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CO oxidation catalysis at multiple length scales

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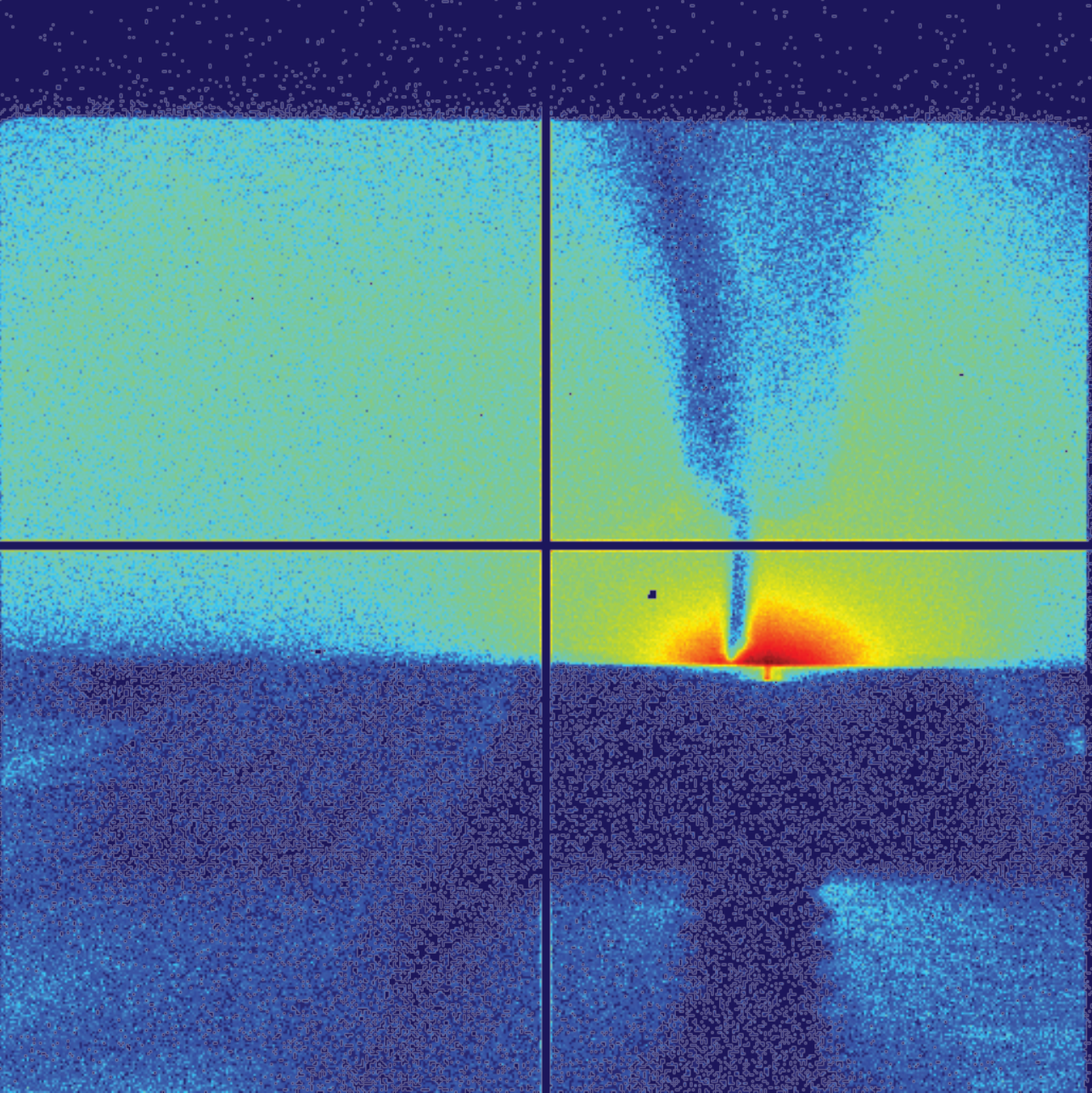


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Willem Onderwaater

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aan mijn ouders

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Preface

The use of catalysts has become an essential part in many industrial production processes. Exerting control over chemical reactions with the help of catalysts is an important aspect of our chemical industry. From the petrochemical to the pharmaceutical industry and in the production of many materials, catalysts are widely used to create the chemicals society relies upon. In order to expand and refine the application and usefulness of catalysis, a detailed, atomic-scale understanding of all aspects of catalytic reactions is fundamental.

The oxidation of CO forms a popular model system for heterogeneous catalysis. In this reaction, two types of molecules, carbon monoxide and oxygen, adsorb on the catalyst surface. Upon adsorption, each oxygen molecule dissociates into two atoms. When a carbon monoxide molecule and an oxygen atom meet, they can react to form carbon dioxide, which desorbs after the reaction. The task of the catalyst is to bring together the reactants and possibly lower the barrier for formation of the product. In this way, the effective activation energy of the reaction is reduced, which lowers the temperature at which the reaction can take place. This is one of the general roles of a catalyst. In addition to making the reaction conditions more favourable, catalysts are also developed to improve the selectivity of desired products over side products.

The basic mechanism of even a simple, heterogeneous catalytic reaction, such as CO oxidation, involves a wide variety of physical and chemical concepts. These range from basic considerations of the atomic-scale structure of the catalyst's surface and its interactions with the reactant molecules to the large-scale architecture of the catalyst itself and the reactor vessel in which the chemistry is to take place. Each of these individual elements forms an important research field in itself. In addition, understanding the interplay between all these aspects forms a formidable challenge of catalysis.

Let us inspect a few of the elementary reaction steps in more detail by considering a catalytic process at a modest pressure of 1 atmosphere and a modest temperature, namely room temperature. Under these conditions,

every active atom on the catalyst surface is visited approximately every nanosecond by a reactant molecule from the gas phase. If the molecule adsorbs, its location on the surface may not be its last resting place. The molecule may diffuse over the surface to other, possibly more favourable locations. The molecule can dissociate upon adsorption. It can dissolve and travel into the bulk. The dissociated molecule can chemically engage with the catalyst to form a new chemical compound together with catalyst atoms. Reactant molecules that are attached to the surface, can execute a chemical reaction with each other. In many cases, more than a single reaction pathway is available, leading to more than a single possible type of product molecule. If the catalyst functions properly, the product molecules will desorb from the surface and make place for new reactants to adsorb.

Which of the reaction pathways is followed, depends on the energy landscape of the reaction, i.e. the total potential energy of the combination of the catalyst and the molecule or molecules that reside on it as a function of all spatial coordinates of the atoms of the catalyst and the molecules involved. The shape of this energy landscape depends on the chemical and physical characteristics of the relevant molecules and the catalyst and their interaction. It contains all the details of the Van der Waals type interactions that the molecules experience at a large distance from the catalyst and the electronic interactions that lead to the possible binding and dissociation of the molecules at close distance. This landscape is a very-high-dimensional potential energy surface, in which many parameters can be relevant, such as the precise position and orientation of each molecule, the internal deformations of the molecules and the detailed rearrangements of the catalyst surface, in response to the presence of the adsorbate. As such, it contains all information on energy barriers for diffusion, dissociation, reaction, desorption and all other processes that the molecule-catalyst system can engage in.

It may be clear from this introduction that catalysis is typically so complex that no single experiment can reveal all relevant details of a reaction, for example finding the reaction pathways, the precise geometrical configurations, the corresponding electronic rearrangements and the energy barriers that are involved in each of the reaction steps. In practice, one has to combine a multitude of information obtained with various experimental techniques, in order to unravel a catalytic reaction. Usually, microscopy is required to identify bonding geometries, often under conditions that are remote from real reaction conditions, spectroscopic techniques are employed to acquire information about the electronic and chemical bonding characteristics of reactants, intermediate products and final products, and dynamic,

temperature-dependent measurements are used to measure rates, binding energies and energy barriers.

Theoretical predictions of the potential energy surface are often obtained with the use of Density Functional Theory (DFT). In view of the enormous complexity of the energy landscapes of even the simplest reactions, usually these calculations are restricted to very limited ranges of configurations and reaction pathways. Combining the total-energy calculations with the thermodynamic contributions from the reactants in the gas phase, one can construct the more relevant free-energy landscape, with the most probable surface and adsorption geometries. Additional calculations are then still required to determine energy barriers and model the kinetics of a catalytic process, which is necessary to establish to what extent the reactions define a dynamic equilibrium configuration that deviates from the thermodynamic equilibrium structure.

The catalyst can take a variety of shapes. For fundamental research studies, usually simple shapes are used, such as that of a flat, single-crystal surface. Practical catalysts, such as in the car catalyst or in most industrial processes, often take the form of an ensemble of nanoparticles. Usually, these are residing on a support structure, such as an oxide or a zeolite. On a larger scale, the catalyst material is often shaped in the form of pellets. On a macroscopic, industrial scale, these pellets are loaded into a reactor vessel. This hierarchy of length scales and materials brings in additional elements of complexity in the behaviour of catalysts. For example, the geometry of the reactor and the material loaded into it, will influence the flow pattern of the reactants and products, the distribution of the composition of this flow, and the temperature distribution. In turn, all of these parameters may influence the local state of the catalyst, the local reaction mechanism and the local reaction rate and these can all vary from one side of the reactor to the other.

Even though some of the basic catalytic mechanisms may be unraveled in great detail under laboratory conditions that are very remote from actual reaction conditions, in particular under low pressures or even ultrahigh vacuum, it is essential that sensitive experiments are also conducted with a variety of techniques at elevated temperatures and elevated gas pressures. To this end, the last decade has seen an enormous effort to develop new equipment for catalysis research. Techniques like Transmission Electron Microscopy (TEM), Surface X-ray Diffraction (SXRD), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS) have been successfully adapted to study catalysis at high pressures. Part of the present PhD thesis is devoted to such devel-

opments. Chapters 1 and 2 present two new setups to investigate catalytic reactions. In chapter 1 we present a setup that combines SPM with SXRD. Both techniques are able to resolve features at a length of Ångströms. With the combination of a scanning probe technique and a diffraction technique we aim to couple structural information on the surface over length scales ranging from atoms to micrometres. To investigate the behaviour of the catalyst at millimetre length scales we present a simple optical technique in chapter 2. This technique monitors the optical response of a flat catalyst with 1 centimetre diameter during a reaction. At this length scale the influence on the surface composition and roughness due to variations and gradients in the composition of the gas phase becomes visible.

To make optimal use of the available techniques we have developed new software to combine, reduce and analyse large volumes of x-ray data. Chapter 3 presents the analysis program BINoculars for SXRD data. This software package allows one to handle and combine large amounts of data from a surface diffraction beamline and to analyse these in a convenient and natural way.

Spontaneous reaction oscillations are one of the manifestations of complex behaviour that can result from the collective interplay of different aspects of a catalytic reaction. In chapter 4 we investigate reaction oscillations in the CO oxidation reaction on a palladium(100) surface. Intervals of high surface reactivity are periodically followed by an intervals of low reactivity. This oscillatory behaviour results from interaction between the surface reactivity and the gradients of the CO partial pressure in the reactor. We analyse in detail the structure and morphology of the catalyst surface in order to investigate the origin of the specific oscillation characteristics. A possible ingredient of the oscillation is the distribution of length scales of surface roughness that can form during the intervals with high reactivity. This concept is explored further in chapter 5 where we calculate if the observations of chapter 4 can be explained by the evolution of the roughness characteristics.

By changing from a single-crystal catalyst to a nanoparticle system in chapter 6, we attempt to study catalysts in an in a geometry that is closer to what is used in practical applications. The technological step required to analyse nanoparticles as opposed to single-crystal surfaces is considerable. Dedicated experimental tools to analyse nanoparticles under operating conditions, like in situ TEM, have become available only recently. We use three experimental tools, TEM, STM and SXRD, to investigate how palladium nanoparticles change shape during the oxidation of CO.

Chapter 1

Combined scanning probe microscope and X-Ray Scattering instrument for in situ catalysis investigations

We have developed a new instrument combining a scanning probe microscope (SPM) and an x-ray scattering platform for ambient-pressure catalysis studies. The two techniques are integrated with a flow reactor and an ultrahigh vacuum system that can be mounted easily on the diffractometer at a synchrotron end station. This makes it possible to perform simultaneous SPM and x-ray scattering experiments under conditions that are relevant for catalysis.

1.1 Introduction

In recent years, operando catalysis research has witnessed the development of a number of experimental surface-science techniques for application under harsh conditions, in some cases even approaching those of industrial catalysis. Examples are X-ray Photoelectron Spectroscopy (XPS) [1], X-ray scattering techniques [2, 3], Transmission Electron Microscopy (TEM)[4, 5], Scanning Tunnelling Microscopy (STM) [6–8] and Atomic Force Microscopy (AFM) [9], which have been developed to investigate a wide array of relevant catalytic systems. Each of these techniques contributes only a specific component to our understanding of heterogeneous catalysis. In view of the complexity of the catalytic process, techniques have to be combined in order to arrive at a sufficiently complete description of the working mechanisms of a catalyst. Unfortunately, combining information from different techniques is not straightforward since a catalyst under operating conditions is a dynamical system that depends on numerous other factors, such as reactor geometry, sample size, gas flow rates etc. Every technique introduces constraints that often make it difficult to study catalysts in precisely the same environment.

This chapter describes the integration of a scanning probe microscope with an x-ray scattering platform in a flow-reactor, combined with an ultrahigh vacuum (UHV) system that can be mounted on a diffractometer. With this experimental setup we can directly combine x-ray scattering data with real-space data obtained with the microscope. Independently, both x-ray techniques and SPM have proven to be powerful tools for understanding surface structures in operando conditions [10–13]. Nonetheless both techniques possess a number of limitations that can be circumvented by combining the two techniques in one setup.

One of the limitations of the generally employed x-ray techniques, such as Surface X-ray Diffraction (SXRD) and Grazing Incidence Small Angle X-Ray Scattering (GISAXS), is that these are averaging techniques, i.e. they rely on the addition, coherent or incoherent, of photons originating from a large volume of scatterers[14, 15]. For in situ catalysis experiments this volume consists of a collection of nanoparticles or a large single-crystal surface area. In the interpretation of these averaging experiments, the assumption is usually made that the entire area illuminated by x-rays exhibits the same characteristics. This assumption, however, is not always justified. In the case of nanoparticles, signal averaging results in a convolution of the signals originating from the individual particles. These are impossible to disentangle without additional information. A frequently employed work-around for this limitation is to analyse the nanoparticle ensemble before

and after the catalysis experiment, with a measurement technique such as Scanning Electron Microscopy (SEM). This way, the size distribution of the nanoparticles can be measured accurately but because the distribution changes during the catalytic activity of the nanoparticles, the connection between the x-ray data and the particle distribution can be still hard to make.

In contrast, the STM and AFM only probe a small area of the catalyst, so that the results obtained with these scanning probe techniques do not suffer from averaging effects. But, as mentioned before, there is no guarantee that the imaged area is representative of the entire surface. A second limitation of SPM is that it only probes the top layer, while interesting phenomena might be occurring below. Even though the STM and AFM images display clear, atomic-scale features, it is challenging to extract quantitative structural information directly from the images.

The limitations of the two classes of techniques, real space and reciprocal space, can be largely overcome by combining them in a single instrument. For example, for a catalyst composed of nanoparticles, the combination will make it straightforward to obtain information about their size distribution, spatial ordering and internal structure. By gathering the SPM and x-ray data in the same setup under the same experimental conditions, one can be certain that they reflect precisely the same state of the model catalyst. Although simultaneous measurements are preferred, the ability to perform the measurements sequentially under identical conditions improves the comparability of the data.

The use of SPM techniques at synchrotron beamlines is well established. AFM and STM are used in combination with synchrotron radiation for combined imaging and spectroscopy [16–18]. X-ray interaction with the sample is used as a contrast mechanism for imaging to create chemical maps of the sample. Using this technique, atomic-scale resolution can be achieved [19]. AFM is also used for applying stress and inducing strain in nanopillars by indenting them from above. The lattice deformation caused by the stress can be investigated using nanometer-wide x-ray beams [20]. The SPM-X-ray combination presented here, integrated with a UHV chamber and a flow reactor, is novel and enables the application of this combination of techniques to the field of catalysis.

In this chapter, we describe the design and performance of the combined SPM and x-ray scattering setup. A complete view of the setup is presented in figure 1.1. Our design is based on the ReactorSXR setup [21] that has been developed previously at the ID03 beamline of the European Synchrotron Radiation Facility for in situ study of catalyst surfaces by surface x-ray

diffraction [22], and on the ReactorSTM [7] and ReactorAFM [9] setups that have been developed earlier at Leiden University. It combines a UHV system for sample preparation procedures with a flow reactor, in which gas pressures up to 1 bar and sample temperatures up to 1000° C can be achieved. The SPM part of the new instrument is integrated with the flow reactor. This enables us to 'image' catalytically active systems in situ in real space with the SPM and in reciprocal space with the x-rays.

1.2 Design Specifications

The design should be optimised for high-pressure catalysis studies with the combination of synchrotron-based x-ray scattering and scanning probe microscopy on well-defined model catalysts, such as flat, single-crystal surfaces and nanoparticle ensembles on flat substrates. This combination imposes heavy constraints on the design of the SPM part of the instrument.

For our studies of heterogeneous catalysis, we require a low level of contaminants in the reactor. Atomically clean surfaces of a model catalyst can be obtained by thoroughly cleaning a sample in a UHV environment before installing it in the reactor. Such cleaning typically involves multiple cycles of ion sputtering and annealing. The UHV chamber should therefore facilitate ion bombardment, sample heating and direct transfer of the sample into the reactor, without exposure to the ambient. Additional sample treatment, e.g. for the preparation of nanoparticle ensembles, may further require the possibility for controlled deposition of metals and other materials, prior to introduction of the sample into the reactor. The requirement of low contamination levels also applies to the gas supply system and the reactant gases that are to be supplied to the flow reactor. Special care has to be taken to select only catalytically inactive materials for all parts that are exposed to the gas mixtures. The pressure range that we address with this setup reached from 200 mbar to 1 bar. The temperature window runs from room temperature to 1000° C. Over these ranges of pressure and temperature, a large number of relevant catalytic processes occur. It should also be possible to change the temperature and the pressure during the experiments. Since one of the goals of the experiment is to correlate the detailed information that we obtain on the catalyst structure with its catalytic performance, mass spectrometry is required, in order to measure the composition of the gases flowing out of the reactor, during the x-ray scattering and SPM experiments.

