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The front cover shows the fast Fourier transform of the perfect spoked-wheel pattern, which is depicted on the back cover. It illustrates the complexity that a simple system can show. The insets on the front cover display scanning electron micrographs of sharp tips for scanning probe microscopy; from top to bottom: a shattered sapphire chip, a Au-coated, etched W tip, and an etched Mo tip. Top and middle image were recorded by Dr. Sander B. Roobol. Middle image is presented on an artificial background (downloaded from wallpaperswa.com). On the back cover, the insets show various scanning tunneling micrographs of different surfaces adapting to high-pressure conditions; from top to bottom: Pt(111) exposed to NO₂, Co(0001) to H₂, and Ag(111) to S-contaminated ethylene.
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Chapter 1

Introduction
Several opportunities arise to a chemist to make oneself useful. One can unravel the origin of life and try to understand the workings of a living cell [1], without a doubt the most sophisticated chemical system known to man. One can even go beyond life on this planet, by studying the role of chemistry in the history of the universe [2]. Chemists with a more practical mindset can design and synthesize new materials, such as solar cells or batteries [3], or synthesize the most complex molecules [4], such as maitotoxin, with the chemical formula $\text{C}_{164}\text{H}_{256}\text{O}_{68}\text{S}_{2}\text{Na}_{2}$ [5]. Instead of making small amounts of novel and daunting molecules, I am interested in the understanding of how to make rather simple molecules in the largest quantities and with the highest efficiency. These are the goals of the field, called heterogeneous catalysis.

Catalysis and the catalyst, the active agent of this process, are widely familiar terms for the general public because the catalytic converter is a vital component of the modern-day car. In an automotive exhaust, it plays an important role: Toxic pollutants are transformed into less harmful gases in a fraction of a second.

A second immensely important example of catalysis is the production of fertilizers. To make fertilizers, hydrogen produced from, e.g., natural gas, and molecular nitrogen are catalytically converted in several steps via ammonia to nitric acid. One of these steps, the synthesis of ammonia, has been awarded with two Nobel prizes [6, 7] and has been labeled as the most influential achievement of the twentieth century [8]. This process is highly energy demanding thus making improvements in catalyst efficiency both economically and environmentally attractive. A final illustration of catalysis is the formation of liquid fuels from syngas\textsuperscript{1} [9]. These fuels can be carbon neutral if syngas is made from biomass. These examples show that catalysis plays a key role in two of the eight millennium goals [10].

### 1.1 Foundation of catalysis

Any spontaneously occurring chemical reaction proceeds by virtue of a decrease in the so-called free energy. This is analogous to a stream of water that will only flow if the destination is lower than the starting point. The spontaneity of a chemical reaction does not give us any information about the activity. For example, it is well known that diamond transforms to graphite under everyday conditions. The rate of this reaction is, luckily, completely negligible.

Reactants in a chemical process often need to cross an energetic barrier, which finds its origin in unfavorable configurations the molecules have to adopt while transforming from reactant to product. The most unfavorable configuration has the highest energy and is called the transition state. These transition states are either stabilized by the interaction with a catalyst, or the catalyst has the ability to provide an alternative pathway with a lower energy transition state. In both cases, the catalyst decreases the reaction barrier and increases the reactivity. This principle is depicted in Figure 1.1.

\textsuperscript{1}a mixture of CO and H\textsubscript{2}
1.2 Challenges in catalytic research

Industrial catalysts are highly complex systems. A typical class of catalysts consists of metallic particles ranging from a few to several tens of nanometers in diameter. These particles are often supported on porous oxides, from which three-dimensional pellets are formed. These structures at different length scales are shown in Figure 1.2 for typical heterogeneous catalysts.

The first step in understanding catalysis is to gain insight into the structure and reactivity of the different parts of the catalyst and their interfaces. The chemical reactivity can be obscured by physical processes, such as gas phase diffusion and heat transfer. The total reactivity depends on both chemical and physical properties of the catalytic materials. These properties are not static, however, and can change as a function of temperature, gas composition, and time.

The difficulty in understanding catalysis is not so much the catalyst’s inherent complexity, but rather the poor experimental capabilities to fully characterize its properties. This characterization needs to be performed either under so-called operando conditions or under in situ conditions, i.e., on a working catalyst under reaction conditions or in an environment that mimics the reaction conditions. The definitions of operando and in situ are not very strict and the terms have been used interchangeably. However, the main difference between operando and in situ conditions is that the former requires a working catalyst. The active catalyst changes the local gas environment into a
mixture of reactants and products, which leads to a more realistic measurement, which is better comparable to the industrial process. The activity of the catalyst should be measurable and measured in order to qualify as an operando measurement.

Both operando and in situ mean that experiments need to be performed under (semi)realistic conditions, i.e., at high pressure and elevated temperature. However, most techniques are not capable of measuring under these conditions. The tools that can be applied under these harsh conditions usually require specialized experimental setups and often only give a fraction of the information needed to fully characterize the catalyst chemically and physically.

An alternative strategy that has allowed characterization of the catalysts to a higher degree is the so-called *post mortem* research. In this method, a fresh catalyst is studied in great detail after synthesis, but before being used, and after serving as catalyst for a certain amount of time. However, the additional information comes at the price of missing the evolution of the catalyst under working conditions.

From a practical point of view, it can also be useful to relate key descriptors, such as activity or selectivity, to parameters in the preparation of the catalytic material. In this approach, understanding has been pushed to the background: catalyst characterization has been replaced by testing for reactivity. This empirical way of developing catalysts has a strong trial-and-error nature. To successfully apply this approach, reactions are being run in parallel in great numbers, which allows the parameter space to be explored relatively quickly.

The drawback of the trial-and-error-based approach is that it may result in an improved catalyst, within the explored parameter ranges, but it cannot guarantee to find the best catalyst. In order to find the most efficient catalyst, the catalyst needs to be designed based on understanding, after which it may be optimized by following traditional approaches. To understand catalysis, we need to answer several key questions:
What is the atomic structure of the working catalyst, how does it adapt its structure depending on its environment? How does it evolve over time? If we know the active phase under reaction conditions, we can begin to understand its chemical interaction with the gas phase reactants. How do they adsorb, diffuse, and react on the catalyst? If we obtain this understanding on an atomic level, we can shift the focus to larger scale problems, such as diffusion, gas flow, and the thermal properties of the catalytic reactor.

1.3 In situ and operando experiments

Measuring interfacial properties of materials is inherently rather difficult, since the region of interest is only a few atomic layers thick and is frequently deeply buried by the phases that form the interface. For example, to study the solid-gas interface one needs to traverse the gas phases, without penetrating the bulk of the solid. This is rather straightforward if the gas is extremely dilute, such as a vacuum. However, catalysis does not occur in vacuum and to study it, the partial pressure of the reactants needs to be sufficiently high.

The main difficulty lies with the gas atoms that will disturb or completely inhibit most measurements that one would like to perform on the catalytically active interface. All surface-sensitive measurements involve particles, such as photons, electrons, ions, atoms or molecules, that are either impinging on the interface or originating from it. Most types of particle will not penetrate deep into a condensed phase, such as a solid, because their cross section for absorption or scattering is too large. This makes those techniques very surface sensitive. However, they have similar cross sections for interaction with gas molecules. If the gas phase layer is too thick or its pressure too high, then none of the particles will reach the interface or detector. If they do reach the detector via the interface, the information that they carry (momentum, energy, charge state, etc.) will be strongly deteriorated.

The usual strategy to overcome this problem (at least partly) is to make the gas phase layer as thin as possible. This can be achieved by moving the detector and/or source very close to the interface. A second solution is to construct a high-pressure cell with semitransparent windows that can be used within a vacuum chamber that houses the measurement instrumentation. Recent technical developments in surface science proved both strategies successful: X-ray photoelectron spectroscopy (XPS) measurements are possible at several mbars by moving the electron analyzer close to the surface, while focusing the X-ray beam to a small spot size [13]. The latter strategy is employed in high-pressure transmission electron microscopy (TEM), which uses high-pressure cells to image surfaces of catalytic nanoparticles under reaction conditions [14].

Another way to be less sensitive to the gas phase is to use high-energy photon techniques. For these techniques, the photon energy determines the interaction strength with atoms and molecules. For high-energy X-ray beams, these photons penetrate deeply into the solid phase and the surface information is entangled with bulk information. Several strategies can be adopted to increase the surface sensitivity. A general method to achieve this is to use a grazing-incidence angle. This increases the path length of the photons through the surface layers and decreases the probing depth. Some high-
energy X-ray techniques are inherently surface sensitive, which is the case for surface X-ray diffraction (SXRD). The surface ends the extended periodicity of the bulk crystal and, therefore, changes the diffraction pattern [15]. Because all of these techniques have their limitations in both the conditions that can be probed as in the information that can be extracted, a combination of these techniques can be very powerful [16].

The in situ or operando measurements in this thesis are based on scanning tunneling microscopy (STM) [17], which is an example of scanning probe microscopy (SPM). These microscopes operate by sensing the interaction between surface atoms and a nanosharp probe. This probe is raster scanned in the region of interest, while the interaction is measured at every point. In STM measurements, this interaction is the tunneling current. In a typical measurement, the detector (the STM tip) is at a distance of $\sim 1.0$ nm from the surface. The tip sample separation is much smaller than the mean free path of molecules in a gas phase (in the order of 100 nm at 1 bar at room temperature). This makes it possible to apply STM, in principle, almost irrespectively of the atmosphere, i.e., the choice of gas and the pressure. Actually, STM can be performed even in liquid environments and, with some care given to the tip and to the management of all potentials, even under electrochemical conditions [18].

The pressure insensitivity of SPM has been used to construct a dedicated high-pressure STM setup specialized to image solid, conductive surfaces under reaction conditions [19]. This unique system integrates the STM unit with a small high-pressure flow cell. The flow can consist of a mixture of up to 5 different gases in ratios that can be chosen over wide ranges and at a total pressure of up to 6 bar. This so-called ReactorSTM forms the current generation of a high-pressure STM concept, first described in our group by Rasmussen et al. in 1998 [20] and later refined by Hendriksen et al. [21] After almost 20 years of high-pressure STM experiments and technical development, this technique has become mature. This is illustrated by the STM experiments described in this thesis, which show true atomic resolution for the first time. Furthermore, true atomic resolution is achieved in almost every measurement. The latest developments include technical adjustments to the gas handling system that allow the absolute pressure to be increased to 20 bar. In addition, in the newest realization, the microscope can operate simultaneously in STM and atomic force microscopy (AFM) [22] mode. Combining STM and AFM has as major advantage that insulating surfaces can be imaged, while the current can be recorded as a function of the sample bias to obtain electronic information from the surface.

1.4 This thesis

In my PhD thesis, I will describe the experiments that I performed to (partially) answer the key questions mentioned at the end of section 1.2. To obtain fundamental knowledge on the elementary steps governing the catalytic process, I employed model catalysts. Model catalysts ideally capture the essence of the catalyst’s activity, while greatly reducing the complexity of the system. In this way, I was able to study adsorption, reaction, and desorption in a precise manner. The model catalysts consisted of extended, flat versions of a metallic particle’s surface. These model surfaces are created
by cutting and polishing bulk single crystals in a specific orientation\textsuperscript{2}. An example is shown in Figure 1.3. The precise orientation determines the arrangement of the atoms in the surface. The facets that define the shape of nanoparticles can be viewed as small regions with the structure of these flat surfaces and much of their properties can thus be derived from studies on the extended, flat surfaces. In my studies, I have found almost invariably that changes in reaction conditions, i.e., in temperature, in total pressure or in the ratio between the partial pressures of the reactants, can result in significant changes in the structure and composition, and, thus, the free energy of a surface. Precise knowledge of all these changes for all relevant surface orientations, would, in principle allow one to predict shape changes; a first and large step in understanding catalysis.

The first 3 chapters of this thesis focus on Pt, of which two model catalysts, the Pt(111) and the Pt(110) surface, were studied. In these experiments the ReactorSTM was used to obtain the atomic structure of these model catalysts under various reaction conditions. The first model catalyst, the Pt(111) surface, is the most stable Pt surface and should therefore be the dominant facet of Pt nanoparticles. Although the structure of this model catalyst is very straightforward and well studied\textsuperscript{3}, significant unclarity still exists about the way the surface oxidizes. Oxidation catalysis is an important application of Pt, thus justifying an in-depth study to elucidate the oxidation of the Pt(111) surface. This study is described in Chapter 2. In the following chapter,

\textsuperscript{2}These orientations are defined by their Miller indices, notated as \((hkl)\) [23].

\textsuperscript{3}One of the first papers using this Pt(111) model system dates back to 1969 [24] and over 3800 papers have been published since.
experiments are described that investigate the growth conditions of these surface oxides. Furthermore, the stability of these surface oxides was investigated by evacuating the reactor after forming the oxides. Finally, an estimate of the O coverage is obtained from XPS measurements performed under UHV conditions.

Chapter 4 presents a review dedicated to reactions on the Pt(110) surface. These reactions include CO oxidation and the reaction between NO and H$_2$. The CO oxidation experiments were performed by my predecessor, Dr. Kees T. Herbschleb. This review was published in a special edition of Catalysis Today, celebrating 50 years of research in heterogeneous catalysis at Leiden University [25, 26].

The second part of my PhD thesis follows a different approach. It describes a typical UHV surface-science study focused on low-temperature CO oxidation on a Au model catalyst. This field is much younger compared to CO oxidation on Pt and was started by Haruta et al. in 1987 [27]. They discovered an unusual and very high activity of Au nanoparticles for CO oxidation. One explanation for this reactivity is that Au nanoparticles deviate from the nobility of the bulk metal due to an increased number of low-coordinated atoms. Moreover, the addition of H$_2$O to the reactants was found to strongly enhance the activity [28]. In this project, I studied the interaction of water with low-coordinated Au atoms (see Chapter 5). In Chapter 6, I went one step further and created an activated water layer by electron-induced fragmentation and was able to follow the reaction of CO with O at very low temperatures.

The UHV surface-science study should be complemented at a later stage with an in situ or operando study to check if the metallic phase is indeed the active phase of these model systems. For Au, it is very realistic that the metallic phase is the stable phase under reaction conditions, since it is much more noble than Pt, of which only the top most layer oxidizes under reaction conditions.
Part I

In situ STM on Pt model catalysts
Chapter 2

Oxidation of Pt(111) at high pressure and temperature; formation of surface oxides
2.1 Introduction

Platinum serves as one of the components in the automotive catalyst. In this car catalyst, CO and residual hydrocarbons are oxidized to CO$_2$. In addition, NO is reacting with O$_2$ to form NO$_2$ when the car catalyst is operating in lean burn, i.e., in excess oxygen.

To improve catalysts by rational design, it is crucial to fully understand the interaction of oxygen with a realistic Pt catalyst as used in the catalytic car converter. A first step towards this goal is to gain understanding on the O$_2$ interaction with a well-defined model catalyst. In its most essential form, this is the extended Pt(111) surface. This surface is the lowest in surface energy and expected to be the dominant facet of (larger) particles [29].

The adsorption and dissociation of O$_2$ on Pt(111) have been extensively studied under traditional surface science conditions, i.e., UHV. It was found that O$_2$ binds molecularly below 160 K with a saturation coverage of $\frac{1}{4}$ monolayer (ML) [30, 31]. At higher temperatures, O$_2$ dissociates readily to form a p(2$\times$2)-O chemisorbed overlayer with a saturation coverage of 0.25 ML. Oxygen structures with higher coverage could be obtained by O$_2$ exposure at elevated temperatures [32]. Using NO$_2$ the saturation coverage was doubled and a p(2$\times$1) structure was observed by STM [33].

Stronger oxidants, such as O$_3$ [34] and atomic oxygen [35, 36], were needed to create Pt oxides. These oxides resulted in O coverages above approximately 1 ML and were accompanied by chemical shifts in XPS and so-called explosive desorption in temperature-programmed desorption (TPD). An interesting surface oxide was discovered after oxidizing the Pt(111) surface with NO$_2$ [33]. This surface oxide has a structure distinctly different from $\alpha$-PtO$_2$. The surface oxide’s structure was a one-dimensional (1D) chain of 7 Pt atoms each surrounded by four O atoms and expanded along the direction of the chain, to acquire a separation comparable to the lattice of $\alpha$-PtO$_2$. These chains were interpreted as having a chemical composition of PtO$_2$. To derive this composition, only the Pt atoms in the chain were considered as being oxidized. The chains assembled in a ‘honeycomb’-superstructure, between which O resided.

Surface science studies performed under vacuum conditions do not guarantee to identify the surface structure under realistic reaction conditions for catalytic oxidation. The relevant structure can only be elucidated when the structure is probed in situ, i.e., at high pressure and elevated temperatures. Two independent in situ SXRD studies showed the formation of bulk-like $\alpha$-PtO$_2$ [37, 38]. Both studies do not report the formation of any surface oxide. These observations seem to contradict with a near-ambient-pressure XPS study [39], which showed the formation of a surface oxide at similar temperatures as in the SXRD experiments, but at much lower pressures. This surface oxide was found to be an intermediate in the bulk oxidation of Pt.

The most important questions remain unanswered. What is the structure of Pt in an oxidation catalyst under catalytically relevant conditions, i.e., at high temperature and high O$_2$ partial pressure? Is this a surface oxide or a bulk oxide? If it is a surface oxide, is its structure identical to the UHV-formed surface oxide?

Using the ReactorSTM [19], we studied the oxidation of Pt(111) with O$_2$ pressures of 1–5 bar in a temperature range of 300–538 K. We observed the formation of two
stable surface oxides. The first had a spoked-wheel structure, in which equilateral triangles were arranged into spoked wheels. The lattice constant within the spokes was expanded similarly to the building blocks of the surface oxide formed after NO$_2$ exposure of Pt(111) in UHV [33]. The spoked-wheel structure can be regarded as an oxygen-rich version of the previously reported surface oxide, which lacked the spokes and showed only a hollow honeycomb. The second discovered structure consisted of a pattern of rows with a periodicity of $\sqrt{3}a$. These rows were lifted from the surface and consisted of half the Pt atoms in the top layer. The structure’s unit cell was $(2\times n)$ with $n=8$ if we would assume similarly expanded rows as building block. Based on the expanded rows which agreed well with the $\alpha$-PtO$_2$ lattice constant, we conclude that both structures were surface oxides and not mere chemisorption structures. For these surface oxides, it is not trivial to determine the chemical composition, because it is not clear if only the Pt atoms in chains were oxidized. If this would be assumed, than the Pt oxide would best be described as PtO$_2$ chains. Interestingly, the formation of $\alpha$-PtO$_2$ was not observed. The conclusions from the experiments described in this chapter will be given at the end of Chapter 3, together with the conclusions derived from the experiments presented in that chapter.

2.2 Experimental

All experiments were performed in a ReactorSTM. This system has recently been described in great detail [19]. Therefore, only its most important aspects are repeated here. The ReactorSTM is a UHV system housing a small-volume (0.5 ml) flow-cell reactor. This reactor is integrated with a home-built miniature STM. The design is such that all delicate STM parts are outside the reactor and not exposed to gases or to elevated temperatures. Only one surface of the sample and the tip with its sliding tip holder are inside the reactor. To seal the high-pressure reactor from the UHV chamber, a fluoroelastomer seal$^1$ is used. In this way, we maintain UHV conditions in the surrounding chamber, even when the reactor pressure reaches 6 bar. The fluoroelastomer limits the temperature of the high-pressure experiment to 600 K. The temperature is measured with a K-type thermocouple, laser spot welded to the side of the sample. In both the sample holder and transfer system, the thermocouple connections include some non-thermocouple material. An extensive calibration was performed with a second true K-type thermocouple. This resulted in an error of all temperatures of less than 1%. Details of this calibration are included in the supplementary information (SI). The sample is heated with a filament placed on the vacuum side of the sample. In addition, the system houses equipment to study the sample with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), and XPS, which we can employ before and after high-pressure exposure of the sample.

The platinum single crystal was polished to the (111) plane within 0.1°, confirmed with Laue diffraction$^2$. After polishing, it was cleaned in the UHV system by Ar$^+$

$^1$Kalrez® 7075 [40]
$^2$Surface Preparation Laboratory [41], Czochralski-grown, purity of 5N
sputtering\(^3\) and annealing both in O\(_2\)\(^3,5\) and in UHV\(^6\). At least 60 to 70 of these cycles were performed before starting the first experiment and around 5 cycles were completed between consecutive experiments. The preparation method was routinely checked with both LEED\(^7\) and AES\(^8\). The LEED pattern showed sharp spots with a \((1\times1)\) periodicity (SI, Fig 3.8), at energies down to 35 eV. In addition, AES showed that the surface was free of contaminants, such as O or C.

Gases were handled with a dedicated gas handling system, previously described in detail [19, 42]. This system allows exposing the surface to a mixture of up to 5 different gases in a wide range of partial pressure ratios and flows. The gases\(^3\) were used without further purification. Unless specified otherwise, all experiments were performed at a total normal flow, i.e., the flow at a pressure of 1 bar, of 10 ml/min with 83.3 % O\(_2\) and 16.7 % Ar.

STM tips were prepared by mechanically cutting a PtIr wire\(^9\). These tips were used without further in situ treatments. STM measurements were performed in constant-current mode using a video-rate STM controller [42, 43]. All images were recorded from top to bottom with the fast scan direction from left to right. Both planar and linear line-by-line background subtractions were employed. In order to emphasize local height variations, several images are presented in differentiated form with the color indicating the local slope measured from left to right. No nonlinear filtering was applied unless stated otherwise. To calibrate the piezoelectric scan element, atomically resolved Au(111)\(^10\) STM images were used. These images were recorded with a closed reactor, with a seal in place at room temperature. This resulted in a calibration with a standard deviation of 1.5 %. Additional inaccuracy could stem from changes in the behavior of the scanner at reaction conditions compared to UHV. However, test observations of Au(111) under reaction conditions suggest that this effect is small.

### 2.3 Results

#### 2.3.1 Exposure to 1.0 bar O\(_2\) at 530–540 K

**Network of islands**

Figure 2.1a shows an STM image of the freshly prepared Pt(111) surface, in the reactor with the seal in place, at room temperature, prior to high-temperature O\(_2\) exposure. It demonstrates that we started with a flat surface with wide terraces of typically between 10 nm and 120 nm. In addition, the steps were generally straight with only very few pinning sites. In the STM image, some slightly brighter spots

\(^{3}\)O\(_2\): Praxair 5.0N and CK 4.5N and Ar: Linde 6.0N, Westfalen 5.0N, and Praxair 5.0N
\(^{4}\)≈20 minutes, beam energy of 1.0 keV, and sample current of 3–4 µA
\(^{5}\)≈2 minutes at 948 K in 1×10\(^{-7}\) mbar O\(_2\)
\(^{6}\)at 1130 K for ~10 minutes; last cycle at 1129 K
\(^{7}\)Omicron SPECTALEED, 4 grid
\(^{8}\)Omicron SPECTALEED, retarding-field analyser
\(^{9}\)Goodfellow, Pt/Ir ratios of 90/10 or 80/20, \(\varnothing = 0.25\) mm
\(^{10}\)Surface Preparation Laboratory [41], polishing accuracy of ~0.1°, Czochralski-grown, purity of 5N
2.3. Results

Figure 2.1: Two STM images showing the change in large-scale morphology upon high-pressure O₂ exposure. (a), freshly prepared Pt(111) surface in the reactor in high vacuum at room temperature (382×386 nm², U₉ = 0.25 V, I₉ = −0.07 nA, t₉ = 71 s). (b), stable, oxidized surface at 1.0 bar O₂ and 531 K after 43 minutes exposure (94×92 nm², U₉ = 0.04 V, I₉ = −1.08 nA, t₉ = 35 s). Nonlinear filtering was applied to remove artefacts due to vibrational interference of the microscope.

were visible. The nature of these spots was unknown but we assumed that they originated from the residual gas that the surface was exposed to in the reactor, prior to high-pressure gas exposure. In this initial part of the experiment, the reactor volume was connected to the vacuum of the surrounding UHV chamber via a set of narrow pumping lines. In general, the spots disappeared when the O₂ flow was started.

Upon admission of the high-pressure O₂ atmosphere, the surface immediately started to change. This phase was very dynamic and contained rapidly changing structures. These will be discussed later, after we focus on the stable structure. This dynamical phase lasted around 30–50 minutes, after which the surface adopted a large-scale stable configuration. A typical example of this configuration is visualized in Figure 2.1b. This in situ STM image exhibits a monoatomic step from the top left corner to the middle of the bottom edge. The step height equaled 0.22±0.04 nm as measured on four separate height profiles. Although the error bar was large, it agreed very well with a monoatomic step of Pt(111) of 0.23 nm. Hence, the imaged surface consisted of two levels of terraces. Within each terrace, the surface showed a complicated network of worm-shaped islands.

The islands divided each terrace in two levels. Figure 2.1b suggests that the top level of the lower terrace was at the same height as the lower level of the upper terrace. In other words, the image seems to indicate that the island structure divided each terrace over two height levels of the Pt(111) surface.

To further substantiate this notion, we quantified the depth of the valleys in between the islands. The measured depths were most reliable for the widest valleys. This
was because the macroscopic tip could not penetrate the narrowest valleys if their width was smaller than the tip apex. The depth was analyzed for several line profiles and a value of \(0.21 \pm 0.02\) nm was obtained and agreed well with a monoatomic step. Therefore, we conclude that solid, flat terraces transformed into networks of monoatomic-high, worm-shaped islands upon \(O_2\) exposure. Through the valleys, the lower lying terrace became visible. This resulted in a two-level terrace structure.

**Spoked-wheels structure**

Parallel to the formation of the large-scale structure, both the islands and the valleys in between developed an extended pattern of triangles. These structures were not observed directly after the onset of the exposure. The first triangles were observed after a time period of 17–33 minutes, which was on the same time scale as needed to form the stable worm-shaped island network discussed in the previous section. During this period, the dynamics of the surface was too prominent to obtain atomic resolution.

The triangles formed a close-packed network resulting in a ‘spoked-wheel’ superstructure. This structure is presented in Figure 2.2. In the left panels of this figure, the background-subtracted height images are given. In addition, the right panels show differentiated versions of the same images, in order to highlight the atomic contrast more strongly.

These images show that the spoked-wheel structure extended over tens of nanometers covering multiple islands. Figures 2.2a and 2.2a’ show the spoked-wheel structures in one island. The island slowly moved to the bottom left due to thermal drift. In Figures 2.2b and 2.2b’, a second island is visible. The third STM image (Figures 2.2c and 2.2c’) shows the atomic resolution on the second island. More interestingly, it shows that the spoked-wheel structure continued in the valleys between these islands. This can be clearly seen when the differentiated STM image is compared to the linearly corrected STM image. The former shows a continuing network of spoked wheels in a large region of the surface. The latter, nondifferentiated STM image, clearly showed that this network spanned (part of) two islands and the void in between.

An intrinsic determination of the in-plane drift velocity was established by studying the triangle angles. These angles should all be 60° for equilateral triangles. The assumption that the observed structure formed equilateral triangles was justified by the three-fold nature of the surface and the fact that different rotational domains were not observed. After drift correction, the length of the spokes was found to be \(2.2 \pm 0.1\) nm. This length corresponded to \(7.9 \pm 0.4\) Pt(111) lattice constants.

Interestingly, the highest atomic contrast was obtained for very small bias voltages of \(\sim 50\) mV. Several images, such as Figures 2.2c’ and 2.3c show clear atomic resolution within the rows. The interatomic distance in the spokes was quantified by exclusively analyzing the spokes parallel to the fast scan direction. Measurements in this direction should hardly be affected by in-plane drift [44]. Consequently, they should also hardly depend on the quality of drift correction. The measured atomic periodicity in the rows was \(0.30 \pm 0.01\) nm, which was significantly larger than the Pt(111) lattice constant of \(0.28\) nm. The measured value was very close to the lattice constant found for the previously reported surface oxide, which was \(0.31\) nm. Also, it was close to the
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Figure 2.2: STM images (25×25 nm², $U_{\text{bias}} = 0.05$ V, $I_{\text{tunnel}} = -(0.86–0.87)$ nA, $t_{\text{image}} = 8.4$ s) illustrating the formed spoked-wheel structure on the islands and valleys on a single terrace upon exposure to 1.0 bar O$_2$ at 529 K. Field of view was gradually moving to the right of the images due to thermal drift. The white star provides a marker of reference. The STM images are shown with linear background subtraction (a, b, and c) and with a line-by-line differentiated background correction (a', b', and c'). The latter enhances the contrast of the spoked wheels. The exposure times to O$_2$ were around 32–33 minutes. The white rectangle in (a)' shows a small patch of remaining, transient, distorted-hexagonal structure.
Figure 2.3: STM images (line-by-line differentiated) showing the detailed atomic resolution of the spoked-wheel structure. (a), STM image with typical resolution of the surface exposed to 1.0 bar O\textsubscript{2} at 529 K for 33 minutes (25×25 nm\textsuperscript{2}, U\textsubscript{bias} = 0.05 V, I\textsubscript{tunnel} = -0.87 nA, t\textsubscript{image} = 8.4 s). (b), subsequent STM image, in which a switch in the tip state resulted in significantly improved resolution, STM settings as in (a). (c), enlargement of the central region in (b) with adjusted color scale to enhance the atomic contrast.

α-PtO\textsubscript{2} \cite{45–49} and PtO \cite{45, 49, 50} lattice constants of 0.31±0.00 nm.

The atomically resolved STM images revealed that most spokes consisted of 8 atoms including both endpoints, with very few being extended to 9 or more atoms. This suggested that there was a clear preference for this structure to form spokes with a length of 8 atoms, including both endpoints, corresponding to 7 interatomic distances. Given the spoke length of these spokes of 2.2±0.1 nm, this would lead to a periodicity within the row of 0.31±0.01 nm. The measured periodicity matches very well to the previously observed surface oxide \cite{33} and to the bulk oxides, α-PtO\textsubscript{2} and PtO.

