dies führt zum Auftreten von zusätzlichen lateralen Ligandeneffekten und lokalen Spannungs-Modifikationen sowie zur Bildung von Ensemble-Plätzen mit unterschiedlicher chemischer Zusammensetzung. Die höchste Aktivität wurde für eine Oberflächenlegierung mit $x_{Pt} = 0.30$ beobachtet, was im Widerspruch zum klassischen bifunktionalen Mechanismus steht, bei dem die höchste Aktivität bei $x_{Pt} = 0.50$ erwartet werden würde, da dann die Anzahl an Pt$_1$Ru$_1$ Dimeren maximal ist. Stattdessen zeigte der Vergleich der beobachteten Aktivitätstrends mit dem statistisch bestimmten relativen Vorkommen von bimetallischen Pt$_m$Ru$_n$ Ensembles, dass Pt$_1$Ru$_3$ Tetramer die aktivsten Ensembles für diese Reaktion darstellen sollten. Dies wurde begründet durch präferierte Adsorptions-Eigenschaften der Reaktanden auf diesen Tetramer Ensembles, welche durch kombinierte elektronische Effekte und durch Ensemble Effekte auftreten. Hier adsorbiert CO$_{ad}$ atop auf Pt Plätzen, während OH$_{ad}$ auf dem dreifach Lückenplatz eines benachbarten Ru$_3$ Trimers adsorbiert. Während die oben genannten Adsorptionsplätze bereits zuvor in theoretischen Kalkulationen als bevorzugt für die entsprechenden isolierten Reaktanden bestimmt wurden, würden weiterführende Berechnungen zur Co-Adsorption von CO und OH auf solchen Tetramer Ensembles zur Validierung beitragen. Da solche Berechnungen eine eigenständige theoretische Arbeit darstellen, wurden sie in der vorliegenden Arbeit nicht durchgeführt. Unterschiede in der Form der CO Oxidations Polarisationskurven zwischen Pt modifizierten Ru(0001) Elektroden und Pt(111) wurden erklärt durch unterschiedliche Adsorptions-Eigenschaften von spezifischen Ensembles auf atomarer Ebene und durch einen abweichenden Oberflächenzustand der Pt(111) Oberfläche. Zusammengefasst stellen diese Ergebnisse die Wichtigkeit von elektronischen und geometrischen Effekten bei bimetallischen PtRu Elektroden für deren CO Elektrooxidations-Aktivität jenseits des bifunktionalen Mechanismus dar.

**Der Einfluss der Pt Filmdicke auf Ru(0001) für die MOR Aktivität:**
Vor dieser Arbeit wurde die MOR auf Pt$_{X-ML}$/Ru(0001) Proben lediglich unter UHV-Bedingungen untersucht, während elektrochemische/-katalytische Untersuchungen fehlten. Pt$_{X-ML}$/Ru(0001) Modellelektroden mit Filmdicken zwischen 1.1 ML und 5.5 ML wurden unter UHV-Bedingungen präpariert und strukturell durch STM charakterisiert. CV Messungen zeigten, dass die Adsorptionsstärke von Wasserstoff auf
Pt_{X,ML}/Ru(0001) verglichen mit Pt(111) reduziert ist, was im Einklang mit vorherigen Studien auf Ru(0001) induzierte kombinierte vertikale Liganden- und komprimierende Spannungseffekte zurückgeführt wird. Weiterhin steigt die Adsorptionsstärke von H_{ad} mit ansteigender Pt Filmdicke, aufgrund eines geringeren vertikalen Liganden-effektes. Alle Pt_{X,ML}/Ru(0001) Elektroden, bis auf den Ru(0001) getragerten Monolagen hohen Pt Film, wiesen höhere Aktivitäten für die MOR auf als Pt(111). Dies wird begründet mit dem Sabatier Prinzip. Auf Pt(111) binden die adsorbierten Reaktanden/Reaktionsintermediate zu stark, während sie an den Ru(0001) getragerten Monolagen hohen Pt Film zu schwach binden. Die dazwischenliegende Bindungsstärke auf Pt_{5.5,ML}/Ru(0001) führt innerhalb der betrachteten Elektroden zu den höchsten MOR Raten. Dickere Pt Filme könnten zu noch geeigneteren Adsorptionsstärken führen, was aus den Messungen dieser Studie jedoch nicht aufgeklärt werden konnte. Die beobachteten Trends demonstrieren, dass elektronische und geometrische Effekte die Reaktivität von PtRu Elektroden, selbst in Abwesenheit von bimetallischen PtRu Plätzen an der Oberfläche, erhöhen können. Während die MOR Aktivität stetig mit ansteigender Pt Filmdicke ansteigt, wurde gefunden, dass die Selektivität zur CO_{2} Bildung nicht von der Filmdicke beeinflusst wird. Dies deutet darauf hin, dass sich entweder die ratenbestimmenden Schritte für die beiden unterschiedlichen Reaktionspfade der MOR in ähnlicher Weise ändern, oder dass sich der ratenbestimmende Schritt vor der Aufspaltung des Reaktionsmechanismus zu den beiden unterschiedlichen Pfaden befindet.