For surface characterisation studies such as SXRD, the rigidity of the sample support is important. It should be sufficient to ensure the alignment

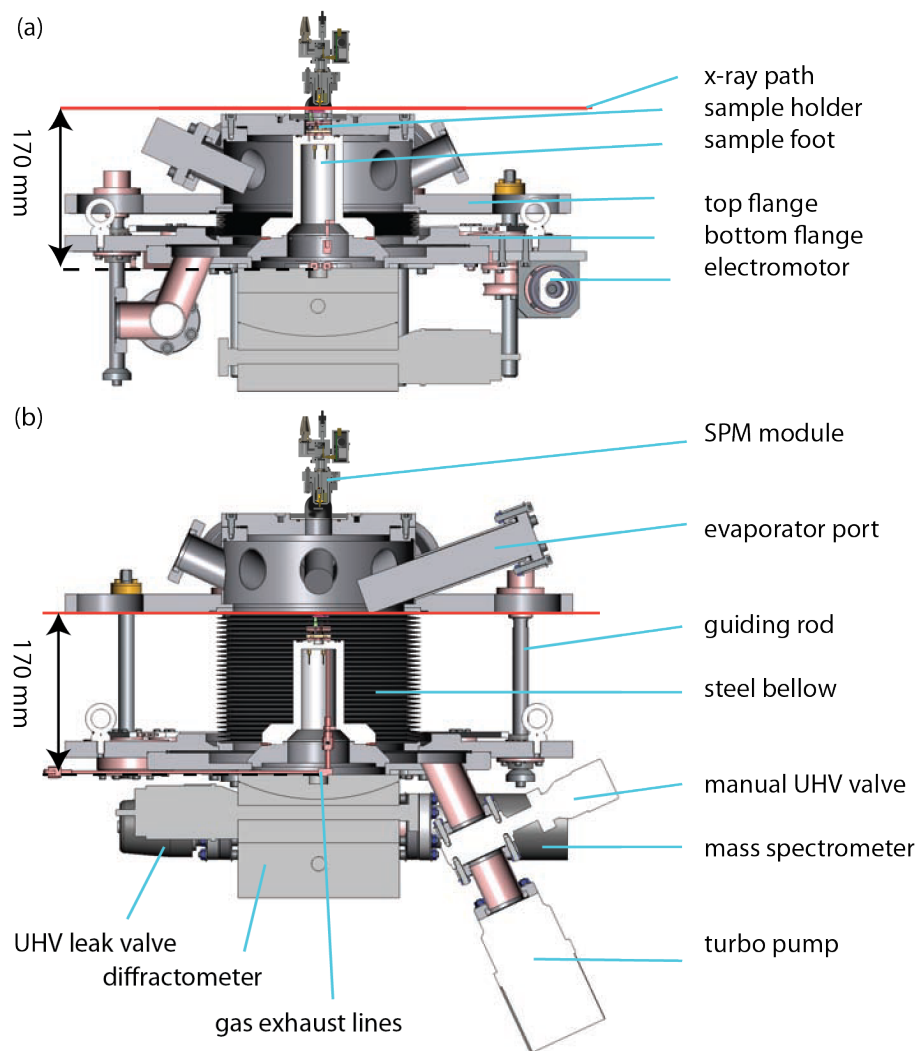


Figure 1.1. Cross section view of the complete SXRD+SPM system. The top flange of this chamber can be translated vertically. When the flange is at its lowest point, (a) the chamber is in measurement configuration. The sample is enclosed by the dome-shaped reactor, which is sealed off from the UHV part of the system. The x-ray beam now has a pathway to the sample. A quadrupole mass spectrometer is used to measure the composition of the gas that leaves the flow reactor via an exhaust capillary. When the flange is in the highest position (b) the chamber is in the UHV preparation configuration. The SXRD system in Figure (b) is shown 90° rotated with respect to the view of figure (a). The sample is exposed to UHV and is available for preparation purposes (ion bombardment, deposition, etcetera). The SPM part is the unit on top of the dome-shaped reactor, which is shown in more detail in figure 1.2

of the sample and to keep its position on the diffractometer completely unchanged over the course of an experiment. The sample has to be accessible for the incident x-rays and the diffracted x-rays require a wide window of exit angles for detection. The experimental setup should fit on a six-circle diffractometer and be rotatable over 90 degrees around central axis (a vertical axis through the sample foot and sample holder in figure 1.1). This ensures that a sufficiently large volume of reciprocal space is available for x-ray scattering. Slits separating the diffracted signal from the background should be mounted on the detector arm as close to the sample as possible. This restricts the space available to the SPM part of the setup to a narrow cone, extending above the sample surface around the central axis of the chamber.

In a typical beamline environment, a combination of pumps and other necessary equipment generates electrical, mechanical and acoustical noise. The diffractometer and the experimental setup are positioned in an experimental hutch that is inaccessible when the x-ray beam is in the hutch. These conditions are far from ideal for high-resolution SPM imaging. The best image quality that can be achieved, largely depends on the degree to which the SPM part can be isolated from these interference signals. Most problematic in this respect are the mechanical vibrations. Since the x-ray scattering experiments require the model catalysts to be rigidly connected to the diffractometer, the SPM cannot be isolated from mechanical vibrations by the typical combination of isolation legs, internal spring suspension and eddy current damping that would otherwise be used to reach atomic resolution. Our only option to keep the resulting mechanical interference to a minimum is to keep the so-called mechanical loop between the tip of the SPM system and the sample surface as small and rigid as possible. This will ensure that the resonance frequencies of the loop are much higher than the frequencies of most of the mechanical vibrations that the microscope is forced to participate in, so that these external vibrations cannot distort the loop significantly. In view of the expected residual sensitivity to mechanical vibrations, our target for the SPM has been to reach sufficient resolution to image monatomic steps on model catalyst surfaces, rather than to reach full atomic resolution. The design and construction have been performed on a best-effort basis. Another element of concern is the response of the piezo element that is used to actuate the SPM to the high-temperature, high-pressure conditions. The element has to remain below its Curie temperature, even when the model catalyst is significantly above that temperature. The combination of the necessary temperature gradients between a hot sample and a much cooler piezo element with the high gas pressure introduces

fluctuating, convective gas flows that can lead to erratic expansions and contractions of the piezo element and other components of the mechanical loop, which introduces strong, varying distortions in the images.

1.3 Design

As the basis for our design, we have used the ReactorSXRd setup that has been developed previously for high-pressure, high-temperature SXRd experiments on model catalyst. This instrument satisfies all requirements that we formulated for the x-ray scattering experiments [21]. Here, we first summarise the special features of this setup and then discuss the combination of it with the SPM unit. For further details of the ReactorSXRd design and performance, we refer to Ref. [21].

In short, the ReactorSXRd setup is configured as the combination of a sample, mounted in a holder on a rigid support inside a UHV system with an adjustable volume and a flow reactor. The UHV chamber is formed by a large-diameter bellow between two horizontal flanges. The bottom flange is bolted on the diffractometer. Using a motor drive and a set of spindles, the top flange can be translated up and down in a controlled manner. In this way, one can choose for a geometry with the top flange in a high position, in which the sample is fully in the UHV environment, while an evaporation source and an ion gun are pointing at its surface; this is the configuration that is used for sample preparation. With the top flange in the lower position, a seal structure between the sample support and the top flange makes a nearly UHV-tight separation between the reactor volume and the UHV chamber. In this configuration, the sample is surrounded by a spherical dome of an x-ray transparent material. Gas tubes in the sample support column are used to supply the small, 60 ml, reactor volume with a flow of a gas mixture, of which we independently control the composition, the pressure and the flow rate over relatively large ranges.

For x-ray scattering experiments, we use a beryllium dome, in view of their excellent transmission for x-rays. We have developed an alternative, dedicated aluminium dome for the combined x-ray and SPM experiments. A miniature SPM unit has been constructed that meets all requirements of available space, compactness and insensitivity to high sample temperatures and gas convection effects. It is mounted on top of the aluminium dome.

The geometry of the combined instrument has been kept completely modular, which enables us to exchange components easily and switch between STM, AFM or purely SXRd modes of operation.

In the remainder of this section, we will provide a more detailed descrip-

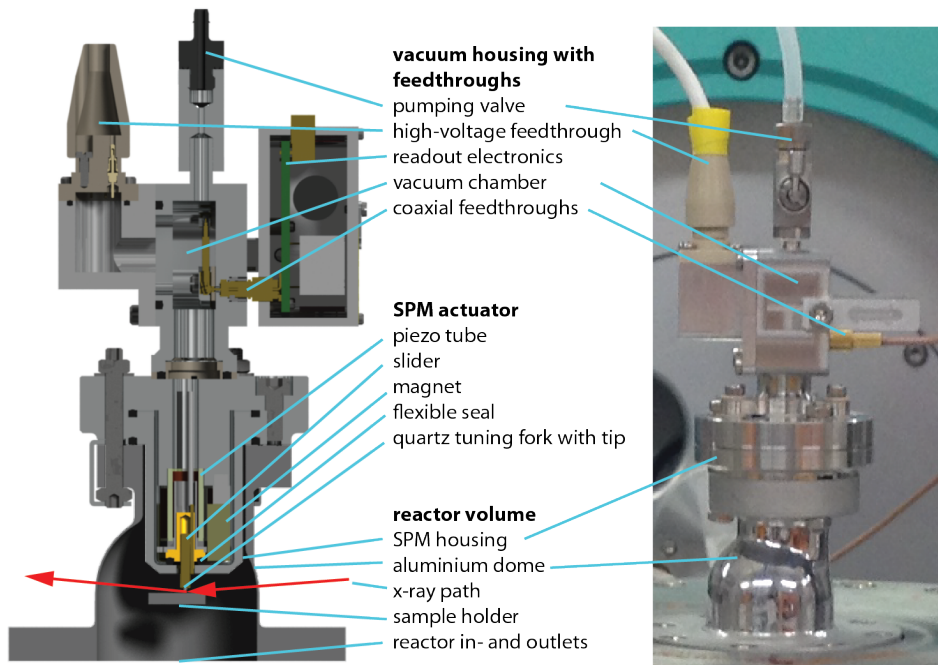


Figure 1.2. Schematic cross section (left) and photograph (right) of the x-ray transparent aluminium dome that defines the reactor volume. In the cross section, the sample is indicated together with incident and reflected x-rays (red arrows). The SPM part of the system is mounted on top of the dome and partially reaches into the dome. The STM tip or the AFM tuning fork with tip are located on the central axis of the dome and the sample. A flexible seal separates the high-pressure reactor volume from the vacuum that surrounds the piezo element. In the photograph the electronics are replaced by cables connecting to a pre-amplifier at 30 cm distance

tion of the part of the setup that is shown in figure 1.2, which contains the essential, new elements, such as the aluminium dome and the SPM part. As mentioned already, details of the rest of the ReactorSXR setup have been described before in Ref. [21].

1.3.1 X-ray transparent dome

The dome is made by 3D printing of aluminium. The wall thickness equals to 1 mm, which results in a transmission coefficient of 0.6 at 24 keV. The dome thickness currently restricts the x-ray experiments to hard x-rays, with energies above 18 keV. Construction of a thinner beryllium dome would allow one to also use lower-energy x-rays. The SPM part of the instrument

is mounted on top of the dome and reaches in towards the sample surface along the central axis of the dome and the sample. This is ideally the axis of rotation of the sample, when it is aligned on the diffractometer. The shape of the SPM part is kept as slender as possible, so that scattered x-rays can take off from the surface without being blocked by SPM components up to an angle of 40° with respect to the sample surface, and over a 130° range of azimuthal angles. The dome serves as the reactor and has a volume of 60 ml. The SPM part that sticks into the dome reduces the effective reactor volume to 40 ml.

1.3.2 Sample holder

The sample holder consists of a ceramic base with two protruding tungsten rods. The tungsten rods carry a boralelectric heater. On top of the heater a tantalum or molybdenum clip holds a sample in place. Two thermocouple wires can be attached to the sample. Four stainless steel pins in the ceramic base make the electrical connections in the sample support. Special care has to be taken when mounting the sample with the clips, not to fix it in a way that makes it easy for the sample to participate in vibrations. Even when minor vibrations have no effect on the SXRD performance, they can be detrimental to the SPM performance.

1.3.3 Mechanical design of the scanning probe microscope

The basic configuration of the SPM part of the system is the same as that of the ReactorSTM and the ReactorAFM that have been described in detail in Refs. [7, 9]. Central to the design is a cylindrical piezo element that is used for the X-, Y- and Z-motion. The same piezo element serves as the actuator of a stick-slip translation stage for the coarse approach of the tip or the quartz tuning fork with tip to the surface. This motion is carried out by a compact slider that moves inside an aluminium tube and is pulled against isolated contact rails, embedded in the inner wall of that tube by a CoSm magnet. In this way, the slider provides the required electrical connections to the tip or the tuning fork with tip. The system is configured such, that the piezo element is not in contact with the gas atmosphere inside the dome. Only the aluminium tube, with the slider and the tip or tuning fork with tip are exposed to the dome's atmosphere (figure 1.2). The piezo element and the wiring of the microscope are kept in a separate housing that is pumped down prior to the experiment to a moderate vacuum. Feedthroughs in the top of this housing connect the wiring of the microscope to external cables that are guided away in order not to block the in- or outgoing x-rays (see

below). The piezo housing is electrically isolated from the dome. Thus, a separate ground path can be chosen, which is necessary to avoid electronic interference caused by ground loops.

The complete SPM unit, including the aluminium dome, has a height of 20 cm (figure 1.2). This compact SPM design naturally leads to high mechanical resonance frequencies, which is beneficial for making the instrument minimally sensitive to external vibrations. Switching between STM and AFM modes is easy, as it merely requires replacing the slider carrying the probe - either the tip or the quartz tuning fork with tip - and the electronics that connect to the probe.

The mechanical loop that determines the sensitivity of the microscope to external vibrations, runs through the sample, the sample holder, the holder support structure, the top flange of the UHV chamber, the aluminium dome, the base plate on which the piezo tube is mounted, the piezo element itself, the aluminium tube, the slider and, finally, the tip or combination of tuning fork with tip. In order to eliminate all flexibility in this loop, the top flange of the UHV chamber has to be maximally lowered. Unfortunately, this reduces the leak from the reactor volume to the UHV chamber effectively to zero, so that we cannot use the mass spectrometer on that chamber for gas analysis simultaneously with SPM imaging. We have solved this by attaching an additional UHV chamber with residual gas analyser to the exhaust gas line of the reactor.

In order to isolate the microscope as much as possible from external, mechanical and acoustical vibrations, the pumps connected to the reactor exhaust, the turbomolecular pump of the UHV chamber and the gas manifold are all placed outside the experimental hut. The roughing pumps backing up the turbomolecular pump and pumping the gas flow from the reactor exhaust are connected with 10 m long, plastic bellows via a lead mass, separating most of the pump vibrations. The other pumps also have 10 m plastic bellows, but are directly connected to the gas manifold and the connector plate.

1.3.4 Control electronics

The microscope is controlled by the SPM electronics from Leiden Probe Microscopy BV [23], which features a digitally controlled, fast, analog scan generator and a high-bandwidth analog feedback system for high-speed imaging. As a complicating factor, the feedback settings of this system are controlled by hand. Therefore, it was necessary to place the entire SPM control system inside the control room, at a distance of 20 m from the microscope in the experimental hut. One of the consequences of this large

distance is the extra capacitance of 1 nF per electrode on the piezo element, introduced by the long cables to the high-voltage amplifiers. In STM mode, the bias voltage is applied to the sample via the thermocouple wires. We use a differential cable to bridge the 20 m to a separate amplifier, close to the diffractometer. This amplifier is designed to reject the common noise on the differential cable, which results in a low-noise bias voltage on the sample. The use of the thermocouple wires eliminates the possibility to measure the temperature during imaging. This should not be a problem, since we avoid changing temperature during STM or AFM imaging, as the sample would otherwise drift out of the piezo range. In STM mode, we use an IV converter close to the microscope to convert the tunnelling current into a voltage. Again, differential cabling is used, to transfer this voltage over the 20 m to the SPM electronics in the control room. For the AFM mode we use the same electrical readout circuit as the ReactorAFM [9]. A Zurich Instruments HF2LI lock-in amplifier is placed in the experimental hutch, close to the microscope [24]. It is connected to the LPM control system via four 20 m long BNC cables carrying relevant signals from the force sensor.

1.4 Performance

In practice, we find that the modularity of this system works very well. With the top flange of the UHV system in the lower position, the UHV side is sealed off from the reactor volume, which can be opened readily to change tips and samples or to change from STM to AFM mode or vice versa. This can be done on a timescale of minutes. Via the gas lines, the reactor volume can be pumped down to a moderate vacuum, prior to raising the top flange and connecting the reactor with the UHV chamber. The complete assembly fits well on the diffractometer and can be rotated comfortably around all diffractometer axes, without problematic situations arising from the connecting cables and capillaries. As will be demonstrated below the x-ray scattering performance instrument is completely uncompromised by the combination with the SPM part. As expected, the SPM resolution is modest, but atomic steps are imaged routinely with the instrument.