The apparent height of the spokes depended on the exact state and/or shape of the tip apex and was found to range from 0.03 nm to 0.11 nm at the same bias voltage of 0.05 V (Table 3.1, SI). Both measurements were taken with the same STM tip, but
between the experiments the tip (gently) crashed into the surface, which most likely had changed the apex of the tip either in shape or in chemical composition. In addition, when the bias voltage was changed between 0.01 V and 0.10 V (in the same experiment), a small variation was observed. In these measurements, the apparent height changed from 0.10 nm for 0.01 V to 0.12 nm for 0.10 V, but this variation was less than the standard deviation on these measurements (0.03–0.06 nm). In all cases, the measured apparent heights were much smaller than the Pt(111) monoatomic-step height.

**2.3. Results**

**Transient, distorted-hexagonal structure**

Before a stable, extended area of spoked wheels was formed, the surface was dynamic and transient structures were observed. This stage is summarized in Figure 2.4a, which shows a high-resolution STM image of typical transient structures. In this STM image, several triangles could be noticed in a few locations and they were starting to form spoked wheels. In addition to these emerging spoked wheels, a row-like structure could be distinguished. This structure, in fact, showed a hexagonal-like symmetry in the highest resolution regions of the image (see regions close to the arrows, Figure 2.4a).

A perfect hexagonal lattice can appear as rows in one of the directions of the lattice due to a minor asymmetry in the tip apex, i.e., the STM tip is not as sharp in one of the directions as in the other two. This asymmetry results in a somewhat poorer resolution and the image appears to have rows in that direction. However, in Figure 2.4 this was definitely not the case, since the upper region of the STM image showed three rotational domains (blue, black, and green arrows, Figure 2.4a) within single scan lines. For this to be an STM tip artefact, the STM tip should have changed its apex several times per scan line at more or less the same positions. This seems highly unlikely since the STM conditions were such that very stable STM feedback was obtained in this part of the experiment.

There is a second explanation for the observation of these rows, which requires anisotropy in the observed lattice, i.e., different lattice constants in different directions. If these lattice constants are in the order of the best attainable resolution of a particular STM tip, then the direction of the smallest lattice constant is not resolved completely and the structure appears as rows. This occurs even with a perfectly symmetric STM tip. This means that the observed lattice (Figure 2.4a) had, in fact, a distorted-hexagonal structure, in which the lattice was expanded perpendicular to the rows. The three rotational domains were all distinguished in Figure 2.4a (blue, black, and green arrows).

The distorted-hexagonal structure was characterized by studying the fast Fourier transform (FFT) of the region indicated by the white square in Figure 2.4a. The FFT image is represented in Figure 2.4b. It clearly shows the distorted-hexagonal pattern. The pattern was compressed along the white line indicated in Figure 2.4b. This compression in reciprocal space is equivalent with an extension in real space. The other rotational domains showed similar but rotated patterns. Therefore, the distortion could not be explained by thermal drift, because that would have affected all regions equally as they were imaged in the same time interval.

Figure 2.4a shows atomic resolution both perpendicular and parallel to the rows.
Figure 2.4: STM image (a) showing the transient structures observed before a stable spoked-wheel structure had developed on a large scale ($25 \times 26$ nm$^2$, $U_{\text{bias}} = 0.05$ V, $I_{\text{tunnel}} = -1.01$ nA, $t_{\text{image}} = 8.4$ s, line-by-line differentiated). Surface was exposed to 1.0 bar O$_2$ at 527 K for 18 minutes. Colored arrows indicate different rotational domains of the distorted-hexagonal structure. (b), fast Fourier transform (FFT) calculated from the region in the white square of (a). The white line indicates the axis of reciprocal-space compression of the hexagonal structure.

The lattice constant within the rows was determined by measuring the corresponding spots in the FFT image (Figure 2.4b). A lattice constant of $0.30 \pm 0.01$ nm was found, which corresponded well to the in-spoke lattice parameter of the spoked-wheel structure, the previously observed surface oxide [33], and the lattice constant of $\alpha$-PtO$_2$ [45–49] and PtO [45, 49, 50]. The average distance between the rows was determined directly from height profiles across several rotational domains. A value of $0.37 \pm 0.04$ nm was found, which was midway between 0.24 nm and 0.48 nm ($\frac{1}{2} \sqrt{3}$ and $\sqrt{3}$ times the Pt(111) lattice constant). So, the distorted-hexagonal structure was nonepitaxial with respect to the Pt(111) lattice, perpendicular to the rows.

Minute patches of this structure remained present in the stable spoked-wheel structure. This can be seen in the region indicated by the white rectangle in Figure 2.2a’. The STM image quality was not good enough to resolve the atomic structure within the rows, but the distances between the rows matched that of the distorted-hexagonal structure.
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Under the high-pressure O_2 conditions, the spoked-wheel oxide formed large domains all across the surface. However, the formed structures were not perfect and contained many defects. Some of these defects occurred only during growth, while others persisted in the stable structures. These defects can be seen in Figures 2.2 and 2.3.

The presence of these defects became clear when the FFT of Figure 2.3b was compared to the FFT calculated for a perfect spoked-wheel pattern (inset of Figure 2.5b). These FFTs are depicted in Figure 2.5a and b, respectively. The FFT of the perfect spoked-wheel structure (Figure 2.5b) was a 30° rotated spoked-wheel pattern. The spokes were comprised of individual higher order spots reflecting the distance between parallel spokes. These spots were also clearly visible in the experimentally obtained pattern (Figure 2.5a). However, the experimental spots were elongated in the vertical direction.

This vertical streakiness indicated that the structure of Figure 2.3b exhibited a translational defect that divided the pattern in two translational domains. This is visualized in Figure 2.5c in which a calculated FFT is depicted of a spoked-wheel pattern containing a horizontal translational defect. More specifically, one diagonal (top left to bottom right, Figure 2.5c) was streaked symmetrically while the other (top right to bottom left, Figure 2.5c) was asymmetrically elongated alternating in top and down direction. This asymmetric behavior was also visible in the experimental FFT. Evidence of these translational defects was also frequently observed in STM, which can be clearly seen in the detailed STM image depicted in Figure 2.6a and the corresponding model (Figure 2.6a’).

In addition to translational defects, also other structural defects were observed. Most prominently, the incorporation of several smaller triangles in the structure. This is illustrated by Figure 2.6b. This figure shows that smaller triangles clustered. These clusters need to occupy the same space as an integer number of regular triangle(s) in order for the structure to remain close packed without voids. The smaller triangles had a minimal edge length of 1.3 nm or 4–5 Pt(111)-lattice constants.

A third class of defects was the doubling or tripling of spokes. Similar defects were
Figure 2.6: STM images with models showing various structural defects (depicted by red lines), such as translational defects (a and a'), incorporation of smaller triangles (b and b'), and doubling and missing of spokes (c and c'). All STM images were obtained at $p_{O_2} = 1 \text{ bar}$ and $T = 529 \text{ K}$, $U_{\text{bias}} = 0.05 \text{ V}$, $I_{\text{tunnel}} = -(0.89-0.98) \text{ nA}$, and the exposure times were 31, 33, and 18 minutes, respectively. The STM images are shown after line-by-line differentiation. (c) was rotated by 31° to correct for a different scan orientation and to match other STM images.
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reported by Devarajan et al. [33] and Weaver [51] for the previously reported surface oxides. However, confirming the existence of multiple spokes is rather difficult by STM. The images can be heavily distorted when the tip does not end in a single apex. In this case, the STM image appears as an overlap of multiple translated images and double or triple spokes could be the result. Generally, double spokes were not frequently occurring in stable structures. In the early stages of growth, this defect was commonly observed. One example is presented in Figure 2.6c. In this case, an STM tip artefact could be excluded. This was because doubling of spokes was observed in all three directions, but not all spokes were doubled, which would be expected when a multiple tip was used for the imaging. This image also illustrates that doubling of spokes usually concurred with missing spokes.

The separation between the spokes in Figure 2.6c was equal to 0.38±0.03 nm. The error bar was rather high but not related to the thermal drift, which was estimated by following large-scale morphology movement and was, at its maximum, 1 % of the image dimensions. The calculated separation was almost equal to the row-to-row distance of the transient, distorted-hexagonal structure discussed in the previous subsection.

2.3.2 Increasing O\textsubscript{2} pressure

After a stable spoked-wheel structure was formed at a pressure of 1.0 bar and at 530–540 K, the O\textsubscript{2} chemical potential was increased by stepwise raising the O\textsubscript{2} partial pressure up to 5.0 bar. Starting at an O\textsubscript{2} pressure of 2.22 bar, a new structure was observed. An STM image showing this structure is shown in Figure 2.7. The image shows a pattern of parallel rows. This structure, that we will refer to as a lifted-row structure (see Section 2.4.1), was different from the transient, distorted-hexagonal structure discussed in section 2.3.1. It differed in two important ways, namely, it was a stable structure and the average distance between the lifted rows was much larger than the rows of the distorted, hexagonal structure (vide infra).

It is very important to note that at all the experimentally probed O\textsubscript{2} pressures, the spoked-wheel structure was still observed. The domains of both the spoked-wheel and lifted-row structures were rather large and estimated to be above hundred nanometer. A region several times larger than this should be analyzed to determine a statically relevant surface coverage ratio of the two structures. The large domains together with the local character of STM made determination of this ratio experimentally infeasible. Further complicating was the fact that this ratio could have been time dependent. Therefore, we cannot state anything about the surface coverage ratio of these structures nor its evolution over time.

Considering the symmetry of the lifted-row structure and that of the (111) surface, three translational domains should experimentally be observable. Different rotational domains were indeed observed in this experiment. The size of the translational domains was estimated to be in the same order as the domain size of the lifted-row structure in the mixture of lifted rows and spoked wheels. This was concluded from the absence of rotational domain boundaries.

Quantification of the thermal drift was much harder for those STM images that showed only the lifted-row structure. In these images, there was no possibility to
Figure 2.7: STM image in which the lifted-row structure was clearly visible, recorded at 535 K, 3.8 bar O\textsubscript{2}, and 98 minutes in the experiment, while increasing the total pressure from 2.7 to 6.0 bar (35×27 nm\textsuperscript{2}, U\textsubscript{bias} = 0.05 V, I\textsubscript{tunnel} = -1.03 nA, t\textsubscript{image} = 15.0 s). The image is shown after drift correction and some nonlinear filtering to remove a few horizontal scan vibrations.

inherently determine the drift by the distortion of shapes with precise features, such as with the equilateral triangles of the spoked-wheel structure. In the lifted-row structure, the only atomic features consisted of parallel rows and without a priori knowledge about the row-to-row distance, drift vectors could not be determined. Instead, monoatomic steps were used to access the thermal drift velocity and a first inspection showed that thermal drift was strong in these images. A drift correction was performed based on the best overlap between consecutive images. This resulted in the elongated and sheared representation of Figure 2.7. The thermal drift was at its maximum around 30 % of the image dimensions with both the magnitude and direction changing between images.
Although the overlap was carefully optimized, it could not be guaranteed that this led to perfect drift correction, since the global morphology mainly had a one-dimensional character and because the STM images contained considerable dynamics.

After drift correction, the row-to-row distance was determined to be 0.46±0.01 nm, while it was 0.44±0.01 nm before the correction. Both these values are close to \( \sqrt{3} \times \) the Pt lattice constant, which equals 0.48 nm. The measured row-to-row distance is commensurate with the Pt(111) substrate and it is significantly larger than the distance between the rows of the transient, distorted-hexagonal structure (0.37±0.04 nm, Section 2.3.1).

Within the rows, the STM image of Figure 2.7 revealed weak atomic features. However, these were not ordered enough to determine a reliable lattice constant. Therefore, we derived at a (hexagonal) unit cell of \((2 \times n)^{11}\). If we would assume that the rows have a similar lattice constant as the spokes of the spoked-wheel structure, \(n\) would be equal to 8. The measured height corrugation across these rows was very modest with an average value of 0.03±0.01 nm, which was in the order of a tenth of a monoatomic Pt step. Interpretation of this value requires caution as both the shape of the tip and electronic states of the tip and sample could strongly influence the measured heights.

Two translational domains should be observable, which are translated by \(\frac{1}{2} \sqrt{3}\) times the Pt(111) lattice constant. In other words, either the odd or the even row in a \((2 \times 8)\) unit cell can be lifted. These domains were both observed and they are indicated by the cyan and light green lines in Figure 2.8a’, which is an annotated replica of Figure 2.8a. The dashed lines in Figure 2.8a’ correspond to rows that were missing. In two cases, those missing lines were defects within a translational domain, while the third one was a boundary between two translational domains. Because the row was missing, this boundary was identified as a light domain wall. In addition, two point defects were observed, in which a single row switched domain.

### 2.4 Discussion

#### 2.4.1 Observed surface oxides

**Spoked-wheel oxide**

The structure observed between 1 and 5 bar O\(_2\) consisted of closed-packed triangles, which led to the formation of a spoked-wheel superstructure. The building blocks of these triangles, i.e., the edges or spokes, consisted of Pt atoms that were expanded with respect to the metallic Pt lattice constant (0.30 ± 0.1 nm vs. 0.28 nm). This expanded lattice constant matched very well to the experimentally determined lattice constants of \(\alpha\)-PtO\(_2\) \([45–49]\) and PtO \([45, 49, 50]\) of 0.31 ± 0.00 nm. This was supported by density functional theory (DFT), calculating values of 0.32±0.00 nm \([52–56]\) and 0.31±0.00 nm \([54, 55, 57]\), respectively. Furthermore, \(\beta\)-PtO\(_2\) contains Pt atoms with similar separation \([58]\). Based on this agreement, we believe that the best way to describe this structure is as a surface oxide comprised of 1D oxide rows. This

\[\frac{\sqrt{3}}{\sin(60^\circ)} = 2\]

\(^{11}\sqrt{3}/\sin(60^\circ) = 2\]
Figure 2.8: Two replicas of a zoom-in of an STM image of the Pt(111) surface exposed to 3.7 bar O\textsubscript{2} at 535 K and 98 minutes in the experiment, while increasing the total pressure from 2.7 to 6.0 bar. In this region, the lifted-row structure covered the surface. The lines indicated in (b) showed several interesting features, missing rows, a light domain wall, and point defects. (8×25 nm\textsuperscript{2}, U\textsubscript{bias} = 0.05 V, I\textsubscript{tunnel} = −1.02 nA, t\textsubscript{image} = 4.7 s). The image is shown without drift correction but with a modest amount of nonlinear filtering to remove a few horizontal scan vibrations.

description was supported by the XPS measurements that will be discussed in more detail in the next chapter. In short, in these experiments, the Pt(111) sample was removed from the high-pressure reactor after O\textsubscript{2} exposure and transported in UHV to the XPS chamber. The spectra showed a shift of the O 1s peak to 530.7 eV. This value was in the range of oxidized Pt and, more specifically, it matched very well to the surface oxides on Pt(110) [59] and Pt(531) [60]. The observed expansion suggested that Pt-Pt bonds were broken to accommodate more O atoms [33, 61]. Unfortunately, we had no direct evidence on the Pt oxidation state, so that this classification relies strongly on the comparison to related structures.

The spoked-wheel superstructure was never identified before at the low pressures of most other oxidation studies on Pt(111). It was also not predicted by theory. Nevertheless, related surface oxides were found earlier that consist of 1D oxide chains. These structures were all obtained in an artificial way, by oxidation with stronger oxidants. On Pt(111), one of these structures resembled the spoked-wheel structure and was formed by exposing the surface to a beam of atomic O [51]. Another structure was observed after exposing the Pt(111) surface to NO\textsubscript{2} at 450 K in vacuum [33]. The chains in this structure had a similar length (1.9–2.4 nm in Reference 33 vs.
2.2±0.1 nm in this work), but were forming “Y”-shaped structures that were assembling in honeycombs at a higher coverage. This honeycomb oxide can be thought of as a spoked-wheel superstructure without the inner spokes. On Pt(110), it was observed that the rows of the (1×2) reconstruction adopt an oxide-chain configuration with a (12×2)-22O unit cell [53, 62]. In both cases, the structures were formed from expanded Pt chains, although the structure on Pt(110) was described both as a chemisorption structure [59, 62] and as a surface oxide [53, 63].

In addition to flat surfaces, there was some experimental evidence that stepped surfaces also formed structures similar to the 1D oxide chains along the ⟨110⟩ steps of the close-packed, {111}-facet type [64, 65]. The experiments in these papers relied heavily on DFT calculations to confirm the presence of the 1D structures. For the 1D oxides along the steps, a lattice expansion was not considered in the calculations and it is not certain that it was present.

STM images with the highest resolution (Figure 2.3) revealed that most spokes were 7 atoms in length, which resulted in a length of 2.1±0.1 nm given the expanded lattice constant. This value was close to the spoke length of 2.2±0.1 nm derived from the FFT analysis. This spoke length corresponded to 7.9±0.4 lattice constants and, as a consequence, the structure had an (8×8) unit cell with the distance between the Pt atoms in the oxide rows showing an expansion close to $\frac{8}{7}$.

Figure 2.9a shows a ball model of the spoked-wheel oxide. In this model, the spoked wheels are not formed on top of the surface layer but within, from where the 1D oxide rows are lifted. This conjecture is based on the measured height corrugation, which was well below the monoatomic Pt(111) step and is consistent with previous experiments [33] and DFT calculations [61, 66, 67].

In this model (and the following ones), the positions of the O atoms are based on an educated guess, as we had no direct observations of the O atoms in our experiments. The O atoms in the chain are forming square planar units with a single Pt atom in the middle. This geometry is based on the DFT calculations by Hawkins et al. [61]. These oxide rows have a chemical composition equal to PtO₂ and hence they were described as PtO₂ stripes, rows, or chains [61, 63, 66, 68]. Structurally, however, they share no resemblance with the hexagonal $\alpha$-PtO₂. Instead, they are closely related to PtO and Pt₃O₄ with which they share the square planar PtO₄ motifs. Therefore, the 1D oxide rows should be considered as an intermediate oxidic phase [33].

The model shows a p(2×1)-O chemisorption phase inside the triangles, based on the observation of Derajavan et al. [33]. They showed that p(2×1)-O chemisorbed O filled the inner regions of the honeycombs. The O coordination of the Pt atoms in the corners of the triangles is more unclear as for this neither experimental nor theoretical evidence is available.

After having made these assumptions on the configuration of the O atoms, we derive an O coverage of 0.75 ML (see SI). This is 0.5 ML more than the (2×2)-O chemisorption structure, which is generally accepted to be the highest coverage obtainable with O₂ in UHV [30, 31, 69–71]. It is also higher than the O coverage of the honeycomb oxide of 0.60 ML (see SI). Although the honeycomb oxide resembles the spoked-wheel structure, our experiments showed that UHV oxidation with stronger oxidants is not guaranteed
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to yield the same structure that is relevant at high pressure and temperature, although similar structures might be formed under the appropriate growth conditions [51].

The formation of the spoked-wheel oxide (and of the lifted-row oxide) resulted in large-scale restructuring of the surface. This roughening is illustrated in Figure 2.1b. The roughening led to a network of worm-shaped islands, dividing every terrace in two levels separated by monoatomic Pt(111) steps. We interpret this large-scale roughening as the consequence of the stress exerted by the surface oxides on the surface. This stress was relieved by forming the two-layer network.

Lifted-row oxide

At higher O$_2$ pressure, domains of the spoked-wheel oxide were observed coexisting with domains of the lifted-row structure. Although the atomic resolution within the rows was not good enough to measure a reliable lattice constant, we assume that the structure consisted of the same 1D oxide rows, making this a lifted-row oxide. The structure of this surface oxide was proposed previously, based on DFT calculations [61]. The same model was used to fit X-ray absorption spectroscopy (XAS) data after exposing the Pt(111) surface to a near-ambient O$_2$ pressure [39]. However, the effect of an expanded lattice constant was mentioned but neither evaluated in the XAS fitting nor in the DFT calculations. Two examples of the structural model that we propose with the 1D lattice expansion are depicted in Figure 2.9b. Due to the expansion within the rows, there are eight non-equivalent ways for the row to be positioned, along its own length direction. We can formally translate this into eight possible ‘phases’ for each row, which we will indicate by $n \times \frac{1}{8}$, with $n$ running from 0 to 7.

The phases of neighboring rows can show order, such as the two examples in Figure 2.9b or they can be disordered. In the first, the lifted rows are ‘in phase’ ($\Delta n = 0$), which minimizes the O-O separation between adjacent stripes and is expected for attractive O-O interaction. The O-O separation is at its maximum for the second example, in which the phases between adjoining rows are shifted with half a period ($\Delta n = 4$). The latter example is more plausible for repulsive O-O interactions. The unit cells for these two configurations are (2×8) and c(4×8), respectively.

The experimental findings excluded the possible formation of structures, recently proposed on the basis of DFT calculations, such as the hybrid buckled/place-exchanged structure [66] and the (4×1) lifted-row structures enhanced with subsurface O [67]. These structures were found to be lower in energy than the (2×1) lifted-row structure proposed by Hawkins et al. [61]. The relative instability of the lifted-row structure in these calculations could be due to the neglect of the expansion of the Pt oxide rows. This expansion could lower both the repulsive interaction along each row and between adjacent rows.

The chemical composition of the complete top layer of the lifted-row model is equal to PtO. Although the literature on PtO is scarce and slightly controversial, PtO was found as a (meta)stable phase [45, 49, 50, 72–79] and, if crystalline, formed a tetragonal cooperite (PtS) structure [49]. Because PtO is isostructural to PdO [45, 50],
it is insightful to mention the PdO(101)-like\textsuperscript{12} surface oxide on Pd(100) \cite{80, 81}, which bears close structural resemblance to the model in Figure 2.9b. Interestingly, it is this (101) surface that was the most dominant in sputtered, thin PtO films \cite{73}. This makes it very plausible that also a PtO(101) layer could form on an unreconstructed Pt(100) surface under oxidizing conditions.

Of the lifted-row oxide, different rotational domains were observed, caused by breaking of the three-fold symmetry of the (111) surface. The size of the rotational domains was on the same order as the size of the lifted-row oxide domains in the mixture of the two surface oxides. In addition, two translational domains exist of this model, which are translated by $\frac{1}{2}\sqrt{3}a$ in the direction perpendicular to the rows. In other words, every even or odd row can be lifted. These translational domains can result in two types of domain boundaries, a light domain wall with a missing lifted row and a heavy domain wall, in which two adjacent rows are lifted. Only the light domain wall was observed.

In the preceding discussion, we implicitly assumed that the lifted-row oxide consisted of half of the atoms in the surface layer lifted to create these rows. However, a similar structure could be formed by either removing half of the surface atom rows, which is equivalent to adding rows on top of the surface. As for the spoked-wheel oxide, we had no conclusive evidence to make a distinction between removing/adding rows versus lifting rows. Based on the significantly smaller height difference observed in STM and supported by DFT calculations \cite{61, 66, 67}, we conjecture that the observed rows were lifted, but not added on top of the surface plane. The corresponding O coverage of the lifted-row oxide is 0.88 ML (see SI), 0.13 ML more than the spoked-wheel oxide.

The lifted-row oxide was only formed at higher O\textsubscript{2} pressure. This observation indicated that it is only thermodynamically stable if the chemical potential of O\textsubscript{2} in the gas phase is high enough to populate unfavorable adsorption sites with respect to the spoked-wheel oxide. In addition, it is likely that the increase in O coverage induced even more stress on the surface. This increased stress is completely anisotropic due to the breaking of symmetry of the lifted-row oxide in the Pt(111) surface, even leading to faceting, as observed in Figure 3.2d.

In both the spoked-wheel and the lifted-row model, any subsurface oxygen was disregarded. This was simply due to the fact that our STM experiment can neither confirm nor disprove its presence. The same holds for our XPS measurements (see next chapter). Although they seemed to suggest a single O 1s state, it is possible that there were unresolved O states. Drawing conclusions from the XPS measurements, is in particular difficult because there is no consistency in the literature with respect to the binding energy of subsurface O. Values for the binding energy are scarce and scattered: ranging from 528.5 to 531 eV \cite{82–87} for Ag and Pd.

Oxygen penetration to subsurface sites has shown to be kinetically feasible at these temperatures \cite{88}. Subsurface sites below the lifted Pt oxide rows could be energetically accessible \cite{67}. This could function as an important step between the formation of surface and bulk oxides.

The O coverage estimate derived from XPS (see next chapter) was 0.88 ML. This suggested that at these conditions (1.0 bar O\textsubscript{2} and 441–444 K), the surface was

\textsuperscript{12}with a $(\sqrt{5} \times \sqrt{5})R27^\circ$ unit cell
covered by a single layer of surface oxide. The estimated error bar of this value was estimated to be around 0.1 ML based on fitting results. It suggested that a mixture of spoked-wheel and lifted-row oxides was present on the surface. However, that coverage estimate (see next chapter) was a lower estimate due to the instability of the structure under vacuum conditions.

An interesting feature of Figure 2.7 can be observed when inspecting the larger scale morphology of the surface. This morphology showed an alternating pattern of higher and lower lying stripes from the top left to lower right of the image. The period of these alternating stripes was 3.7±0.4 nm, with the lower and upper-lying stripes being almost equal of width. Furthermore, the image revealed that both the higher and the lower lying stripes exhibited the same characteristic row pattern. The height difference between the two levels was determined to be 0.04±0.01 nm. Although this height difference was small, we speculate that the two stripes are small terraces at two different height levels, separated by a monoatomic step. This structure can be regarded analogous as to the two-level-islands structure discussed (vide supra) for the spoked-wheel structure. The origin of these structures could also be similar, i.e., a mechanism to reduce the stress on the surface induced by the formation of these oxygen-rich structures. The low height variation could be explained by an STM tip with a very large radius of curvature that was not able to correctly image the lower lying stripes. This tip should have one atom partially protruding, with which the lifted rows were sharply imaged. The large apex radius of the STM tip was supported by the height of the step separating the top right from the middle region of the STM image (Figure 2.7). This step was 0.15±0.02 nm, which was much smaller than the monoatomic step height of 0.23 nm even though this terrace was relatively wide, around 6 nm. Alternatively, it could be possible that stress relaxation created a pattern of alternating low and high regions with a height difference much smaller than an atomic step.

**Transient, distorted-hexagonal structure**

The reported transient structure showed a distorted-hexagonal lattice. In one direction, it was expanded with respect to the Pt(111) lattice, matching the lattice of α-PtO$_2$ very well. Perpendicular, a lattice constant of 0.37±0.04 nm was found. The Pt content of this structure was around $0.28 \times 0.28 \approx 0.70$ compared to a Pt(111) ML. We had no information on the position and number of O atoms in this structure. If we would assume a PtO$_2$ composition, we would derive an O coverage of around 1.4 ML. This would be higher than the O coverage of the stable surface oxides. This higher O content of the transient structure with respect to the stable surface oxides seems counterintuitive, since it would exceed the O coverage that the surface acquired at even higher O$_2$ pressures. The structure could also have had a chemical composition similar to one of the other Pt oxides, such as Pt$_3$O$_4$, [48, 76, 89–91], Pt$_2$O [92], or Pt$_5$O$_6$ [76, 90]. In view of these uncertainties, we will not speculate further on the O content of this structure. Furthermore, it remains unclear why this structure was anisotropically expanded, but it could be related to stress relief. After initial relaxation in one direction, the resulting stress might be too low to induce similar relaxation in the other two directions.
Figure 2.9: Proposed ball models of the surface oxides observed on Pt(111) with in situ STM at high pressure and temperature. Model (a) shows the spoked-wheel oxide: the spokes consist of expanded rows of Pt atoms (light blue) that are lifted with respect to the other surface atoms (dark blue). In this model, the O (red) positions were taken similarly to those proposed for other row structures [33, 61]. The spoked wheel's inner region is covered with a p(1×2)-O chemisorption structure. This structure can be described by an (8×8) unit cell, indicated by the dashed white line. Model (b) gives two examples of the lifted-row oxide in which the O atoms are ordered differently. The left side of (b) depicts the case where all lifted rows are in phase. This results in straight lines of O atoms and the smallest O-O separation, left side of (b). In the right side of (b), the largest O-O separation is obtained due to shifting of adjacent rows by half a period. These structures have a (2×8) and c(4×8) unit cell, respectively. The radii of the balls are based on the atomic radii of Pt and O.

2.5 Summary

We studied the oxidation of the Pt(111) surface in situ with STM at conditions relevant for catalysis, i.e., at an O$_2$ pressure of 1–5 bar and between 291–535 K. Our main findings are summarized as follows:

1. Two different surface oxides were identified. The first one was stable at all probed O$_2$ pressures and consisted of expanded Pt oxide stripes that assembled into triangles showing a spoked-wheel superstructure. In the proposed model, the chemical composition of this surface oxide was different from the known Pt bulk oxides. The second surface oxide was observed above 2.2 bar and showed a pattern of rows with a row-to-row distance close to $\sqrt{3}a$. We propose that it was formed from the same expanded Pt oxide rows, forming a lifted-row oxide with, most probably, a unit cell of c(4×8). The chemical composition of the top layer was PtO and structurally it resembled the PdO(101) surface oxide formed on Pd(100).

2. Parallel to the formation of these surface oxides, the surface roughened on larger length scale. This roughness was different for both surface oxides. The spoked-wheel oxide induced the formation of a two-level network of worm-shaped islands, while the lifted-row oxides produced an anisotropic surface with facets running parallel to the lifted rows.
3. Under these conditions, $\alpha$-PtO$_2$ was not observed. The formation of the bulk oxide could be kinetically hindered under the experimental conditions, stabilizing the surface oxides. Alternatively, the surface oxides could also be thermodynamically stable phases.
Chapter 3

Oxidation of Pt(111), the effect of temperature and pressure studied with STM and XPS
3.1 Introduction

In the previous chapter, I presented high-pressure STM experiments that showed two different surface oxides that formed while the Pt(111) surface was exposed to high-pressure (1–5 bar) and high-temperature (437–538 K) conditions. The spoked-wheel oxide was stable from 1 to 5 bar, while the lifted-row oxide was only observed above \(~2\) bar.