**Struktur-Aktivitäts Zusammenhänge als Anregung für die zweckmäßige Entwicklung von Pt basierten NP Elektrokatalysatoren:** Es ist zu beachten, dass abgesehen von den oben diskutierten strukturellen Parametern eine NP Oberfläche ebenfalls durch andere strukturelle Elemente charakterisiert wird, welche die elektrokatalytische Aktivität des NP beeinflussen könnten. Nichtsdestotrotz sollten die oben präsentierten Ergebnisse als Anregung für das Design von zukünftigen Katalysator Materialien mit verbesserter elektrokatalytischer Aktivität dienen, was durch das Streben nach einer hohen Anzahl von hoch aktiven Strukturen erreicht wird. Die beobachteten Größen-efekte von Pt NC für die HER deuten zum Beispiel darauf hin, dass für ein PEM Elektrolyseur Katalysator Material, welches aus Kohlenstoff getragerten Pt NP/NC besteht, eine große Menge an NC mit einer durchschnittlichen Größe von 38 Atomen vorteilhaft für die Bildung von molekularem Wasserstoff sein kann. Aufgrund der hohen Massenaktivität dieser Pt_{38} NC könnte dies eine Reduktion der Pt Katalysator Beladung ermöglichen und dadurch die Katalysator Material Kosten reduzieren.
Mit Blick auf Katalysator Materialien, die in DMFCs verwendet werden, deuten die in dieser Arbeit erhaltenen Ergebnisse der CO Elektrooxidation auf Pt(111) geträgerten 2D Pt-Kern Au-Schalen Katalysatoren darauf hin, dass Pt Stufenplätze die Aktivität für die CO Oxidation im Falle von geringen CO Konzentrationen im System erhöhen können. Jedoch wird CO kontinuierlich während der MOR in DMFCs gebildet, was zu hohen CO Konzentrationen führt. Da im Falle von hohen CO Konzentrationen die Aktivität für die CO Elektrooxidation nicht von Stufenplätzen erhöht wird, könnte der Effekt von niedrig koordinierten Pt Stufenplätzen an der Oberfläche von Pt NP für die Leistungsfähigkeit der NP demnach vernachlässigbar sein.

Vielversprechender könnte es sein, bimetallische PtRu NP zu verbessern, um eine höhere CO Toleranz in DMFCs zu erhalten. Wie in dieser Dissertation gezeigt, benötigt es für den letztgenannten Ansatz nicht notwendigerweise eine hohe Anzahl von benachbarten Pt und Ru Atomen, wie es vom klassischen bifunktionalen Mechanismus vorgeschlagen wird. Stattdessen ist es wichtig optimale elektronische und geometrische Eigenschaften anzustreben. Basierend auf den Erkenntnissen für die CO Elektrooxidation auf Pt$_x$Ru$_{1-x}$/Ru(0001) Oberflächenlegierungen könnte eine hohe CO Toleranz erreicht werden, indem ein Katalysator konzipiert wird, welcher aus einem Ru NP besteht, der von einer Monolagen dicken Schale einer Pt$_x$Ru$_{1-x}$ Legierung mit einem Pt Anteil von x$_{Pt}$ = 0.30 ummantelt ist.

Für die MOR wurde bereits zuvor berichtet, dass Ru-Kern Pt-Schalen NP eine höhere Aktivität und eine höhere Lebensdauer als Pt NP ähnlicher Form und Größe vorweisen. Die Erkenntnisse für die MOR auf Pt$_x$-ML/Ru(0001) aus der vorliegenden Dissertation zeigen, dass die Aktivität für die MOR weiter verbessert werden könnte, wenn die Dicke der Pt-Schale auf 5-6 ML erhöht werden würde. Während dies die Reaktivität der Ru-Kern Pt-Schalen NP erhöhen sollte, kann die Selektivität für die CO$_2$ Bildung durch diesen Ansatz nicht variiert werden.

**Wissenschaftlicher Mehrwert**

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Publikationen

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Vorträge


12. F. Argast, A. K. Engstfeld, **J. Klein**, S. Brimaud, R. J. Behm: “Methanol electro-oxidation on UHV prepared Pt modified Ru(0001) model electrodes” *DPG Spring Meeting*, Berlin, 18.03.2015.


**Banner**


**Poster**