The performance of the SPM scanner was tested in air at room temperature on a table top catalysis chamber (figure 2.1). This chamber has the same type of sample holder and mechanical loop as the ReactorSXR chamber, but it was supported by a vibration isolation system, so that it was only exposed to a low level of vibrational input. Therefore we should expect it to show a better SPM performance in this case than in its final

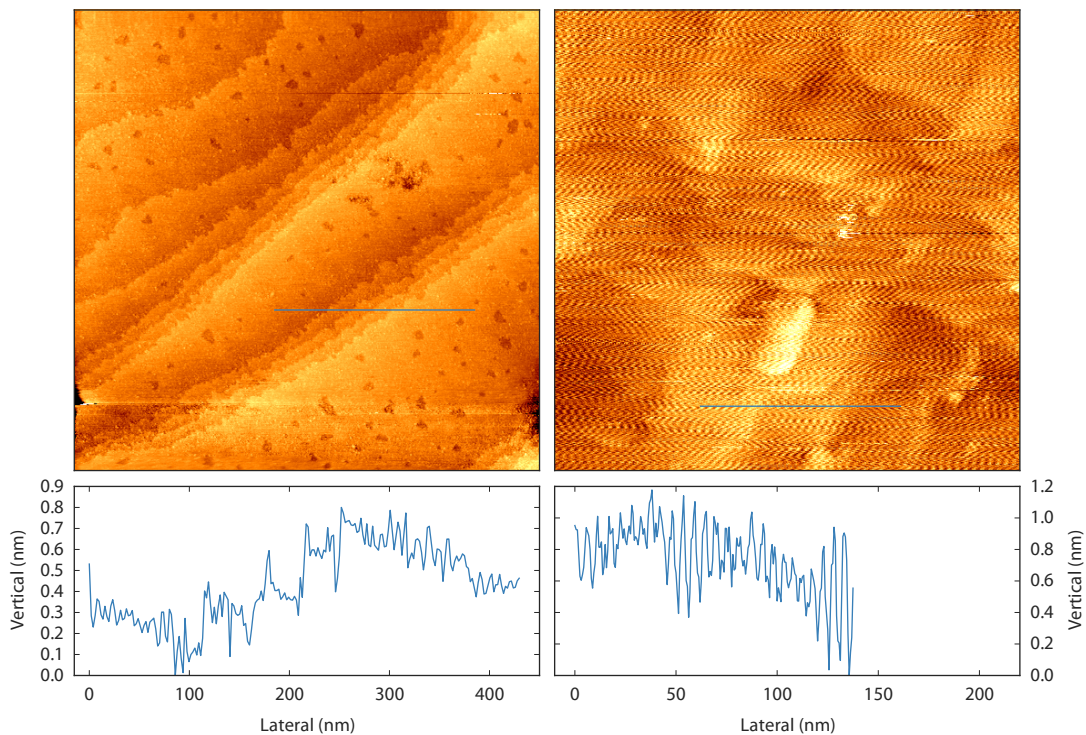


Figure 1.3. Left panel: Au(111) surface scanned by the SPM setup in STM mode. For these measurements, the SPM was mounted on a table-top UHV chamber very similar to the ReactorSXR D chamber and this was placed on a vibration isolation stage. Right panel: similar STM image obtained on another Au(111) surface, with the setup mounted on the diffractometer of beamline ID03 at the ESRF. The lower two panels show characteristic height profiles, obtained along the line segments indicated in the two STM images. Note that in both images, the atomic steps on the Au surface can be distinguished. On the diffractometer, the STM images show a dominant vibration at frequency of 370 Hz and with a typical amplitude of 0.2 nm. Even though such a single-frequency contribution can be removed easily by Fourier filtering, we have chosen to show unprocessed images and line profiles in order to demonstrate the true performance of the instrument. The images have dimensions of 1000 x 1000 nm² and 640 x 640 nm² respectively and were taken with sample bias voltages of 0.5 and 1 V and tunnelling currents of 0.05 and 0.9 nA in acquisition times of 524 and 175 s, respectively.

configuration on the diffractometer. Under these favourable conditions, the images that were taken in STM mode with a PtIr tip on Au(111) showed clear step resolution and even structures can be distinguished on the terraces (left panel of figure 1.3). As the right panel of figure 1.3 shows, when the vibration isolation system is removed and the setup is mounted on the diffractometer, the SPM images still exhibit step resolution. Some of the vibrational eigenmodes of the mechanical loop of the SPM, in particular the one at 370 Hz, provide a dominant contribution to the images. These mechanical resonances are excited mainly by the vibrations of the floor of the ESRF laboratory building.

The first full test of the system on the diffractometer under catalytic conditions was performed in STM mode with a PtIr tip on a Pd(100) surface. We cleaned the surface in the UHV chamber by repeated cycles of 1000 eV argon ion bombardment and annealing at 1150 K. After this, we lowered the top flange to seal off the reactor volume from the UHV chamber. We then used four different techniques to inspect the sample, namely STM (figure 1.4), X-Ray Reflectivity (XRR) (figure 1.5), SXRD (figure 1.5) and GISAXS (figure 1.6). For the x-ray measurements the photon energy was set to 24 keV. We show measurements for three different stages in a mixture of CO and O₂, (i) for the clean surface, in flow rates of 30 ml/min CO and 40 ml/min O₂, (ii) after oxidation of the surface in a mixture of CO to O₂ with flow rates of 3 ml/min CO and 55 ml/min O₂, and (iii) after a subsequent reduction of the sample in a mixture of CO to O₂ with flow rates of 20 ml/min CO and 38 ml/min O₂. All experiments were carried out at a pressure of 1.1 bar at a sample temperature of 300° C.

In a mixture of CO to O₂ at a pressure ratio of 3:4 the Pd(100) surface is flat as illustrated by the reflectivity curve and the crystal truncation rod (red curves) in both panels of figure 1.5. We proceeded by exposing the surface to a mixture of CO and O₂ at a pressure ratio of 3:55. In this environment the surface became oxidised. We obtained a very rough surface, as is illustrated by the STM image in the left panel of figure 1.4. The two blue curves in figure 1.5 show the presence of roughness by the steep decay of the intensity away from the Bragg peaks and the negligible intensity between the Bragg peaks. A similar effect can be recognised in the GISAXS pattern in the left panel of figure 1.6 and the blue curve in the right panel of figure 1.6. The gas mixture was changed again to a CO to O₂ ratio of 10:19. Under these conditions the STM image shows a different surface topography than in the previous conditions which we ascribe to a reduction of the surface. This was confirmed by the disappearance of the diffraction signal of the oxide (not shown). Both the reflectivity curve and the [10L]

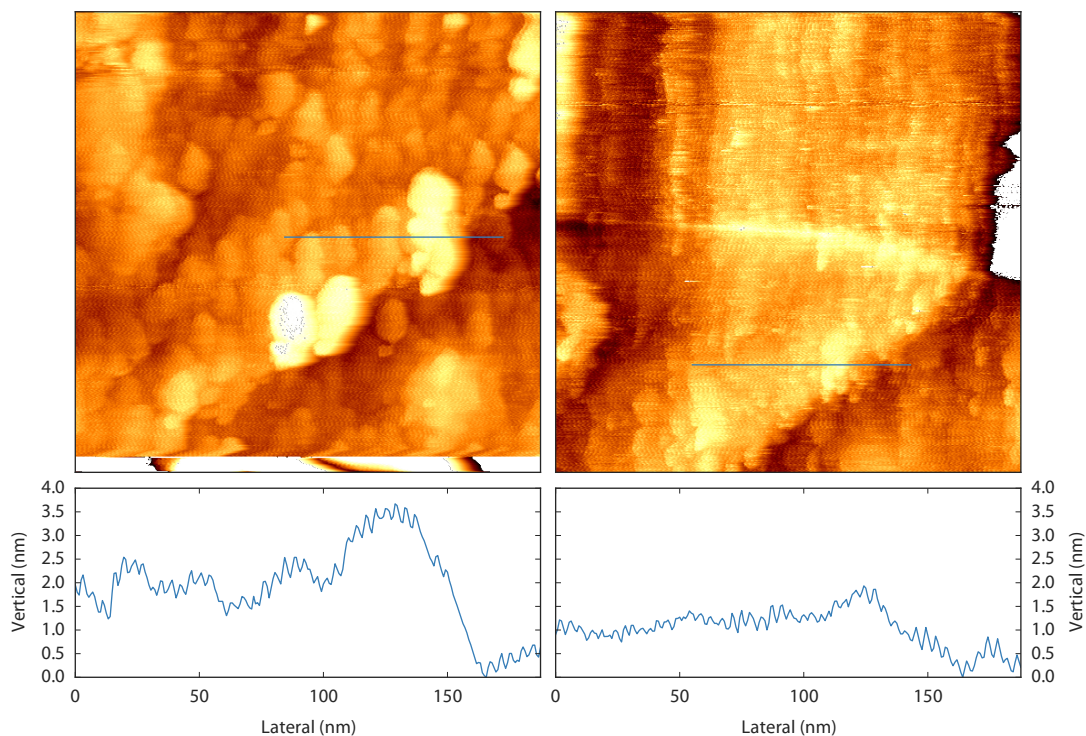


Figure 1.4. Pd(100) surface scanned by the SPM setup in STM mode. The two images show the surface in a mixture of CO and O₂ at 1.1 bar and 300° C. The left image is measured in a pressure ratio of 3:55 CO to O₂. The right image shows the same region, after changing the gas mixture in the reactor to 10:19 CO to O₂. The surface has transformed radically after changing the gas mixture which we ascribe to a reduction of the oxide on the surface. The line cut in the panel below shows more or less the same region in both the panels. The highest point on the height line in the right bottom panel has roughly been halved compared to the highest point on height line in the left bottom panel. Both images have dimensions of 400 x 400 nm² and were taken with a sample bias voltage of -0.2 V and a tunnelling current of 0.1 nA in acquisition times of 105 s.

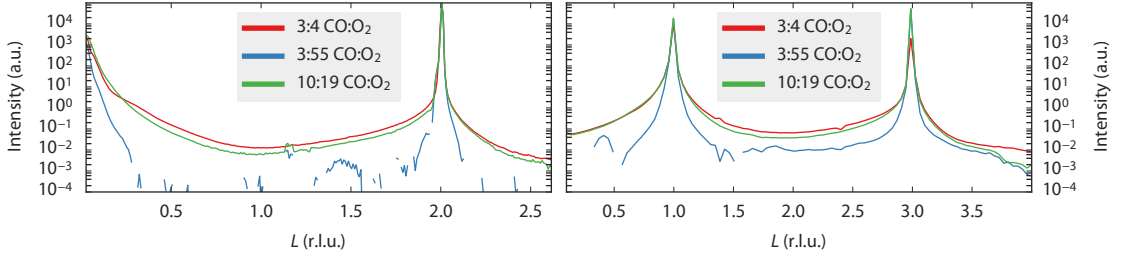


Figure 1.5. X-ray reflectivity curve (left) and $[10L]$ crystal truncation rod (right) during three O_2 and CO mixtures at a temperature of 300°C and under a pressure of 1.1 bar. The reciprocal lattice units ($r.l.u.$) are based on the surface unit cell of the Pd(100) surface with two axes parallel to the surface ($|\vec{a}_1| = |\vec{a}_2| = a_0/\sqrt{2}$) and one perpendicular to the surface ($|\vec{a}_3| = a_0$) where $a_0 = 3.89 \text{ \AA}$. The intensity of the reflectivity curve decreases very fast from low L values upwards in the oxidised regime (blue curve) indicating the surface is very rough. A small peak in the crystal truncation rod resulting from diffraction of the oxide is visible at $0.4 (r.l.u.)$, confirming the sample is oxidised in the 3:55 $CO:O_2$ gas mixture. After switching to the 10:19 gas mixture this peak disappears and the initial intensity from the 3:4 gas mixture is almost fully recovered for both the reflectivity curve and crystal truncation rod, indicating the surface has smoothened considerably.

rod recover their initial shape as can be seen in figure 1.5. The GISAXS pattern for this gas mixture shows a smoothening of the surface as can be seen by the decrease in scattered intensity at high values of $q_{\parallel}$ in the right panel of figure 1.6.

In figure 1.6 we show two GISAXS patterns of the Pd(100) surface. The third panel in figure 1.6 shows two cuts through these patterns with the intensity against parallel momentum transfer $q_{\parallel}$ at a fixed q_z value, corresponding to the Yoneda peak. For the reduced surface, in a 10:19 mixture, the intensity decays more slowly with $q_{\parallel}$. This can be interpreted as the result of the smoothening of the metallic surface, enabled by the increased surface mobility after the removal of the oxide [25].

Like most SPM instruments, our SPM is sensitive to thermal drift. To a large extent, this is due to the construction of the sample holder, which has not been designed to expand symmetrically and with a fixed height of the surface plane, when the temperature is increased. The typical timescale for the system to reach steady imaging conditions, with a drift rate below 50 nm/min , after a large, e.g. 100° C , change in sample temperature, is 3 hours. A line-by-line background subtraction is necessary before displaying the images as long as the drift in the vertical direction has not decreased below a few nm/min . Changes in temperature distribution induced by gas composition changes are within the thermal window of the microscope,

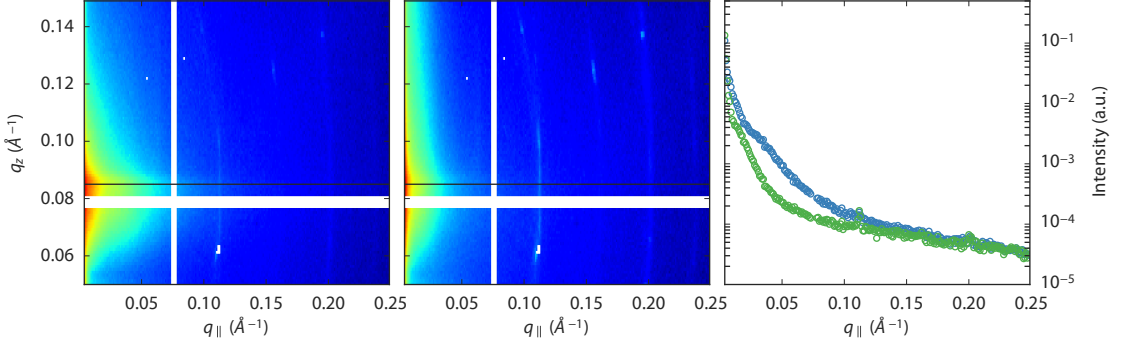


Figure 1.6. Two GISAXS patterns of the Pd(100) surface at a temperature of 300°C and under a pressure of 1.1 bar in a gas mixture of O₂ and CO. The images are measured in O₂ to CO ratio of 3:55 on the left and 10:19 on the right. The GISAXS images have been processed with the BINoculars software (see chapter 3). The white horizontal and vertical bands are inactive areas in the Maxipix detector. The panel on the right shows cuts through both patterns at the location of the Yoneda peak at $q_z = 0.085 \text{ \AA}^{-1}$ for pressure ratios of 3:55 (blue symbols) and 10:19 (green symbols). The rings visible at $q_{\parallel} = 0.1 \text{ \AA}^{-1}$ and $0.2 \text{ \AA}^{-1}$ result from scattering of the reflected x-ray beam and the aluminium window.

provided the heat capacity of the gas mixture does not change too much.

The time it takes to switch from x-ray measurements to SPM operation is mainly determined by the speed of the coarse approach mechanism of the tip. When initiating an x-ray measurement, we choose to retract the tip maximally, in order to avoid a tip-surface crash that could damage the tip. The approach can be time consuming since the initial distance between the sample and the tip apex is unknown, so that the entire approach trajectory has to be traversed in small, sub-micrometer steps. After each approach step, a sensing procedure is performed to establish whether the tip is already close enough to the surface. Alternatively, we can use the x-ray beam to accurately measure the distance between the tip and the sample, reducing the approach time from hours to minutes. After the SPM measurements have been completed the slider can be retracted and x-ray measurements can recommence. Since the sample remains aligned during SPM measurements, no realignment has to be performed.

We have found that it is not easy to perform truly simultaneous SPM imaging and x-ray scattering experiments. Such combined measurements are complicated by the stray currents caused by the interaction of the incident x-rays with the gas environment and the sample. Only by limiting the flux by a factor of 10^8 or more, it is possible to combine both. This however severely limits the type of x-ray experiments that can be performed.

1.5 Conclusion and outlook

We have developed an instrument for combined synchrotron x-ray scattering and scanning probe experiments for in situ catalysis studies. This new instrument allows us to perform a real-space characterisation of the surface topography and a determination of the surface structure under identical high-pressure, high-temperature catalytic conditions. Both scanning tunnelling microscopy and atomic force microscopy can be performed. This instrument contributes to the understanding of fundamental reaction processes by making it possible to follow the evolution of the structure and morphology of active catalytic systems in response to the temperature and gas environment to which they are exposed.

We have constructed the instrument in a modular fashion, combining the previously developed ReactorSXR system for synchrotron x-ray studies with the ReactorSTM and ReactorAFM systems, previously developed for SPM studies under catalytic conditions. The "bolt-on" SPM unit, developed here, can be combined also with other reactor configurations, such as the table-top catalysis chamber, used in some of the SPM performance tests.

The unique sample environment and the suitability of the setup for x-ray experiments also provide the possibility to perform scanning 'X-ray Absorption Near Edge Structure' (XANES) experiments under catalytic conditions [26]. In these experiments the sample surface will be scanned with the STM while the x-ray beam irradiates the surface. Chemical contrast can be provided by choosing the beam energy above the absorption edge of the element of interest. When the STM tip scans atoms of this element, an enhanced photocurrent due to the photoelectrons can be measured by the STM tip. Acquiring real-space information on the chemical composition introduces new possibilities for refined, catalytic studies.

Chapter 2

From dull to smooth: A novel setup for real-time spatially resolved reflectance difference analysis during catalytic conditions

We have developed an experimental setup for optically monitoring a catalytically active surface under reaction conditions. A flow reactor with optical access allows us to image the behaviour of a catalyst at the millimetre length scale. We use reflectance difference measurements with 625 nm light to investigate CO oxidation on Pd(100) at 200 mbar from room temperature up to 400 °C. We conclude that the changes in visible contrast result from the formation of an oxide layer after surface oxidation.

2.1 Introduction

The last two decades have brought us an exciting, new 'look' on heterogeneous catalysis. Where the catalyst surfaces were originally thought of as a mere, two-dimensional playground for the adsorbing and reacting molecules and their products, we now know that these surfaces are intimately involved in the chemical transitions, to the point that they can be heavily affected by the exposure to the high temperature and to the high partial pressures of the reactants. The high temperature alone can already lead to a roughening of metal surfaces [27, 28], thus spontaneously introducing atomic-height steps that can act as efficient binding and reaction sites. The high reactant concentrations can stabilise adsorption structures that would be energetically unfavourable at low pressures. In this way, at sufficiently high pressures, even completely new surface structures can be stabilised, such as the surface oxides that have been found on various metal surfaces that serve as oxidation catalysts.

Most of these changes have been followed on a rather microscopic scale, using for example Surface X-ray Diffraction (SXRD) and high-pressure Scanning Tunnelling Microscopy (STM) [11–13, 29, 30]. As a typical example, we refer to the Pd(100) surface. It has been shown that during the CO oxidation reaction on the palladium surface, a surface oxide can be formed. In the STM images it can be seen that when this surface oxide is formed, the surface is becoming increasingly rough during the reaction. This roughening effect has been thought to be the result of a Mars-van Krevelen-type reaction mechanism. In this reaction mechanism the CO in the gas phase reacts with an O-atom from the surface oxide creating an O vacancy in the oxide. The Pd-atoms from the oxide surface can diffuse around if they become coordinated too poorly, after CO has reacted away several of the surrounding O-atoms, causing the surface to roughen.