In this chapter, several supporting experiments will be discussed that deepen the insight into these surface oxides. All these experiments started similar to the experiments described in the previous chapter: a well-prepared Pt(111) surface was exposed to high pressure in the reactor also holding the STM. During this exposure, the surface was inspected with STM. In the first experiments, I have explored the influence of the kinetics on these oxides by exposing the Pt(111) surface to similar conditions but at lower temperatures, between room temperature and \(~320\) K. These experiments show that similar structural features were formed, but without being ordered on a large scale.

A second set of experiments essentially started after the surface oxide was formed on the Pt(111) surface in the reactor cell. After high-pressure, high-temperature exposure, the vacuum stability was tested by evacuating the reactor. The results indicated that the spoked-wheel and lifted-row structures were not stable without the presence of the high \(\text{O}_2\) pressure. After evacuation, a lower estimate of the \(\text{O}\) coverage under high-pressure conditions was determined with XPS performed under UHV conditions. This estimate was 0.88 ML, which agreed well with the formation of a single layer, surface oxide as presented in the model in Chapter 2.

3.2 Experimental

The in situ STM experiments were very similar in approach to those described in the previous chapter. The high-pressure STM experiments were performed in the ReactorSTM. Details about this system were described in Chapter 2. Also for the experimental details of the sample preparation, the used gases, and the STM experiments, the reader is referred to Chapter 2. In the first set of experiments, the Pt(111) surface was exposed to high pressure of \(\text{O}_2\), but at lower temperature. The experiments probing the vacuum stability were performed in the ReactorSTM after forming the surface oxide under high pressure and high temperature by evacuating the reactor. These experiments were concluded with UHV XPS measurements. The XPS measurements were repeated at various temperatures to study the temperature stability of the formed surface oxides. All XP spectra were collected in UHV, but without exposing the sample to air. We used Al K\(\alpha\) radiation\(^1\), for which we operated the anode at a potential of 14.1 kV. Emitted photoelectrons were detected with a hemispherical analyzer\(^2\) equipped with a collimator aperture to bring the spot size down to \(~8\) mm. The detector was operated with a slit size of 4.0 mm and the electrostatic lenses at 3:1 mode, reducing the spot size further to \(~1.3\) mm. The sample was facing the detector, with the X-ray beam impinging under an angle of 55\(^\circ\) with respect to the surface normal.

\(^1\)VG XR3E2, non-monochromatic  
\(^2\)VG Clam2/IVU, 100 mm radius
To ensure that the inspected area coincided with that exposed in the reactor, the ring-shaped imprint of the fluoroelastomer was used, on which a strong F peak could be discerned. Importantly, the center of the sample did not show any F contamination before or after the high-pressure experiments.

The energy range of interest, around the O 1s and Pt 4p\(^{3/2}\) peaks, was probed with a constant analyzer energy (25 V). The binding energies were calibrated against the known energy of the Pt 4p\(^{3/2}\) peak of 519.5(3) eV [93]. After calibration, the spectra were corrected by subtracting a linear background. The XP peaks were fitted with a Doniach-Šunjić function [94] convoluted with a Gaussian, requiring the following fitting parameters: binding energy, intensity, Lorentzian line width, Gaussian line width, and asymmetry factor. For the temperature-dependent XPS experiments, a simpler procedure was followed, consisting of subtraction of a constant background and normalization to the maximum Pt 4p\(^{3/2}\) intensity. This was followed by fitting the O 1s peaks with a Gaussian function.

### 3.3 Results

#### 3.3.1 Exposure at lower temperature

To investigate the kinetics of the Pt(111) surface oxidation, experiments in the ReactorSTM were repeated at lower temperatures (327–328 K and \(\sim 291\) K) at an O\(_2\) partial pressure of 1.0 bar. These experiments did not lead to large-scale ordered structures. This absence cannot be attributed to a lower resolution, as could have been caused by a blunter tip. The acquired STM images all showed subnanometer features as illustrated in Figure 3.1. These features showed the strongest contrast at very low bias voltages, between 20 and 50 mV, similar to the STM images described in the previous chapter.

Careful inspection revealed that the STM images obtained at lower temperatures at high O\(_2\) pressure have recurring structural motifs. These patterns hinted at the formation of similar structures to those observed at elevated temperature. The predominant structure observed in the STM images (Figure 3.1a) at low-temperature exposure was a pattern of rows. The rows are indicated in the lower right panel of Figure 3.1a (annotated replica of the upper right panel). The periodicity of these rows was 0.49±0.02 nm and matched that of the lifted-row structure observed at high-pressure O\(_2\) exposure, which was 0.46±0.01 nm. Both also corresponded well with \(\sqrt{3}\) times the Pt(111) lattice constant, which is 0.48 nm.

A second observed structure was a triangular unit, the structural element of the spoked wheels, observed in several STM micrographs (Figure 3.1b) at 327–328 K. The small panels of Figure 3.1b show two duplicates of an enlarged region, in which a triangular shape was recognizable. This shape is depicted in blue in the lower right panel. Furthermore, the STM image contained many atomic features of various shapes. These features were true atomic shapes and did not originate from scan vibrations.

Finally, a third returning structure is shown in Figure 3.1c. In this STM image, many isolated clusters could be seen. Several of these clusters were analyzed as indicated in the lower right panel (annotated replica of the upper right panel). The average
Figure 3.1: Several STM images (25×25 nm²), shown together with enlarged regions, measured at 327–328 K at an O₂ pressure of 1.0 bar. Several structural features could be discerned that hinted at the formation of disordered versions of the ordered high-pressure structures found at higher temperatures (Chapter 2): rows (a, 1226 s exposure to O₂, \( U_{\text{bias}} = -0.05 \) V, \( I_{\text{tunnel}} = 0.48 \) nA, \( t_{\text{image}} = 9.9 \) s), triangles (b, 843 s exposure to O₂, \( U_{\text{bias}} = -0.02 \) V, \( I_{\text{tunnel}} = -0.66 \) nA, \( t_{\text{image}} = 8.5 \) s), and clusters (c, 2858 s exposure to O₂, \( U_{\text{bias}} = 0.04 \) V, \( I_{\text{tunnel}} = -1.19 \) nA, \( t_{\text{image}} = 15.5 \) s). Nonlinear filtering was applied to remove some interference. Furthermore, the right panels of (b) have a nonlinear adaptive color scale to enhance contrast.
height between the top of the cluster and its surrounding minima was 0.06±0.02 nm (at a bias of 0.04 V). Although this value was not fully independent of bias voltage, the variations were small and all values were well below the Pt(111)-step height of 0.23 nm (SI, Table 3.2). The average estimated full width at half maximum (FWHM) was 0.32±0.04 nm. The FWHM of these clusters agreed well with the measured lattice constant of the spoked-wheel structure.

### 3.3.2 Evacuation experiments

To test the adsorption strength of the O atoms involved in these structures, we performed a series of experiments in which we evacuated the reactor after having formed the oxygen-rich structures in situ at high O\textsubscript{2} pressures, while the surface was continuously imaged with STM. The decrease in pressure was rapid and the pressure reached the (U)HV-regime within minutes, at which point the STM imaging was resumed. At the same time, heating of the surface was stopped and the sample was allowed to cool down.

The results obtained are summarized in Figure 3.2. The stable structures formed at 1.0 and 5.0 bar O\textsubscript{2} are illustrated by the STM images in Figures 3.2a and c, respectively. In both images the spoked-wheel oxide can be distinguished. In addition, the higher-pressure exposure resulted in a large fraction of the surface covered with the lifted-row structure. After growth, the reactor was evacuated and two representative STM images are shown in Figures 3.2b and d. They show that both well-ordered structures were unstable in the absence of the O\textsubscript{2} atmosphere. However, some hints of the remaining structures could still be distinguished. Some of these vague structures are highlighted in Figure 3.2b'.

### 3.3.3 XPS measurements

**Coverage estimate**

To estimate the O coverage, we performed UHV XPS measurements. The XPS measurements were expected to give a lower estimate for the O coverage, because the oxygen-rich structures were modified somewhat after lowering the O\textsubscript{2} pressure (see Section 3.3.2), which we associate with the desorption (or reaction) of some of the O atoms in these structures.

In order to reliably convert the XPS intensities into O coverages, we used the p(2×2)-O chemisorption structure as reference system. The XP spectrum of this reference structure is shown in Figure 3.3a. It was created by exposing a well-cleaned Pt(111) sample to a total O\textsubscript{2} dose of 400 L (one langmuir, L, is defined as 1×10\textsuperscript{-6} Torr×s) at room temperature. This exposure resulted in a well-known, saturated chemisorption structure. This structure has a (2×2) periodicity and a coverage of 0.25 ML [30, 31, 69–71]. We found the O 1s binding energy at 528.5 eV, which we assigned to chemisorbed O on the metallic Pt(111) surface. This is approximately one eV lower than usually found for chemisorbed O on Pt, as can be seen in Table 3.3, SI. In addition, the table shows that the spread in binding energies, reported in literature, is considerable. This spread could be due to differences in the employed calibration for the binding energy.
Figure 3.2: STM images obtained in situ, while oxidizing the surface (a and c) and after this high-pressure exposure, in high vacuum on a cooling sample (b, b’, d, e). (a), surface mainly covered with spoked wheels, \( p_{O_2} = 1.0 \) bar, \( T_{\text{sample}} = 529 \) K, \( t_{\text{exposure}} = 2715 \) s \((25 \times 25 \text{ nm}^2, U_{\text{bias}}=0.05 \text{ V}, I_{\text{tunnel}}=–2.66 \text{ nA}, t_{\text{image}}=17.8 \text{ s})\). (b), disordered structure, obtained 3436 s after evacuation of (a), \( T_{\text{sample}} = 336 \) K \((25 \times 25 \text{ nm}^2, U_{\text{bias}}=0.05 \text{ V}, I_{\text{tunnel}}=–0.48 \text{ nA}, t_{\text{image}}=17.8 \text{ s})\). (b’) shows the same STM image as (b), highlighting several elements that hint at residues of the spoked-wheel structure. (c), mixture of spoked wheels and lifted rows formed at \( p_{O_2} = 5.0 \) bar, \( T_{\text{sample}} = 538 \) K, \( t_{\text{exposure}} = 9728 \) s \((25 \times 25 \text{ nm}^2, U_{\text{bias}}=0.1 \text{ V}, I_{\text{tunnel}}=–0.95 \text{ nA}, t_{\text{image}}=15.1 \text{ s})\). (d), 2113 s after evacuation of (c), vague row pattern still discernible and many steps following the rows, \( T_{\text{sample}} = 353 \) K \((25 \times 25 \text{ nm}^2, U_{\text{bias}}=0.1 \text{ V}, I_{\text{tunnel}}=–0.71 \text{ nA}, t_{\text{image}}=18.3 \text{ s})\). (e) 4284 s after evacuation of (a), the surface is susceptible to tip-induced restructuring indicated by a changed morphology in the center of the STM image, \( T_{\text{sample}} = 331 \) K \((200 \times 200 \text{ nm}^2, U_{\text{bias}}=–0.03 \text{ V}, I_{\text{tunnel}}=0.26 \text{ nA}, t_{\text{image}}=75.8 \text{ s})\).
3.3. Results

The XP spectrum of chemisorbed O was compared with the graph (Figure 3.3b) obtained after exposing a clean sample to high O$_2$ pressure and temperature (1.0 bar O$_2$, 441–444 K, 60 minutes). While exposing the sample to these conditions, it was confirmed with STM that the spoked-wheel structure had formed. After forming the structure, XPS measurements were performed. The differences were evident: the O 1s intensity had strongly increased and shifted from 528.5 eV to 530.7 eV. The higher binding energy agreed well with the values found for oxidized Pt (see SI, Table 3.4). In this table, a clear trend is missing, although PtO$_2$ seems to be generally lower in binding energy than the surface oxides and PtO. Our shift to higher binding energies matched with the comparison of binding energies of surface oxides with chemisorbed oxygen found in literature (SI, Table 3.3 and 3.4), although it disagreed with the study by Miller et al. on Pt(111) [39].

The FWHM of the new O 1s peak was estimated at 2.4 eV. XPS peaks with similar widths were both attributed to a single O state [32, 95] or to a pair of states [35]. Based on the shape and width of the O 1s peak and the resolution of our XPS system, we associate the peak with a single O state, although we cannot fully exclude the possibility of closely separated states.

The resulting increase in O 1s signal from the p(2×2) structure to the surface oxide was a factor 3.5. This corresponds to an O coverage of 0.88 ML. Based on variations in the fitting results, we expected the uncertainty on the O coverage to be ±0.1 ML. Although the XPS-derived O coverage was a lower estimate, the measurement suggested that the surface oxide had a thickness of a single layer.

Temperature dependence

A second XPS study focused on the temperature dependence of the spoked-wheel structure. The XP spectra were taken at temperatures between 432 and 963 K. The results are presented in Figure 3.4. The spectrum labeled “1056 K” was collected at lower temperatures after annealing briefly to 1056 K. The change in O coverage plotted as function of temperature is depicted in Figure 3.4b. The graph shows a constant, almost linear decrease in O coverage with increasing temperature. After annealing to 1056 K, the O coverage was on the level of the experimental noise, as is indicated by the large error margin for that temperature. Although the oxygen-rich structures were starting to release O between 432 and 564 K, some O was still on the surface at 963 K. This is either above or on the higher edge of O$_2$ desorption from the Pt(111), Pt(100), and Pt(110) surfaces [30–34, 36, 62, 96–100]. The increased stability can be a result of the roughness on the surface [60], but it could also indicate subsurface O [60, 88].

In the first (black) spectrum in Figure 3.4, some intensity was observed around 535 eV. It was not clear whether this was a real peak, noise, or a change in background. This was not observed in the higher-resolution spectrum of Figure 3.3b. Furthermore, it would not be easy to account for a binding energy shift to 535 eV [101].
Figure 3.3: XP spectra collected after exposure of a clean Pt(111) sample to 400 L O$_2$ at room temperature (a) and to 1.0 bar O$_2$ at 441–444 K for 60 minutes (b). Spectra were fitted with a Doniach-Šunjčić function [94] convoluted with a Gaussian: O 1s (green) and Pt 4p$_{3/2}$ (pink). Lower panels show the fitting error. To obtain a good fit, the Pt 4p$_{3/2}$ peak required considerable asymmetry in both spectra.

3.4 Discussion

3.4.1 Effect of pressure and formation temperature

Exposure of the Pt(111) surface to a high O$_2$ pressure (1.0 bar) at lower temperature (327–328 K and ~291 K), did not lead to large-scale ordered structures. At these lower-temperature conditions, thermodynamics predicts an even higher driving force to create oxygen-rich structures. This seems to contradict the observations and, hence, two possibilities remain. The first one is that the disordered structures that were observed contained more O than the surface oxide. In this case, the structures would have to be disordered multilayers or contain subsurface O. The second possibility is that the formation of both surface oxides was kinetically hindered at lower temperatures. This seems to be confirmed by the observation of the basic structural elements, lifted rows and triangles, that are the building block for the ordered, higher temperature structures. The limiting step can either be the rearrangement of the Pt atoms on a larger scale or the dissociation of O$_2$. Similar observations were made on Pt(110) after oxidation at lower temperature [62].

The main extra feature observed at lower temperature were clusters with a diameter of 0.32±0.04 nm. The clusters’ apparent height was much smaller than a monoatomic step and was relatively unaffected by changes in the sample bias. Therefore, we
3.4. Discussion

Figure 3.4: (a), XP spectra measured at different sample temperatures after high-pressure and high-temperature exposure (1.0 bar O$_2$, 433–438 K, 53 minutes, after which the sample was allowed to cool to 332 K in 33 minutes at the same O$_2$ pressure). (b), temperature dependence of the fitted binding energies of the O 1s peak (blue; upper scale) and the integrated O 1s peak areas (red; lower scale). The error bars were based on the uncertainty of the binding energy in the fit and on the variation of coverage with changes in fitting parameters. The latter was estimated to be ± 0.1 ML.
Chapter 3. Oxidation of Pt(111) – 2

propose that these clusters were single PtO units, buckled out of the surface. It could be the building block of both the spoked-wheel and the lifted-row surface oxides. Similar clusters were previously observed [33] and DFT showed that units consisting of a Pt atom surrounded by three O atoms were stable structures [61].

3.4.2 Thermal decomposition and stability with respect to chemisorbed O

After evacuation, the imaged surface appeared very rough and the STM imaging much noisier. This increase in noise in (U)HV conditions compared to high-pressure conditions seems counterintuitive. To explain this, we propose that both structures were thermodynamically unstable without the high O\(_2\) pressure. These unstable structures were releasing O\(_2\), which increased the mobility of Pt atoms. This mobility was responsible for the observed noise in the tunneling current, which affected the quality of the STM images and was observed as single-scan-line noise. Under these conditions, we saw evidence for a significant influence of the tip on the surface structure, possibly via its interaction with the mobile Pt atoms, or by enhancing the rate of departure of O atoms. For example, the STM image of Figure 3.2e was recorded after the central region of the image had been scanned several times, and it showed that this region had suffered a loss of material with respect to its surroundings, while the stripiness indicates significant mobility in or on the depressed region.

There was a clear difference between the surface obtained after evacuation, starting from 1.0 bar O\(_2\) and that from 5.0 bar O\(_2\). After exposure to 1.0 bar O\(_2\) and subsequent evacuation, the terraces exhibited a noisy two-level structure (Figure 3.2c) that was less well organized than the two-level pattern of Figure 2.1b. The STM image following evacuation after exposure to 5.0 bar O\(_2\) showed that the surface tried to avoid steps perpendicular to the lifted oxide rows (Figure 3.2d). The observed step configurations are reminiscent of those on the missing-row-reconstructed Pt(110) surface [25, 26].

The binding energies are remarkably constant as O\(_2\) is desorbing from the surface (Figure 3.4b). Only the last spectrum, taken after annealing to 1056 K, shows a shift to lower binding energies, but this could be completely related to the noise on the measurement, as is indicated by the large error margin for that temperature. The absence of a shift is interesting; it can be explained by a reduction of the surface area covered with this oxygen-rich structures, while an increasing portion of the surface becomes empty, metallic Pt. Alternatively, the surface oxide could have decomposed into a chemisorption structure, but only if that was rather different from the p(2\(\times\)2)-O structure, as it had the same O 1s binding energy as the surface oxide. It could be that such an alternative chemisorption structure is related to the oxygen-induced roughening. The latter explanation is supported by the work of Parkinson et al., in which they observed a (2\(\times\)2) LEED pattern during decomposition of oxygen-rich structures created by atomic O exposure of the Pt(111) surface [35]. The (2\(\times\)2) state, observed with LEED, had an O 1s binding energy of 530.8 eV, very close to our reported values.

All results strongly suggested that the oxygen-rich structures were unstable upon evacuation. However, the loss of oxygen was kinetically delayed within the time
3.4. Discussion

scale of our experiment. In the STM experiments, no structures with lower oxygen coverage, such as the vacuum-stable surface oxide [33], were observed. In addition, the noise characteristics of the tunneling current gave also the impression that the surface remained oxidized.

3.4.3 Tunnel-gap resistance and tip effects

The tip-sample interaction depends strongly on the tip-sample distance, which, in turn, is related sensitively to the resistance of the tunneling gap. The usual gap resistance is around 10 GΩ when the sample is a clean, metallic surface. In contrast, a gap resistance of 20 MΩ was found to result in the highest resolution on the surface oxides. The surprising aspect was that bias voltages of approximately 20–50 mV were used to image the surface oxides. This implied that the surface oxides had no or a very small band gap. This contradicted with an STM finding of a 2D surface oxide and disordered oxide clusters on the Pt(110) surface, which did show a significant band gap of >1 V [62].

Pt oxides do not behave like the typical wide-band-gap oxides, such as SiO$_2$ and Al$_2$O$_3$. For Pt oxides, the band gaps are relatively small and these oxides are generally considered to be semiconductors. For example, experimental values for the band gap of crystalline PtO$_2$ were 1.8 eV [102] and 2.5 eV [103]. The band gap was found to be significantly lower for amorphous PtO$_2$ (1.2–1.3 eV) [75, 77]. For Pt oxides with a lower oxidation state, the band gap is also reduced, although previous results are conflicting. PtO was found to be a metal [79] or a semiconductor [49] with low conductivity [50] in different experimental studies. However, the most recent DFT calculations employing hybrid functionals gave a band gap of 0.9 eV [104, 105]. The decrease in band gap with decreasing oxygen content was also observed when PtO was compared with the hypothetical Pt$_8$O$_7$, which had a 0.3 eV lower band gap. Furthermore, Pt$_3$O$_4$ was suggested to be metallic in nature due to the presence of Pt-Pt bonds in the crystal structure [106], which, however, still requires experimental confirmation. Finally, metallic behavior was also reported for amorphous PtO$_x$, with $x$ between 1 and 2.

Our STM experiments showed that the observed surface oxides had a minute or nonexisting band gap. The lack of a band gap can be explained in two steps. Firstly, the 1D oxide chains in the proposed model are structurally more related to the lower-band-gap oxides, PtO and Pt$_3$O$_4$ than $\alpha$-PtO$_2$ (vide supra). In addition, the Pt atoms in the 1D oxide chains are closely spaced with the Pt atoms not directly involved in the surface oxide and, possibly, these two kinds of Pt atoms can sufficiently bind to eliminate the band gap.

Alternatively, the absence of a band gap can be rationalized by a fractional oxidation state. Oxidation states of Pt oxides deviate strongly from the formal oxidation states of Pt$^{2+}$ and Pt$^{4+}$ and have a significant covalent character. This has been shown consistently with DFT calculations [57, 61, 64, 104–106] and can also be expected for the surface oxides. This fractional oxidation state results in partial occupation of the highest-energy d-orbital. This orbital is the $d_{x^2-y^2}$ orbital for the square planar PtO$_4$

\[^3U_{\text{bias}} \approx 1 \text{ V and } I_{\text{tunnel}} \approx 100 \text{ pA} \]
\[^4U_{\text{bias}} \approx 20 \text{ mV and } I_{\text{tunnel}} \approx 1 \text{ nA} \]
units according to crystal field theory [107]. This orbital is empty for d8-configurations, like Pt$^{2+}$. Partial filling of the $d_{x^2-y^2}$ orbital could as a consequence decrease the Pt-O bond strength, because this orbital could be antibonding with respect to those bonds. Finally, it is possible that the lack of band gap was because of the defects present in these surface oxides. This defects are abundant and clearly discernible in all STM images presented in this work.

Imaging at low values for the tunneling gap resistance had as main drawback that the strong tip-sample interaction resulted in STM artefacts. One example of an STM tip artefact is visible in Figure 3.2e. These effects were generally observed under less-oxidizing conditions and were all destructive in nature, resulting in a rough surface without discernible atomic structure. All STM observations on the high-pressure oxide structures were unrelated to STM-tip effects. This was carefully checked by moving the scan region to a fresh area or by zooming out and comparing the inner region of the STM image with the outer parts (Figure 3.2e).

### 3.4.4 Stability with respect to $\alpha$-PtO$_2$

Equally important as the spoked-wheel and lifted-row oxides, discovered here, is the structure we did not observe, i.e., $\alpha$-PtO$_2$. This directly conflicts with the conclusions of two SXRD studies that probed the Pt(111) surface under similar conditions [37, 38]. The conclusions in these studies were strongly based on the in-plane diffraction spots, which indicated a hexagonal overlayer with a lattice constant close to that of $\alpha$-PtO$_2$. However, the spoked-wheel oxide would give similar in-plane hexagonal diffraction spots. In the SXRD results, the difference would be in the “crystal” truncation rods of the oxide, to which only a model was fitted based on $\alpha$-PtO$_2$. Furthermore, both studies found a hexagonal unit cell parallel to the Pt(111) unit cell. This contradicted both experimental and theoretical studies that showed a 30°-rotated $\alpha$-PtO$_2$ layer [29, 54, 108, 109]. The oxide layer had a $(\sqrt{3} \times \sqrt{3})$ unit cell on a $(2 \times 2)$ Pt(111) unit cell to minimize the misfit between the structures. We conclude that the SXRD observations actually support the identification of the spoked-wheel oxide on the Pt(111) surface at high O$_2$ pressures.

Another scenario would be that $\alpha$-PtO$_2$ was still formed during the SXRD studies. The discrepancy between the SXRD and STM studies could then be explained by a kinetically hindered formation of $\alpha$-PtO$_2$. This hypothesis is supported by a calculated phase diagrams showing that $\alpha$-PtO$_2$ should be the stable phase under these experimental conditions [29, 54, 110]. In this case, the observed spoked-wheel and lifted-row oxides were only metastable with respect to $\alpha$-PtO$_2$. This kinetic limitation that must have been at play in this scenario can hardly be attributed to a lack of mobility. The Pt atoms do not have to move significantly more to form a layer of $\alpha$-PtO$_2$(0001) than to form the spoked-wheel and lifted-row surface oxides. Second, we observed an enormous mobility, which can be seen when Figure 2.1a and b are compared. Therefore, any kinetic limitation should be related to either O$_2$ dissociation or O diffusion into subsurface sites. The differences in O-related kinetics cannot be explained by a difference in temperature between the STM and the SXRD experiments, because similar temperatures were employed in all studies. The difference
can be explained by X-ray-induced formation of O\(_3\). This was already identified by Ackermann and others [38, 59] as a possible artefact in synchrotron-radiation-based experiments. Ozone was observed to strongly oxidize Pt under UHV conditions [34].

In a near-ambient-pressure XPS study, temperature was the important parameter. Only at 720 K, the formation of \(\alpha\)-PtO\(_2\) was observed, below this temperature only the “4O” phase was found. The latter phase was structurally almost identical to the proposed model of the lifted-row oxide, although it is unclear whether XPS or XAS would be able to differentiate between the spoked-wheel and the lifted-row oxides.

To conclude, it remains uncertain whether the surface oxides in this work are the thermodynamically most stable stable phases. They could have been ‘stabilized’ by the kinetic limitation to form \(\alpha\)-PtO\(_2\). More important than thermodynamic stability is the question of stability under catalytic conditions.

### 3.4.5 Implications for catalysis

The surface oxides observed in this study were unstable in vacuum. From the instability in the evacuation experiments, it can be concluded that these oxides contain O atoms that are loosely bound and therefore highly reactive. Although no true distinction between desorption and reaction with background gas could be made, both cases would lead to the conclusion of the presence of highly reactive O atoms. For the spoked-wheel oxide, an interesting question to answer is which O atoms are more reactive. Are those the O atoms forming the Pt oxide stripes or are those the chemisorbed O atoms, which in turn can feel a strong repulsion from the Pt oxide spokes?

The oxidation-induced roughness was very similar to the observed roughness under CO oxidation conditions in an O\(_2\)-rich flow. Under these conditions, a higher reactivity was found [111]. Both the roughness and the higher reactivity phase can very well be explained by the formation of a single layer of the spoked-wheel oxide. In addition, these surface oxides were very recently also identified as the stable phase under NO oxidation conditions. These experiments are not described in this PhD thesis and will be reported in a separate publication.

To translate the results obtained on a Pt(111) model catalyst to real and complex catalysts, one important point to address is the effect of nanoconfinement. This confinement is a direct consequence of the use of nanoparticles as catalysts. The sizes of their (111) facets will be on the same order as the diameter of a spoked wheel for the smallest particles. This could make the spoked-wheel oxide less stable. On the other hand, nanoparticles may have less difficulty to relieve the strain induced by the surface oxide than an extended single crystal. To clarify this point, in situ experiments yielding atomic resolution on particles possibly aided by DFT calculations will be needed.

### 3.5 Summary and conclusions

In summary, in this chapter we have found the following:

1. At high O\(_2\) pressures, but lower temperatures, surface oxides were formed on Pt(111) that did not show ordered structures, although some structural motifs like rows
and triangles were observed, similar to the basic structures of the spoked-wheel and lifted-row oxides that were formed at higher temperatures, reported in the previous chapter. In addition, many small clusters having a width of $0.31 \pm 0.04$ nm were identified that could be clusters of a single Pt atom surrounded by three O atoms [61].

2. Evacuation experiments showed that these surface oxides were not stable without the presence of the high O$_2$ pressure. This resulted in slowly disappearing structures.

3. XPS measurements in UHV after forming the surface oxides in situ, indicated an O coverage of 0.88 ML. This agreed very well with the model of single-layer surface oxides.

Based on these findings, our main conclusions can be stated as follows:

1. On the Pt(111) surface, the stability of the surface oxides depended both on a high chemical potential as driving force to form and possibly a kinetic limitation against the formation of a bulk-like oxide layer. The surface oxides dictated the nature and reactivity of O atoms on the surface.

2. UHV studies cannot be used a priori to make Pt oxides that represent the surface structure under catalytic conditions. The surface oxides were observed in combination with a large-scale roughness. No UHV study to date has been able to capture both aspects with oxidation using stronger oxidants.

3. One must interpret the data of in situ studies with care. This new type of research relies more strongly on a single experimental technique, compared to traditional UHV surface science work, in which it is more customary to combine several experimental tools. For the oxidation of Pt(111), a large apparent discrepancy was found between our STM work and earlier SXRD experiments [37, 38], which could be explained either by the limited range of the structural models considered for fitting the SXRD results or by the formation of $\alpha$-PtO$_2$ as a result of the oxidizing nature of the X-ray-induced O$_3$ species.
Supplementary information – Oxidation of Pt(111)
Temperature calibration

In the current design of the sample holder and sample transfer system of the ReactorSTM [19], the thermocouple connections are not entirely consisting of thermocouple material. To make the transferable connections, gold-plated copper alloy connectors are used. Over these connectors, a temperature gradient will arise upon heating the sample. This gradient results in an erroneous temperature reading.

We performed a temperature calibration to quantify the error in the temperature measurement. To obtain the misreading, a second thermocouple was laser-spot welded directly to the sample and to a true K-type thermocouple UHV feedthrough. The temperature calibration was performed in two environments. One was the UHV environment used for sample cleaning and XPS measurements. The other one was with the sample mounted in the reactor and exposed to a mixture of O₂ and Ar (5:1, flow: 8 ml/min, pO₂: 1.0, 2.66, and 5 bar). All results indicated that the true sample temperature was higher than the temperature measured via the standard thermocouple.