Even though the small-scale features of the CO oxidation reaction on Pd(100) have been resolved by STM, and the oxide structure has been found with x-ray methods, some observations could not be explained by either technique. Spontaneous reaction oscillations between the oxide and the metal phase have been observed by Hendriksen et al.[12]. In these oscillations the intensity of the Bragg reflection that is indicative of the oxide layer disappears and reappears, indicating that the surface switches between a metal surface, and an oxide-covered surface. In the explanation by Hendriksen et al., the stability of the surface oxide is lowered by the increased roughness originating from the Mars-Van Krevelen reaction mechanism. After the oxide has become unstable and is reduced, the accumulated roughness of the surface is removed by the fast diffusion of the Pd-atoms.

Therefore the oxidation and reduction of the surface is accompanied by a roughening and smoothening of the surface. We have also observed a different type of oscillations (see chapter 4). The same Bragg reflection indicating the presence of the oxide on the surface is periodically showing only a partial loss and recovery of the intensity with a higher repetition frequency than the previously seen oscillations. This type of oscillation has yet to be understood.

One of the explanations for these incomplete oscillations is based on the spatial inhomogeneity of the reaction over the sample surface. During the catalysis experiment, the 1 cm cylindrical palladium surface is located inside a flow reactor. The reactant gases are fed into the reactor at a controlled flow rate and the total pressure is set by controlling the pressure at the outlet of the reactor. It has been shown that in the reactor geometry used for the SXRD experiments, the high turnover frequency of the CO oxidation reaction causes lateral variations in the gas composition at the sample surface [31]. In our reactor geometry this results in a lower impingement rate of CO molecules in the center of our crystal than at the edge of the sample. These variations in partial pressures could cause the oscillation between a metal and an oxide state to depend on the sample location. Such differences in local behaviour can be missed by STM, when investigating a relatively small surface area, or by x-ray diffraction methods, when often the beam footprint covers a large area, so that only a spatial average is being recorded. Clearly, it is necessary to inspect the reaction with a field of view that is large enough to cover the entire surface and with a spatial resolution that makes it possible to follow different parts of the surface independently.

In previous experiments, we had noticed that after exposure of Pd(100) to CO oxidation conditions, the surface had changed visibly. It had turned from an almost perfect mirror into a slightly dulled mirror. The origin of this transition has been unknown since our setups did not provide optical access to the sample in its reactor environment. In order to analyse and quantify these optical changes during the catalytic reaction we set out to build a new experimental setup.

Techniques such as photoemission electron microscopy have shown remarkable spatio-temporal patterns on a catalyst during CO-oxidation at $5 \cdot 10^{-4}$ mbar as described by Nettesheim et al. [32]. The features they describe have a micrometre length scale, but they clearly show the spatial and temporal features of the catalyst reaction to behave in complex ways. However this technique is not suitable for higher pressures used in industrial catalysis.

Reflectance difference measurements, where the change in reflectivity

is measured in real time during some surface-altering process, have been used successfully in the past to monitor very subtle surface processes. The non-invasiveness of the technique and the fact that light is only weakly scattered at ambient gas pressures has led to the use of optical tools such as reflectance difference measurements and ellipsometry as diagnostical tools for crystal growth processes [33, 34], but also catalysis processes [35]. Although the diagnostic power is greatly enhanced by the use of multiple wavelengths in reflectance difference spectroscopy, much of the relevant surface behaviour can be inferred already by using a single wavelength, i.e. monochromatic light. Surface anisotropy, when the surface shows different characteristics along its in-plane axes, can be explored by investigating the response of the two different polarisation directions. In view of the square symmetry of Pd(100), however, we expect the surface statistics to be identical in all in-plane directions. Reflection Anisotropy Microscopy (RAM) has been used to investigate CO oxidation on Pt(110) on smaller length scales and at low pressures [36, 37].

To observe the behaviour of the entire sample simultaneously we constructed a new setup using simple optics. The goal of this setup is to image the optical reflectance of a complete, 1 cm diameter model catalyst sample, with high temporal resolution. We are interested in both the specularly and the diffusely scattered light from the sample surface. Resolving the angular intensity dependance of the diffusely scattered light, which is related to the characteristic length scales of the surface, aids us in understanding the catalytic processes.

Techniques such as ellipsometry are very sensitive to the dielectric properties of the surface, but are usually only used with a laser beam to monitor a single sample location. We constructed a setup with which we can follow the reflective properties of the entire sample surface. Limiting ourselves to reflectance allows us to create a flow reactor with an easier design than ellipsometry where the light is required to impinge at a certain angle with the surface, in order to exploit the different reflection coefficients for the two polarisation directions. Our setup can be readily modified by constructing a new reactor window at a suitable angle and adding the necessary polarisers to change the polarisation of the light.

This chapter describes the design of this setup and presents the findings of the first experiments. We investigate the origins of the contrast changes during the CO oxidation reaction on Pd(100).

2.2 Methods

We measure the sample reflectance with a home-built reflectometer. The sample is housed in a small flow reactor, designed by the company Leiden Probe Microscopy B.V. [38], shown in figure 2.1. This mini-reactor is a simplified version of the ReactorSXR chamber [21], with the same sample mounting stage and similar reactor volume but without the UHV sample preparation environment. The chosen geometry enables a direct comparison of the optical data with the SXR results, obtained previously. With a LPM gas supply system [39] we can set the total flow rate, total pressure (200 mbar to 1000 mbar) and partial pressure ratios between all gases at ratios ranging from 1:1 up to 1:100. The maximum flow rate per constituent gas is 10 ml/min. With a reactor volume of ~ 25 ml the refresh rates are in the order of minutes. This has to be taken into account when switching the gas composition in the reactor. The composition of the gas mixture that leaves the reactor is measured with an LPM residual gas analyser [40]. The reflectometer itself consists of two stages. The pre-sample stage starts with a light source. A collimator collects the light and a spatial filter creates a parallel beam. The post-sample stage collects the light, chooses a specific imaging mode and records the result with a camera.

As a light source we use a (Thorlabs M625L3) LED with a 625 nm central wavelength. The light is first collimated after the source with an aspherical lens with a 40 mm focal length and a numerical aperture (NA) of 0.554 to capture a large fraction of the emitted light. After collimation the light is spatially filtered with a lens with 10 cm focal length that focuses the light on a 150 μm pinhole. After the pinhole, a lens with 6 cm focal length collimates the beam, recreating a parallel beam. A diaphragm after the spatial filter allows us to set the beam diameter. We do not measure the LED intensity and therefore cannot correct the measured data for fluctuations in the light.

A pellicle beam splitter reflects half of the beam toward the sample. Half of the reflected beam passes through the beam splitter towards the camera.

After the beam splitter the post-sample stage starts. Figure 2.3 shows four different lens configurations that can be applied to disentangle the different reflected components. In (a) all reflected light is used to create an image of the sample. (b) Corresponds to a bright-field configuration where we use a pinhole in the focal plane of lens L1, in order to select only the specularly reflected components. In the dark-field configuration (c) a beam stop is placed in the focal plane of lens L1. In this way the specularly reflected beam is blocked and only the light that is diffusely

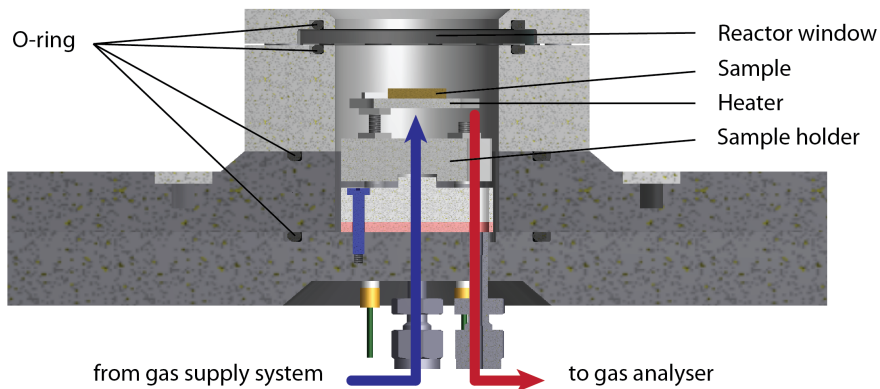


Figure 2.1. Cross section of the Leiden Probe Microscopy mini flow reactor. A transparent window closes the reactor from the top. The sample lies on top of the boralelectric heater that can heat the sample up to 1000°C. With a thermocouple attached to the sample we measure the temperature. The feedthroughs for the gases, heater and the thermocouple are below the sample holder in the bottom plate. Gas flows in from the gas supply system (blue arrow) and out toward the gas analyser (red arrow). The sample holder and reactor enclosure are similar to those of the ReactorSXRD chamber [21] and can be exchanged.

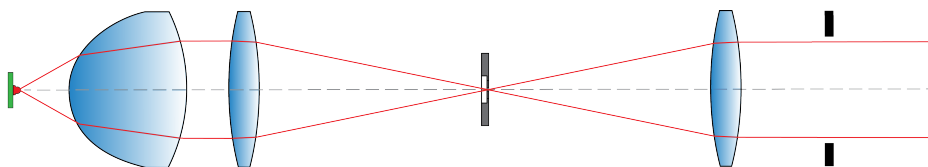


Figure 2.2. Schematic design of the light source and the spatial filter. Light from a high-intensity LED is collected using an aspherical collimator. A second lens focuses the beam onto a pinhole. A third lens with the pinhole in the focal point creates a parallel beam of light. With a diaphragm we match size of the beam to the sample size.

scattered from the sample is allowed to pass. L2 behind the beam stop focuses the remaining light on the camera. In (d) the camera is placed in the focal plane of L1. This creates a far-field image that registers the angles at which the light is reflected at the surface. In principle, the optical system could have been designed such, that it integrated various imaging modes in the same set-up. For simplicity, we chose to simply reconfigure the optical setup between different types of experiments. Because the illumination stage is identical, data collected in different configurations can be directly compared.

To record the images we use a Basler acA2500-14gm [41] CCD camera. This camera is a monochrome camera with 12 bits per pixel and has a resolution of 2592 by 1944 pixels. The camera is fully computer controllable and parameters such as pixel gain, pixel binning, integration time and time between frames can be adjusted. The maximum frame rate of the camera is 14 frames per second. Images acquired at the highest resolution can be up to 10 Mb in size. This makes handling and analysis of the dataset, which can consist of thousands of images for one experimental run, cumbersome and time consuming. Therefore often a low pixel density or a low acquisition rate is chosen.

The sample in the reactor is directly mounted on a boralelectric heater. This heater is connected to a Delta ES 030-5 [42] power supply and can be heated to 1000 °C. The sample holder carrying the boralelectric heater, a graphite heating element embedded in boron nitride [43], is mounted on two tantalum rods that are connected to a ceramic unit. Thermocouple wires connected to pins in the sample holder can be (laser)-spot-welded on the sample to measure the temperature. The pins underneath the sample holder connect to sockets in the reactor base. They are connected to feedthroughs connecting the signal to the outside of the reactor. The power supply, as well as the thermocouple are computer readable and controlled. Feedback is applied between temperature readout and heating power, in order to keep the temperature of the sample constant.

2.3 Performance, first results and discussion.

In this section, we demonstrate the sensitivity of the optical reflection technique by applying it to the (100) surface of palladium, subjected to a range of gas compositions at high temperatures and atmospheric pressures. We will see that, even though the surface changes are very modest, a clear contrast can be observed in the optical reflection signal.

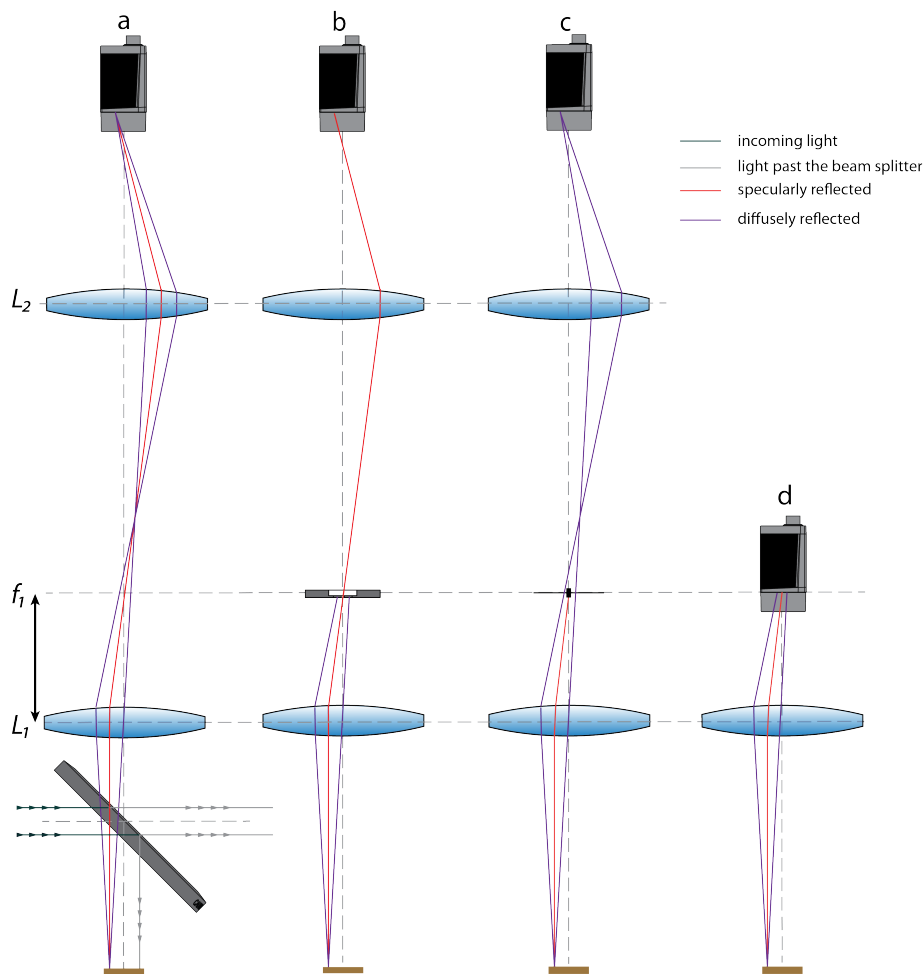


Figure 2.3. Schematics of several possible configurations of the optical system. A parallel light beam arrives from the left where it hits the beam splitter. Half of the intensity is reflected downwards and half is transmitted. After reflection on the sample surface (gold) the light is transmitted through the beam splitter. Four analysis methods are indicated. (a) Imaging of the surface. (b) In a brightfield configuration diffusely reflected light (purple) is blocked by the pinhole. (c) In a darkfield configuration specularly reflected light (red) is blocked by the beamstop. (d) In an angular configuration the distance to the centre of the camera is determined by the angle of scattering.

2.3.1 Oxidation and reduction

We used the instrument, introduced in the previous section, to monitor the relative reflectance difference (ΔR) of the Pd(100) sample during the CO oxidation reaction. Here we define $\Delta R = (I - I_0)/I_0$ with I_0 the reflected intensity at the start of the experiment and I the measured intensity at later stages of the experiment. We first investigated how the reflectance changes upon oxidation and reduction of the sample surface (figure 2.4). The images in figure 2.4 are a direct projection of the sample on the camera, without beamstop or pinhole (configuration *a* in figure 2.3). We kept the pressure constant at 200 mbar. We started in a CO+Ar mixture to ensure the sample surface was initially not oxidised. After this we flushed the reactor with a flow of pure Ar. We then introduced a mixture of Ar+O₂ to oxidise the sample surface. We subsequently flushed the reactor with Ar and finally we reduced the surface with CO. The intermediate flushing with the inert gas Ar, which was always performed for at least 300 s, was necessary to ensure that the previous active component, i.e. CO or O₂, had been removed always completely before the next active component was introduced, so that this experiment only showed the effects of single gases. Mixtures of gases introduce more complex behaviour, as will be explored later in this chapter.