Figure 3.5 shows the results obtained when the sample was annealed in UHV with a sample voltage of 1 kV. The temperature errors are plotted such that they appear positive. The upper panel shows the total power needed to anneal the sample to a specific temperature. It shows that up to 670 K, the power scaled linearly with temperature. In this regime, the filament was not hot enough to emit electrons and the only source of heating was radiative. Above 670 K, a sample current was measured in the range of 2–10 mA originating from electron-beam (e-beam) heating by the filament. In this regime, the required total heating power was following a superlinear increase.

In the lower panel (Figure 3.5), the temperature error was plotted versus the true temperature. The error approached 200 K at a sample temperature of 1200 K and was showing linear dependence on the true temperature. However, the slope of the curve decreased by 30 % after e-beam heating started. The two resulting conversion formulae ensured an error in the temperature below 1 % for UHV annealing.

The temperature calibration of the sample in the reactor at high pressure is shown in Figure 3.6. In this case, the sample was solely heated by thermal radiation by the filament. The investigated temperature range was much smaller as it was limited by the degradation temperature of the fluor elastomer seal5. The figure illustrates that the error was strongly nonlinear. It increased linearly between 294 K and 425 K. The maximum error was 13.5 K at 425 K. Further heating resulted in a decreasing error. In fact, the smallest error (4–5 K) was measured at the highest temperature (530 K). Changing the absolute pressure at this temperature from 1.2 to 6.0 bar did not significantly influence the error. Although this temperature behavior was complex, its effect was small and with this calibration we estimate the error to be around 0.25 K for temperatures recorded in the high-pressure experiments.

In the discussed calibrations, long time intervals between data points were included in order to ensure thermal equilibrium. Deviation from thermal equilibrium, gave a time-dependent misreading. This error originates in different heating rates of various parts of the microscope. This effect was studied by making a single, sufficiently large step in the

5TMKalrez® 7075 [40]
Figure 3.5: Calibration of the effect of the ReactorSTM’s non-thermocouple connectors on the sample temperature, measured with a true K-type thermocouple. Sample is in the UHV environment with a sample-to-ground voltage of 1 kV. The upper panel shows the total heating power (sum of the power to heat the filament and the e-beam heating power on the sample) needed as a function of the true temperature, while the lower panel shows the underestimation by the regular temperature reading.

Figure 3.6: Temperature error versus the true sample temperature with the sample in the reactor at high pressure (p = 1.2 bar, O₂:Ar mixture of 5:1, flow of 10 ml/min), simulating the high-pressure experimental mixture. The data points were measured after the temperature error was stabilized.
heating power. After this step, the heating power was kept constant and the temperature error was recorded as a function of time. The results are depicted in Figure 3.7.

After the stepwise increase in power from 0 to 5.8 W, the error quickly increased to a maximum of 22 K after 300 s. After this maximum, the temperature error decreased to a value of 11.3 K after 7.5 hours. In spite of a very long equilibration time, the error is already within 1 K (light blue band, Figure 3.7) of the final value after 1.1 hours. This time interval is in the same order as needed for thermal drift in the STM to stabilize before starting the experiment. Therefore, all reported temperatures during the experiment were not affected by the time dependence of the temperature error.

Figure 3.7: Time-dependent error in the temperature reading due to the fact that the microscope is out of thermal equilibrium after a step in the heating power. Upper panel shows the temperature error as a function of the time, while the lower panel shows the true temperature versus the time. The light blue band in the upper panel gives a $\pm 1$ K interval around the final error found after a equilibration time of 7.5 hours.
LEED

**Figure 3.8:** Two photographs of LEED patterns from a freshly prepared Pt(111) surface taken at an electron energy of 64.4 (left) and 106.1 eV (right).

**Apparent height - spokes**

The apparent height of the spokes of the spoked-wheel structure was measured at three different bias voltages (10–100 mV) with the same tip in the same experiment. The bias range was small due to the fact that low positive voltages were required to obtain atomic resolution of the spoked-wheel structure. The apparent height showed a small variation with bias voltage as present in Table 3.1, but the effect is very small with respect to the error bars.

A second measurement at 0.05 V in a different experiment showed much less height corrugation, i.e., 0.03±0.01 nm. This was only about one third of the corrugation that was found in the first measurement at the same bias voltage. Both experiments were performed with the same Pt/Ir tip, but the tip apex was altered between the experiments due to a crash in the surface. It showed that the apparent height was much more sensitive to the shape and/or state of the tip apex than to the applied tunneling bias voltage.

**Apparent height - clusters**

In the experiments at lower temperature (≈328 K and ≈291 K), clusters were observed while the surface was exposed to 1.0 bar O₂. The apparent height was measured at several different sample bias settings. The results are presented in Table 3.2.
Table 3.1: Apparent height of the spokes of the spoked-wheel structure observed during the exposure of the Pt(111) surface to 1.0 bar O\textsubscript{2} at 529–537 K at three different sample bias voltages. The second measurement at 0.05 V was performed with the same STM tip, but in a separate experiment with, most likely, a different tip apex.

<table>
<thead>
<tr>
<th>Bias/V</th>
<th>App. height/nm</th>
<th>Stand. dev./nm</th>
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<tbody>
<tr>
<td>0.10</td>
<td>0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>0.05</td>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>0.01</td>
<td>0.10</td>
<td>0.03</td>
</tr>
<tr>
<td>0.05</td>
<td>0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 3.2: Apparent height of clusters observed during the exposure of the Pt(111) surface to 1.0 bar O\textsubscript{2} at lower temperatures (327–328 K) at three different sample bias voltages.

<table>
<thead>
<tr>
<th>Bias/V</th>
<th>App. height/nm</th>
<th>Stand. dev./nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.69</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>0.04</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>-0.05</td>
<td>0.12</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Calculation of ideal O coverages**

**Spoked-wheel oxide**

The (8×8) unit cell contains 4 Pt oxide spokes on the edges of the unit cell (sharing O atoms between two adjacent unit cells) and one spoke in the inside of the unit cell. Every spoke contains 7 Pt atoms with a PtO\textsubscript{2} stoichiometry, thus 14 O atoms. One O atom between spokes is shared, so the six corners reduce the number of O atoms with 6. This leads to:

\[
4 \times 14 \times 0.5 = 28 \\
1 \times 14 \times 1 = 14 \\
6 \times -1 = -6 + \\
36 \text{ O atoms per unit cell}
\]

Additionally, 6 chemisorbed O atoms reside in the inner region of the triangle. So, the total number of O atoms is 48, 36+(2×6). In a (8×8) unit cell on the Pt(111) surface, 64 Pt atoms are located and this leads to \( \frac{48}{64} = 0.75 \text{ ML} \).

**Honeycomb oxide**

One complete honeycomb (Figure 3.9) is described by a nonprimitive hexagonal unit cell, which spans the area of 3 (8×8) unit cells and contains 6 spokes on the unit
Figure 3.9: Ball model of the honeycomb-shaped surface oxide observed in Reference 33. Honeycomb’s edges consist of the expanded Pt atoms (light blue), which are lifted from the surface plane (blue). In this model, the O (red) positions were deduced from literature [33, 61]. The inner region is covered with a p(1×2)-O chemisorption structure. The radii of the balls are based on the atomic radii of Pt and O.

cell’s edges. Each spoke contains 7 expanded Pt atoms with PtO$_2$ stoichiometry. This equals to 42 O atoms. Counting the chemisorbed layer leads to an additional 74 O atoms. All O atoms together, it adds up to 116 O atoms and the total O coverage corresponds to $\frac{116}{3\times64} = 0.60$ ML.

This is lower than the experimental coverages of the honeycomb oxide obtained with temperature-programmed desorption (TPD) [33]. This could be attributed to formation of subsurface oxygen species or due to doubling of Pt oxide spokes.

**Lifted-row oxide**

The following calculation was based on the lifted-row oxide model with the (2×8) unit cell as depicted in Figure 2.9b. A calculation based on the (4×8) unit cell, would
lead to the same result. The lifted-row oxide holds one row of 7 expanded Pt atoms with a stoichiometry of PtO$_2$. This amounts to 14 O atoms. A (2×8) unit cell on a Pt(111) surface contains 16 Pt atoms. The total O coverage equals $\frac{14}{16} = 0.88$ ML.

**O 1s binding energy - references**

<table>
<thead>
<tr>
<th>O 1s B.E. / eV</th>
<th>Sample</th>
<th>Reference</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>529.4</td>
<td>Pt(111)</td>
<td>112</td>
<td></td>
</tr>
<tr>
<td>529.5</td>
<td>Pt(531)</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>529.55</td>
<td>Pt(332)</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>529.7</td>
<td>Pt(111)</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>529.7</td>
<td>Pt(110)</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td>529.75</td>
<td>Pt(111)</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>529.8</td>
<td>Pt(111)</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>530.2</td>
<td>Pt(111)</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>530.8</td>
<td>Pt(111)</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>530.8</td>
<td>Pt(111)</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>530.8</td>
<td>Pt(100)</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

*Table 3.3:* O 1s binding energies of species attributed to chemisorbed O on Pt. $^1$After decomposition of Pt oxide.

<table>
<thead>
<tr>
<th>O 1s B.E. / eV</th>
<th>Assignment</th>
<th>Reference</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>529.5</td>
<td>surface oxide</td>
<td>39</td>
<td>Pt(111)</td>
</tr>
<tr>
<td>530.1</td>
<td>PtO$_2$</td>
<td>39</td>
<td>Pt(111)</td>
</tr>
<tr>
<td>530.2</td>
<td>PtO$_2$ on Pt</td>
<td>95</td>
<td>Pt(111)</td>
</tr>
<tr>
<td>530.3</td>
<td>PtO$_2$ (bulk)</td>
<td>95</td>
<td>Pt(111)</td>
</tr>
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<td>530.3</td>
<td>PtO$_2$</td>
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</tr>
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<td>530.4</td>
<td>PtO$_2$</td>
<td>113</td>
<td>2</td>
</tr>
<tr>
<td>530.5</td>
<td>oxidic layer</td>
<td>35</td>
<td>3</td>
</tr>
<tr>
<td>530.6</td>
<td>PtO$_{1+x}$</td>
<td>74</td>
<td>1</td>
</tr>
<tr>
<td>530.6</td>
<td>PtO$_2$</td>
<td>74</td>
<td>1</td>
</tr>
<tr>
<td>530.8</td>
<td>surface oxide</td>
<td>60</td>
<td>Pt(531)</td>
</tr>
<tr>
<td>530.8</td>
<td>surface oxide</td>
<td>59</td>
<td>Pt(110)</td>
</tr>
<tr>
<td>531</td>
<td>PtO</td>
<td>[74]</td>
<td>1, broad</td>
</tr>
<tr>
<td>531.4</td>
<td>PtO</td>
<td>[74]</td>
<td>1</td>
</tr>
</tbody>
</table>

*Table 3.4:* O 1s binding energies assigned to oxidized Pt.

$^1$ Sputtered Pt ox films.

$^2$ O$_2$ plasma of polycrystalline Pt film.

$^3$ Fitted with peaks at 530.8 eV (chem. O) and 530.2 eV (oxide).
Chapter 4

High-pressure operando STM studies giving insight in CO oxidation and NO reduction over Pt(110)
4.1 Introduction

Much of our current knowledge of the precise mechanisms underlying chemical reactions at catalytic surfaces is derived from experiments under UHV or high vacuum (HV) conditions. This discrepancy with respect to the typical working conditions of practical catalysts (i.e., high pressure (HP) and elevated temperatures) comes from the fact that many surface sensitive techniques such as LEED, AES, and XPS cannot be easily combined with the environment to which a catalyst would normally be exposed. Typical examples of catalysis would be the three-way catalyst in an automotive exhaust system, or catalytic processes in the petrochemical industry. Moreover, UHV conditions provide a clean and easily controllable environment for accurate experiments [114, 115]. Although such low-pressure model studies have contributed extensively to our fundamental understanding of catalysts, recent investigations at high gas pressures have yielded new insight that goes beyond the mere extrapolation of the low-pressure results [21, 116–118]. This difference is often referred to as the “pressure gap” [119, 120]. Recently, several surface analysis techniques have been adapted to realistic conditions. Examples are TEM [121], SXRD [122], STM [20, 120, 123], and AFM [22].

Scanning tunneling microscopy is one of the few atomically sensitive surface science techniques that do not introduce fundamental problems or limitations when bridging the pressure gap. This technique can operate in the full range from UHV to HP of, e.g., 1 bar and beyond, and from cryogenic temperatures to temperatures well above 1000 K [124, 125]. With its capability to image surfaces with atomic resolution, STM holds the promise to determine the detailed dependence of the structure of a model catalyst’s surface on various gas environments, to identify the active sites for catalytic reactions, and to elucidate the role of possible promoters, all under the relevant, high-pressure, high-temperature conditions of the catalytic processes of interest. The weak, local interaction of the tip with the surface provides confidence that in most cases this interaction will not significantly affect the structure and the properties of the catalyst. These advantageous properties of the technique go hand-in-hand with a demanding combination of technical difficulties, involving, e.g., the imaging stability of the instrument in terms of drift and noise resulting from temperature and pressure variations, and from the presence of a gas flow. In addition, the signal-to-noise ratio in the detection of the reaction products in the gas mixture is demanding as well.

In order to investigate the relationship between surface structure and activity of a catalyst under industrially relevant conditions, we have developed the ReactorSTM system [19]. This system combines a small flow reactor, integrated with STM into a UHV system that is equipped with standard, high-quality surface preparation and analysis techniques, such as ion bombardment, metal deposition, XPS, AES, and LEED. The architecture of the system is such that the sample can be transported from the various sample preparation and analysis tools into the ReactorSTM without breaking the UHV conditions. During the HP STM experiments, the UHV stays uncompromised even at pressures inside the reactor well above 1 bar. The flow-reactor geometry and the special design of the low-volume, high-purity gas supply system allows us to continuously control the gas composition in the reactor, the flow rate, and the reactor pressure, and it allows for rapid, time-resolved analysis on the gas effluent from the reactor during STM
imaging, without the need to retract the tip, which would result in a ‘blind moment’. In this way, the system enables us to study the surface structure of an active catalyst with atomic resolution, combined with simultaneous reactivity measurements. Thereby, we can directly correlate structural changes with chemical activity. The system is a strongly improved version of the prototype that we reported on earlier [20, 21] and a commercial version has been developed by Leiden Probe Microscopy BV [42]. In this chapter, we report on the first results from this new instrument applied to two different catalytic reactions, both on the Pt(110) surface: CO oxidation and NO reduction. CO oxidation is one of the reactions occurring in the catalytic cleaning of exhaust gases from automotive engines. Selective oxidation of CO to CO$_2$ has also received major attention in order to clean H$_2$ streams for fuel cells [126]. Typical catalysts used for this reaction include the noble metals, such as Pt [127]. The (110) surface of Pt is perhaps the best studied surface after Pt(111) for the oxidation of CO. Early studies of this reaction system have revealed highly interesting phenomena, such as, kinetic oscillations [128] and reaction induced faceting [129]. However, these phenomena were observed in a pressure range from high vacuum to UHV and using traditional surface science techniques. This experimental window in which detailed information of the surface can be obtained has been dramatically increased by the recent developments of in situ and operando techniques. Because of the interesting discoveries obtained in vacuum, it is easy to understand that this surface received much attention from researchers using these newly developed techniques. One of the key questions is whether the behavior observed under vacuum conditions can be extrapolated to real reaction conditions and which new surprises can be found on the other side of the pressure gap.

High-pressure STM [21] and SXRD combined with DFT [116] have revealed the appearance of new surface structures and compositions, depending on the gas composition. Two of these structures are oxidic in nature. One is a surface oxide probably stabilized by carbonate ions and oxygen atoms. This oxide is observed when the ratio between the partial pressures of CO and O$_2$ is not too low. The other oxidic structure is a thin film of bulk-like $\alpha$-PtO$_2$ and is formed at lower CO to O$_2$ partial-pressure ratios. Interestingly, both oxides show a higher reactivity towards CO oxidation compared to the metallic surface. The formation of $\alpha$-PtO$_2$ and the reactivity to CO has been confirmed by one near-ambient-pressure XPS study [59], while a second study at slightly different pressure and gas compositions compared to the STM and SXRD studies showed only the metallic surface [130]. In addition to the surface oxide observed by SXRD, a different structure has been observed in which O atoms bind to the fcc hollow sites of a reconstructed (1×2)-Pt(110) surface. In this surface oxide, the O-atom-induced stress leads to the ejection of Pt atoms in a highly ordered manner, so that a Pt(110)-(12×2)-22O structure is adopted [62]. However, DFT combined with ab initio thermodynamics predicts that this surface oxide is not stable under reaction conditions [68, 110].

The oxidation of CO by O$_2$ serves as a ‘model system’ to demonstrate the improved resolution of the ReactorSTM under catalytic conditions.

The second part of this work describes experiments on the interaction between NO and H$_2$ and the Pt(110) surface. These interactions are key factors in understanding the selective reduction of NO, which is an extremely important process to clean exhaust gases of engines and large turbines. In contrast to the oxidation of CO, there is hardly
any in situ or in operando result reported on the reduction of NO. Previous work from our group shows that results obtained under reaction conditions strongly differ from the results obtained in UHV on the reaction between NO and CO on Pt(100) [131].

Different reducing agents can be used for this reaction, such as unburned fuel remains, CO and H$_2$. Hydrogen can be formed in exhaust gases by a water-gas shift reaction (equation 4.1) or via steam reforming with for example methane (equation 4.2).

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (4.1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (4.2)$$

### 4.2 Experimental

The results presented in this chapter have all been obtained with the ReactorSTM [19] and establish the first scientific output of this unique system, which is an improved version of the HP STM described by Rasmussen et al. [20]. Herbschleb et al. describe the ReactorSTM in full detail elsewhere [19]. Therefore, we only summarize the most important features of the system. The ReactorSTM is a flow cell integrated with an STM setup inside a UHV system. Only a few parts of the microscope are exposed to the reactive gases, i.e., the tip and a slider that form part of the microscope’s coarse approach mechanism. Most parts of the microscope, such as the piezo tube, are outside the flow cell.

The combination between a UHV system and a flow cell gives the best of both worlds, fundamental surface science and the more applied catalytic research. We can use model catalysts and obtain a very clean and controlled starting point for the high-pressure experiment. Because we use a small flow reactor instead of backfilling a large-volume chamber, we can measure the reactivity with a much lower detection limit and higher time resolution. This reactivity is measured by leaking a small fraction of the gas from the reactor into a separate UHV chamber, housing a quadrupole mass spectrometer (QMS).

The Pt(110) sample, which was spark cut and polished to within 0.1° from the (110) plane [41], was cleaned with repetitive Ar$^+$ sputtering and annealing in UHV, at temperatures between 900–1100 K before every experiment. This procedure was complemented with an anneal step at 800 K in an O$_2$ atmosphere (pressure of $1 \times 10^{-7}$ mbar) to remove residual C. The removal of C and other impurities was checked with AES, until the peaks corresponding to impurities were on the level of the noise. In addition to the surface purity, LEED was used to determine the surface structure. The crystal was cleaned until LEED showed a well-defined ($1 \times 2$) reconstruction. This reconstruction, the missing-row reconstruction, is known to occur on the clean (110) surfaces of Ir, Au, and Pt under UHV conditions [132]. The well-known distances of 0.78 nm [133] between the missing rows of the clean Pt(110)-($1 \times 2$) surface in UHV have been used to calibrate the in-plane displacement of the piezo tube scanner of the microscope. Monoatomic steps of the Pt(110) surface have been used to calibrate the vertical direction.

In order to start a high-pressure experiment, the sample must be transferred to the reactor. The sample itself forms the top wall of the reactor and is pressed onto the
reactor body, which holds the STM tip and the electrical connection from the tip to the STM preamplifier. The sample is sealed on the reactor with a fluoroelastomer\textsuperscript{1} O-ring, forming a high-pressure/vacuum barrier that allows to maintain UHV conditions in the STM chamber and a pressure in the reactor of up to 6 bar. After the sample is pressed on the reactor, the reactor volume is no longer being pumped until the high-pressure gas flow is admitted. The pressure in the stage between UHV sample cleaning and the starting of the high-pressure experiment is solely determined by outgassing of the fluoroelastomer and other polymer parts, which is roughly estimated to be lower than $1 \times 10^{-5}$ mbar. This outgassing is both temperature and time dependent with possibly some memory effects occurring between experiments. However, careful baking of the entire reactor should minimize crosstalk between experiments.

Recently, we have implemented a new configuration in which two small pumping lines have been constructed to maintain some pumping of the reactor volume by the UHV chamber in the time lag between UHV and HP conditions. This improved configuration has been used for the NO and H\textsubscript{2} exposure experiments reported here. Before the STM experiment can start, a coarse approach needs to be employed to bring the tip within tunneling distance of the surface. Since there is no optical access to the STM when the reactor is closed, this coarse approach must bridge a few millimeters and roughly takes between 20 and 60 minutes. To keep the sample as clean as possible one needs to question whether it is better to approach in a vacuum determined by outgassing and low pumping speed or to expose the sample directly to a flow of high-pressure inert gases.

When flowing high pressure of a gas mixture, the contamination is limited by the impurity level in the gas feed. The used gases all have typical purities of 6.0N, which corresponds to an impurity level of 1 ppm. This impurity level corresponds to a partial pressure of $1 \times 10^{-3}$ mbar at a total pressure of 1 bar. However, having a gas flow through the reactor has the advantage that partial pressures of impurities outgassing from the polymer components are reduced to lower levels.

To start a high-pressure experiment with a sample that resembles the well-prepared UHV sample as closely as possible, it was found that it was best to execute the coarse approach step before introducing the gas flow.

Mechanically cut Pt/Ir tips have been used in the CO oxidation experiments without any in situ pretreatment. On the other hand, AC etched (in aqueous solution of NaOH) W has been used as a tip in all the NO and H\textsubscript{2} exposure experiments. After introduction into the microscope, the W tip was sputtered with Ar\textsuperscript{+} to remove oxides and other contaminants from the apex of the tip. All STM images have been recorded from top left to bottom right with the fast scan direction from left to right and have been corrected with line-by-line background subtraction and have been analyzed and imaged using Gwyddion [134] and Spacetime [135].

\textsuperscript{1}TMKalrez\textsuperscript{®} 7075 [40]
4.3 Results and discussion

4.3.1 CO oxidation over Pt(110)

Figures 4.1 and 4.2 summarize characteristic STM images obtained during CO oxidation over Pt(110). Figure 4.1 shows three STM images of the Pt(110) surface under different reaction conditions. Figure 4.1a shows the surface in vacuum at room temperature after being transferred to the reactor, and after the coarse approach of the tip. The surface clearly shows a pattern of rows. The distance between these rows is 0.75±0.03 nm determined from the height profile shown in Figure 4.1a, which is in excellent agreement with the theoretical value of the (1×2) missing-row reconstruction of 0.78 nm [133]. Interestingly, in the upper left part of the image the surface deviates from the missing-row pattern and small patches become apparent. At this point, the surface has been exposed to poor vacuum, determined by the outgassing of the reactor walls and seals without being pumped for the time it takes to perform the approach of the tip. Therefore, we attribute the appearance of these patches to the partial lifting of the (1×2) missing-row reconstruction due to adsorption of outgassing molecules.

The sample was heated to 433 K and a flow of a mixture of CO and O\(_2\) (CO/O\(_2\) ratio > 0.2) was introduced at a total pressure of 1 bar. Under these conditions, the STM image shown in Figure 4.1b has been recorded. Excitingly, the high-pressure and elevated temperatures have not significantly deteriorated the imaging quality. The image clearly again shows a row pattern on the two imaged terraces. The distance between these rows corresponds to the (1×1) unreconstructed surface, as can be read off from the height profile in Figure 4.1b. This is the first time that the row structure of this surface has been observed under these reaction conditions. The blurry appearance of the step edge reflects the highly dynamic step fluctuations that are typical, given the high-temperature, high-pressure conditions. To summarize, the high-pressure exposure of the Pt(110) surface to a CO-rich flow lifts the (1×2) missing-row reconstruction and reveals a well-ordered (1×1) structure.

Figure 4.1c shows the sample in an O\(_2\)-rich flow with a CO/O\(_2\) ratio of less than 0.2. In this regime, the surface has switched again, this time to a row pattern with a row distance of 0.72±0.06 nm, corresponding to a (1×2) structure. Remarkably, even with the roughness we observed under these conditions, the atomic rows are resolved and they exhibit the same row distance at all height levels.

This (1×2) structure is not a missing-row reconstruction. If it were, one should expect an abrupt increase in roughness, when the surface switches from the (1×1) to the (1×2) structure, since the top layer of Pt atoms in the (1×1) surface contains twice the number of Pt atoms compared to the top layer of the (1×2) missing-row reconstruction. As a result, one should expect that after the transition the surface would exhibit an island and hole pattern of two height levels. This transition-induced roughness would then decay over time. However, this behavior has not been observed. Instead, the opposite was witnessed. Immediately after the switch, there was no increase in roughness, whereas roughness was observed to build up as a function of time after the transition. Figure 4.1c’ shows a stage in which significant roughness had been built up already, in the form of protrusions with a height of several nanometers.
4.3. Results and discussion

Figure 4.1: STM images and corresponding height profiles obtained with the ReactorSTM during CO oxidation experiments under high-pressure, high-temperature conditions. (a), The missing-row reconstruction, room temperature, vacuum, 25×25 nm$^2$, $U_{\text{bias}} = 2.39$ V, and $I_{\text{tunnel}} = 49$ pA. Partial lifting of the reconstruction is observable in the top left of the image. (b), the unreconstructed (1×1) surface in CO-rich conditions, 1 bar, 433 K, 7.5×7.5 nm$^2$, $U_{\text{bias}} = -0.04$ V, and $I_{\text{tunnel}} = -86$ pA. (c), the (1×2) surface oxide in O$_2$ rich-conditions, 1 bar, 433 K, 12.5×12.5 nm$^2$, $U_{\text{bias}} = -0.10$ V, and $I_{\text{tunnel}} = -39$ pA. A few bad scan lines due to feedback instabilities have been removed to enhance the image quality. (c'), large scale image of the surface oxide showing the formation of protrusions on the surface as a result of the Mars-van Krevelen-like reaction mechanism, same conditions, 210×210 nm$^2$ [21].
Figure 4.2: STM images obtained with the ReactorSTM demonstrating the development of roughness at various stages of the CO oxidation experiment. (a), missing-row reconstruction, room temperature, vacuum, 4.5×4.5 nm², $U_{\text{bias}} = -0.10$ V, and $I_{\text{tunnel}} = -52$ pA. (b), lifting of the reconstruction observed during exposure to 1 bar of CO. Note that the transition from the missing-row reconstructed (1×2) surface to the (1×1) structure has made the surface rough. T = 433 K, 15×15 nm², $U_{\text{bias}} = 0.10$ V, and $I_{\text{tunnel}} = 749$ pA. (c), flat (1×1) structure in a CO-rich flow, T = 433 K, 4.5×4.5 nm², $U_{\text{bias}} = -0.04$ V, and $I_{\text{tunnel}} = -86$ pA. (d), commensurate (1×2) structure, observed immediately after switching to a more O₂-rich gas mixture. Note that the surface is still relatively smooth. T = 433 K, 4.5×4.5 nm². (e), Rough, metallic (1×1) surface, observed after increasing the CO content of the gas mixture again. T = 433 K, 4.5×4.5 nm², $U_{\text{bias}} = 0.08$ V, and $I_{\text{tunnel}} = -1004$ pA.
This increased roughness could be attributed to the catalytic reaction taking place under these conditions. Before discussing this mechanism in further detail, we present results of more experiments where we attempted to decouple both mechanisms (decay of the roughness introduced by lifting of the surface reconstruction vs. building up roughness due to the catalytic reactions). We prepared a clean Pt(110) surface, exposed it to a high-pressure CO flow in order to find the initial roughness that is associated with the lifting of the (1×2) missing-row reconstruction and the decay over time. The results of this experiment are shown in Figure 4.2. Figure 4.2a shows the initial (1×2) reconstructed Pt(110) surface, imaged in vacuum. After setting up the CO flow at 1 bar, we find initially increased roughness (Figure 4.2b) which eventually decays, resulting in the flat (1×1) periodicity (Figure 4.2c).

The experiment was continued by adding O₂ to the flow. The (1×1) surface shown in Figure 4.2c changes to the (1×2) structure when the CO/O₂ ratio is decreased below 0.2 (O₂-rich mixture, Figure 4.2d), which corresponds to the conditions of the measurement shown in Figure 4.1c. Because the dimensions of Figures 4.2c and 4.2d are identical, the images can be directly compared and the doubling of the distance between the rows is clearly observable. In Figure 4.2d, there is no immediate increase in roughness, excluding the possibility that this structure reflects the formation of the missing-row reconstruction, as explained above. Prolonged exposure of the sample to O₂-rich conditions results in the increase of roughness over time, which is intimately related to catalytic turnover. This will be further discussed below. The result of this roughening is still present immediately after switching the flow back to CO-rich conditions and the accompanying transition from (1×2) back to (1×1). Under CO-rich conditions (Figure 4.2e) the surface roughness decreases steadily over time to the level of Figure 4.2c.

The nature of the (1×2) structure occurring under reaction conditions at CO/O₂ partial pressure ratios below 0.2 has been studied previously by STM [21], SXRD, and DFT [116]. The STM study suggested the structure to be an oxide, based on a change detected in the electronic structure inferred from scanning tunneling spectroscopy. The SXRD study identified this structure under similar conditions to be a commensurate lifted-row reconstruction in which every second row is lifted, thus giving a (1×2) periodic structure. The lowest energy structure with such lifted rows, found in DFT calculations, was stabilized by a combination of a row of carbonate ions below each lifted Pt row [116]. In addition to pushing the Pt row up, they also displace it sideways, in accordance with the SXRD analysis. In addition, the DFT results indicate the presence of a row of surface oxygen atoms bonding to each lifted Pt row. Combining the results of these studies, it is convincingly shown that this (1×2) structure formed under O₂-rich conditions is a commensurate oxide in which every second row is lifted by the incorporation of carbonate ions. Figures 4.1c and 4.2d represent the first series of STM images in which this (1×2) lifted-row structure, which only appears under these harsh reaction conditions, is resolved in real space.

The increasing roughness under reaction conditions has been measured before on Pt(110) [21] and on Pd(100) [136, 137], and is explained as a side effect of a Mars-Van-Krevelen-like reaction mechanism [138]. In this mechanism, the catalyst plays an even more intimate role than in other reaction mechanisms in heterogeneous catalysis. One of the reactants actually reacts with the catalyst to form a film of what could be
regarded as an intermediate product in the reaction. Subsequently, the other reactant reacts with this intermediate product. In this model catalyst, we have identified the active structure of the catalyst under $O_2$-rich conditions to be a commensurate surface oxide, as explained above. The oxygen atoms from the oxide layer react with CO to form $CO_2$, leaving behind reduced and undercoordinated Pt atoms.

Pt atoms that become sufficiently undercoordinated, which probably requires the local loss of two or more oxygen atoms, may be expected to become mobile and diffuse over the surface. These Pt atoms will become immobilized again when they are oxidized by oxygen arriving from the gas phase. This reduction-diffusion-oxidation cycle will enhance the roughness of the surface.

When the CO/$O_2$ ratio is decreased even further, the hexagonal and incommensurate $\alpha$-PtO$_2$ is formed on the surface, as observed with HP SXRD [116]. However, this $\alpha$-PtO$_2$ has not been detected in the ReactorSTM, most likely because the CO/$O_2$ partial pressure ratio could not be lowered far enough in this experiment.

A model summarizing the results of this work, previous STM data, the SXRD data, and the DFT results is given in Figure 4.3. The well-prepared surface in vacuum shows the $(1\times2)$ missing-row reconstruction (Figure 4.3a). This reconstruction is lifted in a CO-rich flow, forming a rough $(1\times1)$ surface (Figure 4.3b). The roughness is decreasing over time enhanced by the elevated temperature to a well-ordered $(1\times1)$ structure (Figure 4.3c). When the composition is changed from CO to $O_2$ rich, the commensurate surface oxide forms, with the incorporated carbonate ions (Figure 4.3d). The roughness of this oxide increases as a result of the Mars-Van Krevelen-like reaction mechanism (Figure 4.3e). Increasing the CO concentration again reduces the oxide and a rough $(1\times1)$ surface is obtained (Figure 4.3f). The rough $(1\times1)$ surface smoothens to restore a flat $(1\times1)$ surface as depicted in Figure 4.3c. The cycle between Figures 4.3c, 4.3d, 4.3e, and 4.3f could be reproduced many times. A parallel cycle involves the formations of the incommensurate and bulk-like $\alpha$-PtO$_2$ at an even lower CO/$O_2$ ratio. This oxide also roughens through a similar mechanism, only much more slowly because the reaction rate is lower due to the low concentration of CO present. As mentioned already, this $\alpha$-PtO$_2$ has not yet been observed in the ReactorSTM.

One of the major advantages of the ReactorSTM over other STM setups able to scan at near-ambient pressures is that we can not only go to higher pressures and temperatures, but also measure the reaction kinetics simultaneously with imaging the surface. The kinetic results for the present study of CO oxidation are presented in Figure 4.4. The most obvious features in Figure 4.4 are the broad peaks in the $CO_2$ production, when switching back and forth from CO to $O_2$ rich. These peaks are indicative of LH kinetics in which the reactivity is highest when the CO and O surface coverages are equal. The details in Figure 4.4, however, show more interesting behavior. One feature is the fact that the reactivity of the oxide, which is present under $O_2$-rich conditions, is higher than the reactivity of the metallic surface, which is present under CO-rich conditions. The other interesting detail is the presence of narrow spikes notable just before the LH peaks in the CO$_2$ production but only when switching from the oxide to the metallic surface. These spikes are ascribed to the increase in reaction rate when the CO content above the oxide is raised and the sudden drop in reaction when the active surface oxide is removed at the point where
4.3. Results and discussion

Figure 4.3: A ball model explaining the different transitions observed in studying CO oxidation on Pt(110). (a), shows the missing-row reconstruction in vacuum. This reconstruction is lifted in a CO-rich flow to give a rough (1×1) surface, (b). This roughened surface flattens out with time, (c). When the O$_2$ content is increased, the commensurate lifted-row oxide is formed, (d). The Mars-van Krevelen-like reaction mechanism increases the roughness over time, (e). Increasing the CO partial pressure results in a rough (1×1) surface, (f), which smoothens over time, (c). At high O$_2$ partial pressures the incommensurate α-PtO$_2$ can be formed, (g).
Figure 4.4: Semi-logarithmic plot of the reaction kinetics during CO oxidation, measured with a QMS. The measured ion current is proportional to the partial pressure of the selected mass. (a), two cycles in which the gas composition has been changed back and forth from CO (solid line) to O$_2$ (dashed line) rich. The product of this reaction, CO$_2$ (dotted line) shows broad peaks during the switching between the gases that can be explained with Langmuir-Hinshelwood (LH) kinetics. In the case of random adsorption, the maximum of each LH peak corresponds to a situation with equal O$_{ad}$ and CO coverages. (b) and (c), grey dashed regions are replotted on an expanded time scale. The oxide shows higher activity, compare the tails in CO$_2$ between (b) and (c). The spike in (b) indicates the high reaction rate on the oxide during the initial stage of increase of the CO partial pressure, followed by the drop in the rate, when the oxide is removed due to the high CO partial pressure.
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Figure 4.5: (a), STM image, 84×85 nm$^2$, $U_{\text{bias}} = -0.70$ V, and $I_{\text{tunnel}} = 121$ pA with three height, (b), profiles of Pt(110) obtained with the sample in the closed reactor in vacuum at room temperature prior to the NO reduction experiments.

the CO supply has become too high. To make this effect more visible, Figure 4.4b and Figure 4.4c show two small regions of Figure 4.4a on an expanded time scale.

4.3.2 Exposure to H$_2$ and NO

The second reaction that we investigate in this chapter, is the reduction of NO by H$_2$ on Pt(110). This reaction is related to the reduction of NO by CO, which is again one of the important reactions in an automotive catalyst. The nature of this system is more complicated than the oxidation of CO, in which there is only one major reaction with a single product. To reduce NO using H$_2$ several pathways are possible, creating a combination of NH$_3$, H$_2$O and N$_2$, among others. These products could have a profound influence on the structure of the catalyst. The first stage in our investigation of this reaction system has been to expose Pt(110) to H$_2$ and NO at high pressure (1.2 bar) at room temperature.

In these experiments, the starting configuration of the Pt(110) surface was less well-ordered than that in the CO oxidation experiments, presented in Figures 4.1a and 4.2a. In Figure 4.5a, an STM image of 84×85 nm$^2$ is shown. Before this image was measured, the surface was exposed for several minutes to the poor vacuum of the flow reactor cell. In the STM image, it is clearly visible that the surface shows a pattern of rows with a few distinct widths, which we will discuss first.

Figure 4.5a shows three height profiles taken from Figure 4.5a. These height profiles have been averaged over several lines to increase the signal-to-noise ratio. Profile 1 (black) shows predominantly narrow rows with a repeat distance of 0.74 nm. This measured distance corresponds nicely to the (1×2) period of 0.78 nm [133]. In this height profile, several larger periods can be observed of 1.14 nm. The height corrugation of these wider rows is somewhat larger than that for the rows with the
Figure 4.6: Change in gas composition measured as a function of Ar (red) and H\textsubscript{2} (blue) flow rates. The pressure inside the reactor was kept constant at 1.2 bar throughout the entire sequence. Note that the total flow rate (sum of Ar and H\textsubscript{2} flow rates) was varied. The grey regions indicate the time intervals in which the STM images of Figures 4.7 were obtained.

regular (1×2) period. The increase in both width and corrugation suggest that the wider periods are (1×3) missing-row configurations. Profile 2 and 3 (blue and green) in Figure 4.5a also show mixtures of the (1×2) and (1×3) structures and mono-atomic steps on the Pt(110) surface. Partial lifting as observed in Figure 4.1a has not been witnessed in the low vacuum of the reactor before the NO reduction experiments. This change with respect to the CO oxidation experiments can be attributed to the increased pumping speed of the reactor before starting the high-pressure experiments.

**HP exposure to Ar-H\textsubscript{2} at RT**

After the surface had been characterized in the reactor vacuum, a flow of Ar was established at a pressure of 1.2 bar. After setting this flow, the surface was imaged within a minute. After 10 minutes in the Ar flow, the gas composition was changed stepwise from pure Ar to pure H\textsubscript{2} while the surface was imaged with STM. The change of gas composition over time was realized within 30 minutes and is depicted in Figure 4.6. Figures 4.7a and 4.7f show STM images of the surface in pure Ar and pure H\textsubscript{2}, respectively. When these images are compared to the image of Figure 4.5a taken in vacuum, an increase in noise is apparent at the higher pressure. This increase could be the result of impurities in the Ar flow that interact with the tip. Nevertheless, we still resolve the atomic rows. In addition to atomic steps, rows within the terraces can be observed.

In Figures 4.7b–e, four STM images are shown for intermediate H\textsubscript{2}/Ar gas compositions. Figure 4.7b shows the image in which the gas composition was changed from pure Ar to 1:5 H\textsubscript{2}/Ar ratio. Due to the gas flow-induced change in the vertical drift, the height signal of the STM shows precisely at which point in time the surface was confronted with the change in gas composition (see blue dot in Figure 4.7b). This effect remains visible even after line-by-line background subtraction. It is noteworthy that before the gas switch, a tip change occurred in pure Ar. This tip change greatly
4.3. Results and discussion

Figure 4.7: STM images obtained with the ReactorSTM during exposure of Pt(110) at room temperature to mixtures of Ar and H\textsubscript{2}. (a), surface imaged in pure Ar, 18×18 nm\textsuperscript{2}, I\textsubscript{tunnel} = 60 pA. (b), STM image during switch from pure Ar to 1:5 H\textsubscript{2}/Ar ratio. The blue dot indicates the scan line of the switch. 84×85 nm\textsuperscript{2}, I\textsubscript{tunnel} = 98 pA. (c), 1:5 H\textsubscript{2}/Ar ratio, 79×85 nm\textsuperscript{2}, I\textsubscript{tunnel} = 165 pA. (d), 1:1 H\textsubscript{2}/Ar ratio, 75×82 nm\textsuperscript{2}, I\textsubscript{tunnel} = 165 pA. (e), 1:1 H\textsubscript{2}/Ar ratio, 403×386 nm\textsuperscript{2}, I\textsubscript{tunnel} = 165 pA. (f), pure H\textsubscript{2}, 49×56 nm\textsuperscript{2}, I\textsubscript{tunnel} = 166 pA. All STM images were obtained at room temperature and with U\textsubscript{bias} = -0.70 V.
enhanced the resolution and some additional internal structure became visible within the atom rows. Figures 4.7d and e show STM images for higher H$_2$/Ar ratios. The images show a progressive rounding of the steps and a gradual disordering of the missing-row structure. Figure 4.7e is an image that was zoomed out with respect to Figure 4.7d. A mild, rectangular depression can be discerned in the center of Figure 4.7e, corresponding to the scan area of Figure 4.7d and previous STM images. The structure that is visible in this region seems somewhat smoother than that in the freshly scanned region around it. This smooth depression is probably tip-induced and may be indicative of tip-enhanced surface mobility under these conditions. To separate between changes induced by the gas composition and to minimize tip effects, Figure 4.7f was taken in a completely fresh region of the surface. Figure 4.8 shows height profiles taken from Figures 4.7a and 4.7f, which are reproduced in the insets. Two height profiles (green and blue, Figure 4.8) have been taken from the image in pure Ar (Figure 4.7a), and they predominantly show a regular row pattern. The period correspond to the (1×2) missing-row structure with isolated larger periods, most likely (1×3) missing-row configurations, similar to the structure observed in vacuum (Figure 4.5).

The black curve in Figure 4.8 shows the height profile of the image taken in pure H$_2$. This height line shows structures with both the (1×2) and the (1×3) missing-row periods as well. The observation that both missing-row structures remain intact indicates that the exposure to Ar and (short) exposure to H$_2$ does not significantly change the surface structure.
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Figure 4.9: Gas composition as a function of time and in situ STM data. (a), shows the stepwise change from H₂ (blue, flow in ml/min) to NO (green, flow set point in ml/min) at room temperature at a constant reactor pressure of 1.2 bar. Grey regions indicate in which time interval and in which conditions the four (b–e) STM images were obtained. (b), surface imaged, while switching from pure H₂ to a mixture with NO, 80×82 nm², \( I_{\text{tunnel}} = 139 \) pA. (c), surface in nearly equal H₂/NO ratio, 73×80 nm², \( I_{\text{tunnel}} = 141 \) pA. (d), sample in pure NO atmosphere, 78×80 nm², \( I_{\text{tunnel}} = 141 \) pA. (e), surface after prolonged NO exposure, 158×160 nm², \( I_{\text{tunnel}} = 139 \) pA. All STM images were obtained with \( U_{\text{bias}} = -0.70 \) V. STM images recorded in NO flow show frequent tip changes to a state with strongly enhanced resolution.
Figure 4.10: Enlarged view of selected region out of an STM image measured in a pure NO flow at room temperature showing enhanced resolution after a tip change. 77×45 nm², $U_{\text{bias}} = -0.70$ V and $I_{\text{tunnel}} = 140$ pA.

HP exposure to H₂-NO at RT

Prolonged exposure of the Pt(110) surface (48 minutes after the H₂ was first introduced) to H₂ at 1.2 bar at RT, resulted in a row structure, identified to have a (1×4) periodicity. Also, some deeper missing rows can be observed (Figure 4.9b). The (1×4) reconstructed surface has been exposed to NO at increasing NO/H₂ ratios, see Figures 4.9c–e. Figure 4.9a shows the gas composition as a function of time. During each change of gas composition, the surface was continuously imaged. The blue dot in the first image indicates the switching point from pure H₂ to an NO/H₂ ratio of 0.14. In general, the imaging quality seems to deteriorate only slightly when switching from H₂ to the more reactive NO. This observation is rather remarkable since the material of the tip was W and this is not known as a particularly noble metal. Tip changes are visible in Figures 4.9c and 4.9d, some of which temporarily enhance the imaging resolution significantly. Features of one to several pixels can be distinguished with very high contrast. In both images a single pixel corresponds to 0.21 nm, slightly smaller than the distance between neighboring Pt atoms (0.28 nm [139]). Figure 4.10 shows a selected region from an STM image taken directly before Figure 4.9e in a pure NO atmosphere. This region exhibit enhanced resolution and the row structures can be seen to have disappeared. Directly after the acquisition of this image, the scan region was zoomed out a factor two to check for tip effects, see Figure 4.9e. Although the resolution in Figure 4.9e is not as high as that in Figure 4.10, no tip effect is identified and the loss of the row structure is observed to have occurred also outside of the previously scanned area.

Figures 4.9 and 4.10 demonstrate that when surface and tip are exposed to a gas flow that contains NO, frequent tip changes occur that often lead to a significant improvement in imaging resolution. This effect could be caused by the adsorption of NO on the tip apex, thereby changing the tunneling characteristics. Functionalizing
STM tips to improve resolution or to give chemical contrast in STM images has been achieved before with CO [140, 141], S [142], H$_2$ [143], and O$_2$ [144].

Currently, we are investigating the H$_2$- and NO-induced structural changes of the Pt(110) surface at elevated temperatures, which appear to be more dramatic than the rearrangements reported here for room temperature. These higher temperature observations are complemented with measurements of the reaction rates, e.g., by measuring the partial pressure of the N$_2$ that is produced, as we illustrated in Figure 4.4 for the CO oxidation reaction on the same surface. These higher temperature experiments will form the subject of a future publication.

4.4 Conclusions

In this chapter, we have presented the first results obtained with the ReactorSTM, a setup combining STM with a flow reactor cell. This system was used to study two highly interesting catalytic reaction systems, namely CO oxidation and NO reduction, both on the Pt(110) surface. Under CO oxidation conditions, we have shown that this surface can adopt different structures. The (1×2) missing-row reconstruction exhibited by a clean Pt(110) surface, is lifted under reaction conditions. At high CO partial pressure, the surface shows an unreconstructed Pt(110)-(1×1) structure. At lower CO/O$_2$ partial pressure ratios, the surface transforms into a (1×2) surface oxide. Previous STM, SXRD and DFT studies have identified this oxide as a lifted-row configuration, stabilized by the incorporation of rows of carbonate ions and oxygen atoms [116]. In this chapter, we have presented the first STM images, in which the atomic rows of this structure are resolved. In addition, we measured an increased catalytic activity of the surface oxide compared to the metallic (1×1) surface. This higher activity reflects an alternative reaction pathway of the Mars-Van-Krevelen type. We have also observed that this reaction leads to the build-up of surface roughness. The α-PtO$_2$ structure, that was identified with SXRD under even more O$_2$-rich conditions was not observed in the present STM study, possibly because the CO/O$_2$ partial pressure ratio has not reached sufficiently low values in this experiment.

To acquire more insight into the reduction of NO, another important reaction in heterogeneous catalysis, we have studied the structural changes of the Pt(110) surface as a function of NO and H$_2$ partial pressure. Prolonged H$_2$ exposure produced both a (1×4) missing-row configuration and some deeper nested missing rows. NO exposure of this surface slowly lifted the surface reconstruction and the row pattern disappeared, leaving flat terraces on the surface. Remarkably, the W tip was relatively stable in the corrosive NO atmosphere. Even more interestingly, the tip frequently switched into a state with significantly improved imaging resolution under NO-rich conditions.
Part II

Surface science study of low-temperature CO oxidation on Au
Chapter 5

Hydrophilic interaction between low-coordinated Au and water: $\text{H}_2\text{O}/\text{Au}(310)$ studied with TPD and XPS
5.1 Introduction

Gold is one of few examples of transition metals with only minor industrial or technical applications. In fact, only $\sim 12\%$ of newly mined Au goes into industry, while the majority ends up as either jewelry or financial investment [145, 146]. The industrially used fraction is utilized because of its nobility and its resulting inertness to corrosion. However, modern research shows that this inertness is not guaranteed and significant chemical reactivity can be ascribed to Au [147–149].

The reactivity of metal surfaces is the central focus of heterogeneous catalysis. Its purpose is to facilitate the formation of many chemical products and to control the emission of pollutants. In this field, Au’s remarkable reactivity was discovered by observing a high activity at low temperatures for CO oxidation [27]. In addition, interesting applications for Au as catalyst have been found in the water-gas shift reaction (WGSR) [150] and the selective oxidation of alcohols [151]. All examples show that Au must be dispersed into nanosized structures to show reactivity.

The enhanced reactivity of low-coordinated Au atoms is one of the explanations for the need of nanosized structures. These atoms can be found in steps and kinks, which are increasingly abundant in smaller nanoparticles. To test this hypothesis, we used a stepped Au single crystal for this work. This model catalyst has a high density of steps and, therefore, low-coordinated Au atoms. So, it can be considered a good model system for a nanoparticle catalyst in this respect. Because it is a single crystal, it does not suffer from complicating details (such as support effects and electronic effects due to nanoconfinement) and is perfectly suitable to probe just the effect of low coordination on the reactivity of Au.

A key aspect of gold catalysis is the role of H$_2$O. By adding H$_2$O vapor, it was found that the reactivity in CO oxidation can be enhanced [28]. The role of H$_2$O is even more important in the WGSR, in which it is one of the reactants. The intimate relation between H$_2$O and Au’s reactivity stimulated research in understanding the details of this interaction on well-defined, single-crystal model catalysts both experimentally [152–163] and theoretically [159, 164–171] and on well-defined supported Au clusters (for example see Reference 172).

This effort fits into a wider framework to understand the interaction between H$_2$O and solid surfaces. This interaction has become the subject of one of the most widely studied fields in surface science. Motivations for these studies are almost as numerous as the number of studies themselves. For example, it is also crucial to environmental chemistry, interstellar nucleation of ice particles, material corrosion, and electrochemistry in which H$_2$O is the most used solvent.

The interaction of H$_2$O with transition metals has been reviewed multiple times [173–176]. The early results were believed to widely support an extended-bilayer model. This frequently proposed bilayer model was not able to explain all results obtained with newly developed tools, most notably scanning tunneling microscopy (STM), combined with density functional theory (DFT). These studies led to interesting cases in which the bilayer model was simply incorrect and the structures formed were more complex and beautiful. An important case is the extended overlayer formed on Pt(111). This layer contained pentagonal, hexagonal, and heptagonal rings [177–179].
Even more interesting, one-dimensional (1D) structures can form when the considered surface is anisotropic. This is well illustrated on Cu(110) on which intact H$_2$O forms chains from pentagons in the [00\,1] direction [180, 181]. Furthermore, partially dissociated H$_2$O forms chains in the [\bar{1}0\,1] direction [182]. This anisotropy can be strengthened by going from flat to vicinal surfaces.

The interaction between H$_2$O and stepped surfaces was the focus of a number of studies. Steps generally show a stronger interaction with H$_2$O as determined with temperature-programmed desorption (TPD) on Pt [183–186], Ru [187, 188], Ni [189], and Co [190]. The experimental work was supported by computational studies on Pt [184, 191–194], Cu [195, 196], and Ni [197, 198]. Although the precise orientation of the steps play an important role, details have not been fully understood yet [184–186, 194, 199–201]. In addition to binding H$_2$O more strongly, steps also lower the dissociation barrier on Pt [191–194], Cu [196], Ni [189, 198, 202], Ru [188], Co [190], and Re [203]. Interestingly, the steps of Pt were observed to be covered by 1D chains [199, 204, 205].

The focus of the present work is to study how anisotropy influences the binding of H$_2$O with the much nobler Au and to see if a weakly interacting surface can also show enhanced binding and 1D structures. Of especial interest is the question whether steps are able to dissociate H$_2$O to any observable extent. To study these effects, care was taken to choose one of the most open and expectedly reactive surfaces. This led to the Au(310) surface, which can be considered as a highly stepped (100) surface with steps forming (110) planes. The adsorption and desorption was studied both with TPD and high-resolution X-ray photoelectron spectroscopy (XPS).

## 5.2 Experimental

The (310) surface is depicted in Figure 5.1a–c, showing the single (110) steps and 2 or 3 atom wide (100) terraces. The atoms in this surface have a coordination number which varies between 6 for the atoms in the ridge of the (110) step to 8 in the (100) terrace and 9 at the base of the (110) step. Both the coordination numbers and the surface unit cell are given in Figure 5.1.

Two different Au single crystals were used and polished to the (310) surface with an accuracy of $< 0.1^\circ$ [41] (for the TPD measurements) and $\sim 2.3^\circ$ (for the XPS measurements). To obtain a well-defined and clean surface, the crystals were prepared by Ar$^+$ sputtering with an energy of 500 eV for the TPD experiments and 1 keV for the XPS experiments for a few minutes. Sputtering was followed by annealing in vacuum at 860 K. Multiple cycles resulted in a contaminant-free and well-ordered surface confirmed by low-energy electron diffraction (LEED) and XPS. After preparing the crystal, the surface structure was checked with LEED. A photograph of a typical diffraction pattern is shown in Figure 5.1d. It was recorded with a beam energy of 60 eV and colors were inverted for clarity. In the LEED pattern, the spot splitting arising from the stepped surface was clearly observed. The ratio of spot row spacing to split spot distance was 1.54±0.2. This was close to the theoretical value of 1.58 [207]. The LEED patterns did not show any sign of a surface reconstruction. This was in
good agreement with the STM results of Weststrate et al. [208].

High-purity$^1$ H$_2$O was used for the TPD experiments. It was degassed by multiple freeze-pump-thaw cycles until a quadrupole mass spectrometer (QMS) confirmed the absence of O$_2$. Small amounts of N$_2$ were considered to be irrelevant, due to the expected inertness of Au to N$_2$. The degassed H$_2$O was admitted via a capillary array doser [209]. It was co-dosed with high-purity$^2$ He at $\sim$1.5 bar at room temperature. This resulted in a mixture containing $\sim$1.5 % H$_2$O. Co-dosing of He was used to create reliable and repeatable pressure readings. For the XPS experiments, high-purity$^3$ D$_2$O was used, which was prepared and dosed in the same way. The dose was reported in Langmuir (L), defined as $1 \times 10^{-6}$ Torr s. The pressure was measured with a hot-filament ionization gauge. No gas-specific corrections were applied, because for H$_2$O these correction factors are close to and scattered around 1 [210].

Experimental work was performed using two different ultra-high vacuum (UHV) systems, one was used for the TPD experiments$^4$ and the other for the XPS experiments$^5$. The TPD setup was equipped with a LEED$^6$ system and a QMS$^7$, mounted directly on the main chamber. The main chamber was evacuated with two turbomolecular

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$^1$Milli-Q Ultrapure
$^2$99.96 at.% D, Aldrich
$^3$Chemistry department, Leiden University, the Netherlands
$^4$SuperESCA beamline, Elettra, Trieste, Italy
$^5$VG RVL 900
$^6$Baltzers Prisma 200
pumps in series. These pumps ensured a base pressure of \((1–2)\times10^{-10}\) mbar.

The sample was mounted on a multistage manipulator containing a liquid-nitrogen cryostat, cooling the sample down to 88 K. The sample was heated by a filament mounted close to the rear of the crystal, combining thermal radiation with electron-beam heating. The temperature was measured by a chromel/alumel thermocouple laser spot welded to the side of the crystal. The temperature was controlled with a PID controller\(^8\) to create linear temperature ramps needed for the TPD experiments.

All TPD traces reported in this work were obtained with a heating rate of \(\sim0.9\) K/s. Adsorption of \(\text{H}_2\text{O}\) and subsequent desorption from the walls of the chamber resulted in enhanced background levels during a measurement. This unavoidable behavior was corrected using a hyperbolic tangent to describe the change in background level \([186]\).

The XPS measurements were performed at the SuperESCA beamline, Elettra synchrotron, Trieste, Italy \([211]\). This beamline is designed to give a high-intensity, monochromated X-ray beam tunable between roughly 0.1 and 2 keV.

XP spectra were collected at normal emission and at a beam angle of 70°. The Au 4f\(_{7/2}\) signals were recorded with a photon energy of 170 eV and a dwell time of 50 ms and 650 eV with 30 ms for the O 1s signal. Both the Au 4f\(_{7/2}\) and O 1s signals were measured in a constant-energy analyzer mode with a pass energy of 4.0 and 15.0 eV, respectively. Moreover, the hemispherical analyzer was set to medium-area mode.

The obtained XP spectra were compensated for changes in beam flux and differences in dwell time by dividing the spectra by a linear background. The XP peaks were fitted with a Doniach-Šunjić function \([94]\) convoluted with a Gaussian line shape. This fitting function required the following fitting parameters: binding energy, intensity, Lorentzian line width, Gaussian line width, and asymmetry factor. Fitting parameters were accepted if a time-resolved data set could be successfully fitted with only the intensities as free fitting parameters. The XP binding energies are reported with respect to the Fermi level. This was measured every time after switching to a different photon energy. The uncertainty in the fitted binding energies is estimated to be around 50 meV.

The O 1s signal was quantified in two separate ways. First, it was calibrated by the O 1s signal from a CO-saturated surface at 105 K. CO adsorption saturates when half of the step sites are covered, which occurs at 0.167 ML \([161, 208]\). This calibration was performed both for a photon energy of 650 and 1205 eV, which agreed within 11–12 %. Second, the surface concentration ratio between the \(\text{D}_2\text{O}\) layer and the Au surface was calculated with \([212]\)

\[
\frac{N_{\text{D}_2\text{O},\text{surf}}}{N_{\text{Au,}\text{surf}}} = \frac{\sigma_{\text{Au4f}}\lambda_{\text{Au}}[1-\exp(-\frac{d_{\text{Au}}}{\lambda_{\text{Au}}})]}{\sigma_{\text{O1s}}\lambda_{\text{D}_2\text{O}}[1-\exp(-\frac{d_{\text{D}_2\text{O}}}{\lambda_{\text{D}_2\text{O}}})]} \frac{I_{\text{O1s}}}{I_{\text{Au4f, surf}}}
\]

in which \(\sigma\) are the respective ionization cross sections, which were linearly interpolated for the correct photon energy from the values reported by Yeh and Lindau \([213]\). The recommended, practical effective attenuation length, \(\lambda\), for Au (0.34 nm) was taken from the NIST database \([214]\) and the reported values for solid

\(^{8}\text{Eurotherm 2416}\)
water (1.8 nm [215]) were used. In this formula, d is the layer thickness, 0.193 nm for a Au layer. The water layer thickness on Au has been measured with STM and values of 0.11–0.15 nm [156, 159] have been found, although 0.25 nm was found with helium atom scattering [163]. Values between 0.11–0.15 nm were used for our calculations. In this calculation, the asymmetry factor was assumed to be 1 and the transmission function of the analyzer constant, due to the small (∼32 eV) difference in kinetic energy of the emitted photoelectrons. Both methods gave similar values within ∼20%.

Small amounts of amorphous C were detected during the XPS experiments. This was attributed to beam damage, more specifically to cracking of C-containing gas molecules. However, typical amounts were just at the XPS detection level and they were monitored frequently during the experiment. If the C contamination was significantly increasing, the experiment was aborted and the cleaning procedure repeated.

5.3 Results

5.3.1 TPD experiments

Figure 5.2 shows the results of the TPD experiments obtained after adsorbing various amounts of H$_2$O on Au(310) at a surface temperature of ∼90 K. For low coverages, a single feature was observed (blue traces, Figure 5.2), labeled as peak $\alpha$. For this peak, the leading edges for different doses completely overlap. Furthermore, the temperature at maximum desorption, i.e., the desorption temperature, increases from about 158 to 170 K. Both properties indicated complicated desorption kinetics and a desorption order of less than 1.