Image *a* in figure 2.4 shows the reflectance of the surface before oxidation of the sample. The dark stripes result from a spatial modulation of the initial LED intensity I_0 and are constant during the experiment. Upon exposure of the surface to O₂, the reflectance decreases (image *b*). From surface x-ray diffraction measurements and STM observations, we know that under these conditions, the Pd(100) surface forms a thin surface oxide [11, 30]. Image *c* shows the spatial map of the change ΔR between images *a* and *b*. From the sequence of images we extract a curve with the behaviour of the sample over time. We do this by integrating a small, pre-defined area (indicated in red in image *c*) for each of the images, which results in $I(t)$. From this we calculate ΔR . Small fluctuations in the flow rate, such as the pressure spikes at $t = 430$ s and $t = 1200$ s and the measured O₂ flow at $t = 850$ s are artefacts from the gas supply system. These spikes result from a feedback overshoot of the mass flow controllers responsible for maintaining the gas flow. Note that changes in the gas flow settings also cause small fluctuations of the sample temperature

The shape of the ΔR curve when starting the O₂ flow shows a rapid initial decrease after which a plateau is approached. From the analysis of the images it can be observed that the decrease of ΔR upon introduction of the O₂ in the reactor is first observed closest to the reactor inlet. The same

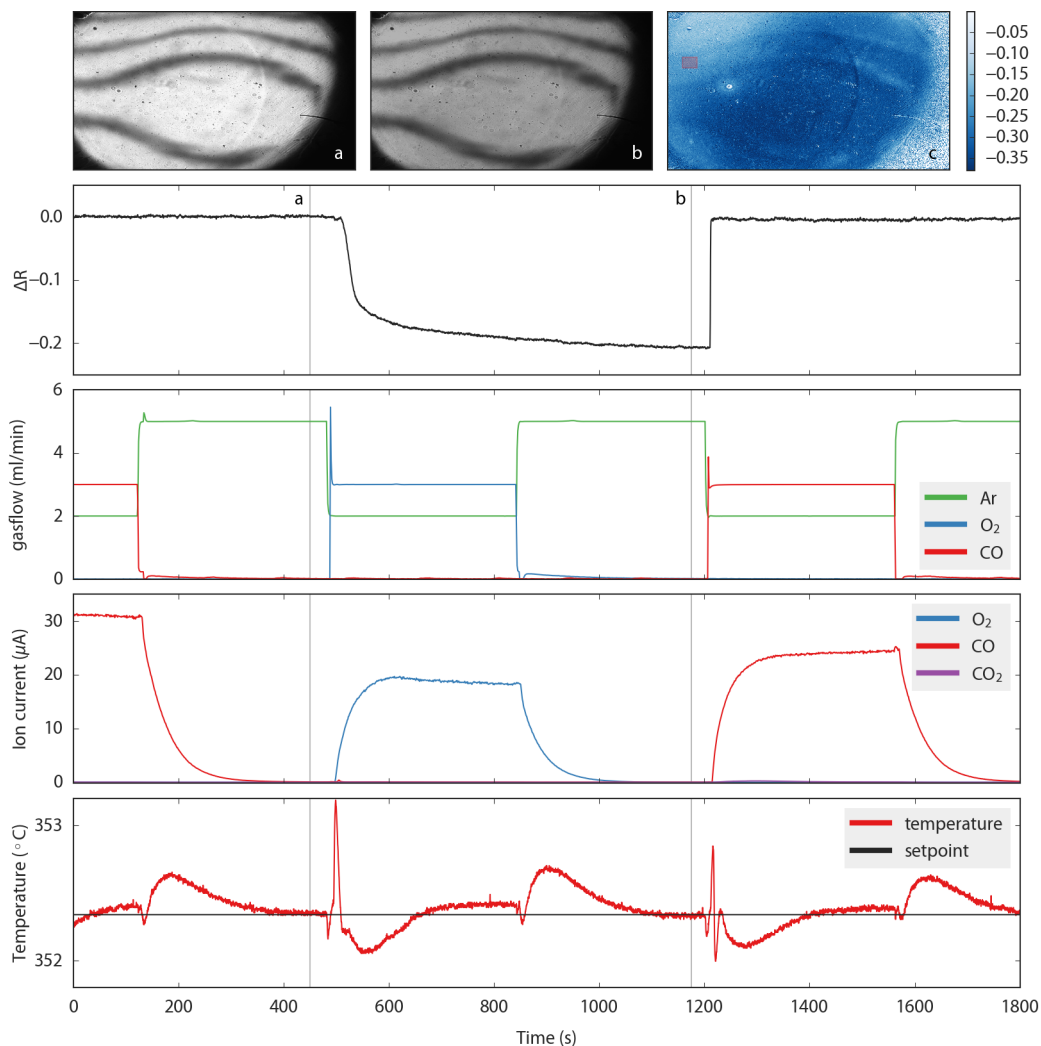


Figure 2.4. Time sequence of the reflectance, the gas composition and the sample temperature. Image *a* shows the reflectance of the surface before oxidation of the sample. After oxidation the reflectance is decreased (image *b*). Image *c* shows the normalised difference ΔR between images *a* and *b*. Below images *a*, *b* and *c* are four graphs. The first graph shows the variation with time of the ΔR value, averaged over the rectangular area indicated in image *c*. The times of images *a* and *b* are indicated as vertical lines. The second graph shows the flow rates at which Ar, O₂ and CO have been fed into the reactor volume. The third graph shows the composition of the gas leaving the reactor, as measured with a quadrupole mass spectrometer in a separate vacuum system. The bottom graph shows the actual sample temperature, which can temporarily deviate from the setpoint to which the temperature is controlled, due to changes in heat conduction through the gas and changes in heat production by the CO oxidation reaction.

holds for the reduction after introducing the CO in the reactor. ΔR varies on the surface from -0.4 to -0.1, with a median intensity of -0.3 per pixel.

2.3.2 Contrast mechanism

The images in figure 2.4 show that the optical properties of the sample surface are changing between different gas conditions. With this setup we are able to follow ΔR over the entire surface while exposing the sample to varying catalytic conditions. Various physical processes can cause a decrease in the reflectance. The oxidation of the palladium increases the roughness, both of the top surface and of the oxide-metal interface, and the optical properties of the palladium-oxide differ from those of palladium, which also changes the reflectance of the surface. Which of these two effects is primarily responsible for the change in reflectance, accompanying the O_2 -induced oxidation of the Pd(100) surface, cannot be concluded from these images. A key question resulting from this experiment is which of the two processes plays a dominant role in the change of ΔR during the oxidation and reduction. Understanding the contrast mechanism will help us to understand the surface dynamics, by examining how ΔR on different locations on the sample correlate.

If the contrast results from oxide formation we expect ΔR to decrease fast initially. Mott-Cabrera theory for oxide growth on metals [44] predicts a decreasing growth rate by an increasing limitation of the diffusion of O-atoms from the surface through the thin oxide layer. Therefore we expect the rate to obey $\Delta R \propto -(\ln(t))^{\frac{2}{3}}$. If the contrast results from roughness generation we expect it to follow $\Delta R \propto -\sqrt{\ln(t)}$ [45]. The observed time dependance of the change in ΔR after oxidation does not favour either of these two models. Although the O_2 partial pressure is identical everywhere we see two regions with different response (image *c* in figure 2.4). ΔR in the top left corner decreases less than in other areas. This suggests that the growth of the palladium oxide depends either on initial conditions of the surface or other growth parameters.

We address the question regarding the contrast mechanism by calculating the effects of both roughening and oxidation on the reflectance separately.

One way of estimating the effect of the oxide layer is by considering a thin palladium oxide film on top of an otherwise smooth palladium surface. The change in reflectance is then caused by a difference in refractive index of the palladium oxide with respect to palladium. We calculate the Fresnel

coefficient for reflection on a single layer with [46]:

$$R = \left| \frac{r_{01} + r_{12}e^{2i\beta}}{1 + r_{01}r_{12}e^{2i\beta}} \right|^2$$

Here the individual Fresnel components r_{ij} for light under normal incidence are given by:

$$r_{ij} = \frac{n_i - n_j}{n_i + n_j}$$

with n_i the (complex) refractive index of layer i . In this notation the index 0 indicates the ambient gas environment, 1 indicates the palladium-oxide layer and 2 the bulk palladium. β describes the phase change of the light in the thin film with thickness d . Under normal incidence $\beta = \frac{2\pi n_1 d}{\lambda}$. If we assume the refractive index of the thin layer to be that of the palladium bulk oxide (PdO) we can calculate the change in reflection coefficient as a function of the layer thickness [47]. The result is shown in figure 2.5. Only a thin layer (~ 10 nm) is needed at this wavelength in order to achieve the observed decrease in the reflectance. Almost complete absorption is calculated around 30 nm. The remarkable sensitivity of the reflected intensity to the oxide thickness occurs because of destructive interference of the light reflected from the gas-to-oxide interface with light reflected from the oxide-to-metal interface below. The near extinction of the reflected intensity around 30 nm thickness indicates that the amplitude of the light reflecting from the gas-to-oxide interface is almost equal to the amplitude of light reflecting from the oxide-to-metal interface.

Next we will investigate the expected effect of the roughness on ΔR . The response of a rough surface to incoming specular light has been investigated extensively for the last sixty years. We recognise three categories of approaches, depending on the in-plane correlation length of the surface roughness. When the in-plane correlation length is large with respect to the wavelength of the employed light, the diffuse reflection of the light can be described with the Fresnel coefficients on the local slopes of the surface. This gives the response a geometrical character, where the angles of the reflection with respect to the incoming beam can be obtained from the distribution of slopes. This decreases the specular reflectance and increases the reflection in the off-specular directions [48].

When the characteristic length scale of the roughness is of the order of the wavelength, a Rayleigh scattering approach becomes more appropriate. Also in this case, roughness leads to an increase in off-specular scattering and a decrease in specular scattering. When the correlation length is much smaller than the wavelength, no off-specular scattering is observed but still

the reflectance decreases [49]. The lost intensity is transmitted through the surface and absorbed. In this regime the roughness can be estimated with the effective medium approximation (EMA) by replacing the roughness with a thin film with a dielectric constant that is an average of the dielectric constants of the ambient and the reflecting medium. As roughness growth models [45] predict that the characteristic in-plane length scale starts small and increases over time, we expect to progress through these three regimes in reverse order.

We can calculate the effective dielectric constant in the effective medium approximation by assuming the layer consists of a random mixture of the ambient and substrate material. The effective refractive index n_{EMA} is given by:

$$v_0 \frac{n_0^2 - n_{\text{EMA}}^2}{n_0^2 + 2n_{\text{EMA}}^2} + v_1 \frac{n_1^2 - n_{\text{EMA}}^2}{n_1^2 - 2n_{\text{EMA}}^2} = 0$$

Here n_0 and n_1 are the refractive indices of the ambient and of the substrate respectively. v_0 and v_1 are the volume fractions of ambient material and substrate material in the mixture respectively which we both choose to be 0.5 [50]. The reflectivity can then be calculated using the method described above for the palladium oxide layer. Using this EMA approach, we find that a mixed layer with a thickness of ~ 35 nm would be required to explain the measured reduction in reflected intensity upon exposure of the surface to O_2 . This corresponds to a short-wavelength roughness with a valley-to-top amplitude of 35 nm.

In the intermediate regime where the correlation length of the surface is of the order of the wavelength we estimate the roughness using the Rayleigh-Rice formalism. Here we have followed the procedure described in [51]. The change in the Fresnel coefficient under normal incidence can be calculated with:

$$\Delta r_{p,s} = \int \int f_{p,s}(q_x, q_y) S(q_x, q_y) dq_x dq_y$$

Here q_x and q_y are the in-plane momentum transfer components of the diffracted wave, $S(q_x, q_y)$ is the spectral density function of the surface and $f_{p,s}(q_x, q_y)$ stands for the optical response for polarisations s and p , which are identical to each other for the case of normal incidence on an isotropic surface. We estimate the spectral density function of the surface to be:

$$S(q) = \frac{\alpha w^2 \xi^2}{\pi} \frac{1}{(1 + \xi^2 q^2)^{\alpha+1}}$$

with w the root-mean-square roughness, ξ the correlation length and α the Hurst exponent. The Hurst exponent defines the scaling relation between

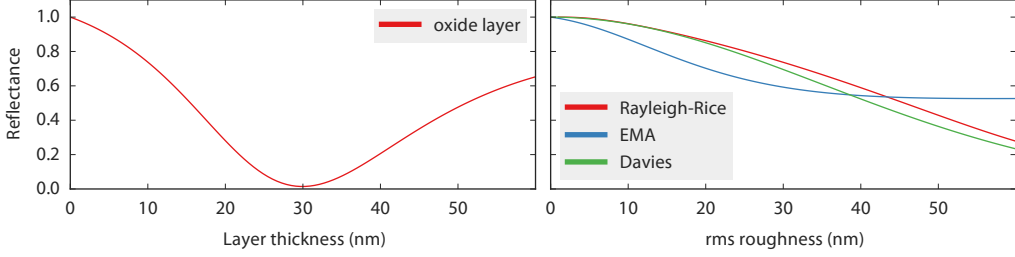


Figure 2.5. Reflected intensity for a surface oxide and various roughness models. The reflected intensity is normalised by the reflectance of a bare, smooth palladium surface of 0.71. A thin oxide layer is a more dominant factor than the roughness for the decrease in reflectance. In order to compare the decrease in intensity calculated with the EMA model with the Davies and the Rayleigh-Rice model we approximate the layer thickness to be 3 times the rms roughness.

the roughness and the lateral length scale: $\langle [h(R+r) - h(R)]^2 \rangle = cr^\alpha$, where $h(R)$ is the height function and c a constant. We use $\alpha = 0.7$ and set ξ equal to the rms roughness. This approach predicts a rms roughness of 30 nm for the observed decrease in ΔR .

The estimated effect of the surface roughness when the wavelength is much smaller than the characteristic in-plane length scale was calculated by Davies with

$$R_s = R_0 e^{-\left(\frac{4\pi\sigma}{\lambda}\right)^2}$$

where R_0 is the reflection coefficient of a smooth surface, σ root-mean-square height variation and λ the wavelength[52]. This approximation assumes that the root-mean-square roughness is small compared to the wavelength and both the height distribution and the autocorrelation function are gaussian distributed. Using this approximation, we find that a roughness value of $\sigma = 28$ nm is required to fit the experimentally observed reduction in reflectance.

Although all described roughness estimates are only applicable in their own respective regimes, they indicate a significantly higher sensitivity of the reflectance to the presence of a thin flat oxide layer than to surface roughness. This suggest that whatever lateral length scale is characteristic for the surface roughness, we should expect ΔR to be dominated by the formation of an oxide at the surface. The oxide thickness estimated on the basis of the measured ΔR is slightly higher than the oxide thickness of 4 nm that was determined previously with SXRD [30]. However, that oxide was grown under different formation conditions and its thickness might be underestimated.

So far, we have considered the separate contributions to ΔR of the presence of an oxidised surface layer and of surface roughness. When the

surface is both oxidised and rough, the two contributions should be summed. An additional effect, involving the excitation of surface plasmons [53], is possible, in principle, when the roughness obeys certain conditions. The characteristics of surface plasmons are highly sensitive to the dielectric properties of the interface as they are purely a surface effect. This renders the reflection coefficient also sensitive to a combination of interface roughness and oxide thickness.

2.3.3 CO oxidation

To differentiate further between oxidation and roughening as the main cause for the decrease of ΔR we performed the following experiment. We started with a by CO reduced surface. The surface was then oxidised in a mixture of O_2 and Ar. Subsequently we lowered the Ar flow rate and increased the CO flow rate to the same value as the O_2 flow rate, to start the CO oxidation reaction. This could be confirmed by the appearance of the CO_2 signal in the gas analyser. After 900 seconds, we interrupted the CO oxidation reaction by flowing only Ar and O_2 for 600 seconds. Afterwards we restarted the reaction. Subsequently O_2 is slowly removed until the surface was reduced. Figure 2.6 shows the results of this experiment.

From this experiment we can see the different behaviour of the CO oxidation reaction versus pure oxidation. When the surface is oxidised in a mixture of O_2 and Ar, ΔR reaches a plateau value. When the CO oxidation reaction is running, ΔR decreases further. When the CO oxidation reaction is stopped, ΔR remains unaffected, only to decrease after the reaction is restarted.

It seems clear that the CO oxidation reaction plays an important role in the decrease of the reflectance. Since it is unlikely that the addition of a reducing agent increases the oxide thickness, we interpret the observation as a strong indication that surface roughness is responsible for further decrease of intensity. This is fully consistent with the observations of STM and SXRD. During the CO oxidation reaction the surface of the oxide layer is seen to become rough in the STM images, while SXRD shows the oxide-metal interface to become increasingly rough during the reaction [11, 30].

A second experimental indication that roughness forms the cause of contrast, can be seen at $t = 3800$ s in figure 2.6, where the surface is reduced after a period of CO oxidation. After CO oxidation, starting at $t = 3800$ s, the recovery of the surface to the initial, zero value of ΔR takes as long as 80 seconds. This should be compared with the much shorter recovery time of 4 seconds found in figure 2.4 at 1220 s after exposure of the surface to pure O_2 .

Although not all regions on the surface vary equally strongly in reflectance, the qualitative behaviour of the entire surface is uniform and completely synchronous. This suggests that the entire oxidised surface is participating in the CO oxidation reaction. For if the oxidised area were completely insensitive to the presence of CO, the reflectance at these areas would not change during the reaction. Furthermore, if the presence of the CO were to lead to a local reduction of the surface, this would either lead to a decrease in the thickness of the oxide, or even to the complete local removal of the oxide and the ensuing smoothening of the surface. In both cases, we should expect the reflectance to stay constant or increase, in contrast with the observed steady decrease.

The origin of the surface roughness has been debated previously. Assuming the reaction follows a Langmuir-Hinshelwood-type mechanism, the roughness generation for Pt(110) has been explained by invoking mass transport due to restructuring of the surface during switches from CO covered to O₂ covered [54]. However this explanation has gained no further support after the discovery of a thin oxide layer present during the roughening phase. Then it was proposed that a Mars-Van Krevelen-type of mechanism causes the surface to roughen. In this reaction, CO molecules react with O atoms in the surface oxide to form CO₂. The O-vacancy, left behind in the surface oxide, is then quickly filled up by fresh O from the gas phase O₂. In the case that a rapid succession of local CO oxidation events leads to a temporary, strong, local reduction of the surface oxide, for example in the form of the simultaneous absence of 3 O atoms, a Pd atom near the multiple O vacancy may become so loosely bound, that it can liberate itself from the oxide matrix and diffuse over the oxide surface. After a brief journey, such a diffusing metal atom will be re-oxidised on top of the oxide. The net effect of this relocation is a local depression at the original location of the metal atom and a new protrusion at its new location, which indeed adds to the roughness of the surface. Our observation of a steady reduction in reflectance during CO oxidation on the oxidised Pd(100) surface is fully consistent with this steady reaction-induced roughening and thus supports the Mars-Van Krevelen hypothesis.

2.3.4 CO oxidation during large temperature variations

A second, convenient way to explore the dependence of the CO oxidation reaction mechanism on the reaction conditions is illustrated in figure 2.7, where the temperature is ramped up and down linearly from room temperature to 300°C and back. During this ramp the gas mixture in the reactor is kept constant at a total pressure of 200 mbar and an O₂:CO partial pressure

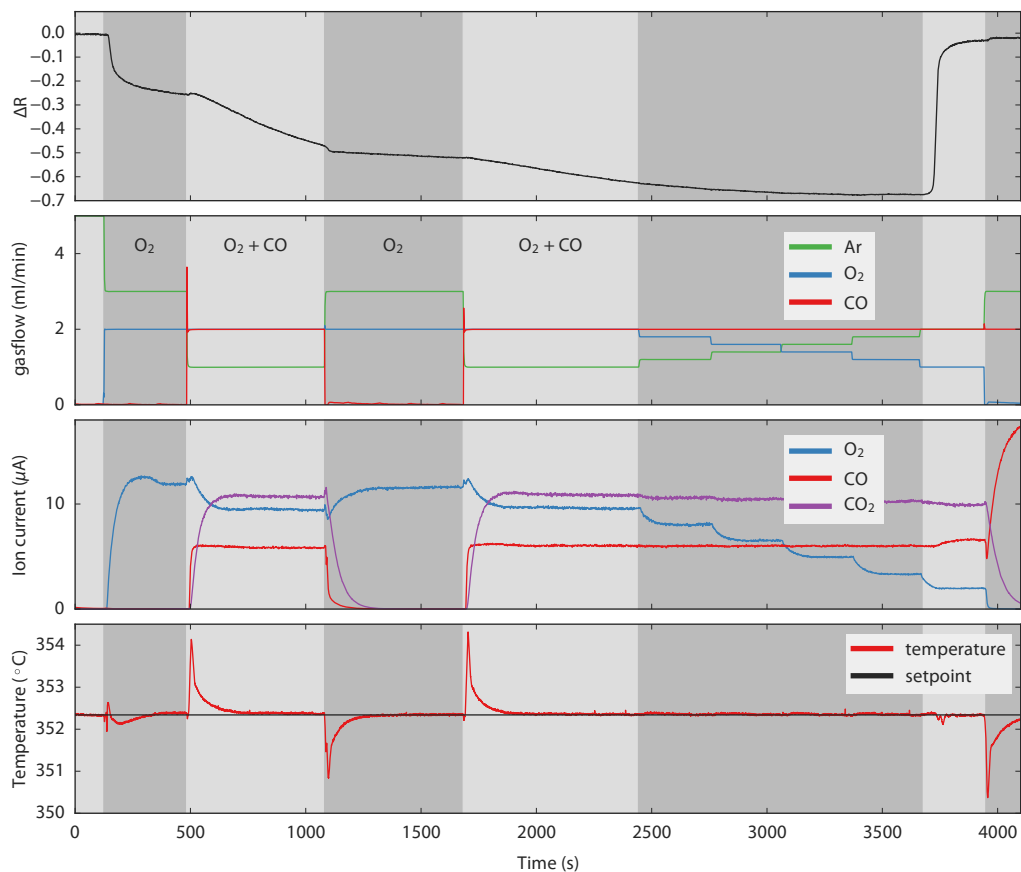


Figure 2.6. Variation in time of the reflectance, the gas composition and the sample temperature. The first graph shows the variation with time of the ΔR value, averaged over the same area as indicated in image *c* in figure 2.4. The second graph shows the flow rates at which Ar, O₂ and CO have been fed into the reactor volume. The third graph shows the composition of the gas leaving the reactor, as measured with a quadrupole mass spectrometer in a separate vacuum system. The bottom graph shows the actual sample temperature and the temperature setpoint. The deviation in this graph is much larger than in the bottom graph in figure 2.4 due to added heat production of the CO oxidation reaction.

ratio of 2:1. We analysed the composition of the gas exhaust to monitor the CO₂ production. The top graph of figure 2.7 shows the behaviour of the surface reflectance, averaged over a small part of the surface, similar to the rectangle indicated in image c of figure 2.4.