When the H$_2$O dose was increased above 1.0 L, a second peak (peak $\beta$) emerged at the low-temperature side. This new peak appeared, while peak $\alpha$ was not fully saturated. The characteristics of this second peak were very similar to those of peak $\alpha$, i.e., overlapping leading edges and increasing desorption temperature (from 161 to 168 K). It is noteworthy that there was no saturation observed up to the maximum H$_2$O dose. The inset of Figure 5.2 shows one example of the hyperbolic tangent used to fit the increasing background pressure during the experiment [186].

A TPD simulation was performed to gain further insight into the observed desorption kinetics. This simulation is included as supplementary information (see Figure 5.14). The comparison between experiment and simulation revealed that desorption followed zero-order kinetics. All together, these results were in very good agreement with van Reijzen et al. [161].

The results are in qualitative agreement with desorption from Au(110) [153]. However, the measured desorption temperatures from that surface were much higher, 185 and 190 K. This difference cannot be completely explained by the higher heating rate used in that work (3 K/s versus 0.9 K/s in this work). A shift to higher desorption temperatures could also be due to stabilization by (partially) dissociated H$_2$O or contamination. Also, there is little structural resemblance with Au(310) due to the missing-row reconstruction present on Au(110). Therefore, we will not further discuss the comparison between Au(310) and Au(110).
5.3. Results

Figure 5.2: TPD traces of various doses of H\textsubscript{2}O adsorbed at \(\sim\)90 K, recorded with a heating rate of \(\sim\)0.9 K/s. Blue traces showed only peak \(\alpha\). Red traces showed, in addition, desorption of H\textsubscript{2}O from a second, lower-temperature peak, \(\beta\). The inset shows an example of a background correction, fitted with a hyperbolic tangent. This accounted for the increase in pressure after the desorption and originated from the low pumping speed of H\textsubscript{2}O.

Peak fitting

To separate the peaks and calculate adsorption energies for both TPD peaks, a polynomial function was fitted through the overlapping leading edges of peak \(\alpha\). This polynomial was extended and subtracted from traces showing both features, resulting in two separate peaks. These are plotted in Figure 5.3a, peak \(\alpha\), and Figure 5.3b, peak \(\beta\).

The separation appeared to produce a reasonable result at first glance. For higher coverages, however, the right-hand side of peak \(\beta\) in Figure 5.3b intersected the x axis almost perpendicularly. Although this behavior is predicted for zero-order desorption, it appeared to be too perfect. Also, peak \(\alpha\) did not seem to saturate up to 3 L, which could be an artifact of the separation procedure.

The insets of these panels show the change in desorption temperature as a function of the integrated TPD signal. Furthermore, the integrated TPD signals of the total signal (red), peak \(\alpha\) (blue), and peak \(\beta\) (green) plotted versus the H\textsubscript{2}O dose are
Figure 5.3: Separation of the two desorption features: (a), peak $\alpha$, ascribed to H$_2$O directly bonded with Au and (b) peak $\beta$, low-temperature peak associated with H$_2$O multilayers. The separation was performed by fitting a polynomial through the leading edges of traces with a single desorption feature (blue traces, (a)) and subtracting the integrated fit from desorption traces showing both features. The insets of (a) and (b) show the peak temperature versus the integrated TPD signal. (c) shows the integrated TPD signals plotted versus H$_2$O dose for the total TPD signal (red trace), peak $\alpha$ (blue trace), and peak $\beta$ (green trace).
shown in Figure 5.3c. In this graph, the estimated error on the dose was based on moderate pressure variations and time inaccuracy and scale with increasing dose. The data for both peaks $\alpha$ and $\beta$ were fitted with a polynomial function to guide the eye.

From this graph, the coverage dependence of the sticking coefficient could be derived. The sticking coefficient of peak $\alpha$ was decreasing with increasing dose, while the sticking coefficient of peak $\beta$ was increasing.

**Leading-edge analysis**

A leading-edge analysis was performed to obtain the adsorption energy of the two TPD peaks. This analysis is shown in Figure 5.4. The leading-edge analysis consisted of plotting the natural logarithm of the TPD signal versus the inverse temperature. Its slope gave the adsorption energy under the assumption of zero-order desorption according to the Polanyi-Wigner equation:

$$\ln(\text{TPD signal}) = \left(-\frac{E_a}{R}\right)T^{-1} + C$$

In this equation, $E_a$ is the adsorption energy, $R$ is the gas constant, $T$ is the temperature, and $C$ is a constant depending on the pre-exponential factor and some experimental constants, such as the sensitivity of the QMS and the pumping speed of the system. In this graph, the original TPD data are also shown on a linear scale (right axis) and the upper axis reads the temperature.

Because the leading edges were overlapping for both peaks, a single TPD trace per peak was analyzed. Specifically, the adsorption energy for peak $\alpha$ was calculated with the highest TPD trace that was showing a single peak. For peak $\beta$ on the other hand, the maximum TPD trace was used to minimize the relative contribution of peak $\alpha$. This resulted in adsorption energies of $55 \pm 2$ kJ/mol for peak $\alpha$ and $48 \pm 1$ kJ/mol for peak $\beta$.

**5.3.2 XPS experiments**

**O 1s during adsorption**

Figure 5.5 shows the O 1s XPS signal with increasing amounts of adsorbed D$_2$O. A single and asymmetric peak was visible at very low D$_2$O dose. With increasing D$_2$O exposure, the asymmetry decreased and the peak shifted to higher binding energy.

The dose-dependent O 1s signal was further investigated by plotting the integrated O 1s signal (top panel, Figure 5.6) and the peak binding energy (lower panel, Figure 5.6) versus the D$_2$O dose. The integrated O 1s signal was linearly increasing with the D$_2$O dose in accordance with the TPD data (Figure 5.3c). However, the slope decreased by a factor of 1.7 above 0.5 L at a coverage of 1.1 ML. It can be partially explained by the onset of the growth of the second layer of D$_2$O. This layer shielded photoelectrons emitted by the first layer resulting in a lower total growth rate. However, this only accounts for a decrease with a factor of roughly $1/(\exp(-\frac{d\text{D}_2\text{O}}{\lambda})) = 1.06-1.09$. So, it is likely that the sticking coefficient of the second layer decreased with a factor of 1.6.

Additionally, the binding energy showed an abrupt change. This change occurred at somewhat lower dose (0.4 L) at a coverage of 0.8 ML. At lower dose, the binding
energy was constant at 532.3 eV; at higher dose, it gradually shifted to 532.8 eV. We attribute this change also to the growth of the second layer of D$_2$O.

A more detailed understanding was derived from the model used to fit the O 1s XPS data. The results are presented in Figures 5.7 and 5.8. In this model, the D$_2$O adsorption is essentially explained by the population of two different O 1s states, one is D$_2$O directly bonded to the Au surface (532.2 eV) and the other is a multilayer D$_2$O state (532.8 eV). The results of these fits are illustrated in Figure 5.7a and 5.7b for 0.1 and 1.6 L D$_2$O. These figures demonstrate that satisfactory fits were obtained as indicated by the small fitting error, depicted in the lower part of the graphs. In addition, a small peak was fitted at 529.9 eV. This minority species accounted for roughly 1% of the total O 1s signal and was assigned to atomic oxygen. This feature could stem from dissociation of D$_2$O as a result of beam damage or by defects in
5.3. Results

Figure 5.5: O 1s signal from a clean surface up to high D$_2$O coverage (blue to green traces) during the D$_2$O adsorption, ranging from 0 to 1.7 L D$_2$O at 106–103 K.

the Au(310) surface with an even lower coordination number.

The resulting peak areas are plotted against the D$_2$O dose in Figure 5.8 and show that the multilayer D$_2$O started to appear from the smallest D$_2$O dose onward. Furthermore, Figure 5.8 shows that a change of growth rate occurred at a dose of 0.4 L, above which growth of multilayers increased. However, the precise coverage where this switch occurred was rather dependent on the values taken for the fitting parameters. In any case, the trend of populating the peak at 532.8 eV even for the lowest D$_2$O dose was robust with respect to differences in fitting parameters. This is an interesting feature, which will be explored further in the discussion.

Au 4f$_{7/2}$ during adsorption

With the focus switched to the Au 4f$_{7/2}$ signal, the D$_2$O adsorption experiments were repeated. The Au 4f$_{7/2}$ spectra with increasing D$_2$O coverages are shown in Figure 5.9, revealing that the Au 4f$_{7/2}$ signal was gradually decreasing upon D$_2$O adsorption. This
Figure 5.6: Integrated XPS signal (brown, pluses) and the binding energy (orange, crosses) plotted versus D$_2$O dose. The coverage increased linearly, however, with a lower rate above $\sim$0.5 L. As the coverage increased (above 0.4 L), the binding energy started shifting to higher values (from 532.3 to 532.8 eV).

tendency can be attributed to shielding of the Au atoms by D$_2$O. However, the shape of the Au 4f$_{7/2}$ features significantly changed with increasing dose. This was most clearly visible by the loss of separation between the peak at 84.0 eV and the shoulder at 83.4 eV. The integrated Au 4f$_{7/2}$ signal showed clear correlation with the D$_2$O dose as displayed in Figure 5.10. The integrated signal was linearly decreasing, when D$_2$O was admitted in the vacuum chamber (indicated by vertical, dashed line in Figure 5.10).

A model to fit the Au 4f$_{7/2}$ data was harder to establish. In principle, one could expect contributions from atoms with the three different coordination numbers. However, both the relative intensity and the core-level shift are not known for this particular stepped surface and material. In fact, research did show that there is not always a direct relation between coordination number and the magnitude of the core-level shift [216, 217]. Furthermore, the relative intensities depend at least on photon energy, detector angle, and step alignment with respect to the plane defined by the
Figure 5.7: Two fitting examples, (a), low D$_2$O dose (0.1 L), and (b) higher D$_2$O coverage (1.6 L). The fitted peaks represented monolayer D$_2$O (red, 532.2 eV), ‘multilayer’ D$_2$O (black, 532.8 eV) and atomic O peak (green, 529.9 eV). In the lower part, the difference between data and fit is shown.
Figure 5.8: Coverages of different oxygen-containing species on the surface during adsorption of 1.6 L D\textsubscript{2}O. Fit model consisted of monolayer D\textsubscript{2}O (red, solid squares, 532.2 eV), ‘multilayer’ D\textsubscript{2}O (black, solid circles, 532.8 eV) and a minute atomic O peak (green, dashed, solid diamonds, 529.9 eV). From low doses on, ‘multilayer’ D\textsubscript{2}O was growing and around 0.9 ML a step increase in the growth rate was visible.

Around 0.5 L, the intensity of the monolayer started decreasing due to screening by the second layer.

X-ray beam and detector [218, 219]. The intensities could also depend on the incident angle of the X-ray beam. In conclusion, there are too many unknown parameters to yield a detailed fitting model without further research into Au surface core-level shifts.

To circumvent these difficulties, a simplified model was used consisting of only one peak for all surface contributions. The results are depicted in Figure 5.11 and it shows that a fairly reasonable fit was obtained. The core-level shift of the surface atoms with respect to bulk Au was found to be 0.42 eV. This shift was larger than shifts reported for the closed-packed Au surfaces (0.28–0.38) [216] and, in line with our expectation, resembles the shift obtained from polycrystalline Au (0.39 ± 0.05) [220].

Upon D\textsubscript{2}O adsorption, one expects a new Au species to appear originating from surface Au atoms interacting with D\textsubscript{2}O. As we represent the surface Au atoms by a single peak, we add one additional, independent Doniach-Šunjić functional form to represent the changes upon D\textsubscript{2}O adsorption. The chemical shift between the clean Au atoms and the ones interacting with D\textsubscript{2}O is only 0.1 eV as shown in (Figure 5.11b). This suggests a very weak interaction between Au and D\textsubscript{2}O.

Figure 5.12 shows the fitted peak areas versus dose. It shows that the contribution from surface Au atoms gradually decreased and stayed constant above 0.8 L at approximately half of the original value. Simultaneous to this decrease, the peak attributed to D\textsubscript{2}O-Au increased, while remaining constant above 0.8 L.

We propose that the first D\textsubscript{2}O layer accumulated to around 0.8 L. Half the surface Au atoms interacted with the molecules in this layer. The second layer had little
5.3. Results

Figure 5.9: Au 4f$_{7/2}$ signal from clean (blue) to high D$_2$O coverage (yellow) during adsorption of a D$_2$O dose ranging from 0 to 1.5 L at 108–104 K. The clean surface showed a peak at 84.0 eV assigned to bulk Au and an intense shoulder at 83.4 eV due to surface Au atoms.

interaction with the Au surface. Therefore, the second layer induced no further shape change to the Au 4f$_{7/2}$ spectra and only accounted for further shielding of the photoelectrons emitted by the Au atoms.

O 1s and Au 4f$_{7/2}$ during desorption

In the final set of the experiments, the XPS signals were monitored during D$_2$O desorption. In these experiments, the surface temperature was linearly increased with 0.10 K/s. The results are presented in Figure 5.13. The areas of the two fitted O 1s peaks are shown as a function of temperature in Figure 5.13a, while Figure 5.13b shows the areas of the three fitted Au 4f$_{7/2}$ peaks. During the temperature ramp, multilayer D$_2$O started to desorb around 142–144 K. Desorption of this feature was observed by a decrease in the corresponding O 1s signal (Figure 5.13a) and an increase in all the Au 4f$_{7/2}$ peaks (Figure 5.13b). This was attributed to decreased shielding
of the diminishing D$_2$O layer. Multilayer desorption was followed by desorption of monolayer D$_2$O at slightly higher temperature, starting at 153–155 K.

Temperature derivatives of these signals are plotted below the respective graphs. These derivatives correspond to the desorption rates and are plotted in such a way that these rates are all positive. These desorption rates showed good resemblance with the TPD experiments (Figures 5.2 and 5.3), although desorption temperatures were about 10 K lower. This difference can be explained by the lower heating rate (0.1 K/s instead of 0.9 K/s) resulting in a 10 K shift as confirmed by the numerical TPD calculations.

5.4 Discussion

5.4.1 Intact or dissociative adsorption

The dissociation of H$_2$O was found to be exothermic on Au(111) and proceeding at high temperature (>750 K) [152]. Furthermore, steps are known to bind H$_2$O more strongly and lower the dissociation barrier [183–205]. However, is this effect strong enough to allow for sufficient H$_2$O dissociation below the desorption temperature on Au(310)? The TPD measurements (Figure 5.2) give the first indication that this is not the case. The high-temperature peak $\alpha$ showed zero-order desorption, which would not be expected from desorption of fragmented H$_2$O. On Au(111) and Au(110), an additional peak was observed after coadsorption of water and O$_{ad}$ [153, 221, 222]. This peak was 20–30 K higher in desorption temperature compared to the desorption
5.4. Discussion

Figure 5.11: Two fitting examples: clean Au (a), and high D$_2$O coverage, 1.5 L (b). Peaks represent bulk Au (black, 84.0 eV), surface Au (blue, 83.6 eV), and D$_2$O-bonded Au (red, 83.7 eV). In the lower part, the difference between data and fit is shown.
of intact water. For the stepped Au(997) surface, a peak difference of even 37 K was found [223]. No such peak was observed in our experiments.

Van Reijzen et al. [161] show that an electron-irradiated H$_2$O overlayer forms a high-temperature shoulder in the H$_2$O desorption spectra. This shoulder was accompanied by the oxidation of CO. The present TPD study did not show such a shoulder to any observable degree.

The XPS data showed (Figure 5.5) that there was a minute peak at 529.9 eV, which we associated with atomic O. However, this peak was around 1% of the total O 1s signal and could stem from beam damage or dissociation at defects sites with even lower coordinated Au atoms. In short, the pristine Au(310) does not significantly dissociate H$_2$O.

### 5.4.2 Adsorption and desorption

The second point we address is the validity of desorption experiments to yield information on the adsorption structure of H$_2$O. Adsorption experiments have a surface temperature of typically tens of kelvin lower than the onset of desorption. This lower temperature opens the possibility that adsorbates stay trapped in a metastable phase. This phase can transform into a more stable phase upon heating the surface. This newly formed phase is probed with TPD and not the original metastable adsorption phase.

This mechanism is believed to explain the discrepancy on Au(111), between desorption and adsorption measurements. On one hand, TPD experiments showed fractional desorption, indicating desorption from ice crystallites and nonwetting behavior [154, 155]. On the other hand, several adsorption experiments resulted in an extended wetting layer [156, 159, 163]. During the temperature increase, a wetting
5.4. Discussion

Figure 5.13: Top panels show fitted O 1s (a) and Au 4f\textsubscript{7/2} (b) peak areas during a linear temperature ramp of 0.10 K/s. They show the desorption of D\textsubscript{2}O from Au(310). Lower panels display the derivative with respect to temperature mimicking TPD spectra. All derivatives were plotted to yield positive rates. Green traces (dashed) show the total desorption rate.

to non-wetting phase transition occurs, similar to H\textsubscript{2}O/Cu(111) [224, 225].

The XP spectra recorded during the temperature ramp (Figure 5.13) indicated no sign of any such transition up to the onset of desorption. However, there was a slight increase in the O 1s ‘monolayer’ signal and the Au 4f\textsubscript{7/2} D\textsubscript{2}O-Au signal. This increase of O 1s ‘monolayer’ was correlated with decreased shielding of desorbing multilayers.

In conclusion, we observe no changes in adsorption between ~100 K and the onset of desorption. Therefore, the TPD experiments can be trusted to yield reliable information on the adsorption of H\textsubscript{2}O on Au(310).
5.4.3 Monolayer adsorption

Next, we will discuss two interesting features of the TPD traces for (sub)monolayer desorption. The first one is the manifestation in a single peak (in addition to the peak ascribed to bulk desorption). In other words, we will explain the absence of separate terrace and step contributions in the TPD spectra. Second, we will explain the zero-order nature of this peak.

Single desorption peak

When we compare the TPD spectra of Au(111) \cite{154, 155} with the ones obtained from Au(310), the differences are obvious. On Au(111), desorption lacked a distinct (sub)monolayer peak and the desorption order was $\sim 0.6$. Both features demonstrated that 3D ice crystallites were thermodynamically more stable than an extended overlayer. In contrary, there was distinct (sub)monolayer desorption on Au(310) and it desorbed at higher temperatures than ice multilayers. This indicated that an extended (sub)monolayer was more stable than ice crystallites.

The difference in desorption from Au(310) and Au(111) can be related to the presence of steps. These steps directly increase the bonding strength of H$_2$O on Au as discussed before. In addition, the steps may play a more subtle role in protecting the surface from reconstructing, thus keeping the coordination of the surface atoms lower. Interestingly, the precise step orientation is very important in stabilizing H$_2$O on Au. Desorption from the stepped Au(997) surface did not result in a separate contribution from (sub)monolayer desorption \cite{223}. Desorption from this surface is remarkably similar to desorption from Au(111). However, both the Au(310) and Au(997) surfaces have steps forming a small (110) facet. The difference between the two steps is the direction of the step with respect to the (110) plane: the steps of the (310) surface run along the [001] direction but the steps of the (997) surface are in the [110] direction.

Surprisingly, no separate contribution from steps and terraces was observed in the TPD experiments, in contrast to desorption from stepped Pt surfaces \cite{185, 186}. This single (sub)monolayer desorption peak on Au(310) was attributed to desorption from (but not limited to) steps, since steps generally bind H$_2$O stronger than terraces.

This interpretation is supported by a coadsorption study of H$_2$O and CO \cite{161}. In this work, van Reijzen et al., preadsorbed CO on Au(310), which is believed to occupy steps \cite{161, 208}. Additional H$_2$O adsorption competes with CO for step sites. This compresses the CO molecules and forces them to occupy closer-spaced step sites.

The absence of a peak originating from terrace-bonded H$_2$O can be explained by either hydrophobic terraces, which are nonwetting. This would result in nucleation of ice crystallites between steps from which desorption would be similar to desorption on Au(111). A second possibility, however, is desorption from an H$_2$O structure covering both step and terrace. To explain the single desorption feature in this case, desorption needs to have a single rate-limiting step. This step could be the release of H$_2$O bonded to steps after which nearby terrace-bonded H$_2$O instantaneously desorbs.
Zero-order kinetics

The zero-order kinetics of the (sub)monolayer peak is also rather remarkable. This can occur in two separate cases. The first one is adsorbate geometry dependent and occurs when desorption takes place from the end points of 1D structures or from the surface of flat multilayers. The other situation of zero-order desorption results from an equilibrium between condensed island and isolated monomers. If desorption is restricted to the isolated monomers and as long as this equilibrium is maintained, the loss of monomers by desorption is replenished by detachment from the islands. If the size of the islands does not change too much, the concentration of monomers remains (nearly) constant [226]. In both cases, the number of desorption sites is constant, which results in a desorption rate effectively independent of coverage.

Zero-order desorption of \( \text{H}_2\text{O} \) is frequently observed for multilayers and monolayers on flat surfaces [174], but on stepped surfaces, examples show that desorption from terraces changes to first order [185, 186]. This occurs when the step density is high enough and terraces too narrow to allow for phase coexistence [227]. In addition, desorption from steps was reported to follow first-order kinetics [184–186].

In our case, the surface had very small terraces and a very high step density but still exhibited zero-order desorption. Instead of a two-phase coexistence model, we propose that desorption occurred from the ends of 1D structures covering either only a step or both a step and (part of a) terrace. This model would also yield zero-order desorption.

The difference between \( \text{H}_2\text{O} \) desorption from stepped Pt and Au surfaces can be explained as follows. For the Pt steps, H bonding between adsorbed \( \text{H}_2\text{O} \) molecules is weaker compared to flat Pt [191, 200] and the Pt-\( \text{H}_2\text{O} \) is relatively strong. This means that desorption could occur from every step site, resulting in first-order desorption. The Au-\( \text{H}_2\text{O} \) interaction, however, is much weaker [228–230] and lateral interactions play a more important role and hinder first-order desorption.

The distance between step atoms in Au(310) is larger than on the stepped Pt(111) surfaces (408 pm for Au(310) and 278 pm for steps on Pt(111)). To have strong lateral interaction and explain the zero-order desorption, it will be necessary that more \( \text{H}_2\text{O} \) is incorporated in the 1D structures on Au(310). The binding of these \( \text{H}_2\text{O} \) molecules could predominantly be with step-bonded \( \text{H}_2\text{O} \) and less with the Au surface. This connective \( \text{H}_2\text{O} \) will most likely directly desorb together with desorption from the step sites. This is consistent with the appearance of a single desorption feature.

XPS data

The O 1s (Figure 5.7) and Au 4f\(_{7/2}\) (Figure 5.11) XP spectra taken during the uptake of \( \text{D}_2\text{O} \) shed more light on the relative step/terrace coverage of the (sub)monolayer structure.

Remarkably, the \( \text{D}_2\text{O} \) ‘multilayer’ peak was populated from the start of adsorption (Figure 5.8), which seems completely counterintuitive. Even when molecules were kinetically trapped on top of the first layer, this growth rate at low \( \text{D}_2\text{O} \) dose would not be expected.

Therefore, we propose to ascribe the O 1s ‘multilayer’ peak to weakly bonded
D$_2$O. This D$_2$O could reside both in multilayers and in the (sub)monolayer. For D$_2$O in the (sub)monolayer, this could be D$_2$O bonded to the ninefold coordinated Au atoms. Similarly coordinated atoms are also present on Au(111) and are the most predominant atoms on Au(997). On these surfaces, H$_2$O adsorption shows single, symmetric peaks with a binding energy of 533.2–532.6 [221, 231, 232] and 532.7 eV [223], respectively. These values are very close to the peak at 532.8 eV, which we assign to D$_2$O bonded to ninefold coordinated Au atoms. A contribution from D$_2$O bonded to ninefold coordinated Au atoms was absent in the TPD measurements. This could indicate that they desorbed at the same temperature as multilayer D$_2$O or that they diffused to six- and eightfold binding sites during the temperature ramp.

The initial growth rate of weakly bonded D$_2$O was half that of the ‘monolayer’ O 1s peak (Figure 5.8). The latter could be ascribed to D$_2$O bonded to both the six- and eightfold coordinated Au atoms and reached a maximum of 0.6 ML. This was a bit lower than the expected value of 0.67 ML, which could be explained by shielding by the second layer of D$_2$O.

The second-layer D$_2$O was indistinguishable with XPS from that of the weakly bonded D$_2$O in the (sub)monolayer. It started growing at a coverage of 0.9 ML after dosing 0.4 L. At this point, around 80% of the ninefold coordinated Au atoms were populated.

Inspired by previous research [168, 181], we overlaid several possible adsorption geometries with the (310) surface (Figure S2). These models agree with our findings; however, without structural information we will not speculate further.

5.4.4 Multilayer adsorption

Finally, we discuss the adsorption and desorption of multilayer H$_2$O from this surface. This desorption occurred at typical temperatures for multilayer desorption. Furthermore, the observed zero-order behavior was not unexpected (Figure 5.3b). However, the calculated binding energy (48±1 kJ/mol) (Figure 5.4) was somewhat higher than that for desorption of ice clusters from Au(111) (44 kJ/mol) [154].

Starting from the second layer, the adsorbed H$_2$O could form 3D clusters on the surface. In this case, a two-phase coexistence with monomers adsorbed on the first layer would explain the zero-order behavior.

An alternative view can be derived from the adsorption of H$_2$O on Au(115) [160, 162]. On this surface, vibrational features remained nearly constant up to at least the tenth layer. These vibrational signatures suggested that the monolayer structure extended in the following layers.

A similar argument could apply on Au(310). If the high step density increased the formation energy of ice clusters, it could be energetically favorable for the multilayers to adapt to the monolayer structures. The multilayer structures could be stabilized by H bonding to the monolayer structures. These H bonds could originate from the upwardly sticking O-H bonds in the first layer.
5.5 Summary and conclusions

The interaction between H\textsubscript{2}O and the stepped Au(310) surface differed significantly from the hydrophobic Au(111) surface. Our findings obtained with TPD and XPS are summarized as follows:

1. Steps did not dissociate H\textsubscript{2}O. They did make the surface hydrophilic.

2. The precise orientation is very important in stabilizing H\textsubscript{2}O: (110) steps parallel to [00\textsubscript{1}] as found on Au(310) bind H\textsubscript{2}O significantly more strongly than (110) steps in the [\overline{1}10] direction.

3. The observed desorption behavior can be explained by 1D adsorption structures. The presence of steps led to a distinct (sub)monolayer desorption peak. The observed zero-order kinetics was rationalized by desorption occurring only at the ends of 1D structures.

During desorption, no separate contribution from steps and terraces was detected. In addition, XPS results suggested that H\textsubscript{2}O occupies multiple adsorption sites. To explain these observation, we propose that 1D structures covered the steps and also (part of) the terrace. These structures were stabilized by step-bonded H\textsubscript{2}O. Desorption of the step-bonded H\textsubscript{2}O was rate limiting and resulted in a single desorption peak.

In addition, XPS measurements showed no dewetting transition while heating the surface, as was found on Au(111) and Cu(111). Furthermore, XP spectra showed no significant interaction between additional H\textsubscript{2}O layers and the Au surface. These additional layers could either have formed clusters or 1D structures, dictated by the monolayer structures.
Supplementary information – Hydrophilic interaction between low-coordinated Au and water
TPD Simulation

A temperature-programmed desorption (TPD) simulation was performed to gain further insight into the observed desorption kinetics. For this simulation, the coverage and desorption rate were evaluated for the experimental temperature range with different initial coverages by calculating

\[ R_{\text{des}} = \theta^n A \exp(-E_a/RT) \]

In this formula, \( \theta \) is the actual coverage, numerically calculated from the initial coverage, \( n \) is the desorption order, and \( A \) is the pre-exponential factor (estimated to be \( 1 \times 10^{13} \)). The \( \text{H}_2\text{O} \) adsorption energy of peak \( \beta \) and a heating rate of 0.9 K/s were used. This simulation was repeated for desorption orders of 0, 1/2, 2/3, and 1.

Figure 5.14: Four simulated TPD experiments showing the effect of the desorption order on the coverage dependence of the desorption rate. These desorption rates are depicted in the top panels and plotted versus temperature, while the lower panels show the temperature-dependent coverage. For every simulations, five initial coverages between 0 and 1.0 ML were used. From left to right, the panels show the desorption behavior for desorption orders of 0, 1/2, 2/3, and 1. Indicative of zero-order desorption are the completely overlapping leading edges and desorption peaks on the leading edges.
First-order desorption occurs when intact molecules desorb without any complicating intermolecular interaction. Fractional desorption is expected when desorption results from the perimeter of either islands (n = 1/2) or clusters (n = 2/3). Zero-order desorption can occur in two separate cases. The first one is adsorbate-geometry dependent and follows when desorption takes place from the end points of 1D structures or from the surface of flat multilayers. The other situation of zero-order desorption results from an equilibrium between condensed island and isolated monomers. If desorption is restricted to the isolated monomers and as long as this equilibrium is maintained, the loss of monomers by desorption is replenished by detachment from the islands. If the size of the islands does not change too much, the concentration of monomers remains (nearly) constant [226]. In both cases, the number of desorption sites is constant, which results in a desorption rate effectively independent of coverage.

When the four simulation are compared, the differences between zero and first-order desorption kinetics are striking. First-order desorption shows non-overlapping leading edges and maximum desorption temperatures independent of coverage. On the other hand, zero-order desorption shows overlapping leading edges and desorption temperature shifting to higher temperatures. Fractional desorption gives intermediate behavior between these extreme cases.

A comparison of the simulated (Figure 5.14) and the experimental (main text, Figures 5.2 and 5.3) TPD traces reveals that the experimental peaks show complete zero-order desorption kinetics.

**Proposed Models**

All experimental results can be explained by (sub)monolayer adsorption in 1D structures or chains with strong H bonding along the chain. However, the nearest-neighbor distance between step atoms in Au(310) is large and disfavors strong H bonds. Therefore, it is unlikely that H$_2$O adsorbs in chains that only cover the step atoms as on Pt [199, 204, 205].