In the episode labelled *a* in figure 2.7 we start at low temperature. The increase in temperature is initially accompanied with a modest, slow decrease of ΔR , which can be ascribed to thermally induced drift of the Pd sample. In episode *b* we see an increase of the CO₂ pressure and a decrease in the partial pressures of O₂ and CO in the exhaust gas mixture. Here we see both a sharp increase in CO₂ production and a sharp decrease in O₂ and CO. Coinciding with these chemical changes in episode *c*, ΔR shows a sudden, small decrease of 0.5 %. The resulting ΔR is maintained for only a few seconds, until episode *d* starts, in which the partial pressures of O₂, CO and CO₂ remain constant, but ΔR decreases rapidly with time. The start of episode *e* marks the point in time where the reduction of ΔR is slowed down significantly. In this episode, the composition of the gas that leaves the reactor is constant. Episode *f* starts at the point in time where we have reached the maximum temperature and start cooling. Initially, ΔR remains constant. In the second half of episode *f*, ΔR increases somewhat. In *g* we see the combination of a temporary decrease in CO₂ production and a very small upward step in ΔR , while in *h* the CO₂ production rate is at its former level. This cycle repeats itself at *i* and *j*, this time with a more pronounced increase in ΔR . In episode *k*, the CO₂ production is severely decreased. This coincides with an almost full recovery of the reflectance. In the final episode, *l*, the measured CO₂ partial pressure falls in the noise level. The slow increase in reflected intensity results from the reverse thermal drift of that experienced in episode *a*.

Armed with only the ΔR and gas composition information in figure 2.7, it is impossible to give a full description of all changes in surface structure and reaction mechanism during the experiment. In our interpretation, we make use of previous experiments on Pd(100), performed under comparable conditions, with other, structurally sensitive techniques, in particular STM and SXRD [11–13, 29, 30]. This brings us to the following scenario. In episode *a* the sample is CO poisoned and therefore in a metallic state. The CO₂ production follows the Langmuir-Hinshelwood mechanism. As the temperature increases, the surface is increasingly populated by O atoms. We speculate that in the last part of episode *b*, the reaction rate increases as a sign of the presence of an alternative and more reactive co-adsorption structure of O and CO on the metal surface. We interpret the sudden decrease of ΔR , accompanied by the jump in CO₂ partial pressure, as

the consequences of the sudden formation of a surface oxide, as has been identified in SXRD and STM experiments [11, 30]. The surface oxide forms the starting point for the rapid growth of a thin film of a few nanometres thick of bulklike PdO. This goes hand-in-hand with the buildup of additional roughness and, hence, a further reduction of ΔR (*d*). This growth of the bulklike oxide is self-terminating and therefore the rapid reduction of ΔR also comes to an end (*e*). Under these conditions, the reaction proceeds according to the Mars-Van Krevelen mechanism. As we have seen before, this reaction mechanism leads to a steady roughening and the corresponding steady reduction of ΔR . When the temperature is decreased again in episode *f*, the reaction rate, which is mostly limited by the diffusion of CO in the gas phase, slows down. This progressively reduces the rate at which ΔR drops. The effects in (*g*, *h*, *i* and *j*) are described in more depth in the chapter 4. We interpret them as reduction and oxidation cycles, induced by the interplay of the decreasing temperature and the changes in surface roughness. In episode *k* the surface is fully reduced. With the removal of the rough oxide the diffusivity of the palladium atoms is increased and the surface smoothens. In the gas analysis we can see that upon reduction of the surface the reactivity is decreased. The reaction is back to the initial Langmuir-Hinshelwood mechanism.

2.3.5 Brightfield versus darkfield

The distance of the first lens to the sample is approximately 12 cm, and this lens has an diameter of 4 cm. Therefore only light reflecting off a part of the surface with a local slope below 10° is captured by the camera. For light to reflect at such angles an average slope of the area of the wavelength on the incoming light is required to be at this angle. For diffracted light to fall within the aperture of the camera, the spatial period of a sinusoidal corrugation has to be larger than 3.6 μm . In kinetic roughening processes the roughness and the correlation length start small and increase over time [55]. Therefore the off-specular contribution only becomes significant after considerable time and mass transport on the surface. Since the STM and SXRD data indicate typical roughness length scales to remain well below 1 μm , we have not pursued the darkfield light scattering in the measurements presented in this chapter.

2.4 Conclusion and outlook

This chapter has presented a new method for performing in situ investigations of model catalysts under reaction conditions. We are able to follow the

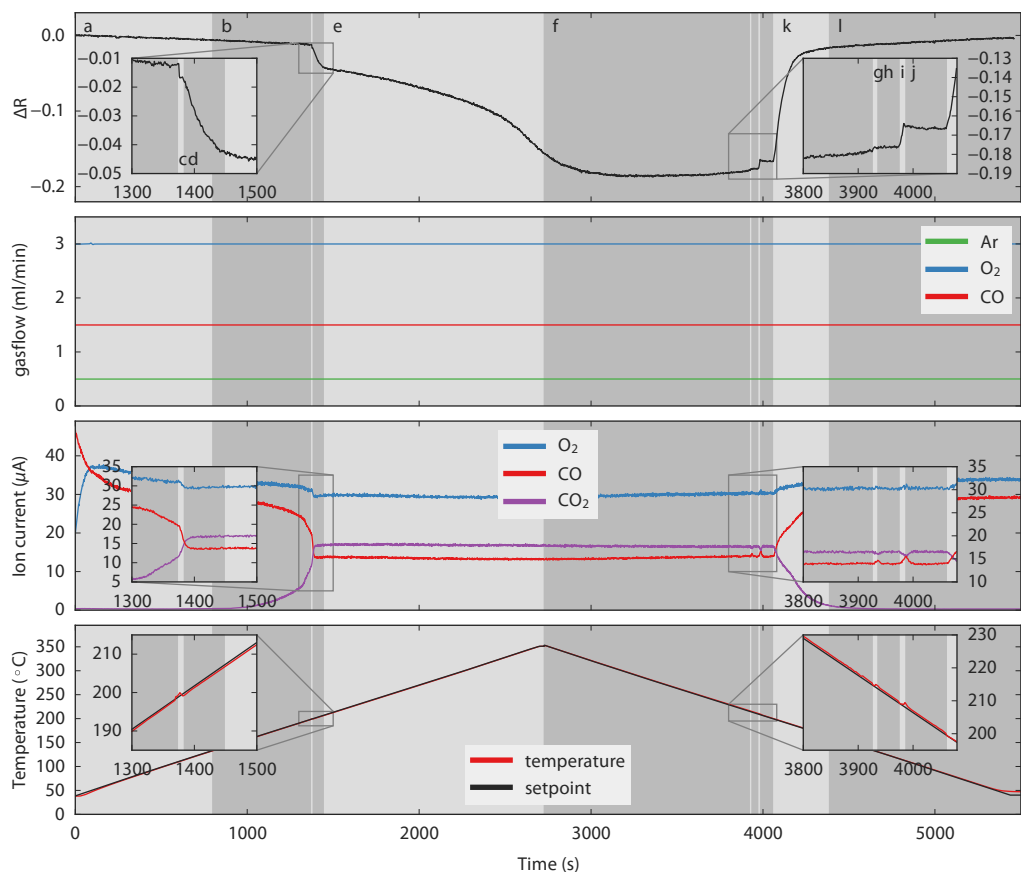


Figure 2.7. Time sequence of the reflectance, the gas composition and the sample temperature. The first graph shows the variation with time of the ΔR value, averaged over a selected area in reflection images. The second graph shows the flow rates at which Ar, O₂ and CO have been fed into the reactor volume. The third graph shows the composition of the gas leaving the reactor, as measured with a quadrupole mass spectrometer in a separate vacuum system. The bottom graph shows the actual sample temperature, which can temporarily deviate from the setpoint to which the temperature is controlled, due to changes in heat conduction through the gas and changes in heat production by the CO oxidation reaction. The insets show enlarged views of two episodes of interest with rapid changes in reactivity and reflectance.

optical response of a catalyst surface under a range of gas conditions and over a broad temperature range. The technique is sensitive to small changes in reflectance of the catalyst surface and has a lateral resolution well below 1 mm. This setup is less complex than instruments previously used, such as those developed for high-pressure STM and SXRD. Therefore a large range of catalytic environments can be easily monitored. This method forms a valuable addition to the full set of techniques available for investigating high-pressure catalysis.

We have concluded that in the case of CO oxidation on Pd(100) the contrast is both caused by oxidation of the surface and by changes in roughness of the surface during the reaction.

The limiting factor for extracting the correlation length of surface features is mainly the acceptance angle of the lens. This could be solved by choosing an off-normal angle of incidence, combined with a different or an additional entrance window. This could also be combined with polarisers to perform ellipsometric microscopy, for increased sensitivity to the surface features.

Chapter 3

BINoculars: data reduction and analysis software for two-dimensional detectors in surface x-ray diffraction

BINoculars is a tool for data reduction and analysis of large sets of surface diffraction data that have been acquired with a 2D x-ray detector. The intensity of each pixel of a 2D-detector is projected onto a 3-dimensional grid in reciprocal lattice coordinates using a binning algorithm. This allows for fast acquisition and processing of high-resolution datasets and results in a significant reduction of the size of the dataset. The subsequent analysis then proceeds in reciprocal space. It has evolved from the specific needs of the ID03 beamline at the ESRF, but it has a modular design and can be easily adjusted and extended to work with data from other beamlines or from other measurement techniques. This chapter covers the design and the underlying methods employed in this software package and explains how *BINoculars* can be used to improve the workflow of surface x-ray diffraction measurements and analysis.

The work presented in this chapter has been performed together with Dr. Sander Roobol.

3.1 Introduction

Over the last decade there have been several developments that have radically changed data acquisition in X-Ray Diffraction (XRD) experiments. The primary development is that nearly all point detectors have been replaced by 2D-detectors, such as the MAXIPIX detector [56], that collect spatially resolved information from a region in reciprocal space in a single shot. Secondly, by synchronising the data acquisition with the actuation of the diffractometer motors, it is now possible to perform continuous scans during diffractometer movements. Even though this has been demonstrated already 50 years ago [57], it has only recently become routine practice [58]. Thirdly, the high photon flux at 3rd generation synchrotrons [59] allows integration times in the order of tens of milliseconds rather than seconds, thus enabling time-dependent observations of dynamic processes rather than the slow acquisition of static information.

The result of these developments is that the data acquisition rate has increased by six to seven orders of magnitude, from typically 1 point per second to millions of points per second, so the amount of data collected during one experiment increased dramatically. Today’s computer hardware can keep up with that increased demand, but the development of software to analyse these large datasets has been lagging behind, which has kept most users from exploiting the full potential of modern surface diffraction beamlines. *BINoculars* aims to fill this gap by taking a novel approach to data reduction in Surface X-Ray Diffraction (SXRD) experiments.

Currently, data reduction is typically performed by integrating a region of the image from a 2D-detector, sometimes coupled with another integration to determine the background level, and then basically treating the data as if it would have come from a point detector. Compared to a traditional point detector the advantages are mostly qualitative: the large acceptance angle of the detector, in combination with its good angular resolution, is very convenient during diffractometer and sample alignment, and makes it possible to visually identify peaks by their shape (i.e. one can easily distinguish between a powder ring, a crystal truncation rod or a region of diffuse background). *BINoculars* improves on this by treating every pixel of a 2D-detector individually, rather than to reduce the 2D-detector to an expensive point detector.

BINoculars takes a series of images from a 2D-detector, calculates for each pixel the corresponding reciprocal lattice coordinates (hkl), and reduces the image collection to a single dataset by averaging the intensities of pixels taken at identical (hkl) positions (within a user-specified resolution). This transformation and averaging is illustrated in figure 3.1. To allow online

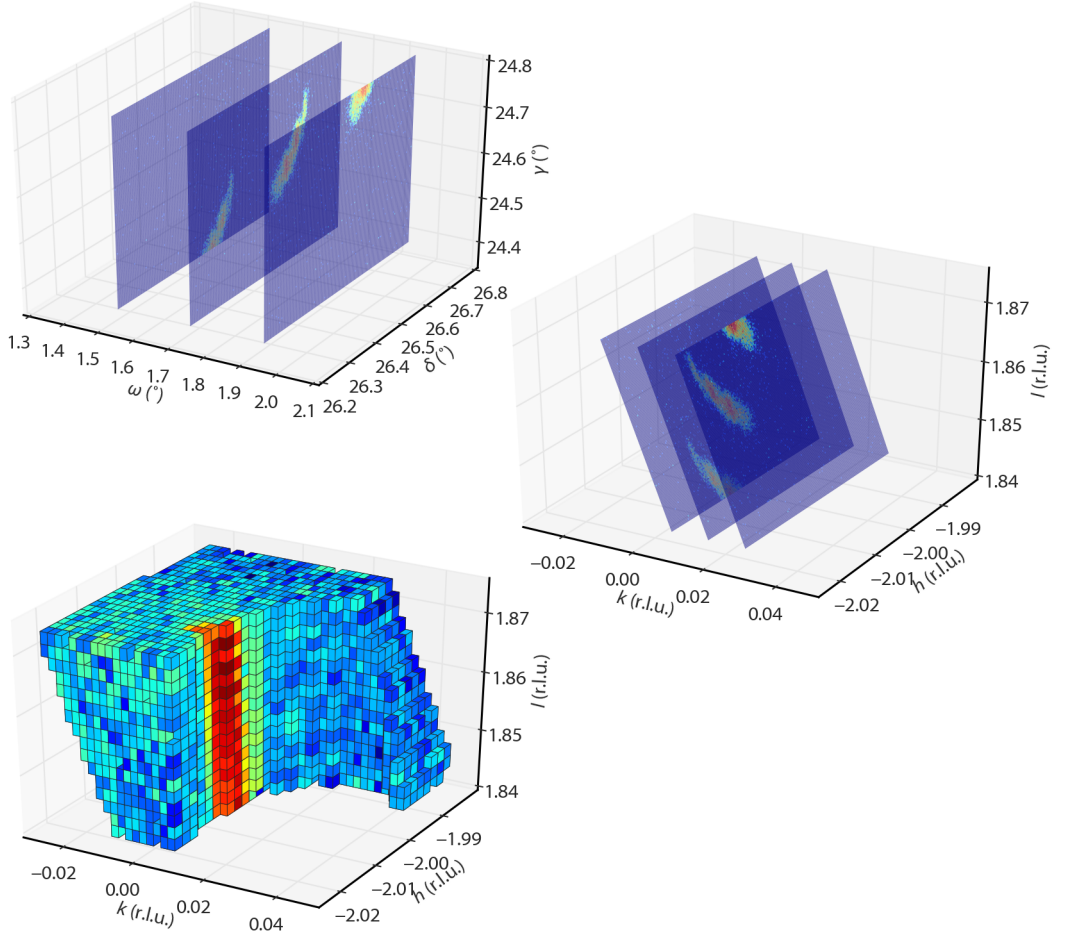


Figure 3.1. A graphical overview of the process performed by *BINoculars*. The data displayed here are from a rocking scan through $(h, k, l) = (-2, 0, 1.85)$ in the diffraction pattern from a Pt(110) surface. Upper panel, raw data acquired by the 2D-detector with the corresponding angles ω , δ , γ from a six-circle diffractometer [60]. Middle panel, the diffractometer angles are mapped onto reciprocal space coordinates $(h k l)$. Lower panel, the averaged intensity of pixels on a regular grid of volumetric bins (voxels) is calculated. Part of the bins are removed for clarity. Note that the data in reciprocal space in the lower panel are constructed from a series of images over a larger range and with a denser sampling in ω than shown in the other panels.

analysis during data acquisition, *BINoculars* can run on a high performance cluster to process large datasets. For example, the result of a full hour of continuous scanning, adding up to a total of approximately 10^{10} pixels, can be processed in a matter of minutes. In addition, *BINoculars* provides tools to further process the data, including visualisation, curve fitting, and crystal truncation rod integration. The latter can be seen as an implementation of the reciprocal-space integration method, recently described by Drnec et al [61]. As a whole, *BINoculars* can be seen as an N-dimensional generalisation of PyFAI [62] and xrayutilities [63], optimised for (but not limited to) surface x-ray diffraction.

3.2 Implementation

BINoculars has been written in Python, an open source scripting language that is very suitable for scientific software, thanks to its powerful and clear syntax and the extensive support for numerical calculations via the Numpy and Scipy libraries [64].

BINoculars has been designed to process large datasets, and its operation is usually cpu-bound. An ordinary desktop computer can easily take many hours to deal with a dataset obtained in one hour (e.g. 10^{10} pixels with 16 bit per pixel). To allow online analysis during data acquisition at a beamline, *BINoculars* can use a computing cluster to distribute the load over multiple computers.

To keep *BINoculars* modular and flexible, the workflow for processing data is separated into four modules: the *dispatcher* is in charge of the whole process and handles job parallelisation and distribution, the *input* class gathers the experimental data, and the *projection* class converts the raw data into the coordinates of choice. Finally, the processed data is binned on a discrete grid and stored in a *space* class, which provides generic tools for further analysis. The specific behaviour of the *dispatcher*, *input* and *projection* modules can be changed independently. For these modules, the user can choose from several different implementations, each having a different set of features.

The *input* class collects the raw 2D-detector images and assigns metadata to each individual pixel. This metadata is used later on by the *projection* class to make the conversion to the desired coordinate system (e.g. (hkl) for a typical SXRD experiment). The *input* class is specific to a certain experimental setup. As an example, for the ID03 beamline at the ESRF [22], a separate class has been written for each of the experimental hutches. In many ways the two experimental hutches are identical, for example the

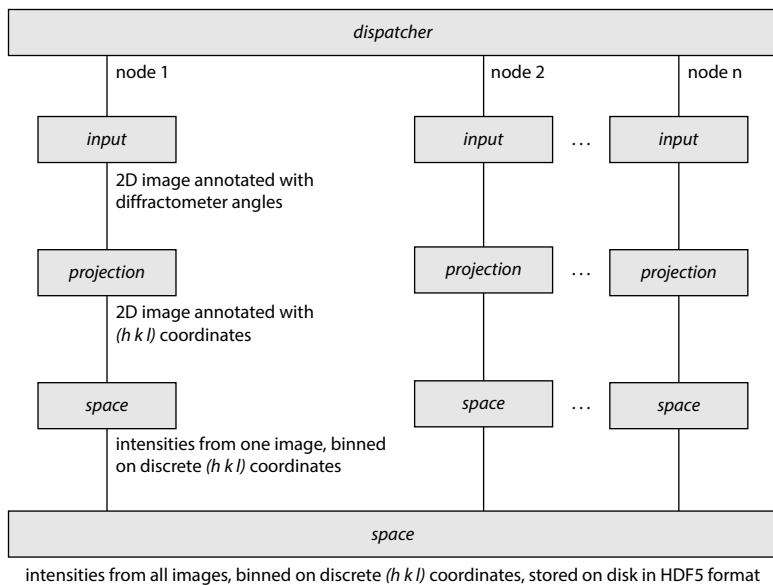


Figure 3.2. Block diagram of the process performed by *BINoculars* for a typical dataset from a diffraction experiment. The *dispatcher* distributes the load over multiple nodes from a computing cluster. The *input* class gathers the experimental data and calculates the diffractometer angles for each pixel. The *projection* class converts the angles to $(h\ k\ l)$ coordinates. The intensities are binned on a discrete grid by the *space* class, and finally the intermediate results from each node are combined into a single *space*.

same numbering scheme is used for the images taken by the x-ray cameras, but one of the diffractometers operates at constant detector-sample distance while the other does not. The *input* class takes care of all these technicalities, and writing a new *input* is the most important task when adding support for another experimental setup. In addition, the work done by the *input* class is often the most computationally intensive step in the entire process of *BINoculars*.

The next step is performed by the *projection* class, which converts the data collected by an *input* class into the appropriate coordinate system for binning. For an SXRD experiment, the *input* class will typically return a series of detector images with corresponding diffractometer angles for each pixel, and the *projection* class will convert the angles into reciprocal space coordinates (hkl) for each image. In some cases, there are several projections that are useful. For example, for the ID03 beamline it is sometimes necessary to project onto the scattering angle 2θ rather than (hkl) coordinates (although an alternative route would be to perform a coordinate transformation afterwards to convert the (hkl) *space* into a 2θ *space*).

Once the data has been gathered and projected on the desired coordinate system, the binning operation is performed by a class called *space*. This class represents an n -dimensional regular grid: it is a discrete subset of a vector space, where each dimension has a fixed step size. Many mathematical operations can be performed with *spaces*, including addition, subtraction, slicing, projections, and coordinate transformations. To bin an image, the (hkl) coordinates of each pixel of the image are mapped onto the nearest discrete *space* grid location. Then the pixel intensities are accumulated at every discrete grid location, using the histogram-operation *bincount* from Numpy. In addition, the number of contributions per coordinate is stored in order to calculate the mean intensity per bin rather than the integrated intensity. This binning operation is the essential data reduction step performed by *BINoculars*, hence the name of the program.

The *dispatcher* orchestrates the entire process: it asks *input* for the sequence of images from the 2D-detector, delegates it to the appropriate *projection* and performs the binning operation by feeding the projection result into a *space*. Two *dispatcher* implementations are currently present: one for local processing using multiple processor cores on a single computer, and one that distributes tasks over a high performance cluster managed using OAR [65]. Support for other types of clusters can easily be added. When running on a computing cluster, the *dispatcher* gathers all intermediate spaces calculated by the individual nodes (for example using a shared

filesystem) and they are added together to form the final resulting *space*. *Spaces* are stored on disk using the HDF5 file format [66].

After a *space* has been created, the size of the dataset has typically been reduced by a factor 10 to 100, and further analysis can usually be performed on a standard workstation. However, loading a high-resolution large-area 3D dataset can require several GB of memory, and for some operations it is required to have several copies in memory. If this is a problem, it is also possible to work with a subset of the data, either by selecting a smaller region, or by reducing the resolution, or by reducing the dimensionality.

BINoculars provides various tools for analysis, including mathematical operations, plotting and exporting. For ultimate flexibility it is possible to directly manipulate a *BINoculars* space from a Python script, but in many cases the standard tools are sufficient. In addition, a fitting and integration tool is available to calculate the structure factors of a crystal truncation rod to be directly inserted into the fitting program ROD [67]. It takes as input a reciprocal mesh which it slices by a user-specified resolution and the resulting data are either fitted (typically with a 2D lorentzian) using a least-squares optimisation, or simply integrated. The error is estimated from equation (3.2), as will be described in more detail in the next section.

3.3 Binning and error handling

BINoculars calculates the average intensity of multiple contributions, originating from different pixels and/or detector positions, to a single reciprocal space bin. This operation is similar but not identical to averaging a series of repeated measurements taken by a point detector at a fixed position. This section discusses the implications of the binning operation for the background intensity and the estimation of statistical errors.

When using a point detector, the typical surface diffraction experiment is set up such that there is a unique detector position for each set of reciprocal space coordinates ($h\ k\ l$). In practice, this means reducing the degrees of freedom of the diffractometer to three, e.g. by working with a constant surface normal and a fixed angle of incidence. When taking series of repeated observations at a certain reciprocal-space location, the systematic error in each measurement can be assumed to be constant (after the usual correction for variations in the total beam intensity), and the only variation is given by the shot noise of the incoming photons.

Using a 2D-detector, the spatial extent of the detector introduces two more degrees of freedom, meaning there is no longer a unique detector position for a given reciprocal space coordinate. This is usually solved

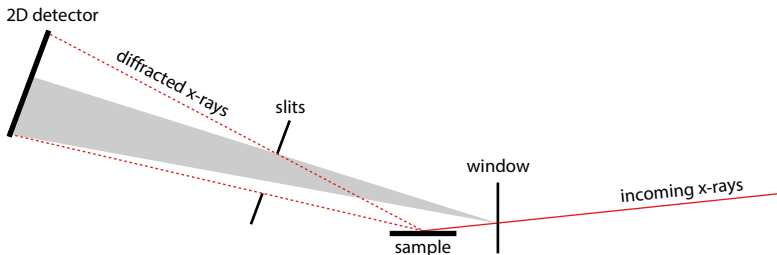


Figure 3.3. The wide opening angle of the slits, which is required to capture a region in reciprocal space with a 2D-detector, results in a non-uniform background across the detector (indicated in grey in the figure). This background originates from scatterers other than the sample, for example a beryllium window. This means that when taking two images at slightly different detector positions such that there is some overlap between the two captured regions, the background intensity in the overlapping region is not constant.

by selecting one pixel of the detector to correspond with “the detector position”, and ignoring the fact that the other pixels are at a slightly different position. However, *BINoculars* does take the spatial extent of the detector into account, and calculates the average intensity at each location in reciprocal space, regardless of the detector position.

This means that multiple measurements, even when spaced closely together in time, exhibit variations not only due to the statistical nature of the process, but also due to a systematic error possibly resulting from different detector positions. This error is caused by differences in background originating from scatterers other than the sample, as is illustrated in figure 3.3. Flight tubes and slits between the sample and the detector can be used to reduce this background, but they also decrease the aperture of the 2D-detector. This reduces the range of $(h\ k\ l)$ -locations over which data can be collected in one acquisition. This means that a careful trade-off needs to be made between acquisition speed and background suppression.

In some cases it is possible to subtract the background I_b , either by measuring it directly when the sample is not in the beam, or by estimating it from the dataset itself in regions in reciprocal space where the sample only weakly contributes to the total observed intensity. The latter approach will be explored in more detail in section 3.4.

The remaining error reflects the counting statistics in the number of detected photons and is typically assumed to obey Poisson statistics [68]. For a single observation of I counts, the standard deviation σ is estimated using $\sigma = \sqrt{I}$. With N independent observations I_i in a single bin, each

with its own $\sigma_i = \sqrt{I_i}$, the average intensity is

$$I = \frac{1}{N} \sum_i I_i, \quad (3.1)$$

and the variance can be estimated under the assumption of normality (N or I_i sufficiently large) using

$$\sigma^2 \approx \frac{1}{N^2} \left(\sum_i \sigma_i^2 \right) = \frac{I}{N}. \quad (3.2)$$

Assuming we have a separate estimate of the background intensity I_b in this bin with a corresponding variance σ_b^2 , the the variance σ_s^2 of the signal $I_s = I - I_b$ is now given by

$$\sigma_s^2 = I/N + \sigma_b^2. \quad (3.3)$$

Of course, if the background was also obtained by averaging N measurements, σ_b^2 would also take the form I_b/N .

3.4 Demonstration

Four different examples will be discussed to show the capabilities and limitations of *BINoculars*.

Figure 3.4 shows a high-resolution (0.0002 reciprocal lattice units or r.l.u.), large-area (hk)-surface in reciprocal space, covering the first reciprocal unit cell of a Au(111) surface, submerged in an electrochemical cell filled with sulphate-containing electrolyte (pH 7) and kept at -800 mV vs. Ag/AgCl reference electrode. The gold surface exhibited the so-called herringbone reconstruction [69], which is a regular structure with a $(22 \times \sqrt{3})$ periodicity that is organised into a zigzag pattern on an even larger scale. The $(22 \times \sqrt{3})$ superstructure peaks originating from this reconstruction [70, 71] are well-resolved in the scan. The differences between this diffraction pattern and the pattern reported in literature for the same surface in ultrahigh vacuum are not fully understood, however, it is likely due to the sample preparation procedure in the electrochemical cell. The dataset was acquired in just 111 minutes.

Figure 3.5 shows a dataset that is strongly affected by background intensity. Like figure 3.4, the dataset is built up from a series of ω -scans and in this case those scans are clearly visible as arcs after processing by *BINoculars*. The problem is that the background intensity not only depends on the position of a pixel, but also on the position of the camera. In other

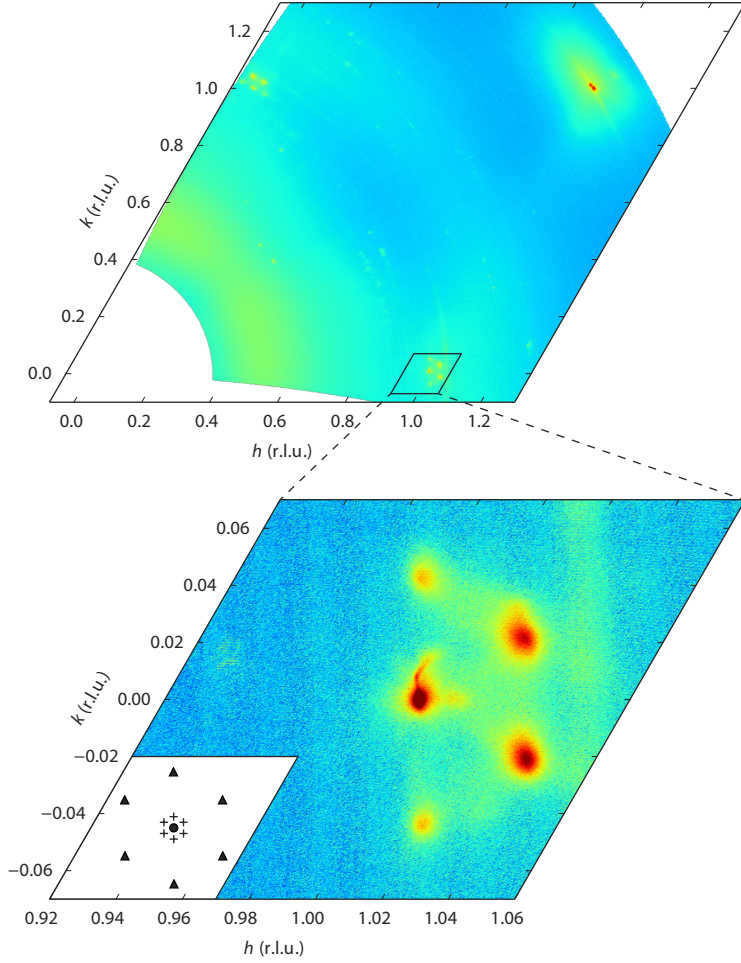


Figure 3.4. A large-area survey (upper panel) in reciprocal space of the heringbone reconstructed Au(111) surface, taken at $l = 0.3$. The dataset has been obtained in 111 minutes using a series of continuous-acquisition ω -scans. A zoom-in (lower panel) around the $[10l]$ crystal truncation rod (indicated by the circle in the inset) shows the satellite peaks caused by the $22 \times \sqrt{3}$ unit cell (indicated by triangles), and those originating from the longer range ordering of the zigzag domains (indicated by crosses). Loading this dataset requires 1 GB of memory.

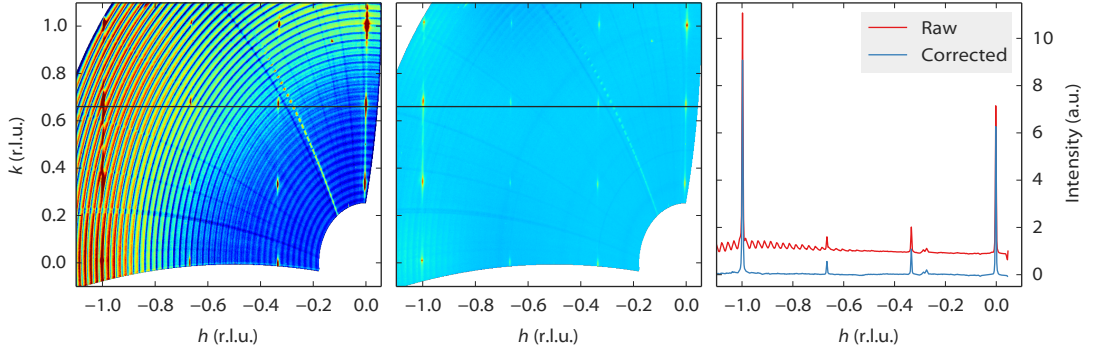


Figure 3.5. Some datasets require further processing to remove the curved background artefacts. This figure shows the $l = 0.5$ plane from a Pt(110) sample in the high-pressure flow reactor setup at ID03. The surface exhibited a (3×3) reconstruction (which has not been described before in literature) during high-temperature, high-pressure exposure to NO and H₂. The setup had a relatively high diffuse background that could be corrected for by estimating the background level for each pixel of the detector, once per scan in ω . The left panel shows the raw data, the middle panel the data after background correction. The right panel shows the intensity profiles along the line $k = 0.66$ for a direct comparison between raw and corrected data. The small peaks at $h = 0.3$ originate from scattering from the Be dome, this is also visible in the left and middle panel as a diagonal line.

words, when moving the camera by only a small amount, such that a certain feature remains in the field of view (in this case a move in γ between the consecutive ω -arcs), the contribution of the background intensity to that feature can change significantly, as illustrated in figure 3.3.

This particular dataset has been obtained using the high-pressure flow reactor setup at ID03 [21], which has a beryllium dome around the sample. The dome acts as a strong x-ray scatterer only 14 mm away from the sample. It is not possible to lower the resulting background intensity using slits without dramatically reducing the aperture of the detector. However, for this sample it proved possible to estimate and subtract the background level, the result of which is shown in the middle panel of figure 3.5. For each pixel of the detector, the background was estimated as the average intensity of that pixel in all images in a single ω -scan. The average is calculated by fitting a Poisson distribution, as this turned out to give better rejection of outliers (which are in fact the diffraction peaks) than a simple mean or median calculation. This process was then repeated for each ω -scan, resulting in an estimate of the background intensity that was subtracted from the raw data.

The background subtraction procedure described here is not generally

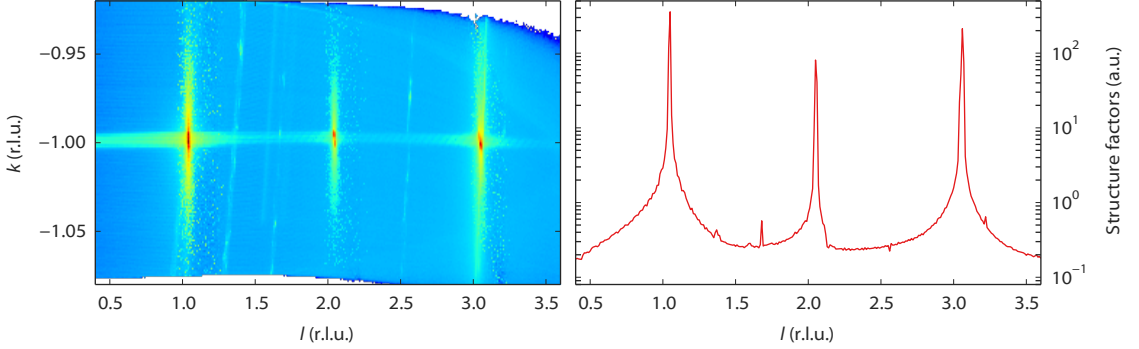


Figure 3.6. The left panel shows an l scan along the $[0\bar{1}l]$ crystal truncation rod of a $\text{SrTiO}_3(100)$ surface [72] projected on the kl plane after processing by *BINoculars*. A series of 2D-Lorentzians has been fitted to slices at constant l (corresponding to small hk surfaces), which has resulted in the structure factors shown in the right panel.

applicable as powder rings are treated as background. In addition, the amount of background is strongly dependent on the experimental setup, and the other datasets shown here did not need any background correction. Therefore this procedure is currently not part of *BINoculars*, although it is likely to become part of the ID03-specific *input* module in the near future.