Figure 5.15 shows three models inspired by previous research [168, 181] overlaid on the Au(310) surface. First, a model covering the step sites and an equal number of terrace atoms to facilitate H bonding is shown in Figure 5.15a. Lin and Gross showed that this is the most stable structure formed on unreconstructed Au(100) [168].

The second and third model depicted in Figures 5.15b and c are adapted from the structures proposed by Carrasco et al. for H$_2$O on Ag(110) and Cu(110), respectively [181]. According to Carrasco et al., the lattice constant of the metal substrate determines the preference to either form chains built from hexagons (Ag) or pentagons (Cu). Following this reasoning, the (unreconstructed) Au(110) would adopt a hexagon-based structure. However, there is significant difference between the (110) and the stepped (310) surface. This leads to hexagons spanning three planes and the pentagons spanning two. This buckling can have detrimental consequences on the relative stability between the hexagons and pentagons and on their total stability. Another complication arises when all steps are covered. In this case, H$_2$O molecules at the outer corners of the hexagons are shared between chains. This is not the case for the pentagon
Figure 5.15: Three possible H$_2$O adsorption geometries overlaid on a (310) surface [206]. No structural optimization was performed. (a), based on DFT calculation on unreconstructed Au(100) [168]. (b), based on DFT calculations on Ag(110) [181]. (c), based on STM and DFT calculations on Cu(110) [181].

chain, but also here lateral interactions between chains can play an important role.

Without further research, we will not try to predict relative stabilities of the three models. Structural measurements, such as scanning tunneling microscopy (STM), in combination with density functional theory (DFT) calculations, are needed to give further insight into the (sub)monolayer adsorption of H$_2$O on Au(310).
Chapter 6

Effect of water on CO oxidation at low-coordination Au sites
6.1 Introduction

The recent history of Au catalysis started with the pioneering work of Haruta et al. [27]. In this and following studies, Au nanoparticles (NPs) were found to be active for CO oxidation, water-gas shift reaction, selective oxidation and hydrogenation/isomerization [147]. In the Netherlands, Au catalysis has successfully been studied amongst others in the group of Prof. B.E. Nieuwenhuys [233, 234].

In addition to being of fundamental, chemical interest, Au catalysis can hold the answer to some challenging problems in catalysis. One of these is the low-temperature and selective oxidation of CO. Traditionally used catalysts, such as Pt, only operate at high temperature. Au does not have this requirement and has the potential to increase the efficiency of the automotive catalysts before the catalyst is at operating temperature. Additionally, Au can selectively oxidize adverse CO in hydrogen fuel cells.

Advances in our understanding of Au catalysis have recognized the importance of three factors: highly dispersed NPs, a reducible oxide support, and the presence of H$_2$O vapor to enhance the reactivity. These have inspired various explanations for the high reactivity of Au. Among these hypotheses are: the modified electron structures of small clusters [172], the presence of low-coordinated atoms [235], the existence of active sites on the NP-support perimeter, or spillover, i.e., diffusion from support to NPs of reaction intermediates.

Proving or disproving these theories on technical catalysts is very difficult. This is because precise characterization of the active sites both chemically and structurally is needed. This is where model catalysts come into play. They can represent one aspect of a real catalyst, while greatly reducing the inherent complexity of the technical catalyst.

Ideally, the full structural and chemical characterization is obtained under reaction conditions. Although recently developed surface science tools can give some of the desired structural [15, 19, 22] or chemical information [236], they have limitations. These tools are very challenging and usually operate at the signal-to-noise limit. As a consequence, these so-called in situ or operando techniques still depend on vacuum-based, surface science experiments to interpret the experimental results.

In this and our previous work, we undertook a surface science study using X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) to answer elementary questions about the interaction of H$_2$O and Au, the oxidation of CO, and the role of low-coordinated atoms. In the previous chapter, we studied the interaction between H$_2$O and a stepped model catalyst, the Au(310) single-crystal surface. This surface is visualized in Figure 5.1. The surface consist of narrow (2–3 atom wide) terraces with a (100) structure separated by monoatomic (110) steps. The high step density provides many atoms with low coordination numbers, going as low as 6. The lowest coordinated atoms are found in the (110) step at the edge of the terrace. The high concentration of low-coordinated Au atoms makes it a good model for small NPs. However, because it is a single crystal the electronic structure remains that of metallic Au. Furthermore, the lack of an oxide support allows us to completely separate the effect of different aspects of the technical catalyst. The main results of the previous chapter are summarized as follows: low-coordinated atoms increase the H$_2$O-Au interaction, however, no H$_2$O dissociation was observed [161, 237].
As the high concentration of low-coordinated atoms is not enough to explain the promoting effect of H$_2$O, we focus on a different hypothesis to explain the role of H$_2$O. Water dissociation or H$_2$O-assisted activation of oxygen could occur on the support or on the NP-support perimeter. This can be followed by diffusion of the reaction intermediates to the facets of the NP, where they are able to react with CO. In our model catalyst, no oxide support was present. The reaction intermediates spilling over to the Au surface were produced in a different way. Adsorbed D$_2$O layers were exposed to low-energy electron irradiation to fragment D$_2$O. This treatment led to a mixtures of D$_2$O:O$_{ad}$ on the surface, based on the XPS measurement. No significant amount of OD was detected. This mixture was tested for reactivity towards CO oxidation. The experiments were repeated at different temperatures to study the kinetic details of this reaction.

6.2 Experimental

The experimental details were thoroughly discussed in the previous chapter and only the most important aspects will be highlighted. All experiments were performed at the SuperESCA beamline, Elettra Sincrotrone Trieste, Italy. We used an ultra-high vacuum (UHV) system designed to study surfaces with high-resolution or time-resolved XPS. This system was equipped with a liquid-nitrogen cryostat, a quadrupole mass spectrometer (QMS), and equipment to measure low-energy electron diffraction (LEED).

A single crystal of Au, polished to the (310) plane$^1$ was cleaned with multiple cycles of Ar$^+$ sputtering$^2$ and annealing$^3$. Surface crystallinity was checked with LEED and cleanliness was confirmed with XPS.

High-purity$^4$ D$_2$O and He were co-dosed after repetitive freeze-pump-thaw cycles to remove dissolved air. D$_2$O was used, because of the low background levels of both D$_2$O and D$_2$ in the residual gas of the vacuum chamber. Reproducible dosing was achieved by monitoring the O 1s signal from the surface while admitting D$_2$O/He to the vacuum chamber. After adsorption at a surface temperature of $\sim$100 K, the D$_2$O was exposed to electron irradiation for 5 to 720 s. These electrons were generated using the electron gun of the LEED system at an energy of 100 eV. For this purpose, the electron gun was completely defocused, with a resulting beam width of $\sim$5 mm and a sample current of 7–8 $\mu$A. The electron dose is reported in monolayer (with 1 ML equal to the number of Au atoms in the (310) surface: $1.14 \times 10^{19}$ m$^{-2}$), based on the integrated sample current and the estimated beam size. The electron irradiation led to a sample temperature increase of 4–5 K.

XPS spectra were recorded at three different photon energies: 170 eV for Au 4f$_{7/2}$, 650 eV for O 1s, and 400 eV for C 1s. Spectra were taken with normal emission and an incident angle of 70°. Furthermore, they were corrected by measuring the Fermi level. After this calibration, every spectrum was scaled by a constant factor, obtained by averaging the background over a 0.5 eV interval on the low binding energy side,

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$^1$accuracy of 2.3°

$^2$energy of 1 keV, for a few minutes

$^3$in UHV, 860 K

$^4$D$_2$O, 99.95 at.% D, Aldrich; He, 6.6 N purity
to correct for changes in beam intensity. After scaling, a linear fit to the background was subtracted. Fitting of the resulting spectra was achieved using a Doniach–Šunjic function \[94\] convoluted with a Gaussian line shape. The D\textsubscript{2}O coverage was estimated by comparing the O 1s integral with that of a saturated CO overlayer at 105 K, which equals a coverage of 50 % of the step atoms or 0.167 ML \[161, 208\]. These integrals were measured at 1205 eV to decrease the effect of energy-dependent fluctuations of the photoemission cross section, caused by photoelectron diffraction. These are stronger, closer to the absorption edge. This calibration of the coverage was confirmed by analyzing the relative intensities of the O 1s and Au 4f\textsubscript{7/2} peaks, see previous chapter.

During the experiments, some increase in C was detected (see SI). It was identified as CO, and possibly some amorphous or graphitic C, and possibly carbidic AuC\textsubscript{x}. This C buildup was unavoidable due to the lengthy nature of these experiments, typically several tens of minutes. These species were unrelated with X-ray beam exposure and only showed a slow increase over time and for CO, a decrease with electron irradiation. The total amount was rather low, typically 2–3 % with a maximum of 4.7 %, which mainly consisted of CO. The coverage estimation was based on the coverage of the saturated CO overlayer (105 K, 400 eV) \[161, 208\]. Furthermore, we believe that they were spectator species, since our results showed no correlation with their coverage.

6.3 Results

6.3.1 Formation of reaction intermediates

H\textsubscript{2}O does not adsorb dissociatively on Au(310) under UHV conditions and, hence, the coadsorption of H\textsubscript{2}O and CO did not lead to CO oxidation \[161, 237\]. To study reaction of water with CO on this Au model catalyst without oxide support, we activated D\textsubscript{2}O by electron irradiation.

Figure 6.1 shows the XPS O 1s spectra after increasing amounts of 100 eV electron irradiation. The figure shows the result of an experiment in which the surface was stepwise irradiated. The experiment started after dosing D\textsubscript{2}O up to a coverage of 0.5 ML, referred to as pristine D\textsubscript{2}O. The electron irradiation induced a strong intensity decrease of the major peak. Furthermore, the peak shifted to lower binding energies (532.3 to 531.4 eV) with increasing electron dose. In addition, the peak around 530 eV grew significantly compared to the pristine D\textsubscript{2}O layer and the peak shifted from 529.9 to 529.7 eV.

A quantitative view of the effect of electron irradiation was obtained by fitting the O 1s spectra with four peaks. Two were used to account for adsorption of pristine D\textsubscript{2}O (black, 532.8 eV and red, 532.2 eV). The origin of these molecular peaks is discussed in the previous chapter. In short, the peak at 532.8 eV was assigned to both multilayer D\textsubscript{2}O and D\textsubscript{2}O bonded to ninefold-coordinated Au atoms. The other peak, at 532.2 eV was attributed to D\textsubscript{2}O bonded to sixfold- and eightfold-coordinated Au atoms. To account for the changes induced by the electron irradiation, one new peak (blue, \(\sim\)531.6 eV) and one peak for O\textsubscript{ad} (green) were needed. To obtain the best fit, the binding energy for the former shifted from 531.9 to 530.9 eV, with an average of 531.6 eV. The appearance of the new species on the surface indicated the
6.3. Results

Figure 6.1: XPS O 1s spectra showing the effect of increasing electron irradiation dose on the adsorbed D$_2$O layer. Several changes are notable: an intensity decrease of the main peak, a shift to lower binding energies, and the growth of the peak around 530 eV. Spectra were recorded at $\sim$100 K.

formation of hydroxides or the O$_{ad}$-stabilisation of D$_2$O. The actual assignment will be given in the discussion section.

Three fitted spectra are presented in Figure 6.2. Figure 6.2a depicts a spectrum prior to electron irradiation, showing intact D$_2$O, fitted with two separate peaks. After a small amount of electron irradiation (36 ML, Figure 6.2b), the feature corresponding to O$_{ad}$ developed into a significant contribution to the spectrum and a peak at $\sim$531.6 eV appeared, while the peaks assigned to intact D$_2$O strongly decayed. The total O 1s intensity decreased considerably from 0.5 to 0.3 ML, which we attributed to electron-stimulated desorption. Thermal desorption could be excluded, since the temperature increase during electron irradiation was too small. This was confirmed by TPD experiments that showed no desorption of H$_2$O at 100±10 K (see previous chapter and References 161 and 237). With increasing irradiation dose (304 ML), the total O coverage decreased to 0.05 ML. The surface was covered by roughly equal amounts of O$_{ad}$ and the unknown species, which was reduced by a factor 3.

The fitted peaks were integrated, normalized to obtain the O coverages and plotted as a function of the electron dose as shown in Figure 6.3. The figure shows a strong exponential decay in the D$_2$O coverage upon electron irradiation. At the same time,
Figure 6.2: Fits of several O 1s spectra to show the model to describe the effects of the electron irradiation. Peaks represent: $\text{D}_2\text{O}$, weakly bonded (black) and Au bonded (red), peak at $\sim 531.6$ eV (blue), and O$_{\text{ad}}$ (green). (a), no electron irradiation. (b), 36 ML electron dose. (c), 304 ML electron dose. Lower panels of figures give the residual spectra. Spectra were recorded at $\sim 100$ K.
6.3. Results

Figure 6.3: Coverage of different O-containing species plotted versus electron irradiation dose. Strong decrease of D$_2$O (red and black) caused by desorption and fragmentation was observed for a small electron dose. In parallel, the peak at $\sim$531.6 eV increased, reaching a maximum after an electron dose of 36 ML, after which it decreased again. The O$_{\text{ad}}$ peak showed similar behavior, but saturated at 0.05 ML. The grey bar indicate the XPS fits obtained after an electron dose of 36 ML (Figure 6.2b).

the intensity of the peak at $\sim$531.6 eV was rapidly increasing for an electron dose up to 36 ML, after which it showed a modest decrease. The O$_{\text{ad}}$ peak increased initially, after which it saturated around 0.05 ML, followed by a slow, gradual decrease. The relative intensity of the peak at $\sim$531.6 eV rapidly increased to 8 times that of the O$_{\text{ad}}$ peak within the first 8 ML of electron irradiation. After this initial increase ($\gtrsim$30 ML), the relatively intensity started to decrease.

Figure 6.4 shows four Au 4f$_{7/2}$ spectra. None of the spectra showed any sign of Au oxides. These oxides would be expected around 85.2–86.0 eV [238–251] (indicated by the yellow region in Figure 6.4) The largest difference can be observed between the spectrum of the clean Au(310) surface and that obtained with 0.5 ML D$_2$O adsorbed. Electron irradiation induced only small changes in the spectra. The total intensity increased with increasing electron dose, due to desorption of D$_2$O. Other changes were an increase in the shoulder around 84.6 eV and the decrease in the shoulder at 83.7 eV. All changes were very modest and the latter two changes were reversed by larger doses of electron irradiation.
Figure 6.4: Au 4f\textsubscript{7/2} spectra obtained during various stages of the experiment: clean Au(310) surface (orange), after adsorption of 0.5 ML D\textsubscript{2}O prior to electron irradiation (red), after an electron dose of 8 ML (blue), and after an electron dose of 973 ML (yellow). Possible Au oxides would be expected in the yellow region between 85.2–86.0 eV.

6.3.2 CO oxidation by activated D\textsubscript{2}O

For the next set of experiments, a reproducible amount of D\textsubscript{2}O (0.5±0.1 ML) was adsorbed while monitoring the O 1s signal. After adsorption, the surface was irradiated with a fixed electron dose (36 ML) to obtain a mixture close to that indicated by the grey bar in Figure 6.3. This resulted in a mixture of D\textsubscript{2}O, O\textsubscript{ad}, and possibly hydroxide or O\textsubscript{ad}-stabilized D\textsubscript{2}O. The total coverage of this mixture was ~0.3 ML. In this mixture, the O\textsubscript{ad} content was 21±1 %. The followed procedure resulted in mixtures with very reproducible composition, with only modest variation in absolute coverage. The prepared mixture was exposed to CO, at the highest attainable pressure (~1×10\textsuperscript{-7} mbar) that allowed us to measure the O 1s spectra simultaneously. This corresponded to a CO flux of 0.03 ML/s.

Even at temperatures as low as 105 K, we observed reactivity. Figure 6.5 presents the areas of the fitted peak as a function of time, measured while exposing the surface to CO. Two distinct cases are shown here: one (Figure 6.5a) of a reaction at 137 K, which is below the onset of H\textsubscript{2}O desorption. The other (Figure 6.5b) shows a dataset recorded at 153 K, i.e., at the onset of H\textsubscript{2}O desorption (see previous chapter and References 161 and 237). Both situations clearly showed a strong decrease in O\textsubscript{ad} and in the ~531.6 eV peak and were directly correlated with the CO exposure.

In both measurements, the photoemission spectra show an increase in the peaks associated with pristine D\textsubscript{2}O. In the lower temperature experiment (Figure 6.5a), this
Figure 6.5: Reaction of the fragmented D$_2$O mixture with CO at two different temperatures one below the H$_2$O desorption temperature, 137 K (a) and one at the desorption temperature, 153 K (b), lines depict the peak areas for the combined D$_2$O peaks of 532.2 and 532.8 eV (dashed, red line with black circles), the peak at $\sim$531.6 eV (blue, solid line with open squares), O$_{ad}$ (dotted, green line with solid squares), and CO (purple line with crosses). Note the shorter time scale on the axis of (b).
Chapter 6. CO oxidation, Au(310)

is most prominent, since the surface temperature was not high enough to facilitate desorption. At 153 K, D$_2$O can desorb and only a transient peak in D$_2$O coverage was observed, which quickly decayed. Interestingly, D$_2$O showed a higher thermal stability before the reaction as it remained adsorbed on the surface. This D$_2$O was indistinguishable with XPS from pristine D$_2$O adsorbed on Au(310).

**Activation energies**

To determine the apparent activation energies, CO oxidation experiments were performed under a constant $p_{\text{CO}}$ of $(8 \pm 1.8) \times 10^{-8}$ mbar. The experiments were repeated for three temperatures: 125 ± 2, 137 ± 0, and 153 ± 2 K. The decrease in O$_{\text{ad}}$ and in the ∼531.6 eV peak was fitted with an exponential decay:

$$\theta(t) = \theta_i \exp(-t/\tau)$$

in which $\tau = k_d/(k_r S_{\text{CO}} F_{\text{CO}})$ (see SI) with $k_d$ and $k_r$ as the rate constants for CO desorption and the reaction with CO, $S_{\text{CO}}$ as the CO sticking coefficient and $F_{\text{CO}}$ as the CO flux impinging on the surface. A plot of $\ln(1/\tau) \times R$ versus $1/T$ yields a line with the slope: $-E_{\text{a,app}} = -E_{\text{a,r}} + E_{\text{ad,CO}}$. In this formula, $E_{\text{a,app}}$ is the apparent activation energy, $E_{\text{a,r}}$ the activation energy of the CO oxidation reaction, and $E_{\text{ad,CO}}$ the adsorption energy of CO. Figure 6.6 gives this plot and it shows that for both the decrease in O$_{\text{ad}}$ and the decrease in the ∼531.6 eV peak a similar slope was obtained. The resulting apparent activation energies were 5 ± 2 and 7 ± 2 kJ/mol, respectively.

The linear fits yielding the apparent activation energies were constructed using the orthogonal distance regression (ODR) algorithm\(^5\). The ODR fit took uncertainties in both temperature and $\tau$ into account.

From the apparent activation energies, the activation energy for the Langmuir-Hinshelwood reaction with CO can be derived by adding the CO adsorption energies [161]. These were reported to be 21 ± 3 and 37 ± 5 kJ/mol, depending on the nearest-neighbor distance of the CO molecules, which were adsorbed on the Au step edges. This resulted in activation energies for the reaction of O$_{\text{ad}}$ with CO of 26 ± 4 and 42 ± 5 kJ/mol or 0.27 and 0.44 eV, depending on the CO adsorption site. These barriers agreed well with the barriers found for CO oxidation with O$_{\text{ad}}$ on Au(211) [252] and Au(111) [221] and Au(110) [253, 254] (see Table 6.1).

During the CO exposure, both the peak ascribed to O$_{\text{ad}}$ and the peak at ∼531.6 eV were exponentially decaying to an asymptotic value that was above zero. In other words, a certain amount of both species remained on the surface and was unreactive towards CO. This unreactive fraction increased with decreasing temperature. This can be observed when the exponential decays of Figure 6.5a are compared with those of Figure 6.5b. For example, the unreactive O$_{\text{ad}}$ fraction increased from 25% of the initial O$_{\text{ad}}$ coverage at 137 K to 36% at 125 K.

\(^5\)Igor Pro 6.05 with ODRPACK95
6.4. Discussion

The effect of electron irradiation on the D₂O layer can be explained in three steps. The most discernible process occurring during irradiation was electron-stimulated desorption of water, which caused the decrease in intensity of the largest peak at 532.3 eV. Second, some D₂O dissociated upon irradiation and formed O_{ad} on the surface. The formation of O_{ad} was observed by the intensity gain of the peak at 529.9–529.7 eV, which we previously assigned to O_{ad} [237]. Because the reported binding energies in the literature
of $O_{ad}$ show significant variation and also overlap with the binding energies of Au oxides, we base this assignment on the absence of any Au oxide peaks in the Au 4f$_{7/2}$ spectra. Third, the shift of the main XPS peak from 532.3 to 531.4 eV, is interpreted as the appearance and growth of a new XPS peak at lower binding energies as compared to the pristine $D_2O$ peaks. It could stem from the formation of hydroxides on the surface.

The possible formation of hydroxides on Au surfaces from coadsorbed $D_2O$ and $O_{ad}$ via

$$D_2O + O_{ad} \rightarrow 2 OD$$

has been debated in literature. Several studies indicate that at least very small amounts of hydroxides form on Au(111). This was based on the observed isotope exchange between isotopically labeled $H_2O$ and coadsorbed $O_{ad}$ [255] as was the case for Au(110) [153]. In similar experiments, it was found that these hydroxides are reactive towards CO [256, 257] on Au(111). However, the hydroxide signature was not detected on the same surface with infrared spectroscopy [255], which had a detection limit of $\sim 0.05$ ML. On the stepped Au(997) surface, the ultraviolet photoelectron spectrum showed a peak accredited to hydroxide [223].

DFT calculations show that the formation of hydroxides on Au(111) from coadsorbed $H_2O$ and $O_{ad}$ is endothermic (0.03–0.21 eV) [257–259], with relatively small barriers of 0.11–0.33 eV [257, 259]. If we make the simplification that the DFT-calculated energies are equal to the free energies, this would lead to equilibrium constants of $0.03 \cdot 3 \times 10^{-11}$ at 100 K and $0.11 \cdot 2 \times 10^{-7}$ at 160 K. This supports the view that if hydroxides are formed on the Au(111) surface, their concentration is small, most likely lower than the detection limit of regular surface science techniques. On Au(110), however, the formation of hydroxides is greatly exothermic [258], indicating that this reaction is strongly structure sensitive. Also on other stepped surfaces, e.g., Pt, the formation of $O_{ad}$ versus OH has been shown to depend on the precise structure of the step [260].

Alternatively, it could originate from $D_2O$ stabilized by H bonding to nearby $O_{ad}$. Three arguments favor the assignment of the $\sim 531.6$ eV peak to $O_{ad}$-stabilized $D_2O$ through H bonding and not to the formation of OD. First, the observed stoichiometry as deduced from the increase in $D_2O$ upon CO oxidation is incompatible with reaction of CO with OD. The ratio of $D_2O$ increase to decrease in area of the $\sim 531.6$ eV peak was 1.20 at 125 K and 0.76 at 137 K. This is significantly higher than 0.5, which would be expected if the peak was originating from hydroxide. In that case, the hydroxide would have either reacted via

$$OD + CO \rightarrow COOD$$  (6.2)

$$COOD + OD \rightarrow CO_2 + D_2O$$  (6.3)

or

$$2 OD \rightarrow D_2O + O$$  (6.4)

$$CO + O \rightarrow CO_2$$  (6.5)
In both cases, half of the hydroxide groups would react (directly or indirectly) with CO, while the other half would form D\textsubscript{2}O. Because the experimentally derived ratio was larger than 0.5, we propose:

\[ \text{O--D}_2\text{O}+\text{CO}\rightarrow\text{CO}_2+\text{D}_2\text{O} \] (6.6)

The expected ratio for this reaction would be 1 or higher, depending on the number of D\textsubscript{2}O molecules that are interacting with every O\textsubscript{ad}. The value found at 125 K was slightly higher than 1, but within the estimated uncertainty of the fits. At higher temperature, this ratio decreased, which can be explained by desorption of some D\textsubscript{2}O during the reaction. At 153 K, only a modest transient increase in D\textsubscript{2}O was observed.

Our second argument to ascribe the peak at \( \sim 531.6 \) eV to O\textsubscript{ad}-stabilized D\textsubscript{2}O relies on the activation energies found for reaction with CO. If the unknown species indeed was O\textsubscript{ad}-stabilized D\textsubscript{2}O, and not OD, similar values were to be expected because the decrease in both species is caused by a single reaction (reaction 6.6). In the case of parallel reactions of CO with O\textsubscript{ad} and OD, it would be coincidental that both CO oxidation with O\textsubscript{ad} and OD would have similar barriers.

Finally, the position of this peak around 531.6 eV suggested that it is not a hydroxide species. The shift of the peak with respect to that of pristine D\textsubscript{2}O was around 1 eV, equal to the 1.0 eV shift reported for Au(111), explained by stabilization of H\textsubscript{2}O by H bonding to O\textsubscript{ad} [221]. In a similar experiment on the same surface, a 2.0 eV shift from the binding energy of H\textsubscript{2}O was detected upon H\textsubscript{2}O and O\textsubscript{ad} coadsorption, which was tentatively assigned to OH formation [231]. On the Au(997) surface, a shift of 0.7 eV was found between the peaks assigned to H\textsubscript{2}O and H\textsubscript{2}O affected by O\textsubscript{ad}, respectively [223]. We note that our spectra show a hint of a peak on the edge of the XPS detection limit at 530.9 eV, which is close to the binding energy (530.7 eV) of the peaks attributed to hydroxides on Au(111) [231] and on Au(997) [223]. The intensity of this species is, however, almost insignificant compared to that of D\textsubscript{2}O and O\textsubscript{ad}.

With three arguments to assign the peak at \( \sim 531.6 \) eV to D\textsubscript{2}O H bonded to O\textsubscript{ad} and no arguments to assign it to OD, we continue with a comparison of the peak areas of O\textsubscript{ad} and of O\textsubscript{ad}-stabilized D\textsubscript{2}O (Figure 6.3). Interestingly, this comparison reveals that up to 6–8 D\textsubscript{2}O molecules were stabilized by a single O\textsubscript{ad} atom. The interaction of O\textsubscript{ad} with several D\textsubscript{2}O molecules makes it very plausible that the adsorbates did not segregate into islands, but were completely mixed.

The D\textsubscript{2}O:O\textsubscript{ad} mixture on the Au(310) was highly reactive towards CO, even at temperatures as low as 105 K. However, the comparison of the activation energies of this surface with the Au(111) surface shows that the presence of steps does not increase Au’s reactivity, contrary to what is often believed to be the effect of surface corrugation. This can be explained by the fact that steps stabilize the reactants more than the transition state of the CO oxidation reaction. On a real supported catalyst, the turnover is not solely determined by the activation energies of reactions 6.5 and 6.6. It also depends on the coverage of the oxidant. This could be greatly affected by the low-coordinated Au atoms, which are likely to bind O\textsubscript{ad} stronger in the vicinity of the steps, perhaps even stabilizing the particle’s shape. The net result could be a more active catalyst.

Our experiments give evidence that OD is not stable with respect to D\textsubscript{2}O and
$O_{ad}$. Therefore, $O_{ad}$ is the major oxidant in CO oxidation. Hydroxide could still be important as a possible spillover product, which would probably be more mobile than $O_{ad}$ on the Au surface. This hydroxide species will form $O_{ad}$ and $D_2O$ near the active site of the Au NP, after which $O_{ad}$ reacts with CO to form $CO_2$.

At lower temperature, less $D_2O$ desorbed in our reactivity measurements and as a result an increasing fraction of $O_{ad}$ remained on the surface. This $O_{ad}$ was completely unavailable for the reaction with CO. Possibly, it was strongly bonded into a H-bond network formed by the $D_2O$. Therefore, the reported, promotional role of water [28] should be fulfilled on the supporting oxide and not on the Au NP itself. On the surface of the Au NP, too much water has a poisoning effect on CO oxidation.

### 6.5 Conclusions

We have shown that a mixture of $O_{ad}$ and $D_2O$ can be created by electron irradiation of a molecular adsorbed $D_2O$ layer without producing Au oxides. This is a major advantage over studies relying on decomposition of $O_3$ to produce active species, as such harsh oxidation may lead to formation of Au oxides. Those do not represent the actual catalyst well. Also, in our mixture of $O_{ad}$ and $D_2O$ with low-coordinated Au atoms, hydroxides are not significantly present. Similar to extended (111) terraces, they seem to highly favour dehydrogenation of hydroxides to $O_{ad}$. Hence, we only observe reaction from atomic $O_{ad}$ with CO. As $H_2O$ was previously shown not to dissociate on Au, we conclude that the role of water in promoting CO oxidation can lie in the supply of O-containing species by the catalyst’s support. Probably in the form of OH, they can spill over to Au NPs, where dehydrogenation to $O_{ad}$ is highly favoured. We have shown here through a kinetic analysis that reaction of $O_{ad}$ with CO is not significantly affected by the stronger binding to low-coordinated Au sites in comparison to terrace-bound $O_{ad}$. Finally, we note that excess water may have a poisoning effect on CO oxidation by overcrowding $O_{ad}$, making it inaccessible for reaction with CO.
Supplementary information – Effect of water on CO oxidation at low-coordination Au sites
Introduction

This chapter provides supporting information to the previous chapter. It includes a set of C 1s spectra and a derivation for the kinetic model. The set of spectra was recorded during the experiments in which a fixed amount of D$_2$O was irradiated stepwise with 100 eV electrons. All spectra were analyzed as described in the previous chapter.

Electron irradiation, C 1s spectra

A small increase in C was noticed during the electron-irradiation experiments. One example of a typical C 1s spectrum is depicted in Figure 6.7. It shows that 4 different carbon species were present. Based on their binding energies, we identified CO (yellow/brown, 288.6 eV) [208] and speculate that graphitic or amorphous C (purple, 284.2 eV), and carbidic AuC$_x$ (light blue, 283.4 eV) [101] were present. The small peak (red/brown) at 286.7 eV remained unidentified.

The C 1s spectrum of the Au(310) surface saturated with CO at 105 K is illustrated in Figure 6.8. CO binds to half of the step atoms, corresponding to a coverage of 0.167 ML [161, 208]. The integral of this spectrum was used to quantify the C contamination.

To learn more about the origin of these peaks, the fitted peaks were integrated.
and plotted versus all experimental parameters to search for a correlation. These parameters included: electron-irradiation dose, time in experiment, number of total XPS scans performed, and number of O 1s, C 1s, and Au 4f\(_{7/2}\) spectra recorded. The results are plotted in Figure 6.9. The peak assigned to CO was largest directly after dosing D\(_2\)O and decreased with increasing amount of electron irradiation, due to electron-stimulated desorption. The peaks assigned to graphitic or amorphous C and carbidic AuC\(_x\) showed a linear increase over time. The coverage of graphitic or amorphous C increased linearly with time, but decreased after higher doses of electron irradiation. In this regime, an interplay between adsorption and electron-stimulated desorption could have determined the coverage. The carbidic AuC\(_x\) showed no dependence on X-ray or electron exposure and, therefore, we do not believe that it was caused by fragmentation of other C species. Instead, it is possible that C segregated from the bulk of the Au single crystal. The unknown peak at 286.7 eV did not show any correlation and had a constant intensity during the experiment. The typical amount of C contamination was 2–3 %, with a maximum of 4.7 %.

**Kinetic model**

The kinetic model used to obtain the CO oxidation reaction barrier was previously explained in detail in References 253 and 254. Therefore, only a brief derivation will be given here.
If we assume a Langmuir-Hinshelwoood reaction between CO and O$_{\text{ad}}$, which react according

$$\text{CO} + \text{O}_{\text{ad}} \rightarrow \text{CO}_2$$

(6.7)

then the rate of CO$_2$ formation can be expressed as

$$R_{\text{CO}_2} = -\frac{d\theta_{\text{O}}}{dt} = k_r \theta_{\text{O}} \theta_{\text{CO}}$$

(6.8)

in which $\theta$ represents the coverage of O$_{\text{ad}}$ and CO, respectively, and $k_r$ the rate constant for this reaction. For the CO coverage, we can assume steady-state conditions, i.e.,

$$\frac{d\theta_{\text{CO}}}{dt} = 0 = S_{\text{CO}} F_{\text{CO}} (1 - \theta_{\text{CO}}) - \theta_{\text{CO}} (k_d + \theta_{\text{O}} k_r)$$

(6.9)

In this formula, $S_{\text{CO}}$ is the CO sticking coefficient and $F_{\text{CO}}$ the CO flux impinging on the surface. Furthermore, the simplification was made that the CO coverage was
not influenced by the coverage of other adsorbates. For the reactivity experiments, a low flux of roughly 0.03 ML/s was used. In this case, we approximate that $1 - \theta_{CO} \approx 1$, which leads to

$$\theta_{CO} = \frac{S_{CO} F_{CO}}{k_d + \theta_O k_r}$$

(6.10)

and

$$-\frac{d\theta_O}{dt} = \frac{k_r \theta_O S_{CO} F_{CO}}{k_d + \theta_O k_r}$$

(6.11)

Equation 6.11 leads upon integration to:

$$\ln\left(\frac{\theta_O}{\theta_{O,i}}\right) + \frac{k_r}{k_d} (\theta_O - \theta_{O,i}) = -\frac{k_r S_{CO} F_{CO}}{k_d} t$$

(6.12)

In this formula $\theta_{O,i}$ is the initial O$_{ad}$ coverage. At least for the initial reaction, when $\theta_O - \theta_{O,i}$ is small, this can be approximated with

$$\ln\left(\frac{\theta_O}{\theta_{O,i}}\right) = -\frac{k_r S_{CO} F_{CO}}{k_d} t$$

(6.13)

which can be rearranged into

$$\theta_O(t) = \theta_{O,i} \exp(-t/\tau)$$

in which $\tau = k_d/(k_r S_{CO} F_{CO})$. The slope of $\ln(1/\tau)\times R$ plotted versus $1/T$ results in the apparent activation energy

$$-E_{a,app} = -E_{a,r} + E_{ad,CO}$$

(6.14)

from which the activation energy for CO oxidation, $E_{a,r}$ can be determined when the CO adsorption energy, $E_{ad,CO}$, is known.
Summary
Oxidation of Pt(111)

The oxidation of Pt(111) by O$_2$ was studied in situ with the ReactorSTM. This unique system houses a small-volume flow cell incorporated within a STM. The combined reactor with STM is housed inside a conventional vacuum system to allow for traditional surface science preparation and analysis techniques. Under the experimentally probed conditions, we did not observe the formation of $\alpha$-PtO$_2$. This observation contradicts both previous in situ experiments and theoretical predictions. Instead, we discovered the formation of two different surface oxides, between 1.0–5.0 bar O$_2$ and 437–538 K. The first observed structure consists of small triangles forming a spoked-wheel superstructure. The STM results show an $\sim$8 % expanded lattice constant of 0.30$\pm$0.1 nm within the spokes. We propose that the driving force for this expansion is the tendency to match the lattice constant of $\alpha$-PtO$_2$. Prior to the formation of the spoked-wheel oxide, we observed a structure with a distorted, hexagonal lattice. This oxidic intermediate was not stable and transformed into the spoked-wheel oxide. When the O$_2$ pressure was increased to 5.0 bar, a second, stable structure was formed. It is proposed that it shared identical structural building blocks with the spoked-wheel oxide, namely the expanded oxide rows. However, instead of triangles, it formed a row pattern, which could be described as a lifted-row oxide with possibly a c(4$\times$8) unit cell.

This discrepancy with the SXRD studies can be explained by the fact that the surface oxides observed in this study give rise to similar in-plane diffraction peaks as $\alpha$-PtO$_2$. A second possibility is that X-ray beam-induced formation of O$_3$ was responsible for oxidizing the surface into $\alpha$-PtO$_2$, during the SXRD measurements.

High-pressure exposure (1.0 bar O$_2$) at lower temperatures did not result in well-ordered structures. However, STM images hint on the formation of both triangles and rows. The surface oxides were only fully stable at high O$_2$ pressure. After evacuating the reactor, STM images show that the structure faded, which we ascribed to O$_2$ desorption or reaction with residual gases. While O$_2$ was disappearing, the order was lost and mobility was very high. Even in high vacuum, some triangles and rows remained visible. XPS measurements (in vacuum, without exposure to ambient conditions) gave a lower estimate for the O coverage, which was 0.88 ML. This is higher than the previously observed surface oxide and supports a model of a single-layer surface oxides of expanded Pt oxide stripes.

CO oxidation and NO reduction over Pt(110)

Two catalytic systems have been studied at high pressures on the Pt(110) surface on an atomic level. The first system was the oxidation of CO by O$_2$ towards CO$_2$. In the framework of the second reaction, namely NO reduction, the effect of room temperature exposure of the surface to NO and H$_2$ was investigated. To study these reaction systems at relevant pressures, the ReactorSTM has been used. The STM images obtained with the ReactorSTM under reaction conditions show the lifting of the (1$\times$2) missing row reconstruction by high-pressure CO exposure. The lifting is followed by the formation of the (1$\times$1) metallic Pt(110) structure for high CO/O$_2$ ratios and a (1$\times$2) lifted-row
type surface oxide for more O\textsubscript{2}-rich conditions. Interestingly, the surface oxide shows a higher reactivity towards CO oxidation. The second study on this surface under a reducing environment shows different reconstructions. The room temperature exposure to H\textsubscript{2} results in the formation of a (1×4) missing-row structure and deeper, nested missing rows. The exposure to high-pressure NO removes these missing-row structures.

**Hydrophilic interaction between low-coordinated Au and water**

In this work, we study the relatively weak H\textsubscript{2}O-Au interaction on the highly stepped and anisotropic (310) surface with TPD and XPS. Compared to Au(111), we report an enhanced adsorption energy of H\textsubscript{2}O/Au(310) as observed from the (sub)monolayer desorption peak. This peak shows zero-order desorption kinetics, which we do not explain with a typical two-phase coexistence model, but rather by desorption from the ends of one-dimensional structures. These could cover both the steps and (part of) the terraces. We do not observe crystallization of ice clusters as observed on Au(111). This leads to the conclusion that this stepped surface forms a hydrophilic template for H\textsubscript{2}O adsorption. We also notice that the precise orientation of the steps determines the H\textsubscript{2}O binding strength. Despite the surface’s enhanced H\textsubscript{2}O interaction, we do not observe any significant H\textsubscript{2}O dissociation. This indicates that the presence of low-coordinated Au atoms is not enough to explain the role of H\textsubscript{2}O in Au catalysis.

**The role of water in Au-catalyzed CO oxidation at low-coordination sites**

We have studied catalytic CO oxidation at low-coordinated Au atoms using a single-crystal approach. We use electron irradiation to activate an otherwise unreactive overlayer of undissociated D\textsubscript{2}O on Au(310). A low-coverage mixture of D\textsubscript{2}O:O is subsequently allowed to react at surface temperatures from 105 K upward with CO supplied from the gas phase. XPS shows the absence of Au oxides and quantifies various O-containing species during the reaction. The dependency of the reaction rate on the surface temperature yields an activation energy for the Langmuir-Hinshelwood (LH) reaction of O\textsubscript{ad} and CO between 26±4 and 42±5 kJ/mol. Our results provide evidence that atomic O and not OH is the active reactant on small Au nanoparticles. Importantly, we observe that water has a negative effect on the reactivity of O. We conclude that the beneficial contribution of H\textsubscript{2}O to catalytic CO oxidation by small Au nanoparticles could rely on the reactive species being provided by spillover from the support.
Samenvatting
Achtergrond

In bijna alle gevallen moeten moleculen een energetische barrière overwinnen voordat ze kunnen reageren en een product kunnen vormen, bijvoorbeeld wanneer het giftige CO met O₂ het (relatief) onschadelijke CO₂ vormt. Deze energiebarrière ontstaat omdat de moleculen tijdens de reactie ongunstige overgangstoestanden moeten innemen, zoals gebeurt bij de splitsing van O₂ in losse O-atomen die daarna pas met CO kunnen reageren tot CO₂. Een katalysator stabiliseert deze ongunstige overgangstoestanden en verlaagt daardoor de reactiebarrière. Hiermee wordt de reactiviteit enorm veel groter. Om dit proces goed te kunnen begrijpen is het van belang dat we weten wat de actieve fase is van de katalysator. In het geval van heterogene katalyse, waarbij katalysator en reactanten zich in verschillende aggregatietoestanden bevinden, bestaat de katalysator meestal uit een vaste stof en de reactanten uit gasmoleculen. Alle actie vindt dan plaats op het grensvlak tussen vaste stof en gas.

De thermodynamica is de tak van wetenschap die onder andere voorschrijft welke structuur een katalysator aanneemt en hoe het grensvlak eruitziet. Deze theorie voorspelt dat de structuur met de laagst mogelijke vrije energie altijd wordt opgezocht. Hoe hoger de druk van de gasfase is, hoe ‘oncomfortabeler’ de moleculen zich hierin voelen. Een aantal van die deeltjes zal adsorberen op het oppervlak van de katalysator. Als de concentratie hiervan voldoende hoog wordt, dan is het mogelijk dat er een nieuwe structuur ontstaat die een lagere vrije energie heeft. Een voorbeeld hiervan is de oxidatie van metalen. De structuur van het oxide staat toe dat er meer zuurstofatomen opgeslagen kunnen worden dan op het oppervlak van het pure metaal.

Nu is het mogelijk de thermodynamica dusdanig te beïnvloeden dat onder vacuümdruk dezelfde structuren zouden moeten ontstaan als onder hoge druk. Dit kan tamelijk eenvoudig worden gedaan door de temperatuur van het systeem flink te verlagen. Het afkoelen zorgt er namelijk voor dat de bijdrage van de entropie aan de vrije energie verlaagd wordt. Ook dit zorgt ervoor dat gasmoleculen opgedrongen worden aan het oppervlak. Op deze manier is het mogelijk zinnige experimenten uit te voeren met meettechnieken die vacuümvraag vereisen.

Het afkoelen van het systeem kent echter een groot nadeel. Om sommige structuren te vormen is het nodig dat metaalatomen van de katalysator significant van positie veranderen. Dit is typisch het geval bij structuren die zich pas onder hoge druk willen vormen, zoals metalloxides. De energiebarrière is daarbij erg hoog en om dit voor elkaar te krijgen is er veel mobiliteit nodig. Deze mobiliteit is niet aanwezig bij sterk gekoelde systemen en de meest stabiele structuur zal niet gevormd worden binnen realistische tijdschalen. Dus ook al schrijft de thermodynamica een bepaalde structuur voor, dan is dat nog geen garantie dat dit de structuur is die bij lage temperatuur onder vacuümccondities wordt waargenomen. Experimenten onder hoge druk én hoge temperatuur zijn daarom absoluut noodzakelijk. De ReactorSTM is speciaal voor dergelijke condities ontwikkeld.
Modelkatalysatoren

Katalysatoren die gebruikt worden binnen industriële toepassingen zijn uiterst complexe systemen. Ze bestaan vaak uit metalen deeltjes van enkele tot honderden nanometers groot. Omdat alleen het oppervlak van deze deeltjes actief is, is het van belang dat ze klein blijven en niet samenkloteren tot grotere agglomeraten. Om dit te voorkomen worden de nanodeeltjes geplaatst op een drager gemaakt van oxide, zoals SiO\textsubscript{2} of Al\textsubscript{2}O\textsubscript{3}. De structuur van deze oxidedrager is op zijn beurt weer ingewikkeld en bestaat uit een samengeperst poeder waarin allerlei poriën en kanalen zitten om het oppervlak te vergroten, opdat de drager meer nanodeeltjes kan herbergen. De complexiteit maakt het nagenoeg onmogelijk de katalysator volledig te karakteriseren en een experiment op te zetten waarbij het effect van één eigenschap onderzocht wordt. Toch blijft het doel van ons onderzoek om belangrijke aspecten zoals reactiviteit en selectiviteit te begrijpen en te koppelen aan bepaalde structuren van de katalysator. Op deze manier wordt het mogelijk nieuwe en verbeterde katalysatoren te ontwerpen. Dus om de katalysator te doorgronden, wordt deze eerst vereenvoudigd tot het simpelste modelsysteem dat nog steeds als katalysator functioneert. Een eerste stap kan zijn nanodeeltjes van één enkel formaat te deponeren op een volledig vlak gepolijst oxide. Dit is een grote stap terug in complexiteit maar laat nog veel overeenkomsten bestaan met industriële katalysatoren.

We kunnen echter nog een stap verder gaan en negeren dat het metaal uit kleine deeltjes bestaat. In dat geval nemen we een vlak oppervlak van een perfect kristallijn metaal, zoals platina. De afmetingen van zo'n kristal zijn tussen de millimeter en centimeter. Om deze modelkatalysator reproduceerbaar en perfect schoon te krijgen is het nodig het oppervlak voor elk experiment met een aantal vacuüntechnieken grondig te reinigen. Als eerste worden met argonionen de bovenste lagen van het kristal inclusief verontreinigingen weggebombardeerd, waarna de kristalliniteit van het oppervlak wordt hersteld door het hierdoor beschadigde oppervlak naar hoge temperaturen te verhitten. Deze procedure wordt meerdere malen herhaald om een schoon en vlak oppervlak te krijgen.

De ReactorSTM

De meetopstelling die ik voor mijn onderzoek heb gebruikt, is een speciale variant van een rastertunnelmicroscoop (Scanning Tunneling Microscope, STM). Deze microscoop geeft de structuur van een oppervlak op atomaire schaal weer. Een STM wijkt af van een standaardmicroscoop waarbij licht gebruikt wordt en tast een oppervlak als het ware af. In een STM gaat een scherpe naald, de zogenaamde tip, vlak boven het oppervlak heen en weer. Wanneer er tussen tip en oppervlak een spanning gezet wordt, dan kunnen elektronen tussen tip en oppervlak overspringen. Hiervoor moet de tip zich dicht bij het oppervlak bevinden, maar zonder het te raken. De grootte van de gemeten stroom is sterk afhankelijk van de afstand tussen tip en oppervlak. Bij de scanbeweging van de tip over het oppervlak varieert deze stroom overeenkomend met de structuur van het oppervlak. STM is één van de weinige meetapparaten die vrijwel evengoed onder ultrahoog-vacuüm (UHV) werken als onder hoge druk. Een verhoogde gasdruk kan atomen op het oppervlak mobieler maken en wellicht zal het gas ook met de tip reageren.
Hoewel een STM bij hoge druk en hoge temperatuur daardoor soms moeilijk werkt, blijft het meestal mogelijk atomaire resolutie te halen. De gebruikte STM is een speciale uitvoering waarbij een kleine hogedrukreactor is geïntegreerd in het hart van de microscoop. Deze ‘ReactorSTM’ is geplaatst in een UHV-systeem, waarin allerlei apparatuur geplaatst is voor standaard vacuümtactieken, zoals voor het schoonmaken van het preparaat, het opdampen van deeltjes, en voor de karakterisering van het oppervlak met elektronendiffrajectie en -spectroscopie.

Met een speciale gaskast kan er een mengsel gemaakt worden met instelbare verhoudingen en een druk van ongeveer 1 mbar tot aan 6 bar. Nadat dit gaseelement de modellkatalysator gepasseerd is, stroomt het naar een aparte UHV-kamer waar een deel van de gasstroom naar binnen lekt. In deze kamer wordt met behulp van een quadrupool-massalspectrometer de gassamenstelling bepaald. Op deze manier kan een verandering in reactiviteit direct worden gecorreleerd aan een structuurverandering, die we kunnen waarnemen in de STM.

**Ultradunne oxidelaag op Pt(111)**

Platina is één van de meest gebruikte metalen in katalysatoren voor oxidatieracties. Deze katalysatoren worden dus aan hoge O₂-drukken blootgesteld. Traditioneel werd gedacht dat edelmetalen zoals platina geen oxideren vormen en metallisch blijven onder deze omstandigheden. Recent werk, onder andere uit onze onderzoeksgroep, laat echter zien dat platina en het net wat minder edele palladium toch structuren vormen die sterk lijken op oxides. Deze ontdekking motiveerde mij de oxidatie van platina nader te bestuderen met de ReactorSTM. Als modellkatalysator is gekozen voor Pt(111). Dit is het platina-oppervlak waarbij de platina-atomen zo dicht mogelijk op elkaar zitten. Daarom is dit het meest stabiele oppervlak en hebben de grootste facetten van nanodeeltjes een (111) oriëntatie. Pt(111) is dus een uiterst representatieve modellkatalysator. Onder vacuümvcondities is het niet mogelijk Pt(111) te oxideren met O₂. Hoewel de thermodynamica voorspelt dat het mogelijk moet zijn om al bij lage O₂-druk platina om te zetten in α-PtO₂, beurt dit niet. De eerste stap in het oxidatieproces is de dissociatieve adsorptie van O₂ tot atomair zuurstof:

\[
O_2 \rightarrow 2O_{ad}
\]

De snelheid waarmee deze reactie verloopt, neemt af naar null naarmate het oppervlak meer zuurstofatomen bevat; de adsorptie komt tot stilstand lang voordat een oxide kan ontstaan. Een ‘woud’ aan verschillende oxides, waaronder α-PtO₂, kan wel gevormd worden indien sterker oxiderende gassen worden gebruikt, als NO₂, O₃ en bundels van atomair zuurstof. Deze waarnemingen beantwoorden helaas niet de vraag wat de relevante fase is onder chemische reactiecondities. Om deze vraag te beantwoorden blijft het nodig metingen onder reactiecondities uit te voeren.

Ik heb het volgende experiment uitgevoerd: een Pt(111)-kristal werd schoongemaakt volgens de gebruikelijke methodes en geplaatst in de reactor. Het reactorvolume werd gevuld met argon tot 1,2 bar en het kristal werd verhit tot 527 K. Terwijl ik het oppervlak voortdurend afbeelde met de ReactorSTM, veranderde ik de
gassamenstelling naar een 5:1 mengsel van O\textsubscript{2} en Ar. Er ontstond een structuur van driehoekjes met zijden van ongeveer 2,3 nm. De details laten zien dat de zijden bestaan uit rijen van 7 tot 8 platina-atomen. De afstanden tussen deze platina-atomen zijn enigszins groter dan die in het onderliggende Pt(111)-rooster, terwijl de structuur in de richting loodrecht op de rijen wel precies op het rooster past. Het is vooral de aansluiting met het onderliggende substraat waarin deze structuur fundamenteel afwijkt van \( \alpha \)-PtO\textsubscript{2}. Het model dat ik uit mijn STM-waarnemingen aflees, bestaat uit een spakenwiel-superstructuur opgebouwd uit driehoeken. Elke zijde van zo’n driehoek kan beschouwd worden als eéndimensionale oxiderij. Onder realistische, katalytische condities vormt Pt(111) dus een oppervlakte-oxide in plaats van het bulkoxide, \( \alpha \)-PtO\textsubscript{2}. De heersende discussie of \( \alpha \)-PtO\textsubscript{2} wel of niet reactief is, blijkt dus niet relevant te zijn. De vraag die we wel moeten stellen is hoe reactief dit oppervlakte-oxide is. De eerste indruk is dat dit oxidaal laagje enorm reactief is, want zodra de reactor werd leeggepompt, verdween de structuur. Dit betekent dat O\textsubscript{2} desorbeert of reageert met restgassen.

**Oppervlakte-oxides en reconstructies op Pt(110)**

Een gelijksoortige studie (deels door mijn voorganger, Dr. Kees T. Herbschleb en deels door mijzelf) is uitgevoerd op een andere oppervlakte-oriëntatie van platina, het (110)-oppervlak. Dit hebben wij blootgesteld aan zowel oxiderende condities, een zuurstofrijke mengsel met wat CO, als aan reducerende condities, zowel H\textsubscript{2}, CO, als NO. Dit oppervlak heeft een lagere dichtheid aan Pt-atomen dan het (111)-oppervlak en is daardoor instabiel. Dit heeft tot gevolg dat het oppervlak reconstrueert wanneer het vrij is van adsorbaten. De reconstructie heeft een missende-rijstructuur, waarbij elke tweede rij mist. Door invloed van de gascondities veranderde dit oppervlak op verschillende manieren: of door een oxidaan te vormen of door van reconstructie te veranderen.

Het zuurstofrijke mengsel met CO zorgde voor een oppervlakte-oxide, maar verschillend van het oxidaan wat zich vormt op Pt(111). Dit oxidaan op Pt(110) is reactiever in de oxidaatie van CO dan het metalen oppervlak. Dit spreekt de heersende opvatting binnen heterogene katalyse tegen die stelt dat oxidaatie van een katalysator de reactiviteit niet ten goede komt.

Na blootstelling aan CO of NO verdween de missende-rij-reconstructie en er ontstond een structuur die men zou verwachten wanneer een bulk Pt kristal wordt doorklieft. Dit is in overeenstemming met de uitkomsten van eerder onderzoek onder vacuüumcondities. In dit geval zien wij geen nieuwe structuren. Wanneer het oppervlak werd onderworpen aan een hoge H\textsubscript{2}-druk, gebeurde het tegenovergestelde. De reconstructie werd nog sterker: in plaats van elke tweede rij ontbraken nu drie van de vier rijen. Dit leidde tot een oppervlak met een soort zaagtandprofiel. De conclusie van dit werk is dat bij reactiere oppervlakken de veranderingen in de gasatmosfeer grote verschillen in de structuur tot gevolg kunnen hebben.
Het effect van $\text{H}_2\text{O}$ op CO oxidatie op Au

Het grootste deel van mijn promotiewerk heb ik uitgevoerd met een STM onder reactiecondities. Vaak zijn deze experimenten niet eenvoudig te analyseren. Daarom maken we dankbaar gebruik van het voorwerk dat is gedaan onder vacuümcondities. Deze combinatie stelt ons in staat de modelkatalysator onder reactiecondities te begrijpen. Het laatste deel van mijn proefschrift beschrijft een reeks experimenten onder vacuümcondities. Hiermee kon gedetailleerde informatie verkregen worden, wat niet mogelijk is onder hogedrukv- en hogetemperatuurcondities.

Het toevoegen van wat $\text{H}_2\text{O}$ aan een mengsel van CO en O$_2$ vergroot de reactiviteit van een Au-katalysator. Het is echter nog steeds de vraag hoe dit precies werkt. Mijn experimenten richtten zich op het vergaren van fundamentele kennis over de interactie tussen $\text{H}_2\text{O}$ en Au en over de Au-atomen in stapranden in het bijzonder. Deze Au-atomen bleken niet reactief genoeg om $\text{H}_2\text{O}$ te dissociëren. Wel zorgden ze ervoor dat $\text{H}_2\text{O}$ veel sterker aan het oppervlak gebonden was; het oppervlak werd hydrofiel in tegenstelling tot Au(111). Ook suggereerde mijn resultaten dat $\text{H}_2\text{O}$ ééndimensionale rijen vormde, die parallel liepen aan de stappen.

Wanneer het $\text{H}_2\text{O}$ moedwillig werd gefragmenteerd door bestraling met elektronen, vormde zich een mengsel van $\text{H}_2\text{O}$ en O-atomen. Dit mengsel bevatte onnoemenswaardig weinig OH-moleculen, wat verklaard kon worden door aan te nemen dat de reactie

$$\text{H}_2\text{O} + \text{O} \rightarrow 2 \text{OH}$$

endotherm is. Het mengsel van $\text{H}_2\text{O}$ en O-atomen was al op zeer lage temperaturen reactief. Onze experimenten laten echter nog niet zien hoe $\text{H}_2\text{O}$ de reaktiviteit van Au-katalysatoren verhoogt. Het is mogelijk dat de oxidedrager bij het effect van $\text{H}_2\text{O}$ een sleutelrol speelt. Dat zou verklaren dat dit effect juist niet bij onze modelkatalysator kon optreden.

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List of publications
Peer-reviewed publications


   *Oxidation of Pt(111) at elevated temperature and high pressure: The formation of novel surface oxides*, to be published

2. P.V. Dudin, Y.I. Yanson, N. Vasiljevic, M.T.M. Koper, J.W.M. Frenken, and M.A. van Spronsen

   *Gold-coated tungsten tips for imaging in reactive environments with scanning tunneling microscopy*, to be published


   *Operando studies of NO reduction by H2 over Pt using surface X-ray diffraction and transmission electron microscopy*, to be published


   *Fast and Reliable Pre-Approach for Scanning Probe Microscopes based on Tip-Sample Capacitance*, to be published


   *The role of water in Au-catalyzed CO oxidation at low-coordination sites*, submitted

6. V. Navarro, M.A. van Spronsen, and J.W.M. Frenken

   *In situ observation of self-assembled Fischer-Tropsch products on a cobalt catalyst*, submitted

*Hydrophilic interaction between low-coordinated Au and water: \( H_2O/Au(310) \) studied with TPD and XPS*

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*High-pressure operando STM studies giving insight in CO oxidation and NO reduction over Pt(1 1 0)*


*Erratum to “High-pressure operando STM studies giving insight in CO oxidation and NO reduction over Pt(1 1 0)” [Catal. Today 244 (2015) 85–95]*


*The ReactorAFM: Non-contact atomic force microscope operating under high-pressure and high-temperature catalytic conditions*


*The ReactorSTM: Atomically resolved scanning tunneling microscopy under high-pressure, high-temperature catalytic reaction conditions*


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**Other publications, interviews, etc.**


*De actieve fase van een katalysator bestudeerd met de perfecte combinatie van experimenten onder hoge druk en vacuüml Protesten*

Article competed for the NEVAC Prize, Dutch Vacuum Society (2015)

Curriculum vitae
Matthijs André van Spronsen was born in Leiderdorp, the Netherlands, on March 8, 1987. He graduated from gymnasiun\textsuperscript{6} at the Bonaventura College in Leiden in 2005, with a major in the natural sciences. Van Spronsen finished his B.Sc. degree in Chemistry with a research project focusing on the interaction between CO and H atoms towards understanding interstellar methanol formation. This was a theoretical project and a collaboration between the group of Prof. Dr. Ewine F. van Dishoeck and the group of Prof. Dr. Geert-Jan Kroes under the daily supervision of Dr. Stefan Andersson.

Van Spronsen’s experimental research project for his M.Sc. degree in Chemistry was conducted in the group of Dr. Ludo B.F. Juurlink and was devoted to the interaction between H$_2$O and CO on a stepped surface of a Au single crystal. Before graduating cum laude, he spent a semester in the group of Prof. Dr. Gabor A. Somorjai at the University of California, Berkeley and the Lawrence Berkeley National Laboratory in California, the United States of America. In this project, van Spronsen performed a kinetic study to probe the role of the support on Pt nanoparticles in several reactions.

Van Spronsen performed the research for his PhD degree in the group of Prof. Dr. Joost W.M. Frenken in the Leiden Institute of Physics (LION) of Leiden University. After Frenken accepted a position as director of the Advanced Research Center for Nanolithography in 2014, Dr. Irene M.N. Groot started leading the research group and became a copromoter of van Spronsen. The original scope of his PhD project was the combination of in situ STM and AFM. During the project, the scope was widened to incorporate the STM studies in this thesis. Van Spronsen did many chemical experiments using the ReactorSTM. Furthermore, he did experiments at the Elettra Synchrotron, Trieste, Italy under the supervision of Juurlink, his second copromotor.

After defending his PhD thesis, van Spronsen plans to continue his scientific career as a postdoctoral fellow in the group of Prof. Dr. Cynthia M. Friend at Harvard University in Cambridge, Massachusetts, the United States of America.

\textsuperscript{6}preuniversity education including ancient Greek


Bibliography