The third example, figure 3.6, shows the output of the crystal truncation rod (CTR) fitting module. The original dataset is a single l -scan along the CTR. After processing by *BINoculars*, during which the *input* module also takes care of the polarisation correction factor necessary to obtain the structure factors [60], the three-dimensional rod can be visualised in reciprocal space. The dataset is then segmented into small intervals along l . Each section is analysed separately by a numerical integration algorithm to calculate the structure factors as a function of l . This method has recently been described by Drnec and co-workers [61].

At lower l the detector is more perpendicular to the surface, and for some samples it might be useful to augment the l -scan with rocking scans at low l . *BINoculars* can easily deal with such a hybrid dataset, since it starts by processing the data into the three-dimensional rod, after which the integration procedure (taking place in reciprocal space) is performed completely independently of the original character of the raw data.

The fourth example demonstrates that *BINoculars* can be used with other coordinate systems than (hkl) . Figure 3.7 shows the reflected intensity from a $(\text{PbSe})_{4+\delta}(\text{TiSe}_2)_4$ sample. It is constructed from images taken at different incidence angles that are projected onto $q_{\parallel}$ and q_z , the in-plane

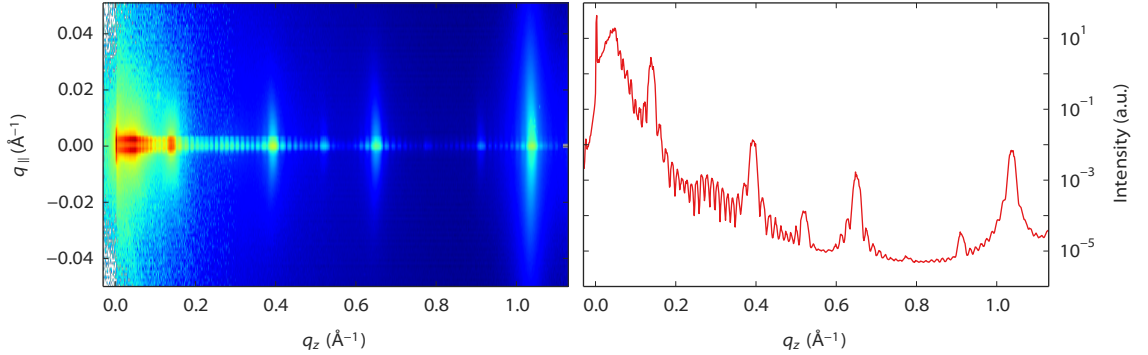


Figure 3.7. Reflectivity scan of $(\text{PbSe})_{4+\delta}(\text{TiSe}_2)_4$, a telluride misfit layer compound [73]. This sample has a multilayer structure with well-defined out-of-plane stacking but rotational disorder between layers. This gives rise to oscillations in the reflectivity curve, combined with broad in-plane scattering. The left panel shows the projection of the images taken at different incident angles onto $q_{||}$ and q_z . The right panels shows the specular rod obtained by integration along $q_{||}$ from -0.005 to $0.005 \text{ \AA}^{-1}$.

and out-of-plane momentum transfer. This two dimensional projection allows detailed analysis of the in-plane x-ray scattering that cannot easily be obtained by conventional methods. In addition, the integration to obtain the specular rod ($q_{||} = 0$) can be easily performed.

3.5 Conclusion

BINoculars brings SXRD into the 21st century by unlocking the full visual power of two-dimensional surface diffraction patterns, something that was previously only achievable with LEED in UHV conditions, or by increasing the x-ray energy and sacrificing k -space resolution and dynamic range [13], or by taking an impractical amount of time. In addition, *BINoculars* simplifies structure determination by providing a quick, easy, and accurate method to integrate crystal truncation rods.

BINoculars is open source under the terms of the GNU General Public License [74] and is available online [75].

Chapter 4

Fast reaction oscillations in the catalytic oxidation of CO on Pd(100)

We have studied oscillatory reaction behaviour of the CO oxidation reaction on Pd(100). We have used 24.3 keV x-ray to examine the structure and morphology of the thin oxide layer throughout these self-sustained oscillations. We conclude that competition between the step density and surface reactivity drives the oscillations.

4.1 Introduction

Although CO oxidation on Pt-group catalysts has been very widely studied, there is no consensus yet about the reaction mechanism under actual reaction conditions. Two competing reaction mechanisms have been proposed [25, 76]. In the traditional Langmuir-Hinshelwood mechanism, oxygen molecules adsorb dissociatively on the metal surface and CO molecules are adsorbed molecularly. On the surface, they react to CO₂ molecules that desorb to make room for new reactants. The observation of the formation of thin surface oxides under CO oxidation conditions has suggested a second mechanism. In the Mars-Van Krevelen mechanism, CO molecules adsorb on the oxide from which they extract O atoms to form CO₂. The oxygen vacancies are refilled by oxygen from the gas phase. The debate hinges on the question whether the oxide is the active phase (MvK mechanism) or, possibly, a consequence of the local decrease in the partial pressure ratio between CO and O₂ due to the reaction on the metallic surface (LH mechanism). In order to distinguish between these two situations, we would need to measure the chemical activity of the metal and the surface oxide separately. Because the tools we have constructed for measuring reactivity, i.e. mass spectrometry, are always aggregating the total turnover of an entire sample, spatially resolving the active phase with nanometre resolution is still not possible. In order to circumvent this problem we have taken a different route.

In this chapter we focus on reaction oscillations of the CO oxidation reaction on the Pd(100) surface. Reaction oscillations have been found in many chemical situations. When self-sustained oscillations occur there exists a 'driving force' and a 'restoring force', with the driving force keeping the system out of equilibrium. Understanding how these two 'forces' work, might provide us with insight on the CO oxidation reaction itself. The self-sustained oscillations provide a unique situation in which the oxidation and reduction behaviour can be observed. In this chapter we present an in-depth analysis of observations during the CO oxidation oscillation reaction. We employ a number of x-ray techniques, all with their own speciality for examining multiple aspects of the oscillation reaction.

Reaction oscillations on Pd(100) at high pressure and temperature have been observed both with Scanning Tunnelling Microscopy (STM) and Surface X-ray Diffraction (SXRD) [11, 12]. In the model of Hendriksen et al.[12] the stability of the oxide is governed by the step density of the metallic palladium surface that is exposed when the oxide is reacted off. The adsorption of CO on the metallic surface is so much stronger on steps than on terraces, that in the presence of a high CO pressure, the free energy of a

rough surface is actually lowered when it is turned from a rough oxide into a metal surface with a high step density. Since the MvK mechanism that is characteristic for the surface oxide also leads to the accumulation of surface roughness, the oxide is naturally driven towards a first-order phase transition to the CO-covered metal surface. After this transition, the palladium surface smoothenes until the oxide configuration is favourable again. Smoothening occurs because the mobility of palladium atoms in the metal phase is much higher than in the oxide phase and the Langmuir-Hinshelwood reaction mechanism does not generate new roughness. If the step density were the only parameter in the free energy equation, the surface would permanently choose for a single structure, either metal or oxide, whichever would be most favourable for the given combination of partial pressures and step density. In this situation, spontaneous oscillations would not occur. However, the free energy also depends on the CO partial pressure. The CO partial pressure at the surface is partly determined by the reactivity of the surface. Because the oxide is assumed to have a higher reactivity in this model, the CO pressure is lowered at the surface when the surface switches from metal to oxide, which shifts the free energy difference even further in favour of the oxide. Similarly, when enough roughness has accumulated for the surface to switch back to the metallic state, the CO partial pressure is increased at the surface, which shifts the free energy difference in the opposite direction, further in favour of the metallic state. The combination of these two effects creates the self-sustained reaction oscillations. The variations in roughness and in the free energy difference between the metallic and oxidic states are illustrated in figure 4.1.

In this chapter we use x-ray scattering techniques to inspect the spontaneous oscillations in the catalytic oxidation of CO on Pd(100) in more detail. We will find that, in addition to the oscillations identified previously, a more rapid class of oscillations occurs that contains information on the lateral length and timescales involved in the roughening and smoothening.

4.2 Methods

We performed experiments at the ID03 beamline of the ESRF with 24.3 keV x-rays, using the high-pressure Surface X-Ray Diffraction (SXRD) flow reactor [21]. Prior to the experiment, the Pd(100) sample was cleaned in situ in UHV by repeated cycles of argon ion bombardment and annealing. Subsequently, the flow reactor around the sample was closed and the sample was investigated in situ by SXRD or Grazing Incidence Small-Angle X-ray Scattering (GISAXS) under high-pressure, high-temperature exposure to

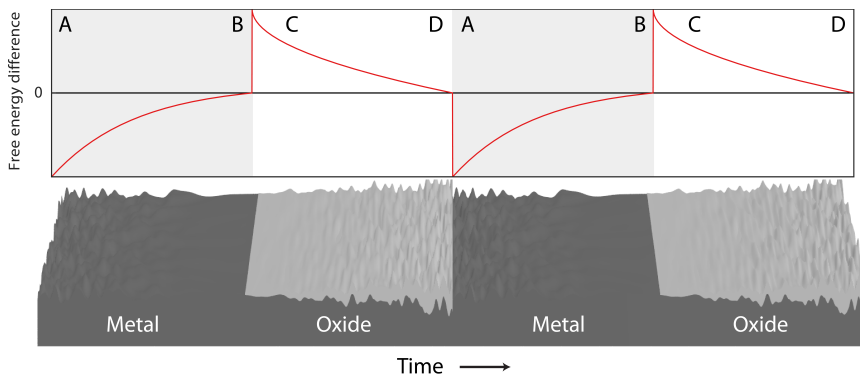


Figure 4.1. Schematic representation of the four phases in the oscillation model of ref[12]. The free energy difference between the metal and a metal oxide is shown through two full oscillations. In (A), a rough metal surface smoothens slowly into (B). This progressively makes the free energy difference between the CO-covered metal and the surface oxide less negative. When the decrease in step density lowers the free energy of the oxide below the free energy of the metal the surface oxidises (C). The increased reactivity of the oxide reduces the partial pressure ratio between the CO and the O_2 , which results in an additional, stepwise increase in the free energy difference. Due to the Mars-Van Krevelen mechanism the roughness of the oxide increases (D). This increase in roughness lowers the free energy difference, until the metal configuration is more favourable again and the oxide reduces to (A). The lower reactivity of the metal now results in a stepwise increase in the partial pressure ratio between CO and O_2 , which makes the free energy difference even more negative, and the cycle repeats from the start.

controlled gas flows.

In order to engage the oscillation conditions we used flow rates of 1.1 ml/min CO, 20 ml/min O₂, and 10 ml/min Ar at a total pressure of 1 bar. The heating power was constant by passing a current of 0.61 A through the 13.5 Ω heater, resulting in a sample temperature of approximately 170°C.

4.3 Results and discussion

We analyse results obtained with three experimental techniques that were acquired under similar conditions but not simultaneously. First we use SXRD to analyse in detail the behaviour of the oxide during the oscillation. Then we discuss the roughening of the surface as seen by X-Ray Reflectivity (XRR). Then we use SXRD again to observe the interface between the palladium and the the surface oxide. Finally we use GISAXS to extract the height-height correlation function of the surface.

4.3.1 Oxide

Figure 4.2 shows a measurement of the diffracted X-ray intensity from the surface oxide at HKL = (0.81, 0.39, 0.75), expressed in reciprocal lattice units of the Pd(100) substrate, where the real-space unit cell is defined by two axes parallel to the surface ($|\vec{a}_1| = |\vec{a}_2| = a_0/\sqrt{2}$) and one perpendicular to the surface ($|\vec{a}_3| = a_0$), with $a_0 = 3.89$ Å. The episode in figure 4.2 covers roughly two periods of the 'regular' reaction oscillation between the surface oxide and the metallic surface, the latter phase appearing from 900 to 1020 s and after 2556 s. During both oscillations, the x-ray intensity exhibits a gradual decrease with time, and a small number (typically one or two) stepwise intensity reductions. In addition, we see a much more rapid variation in x-ray intensity with a very modest amplitude.

We have fitted the surface oxide's Bragg reflection in a reciprocal space region around HKL = (0.81, 0.39, 0.75) to extract the behaviour of the oxide during the oscillation cycle. As illustrated in figure 4.3, we fit the Bragg peak with a Lorentzian shape:

$$S(q_a, q_b) = I \frac{1}{1 + \left(\frac{q_a}{\gamma_a}\right)^2} \cdot \frac{1}{1 + \left(\frac{q_b}{\gamma_b}\right)^2} \quad (4.1)$$

here q_a and q_b are the reciprocal space distances from the peak center ($q_{||0}, q_{z0}$), measured in a frame rotated by an angle ϑ with respect to the $q_{||}$ and q_z directions perpendicular and parallel to the sample surface, as indicated in figure 4.3. The widths of the peak along the peak's principal

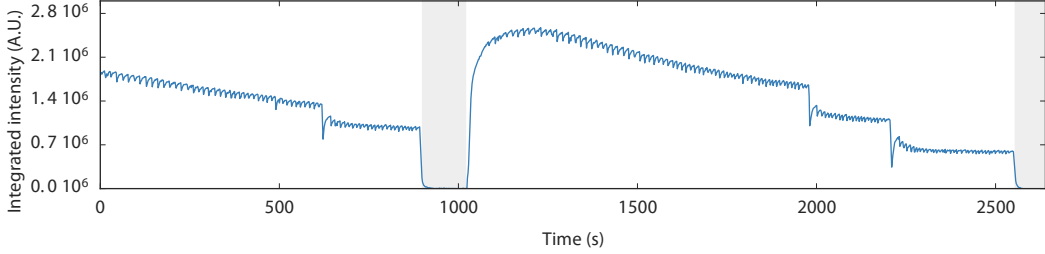


Figure 4.2. Intensity of the palladium oxide Bragg peak at $\text{HKL} = (0.81, 0.39, 0.75)$ during oscillations in the CO oxidation reaction on Pd(100) at 170°C in an atmosphere of 650 mbar O_2 and 30 mbar CO. The grey bands indicate the metal phase, during which the surface is completely reduced.

a - and b -directions are determined by γ_a and γ_b and I the maximum value of the peak. The central panel of figure 4.3 gives an example of such a Lorentzian fit for the measured data in the left panel. The reciprocal space region we use for fitting is 1.962 to $2.143 \text{ \AA}^{-1}$ in the $q_{\parallel}$ direction and 1.125 to $1.411 \text{ \AA}^{-1}$ in the q_z direction. Prior to fitting, the mean of the images between $t = 960$ to 1023 s is subtracted as a reference background.

Figure 4.4 shows the fitted parameters of the oxide Bragg peak over time. Every data point corresponds to one detector image with an integration time of 1 second. We will now try to couple the changes of the parameters to physical processes at the surface.

The oscillations observed in the oxide peak intensity show three separate timescales. The longest cycle lasts approximately 1500 seconds and corresponds to the appearance and complete disappearance of the oxide Bragg peak. This is indicated as the light grey section in panel (a) of figure 4.4. Towards the end of the period, we observe two sharp decreases in the intensity, with a time separation of approximately 250 seconds. The time between them is indicated by the dark grey section. Superimposed on these infrequent events, over nearly the entire oxide episode, is a sequence of very rapid intensity variations, in the form of a fast but modest decrease in intensity, followed nearly immediately by a recovery with a characteristic period of approximately 10 seconds, indicated by the black section. We see this fastest type appearing within 100 seconds of the start of each long cycle.

The fit parameters of the oxide Bragg peak show that the characteristics of the Bragg peak are changing during each oxide episode, from the very moment that the oxide is formed, to the point where the surface is reduced again. This indicates that the oxide layer undergoes a continuous transformation throughout its entire existence. We examine these fitted parameters

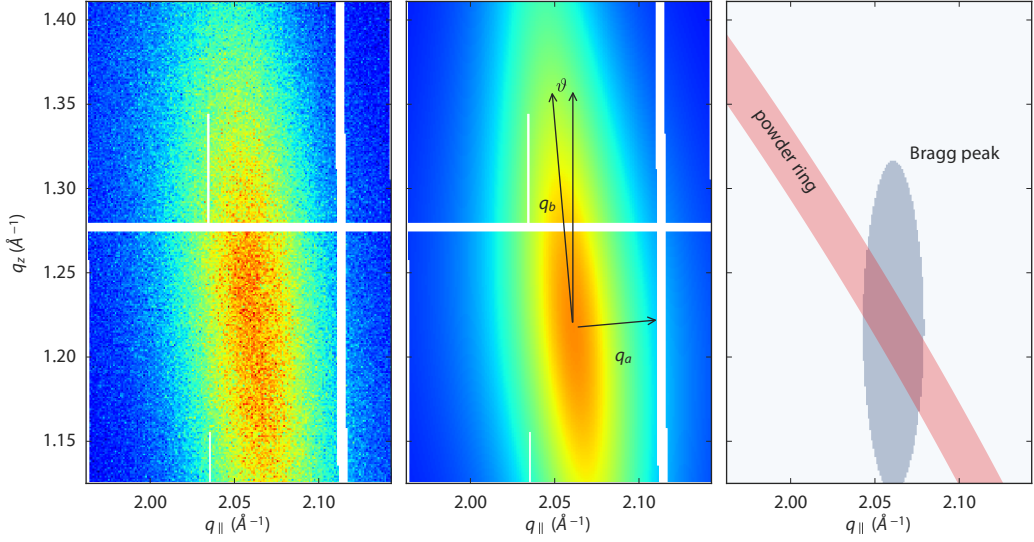


Figure 4.3. The left graph shows one detector image after processing with the BINoculars software (see chapter 3). The Bragg peak is fitted with the two dimensional Lorentzian peak shape from equation 4.1. The result of the fit for the data in the left panel can be seen in the middle panel. An ensemble of randomly orientated palladium oxide nano-crystallites would result in the powder ring as indicated by the red band in the right panel. A well-defined epitaxial palladium oxide layer would result in a Bragg peak strictly along q_z , as indicated in grey in the right panel. The white stripes in the left panel are inactive areas in the Maxipix detector.

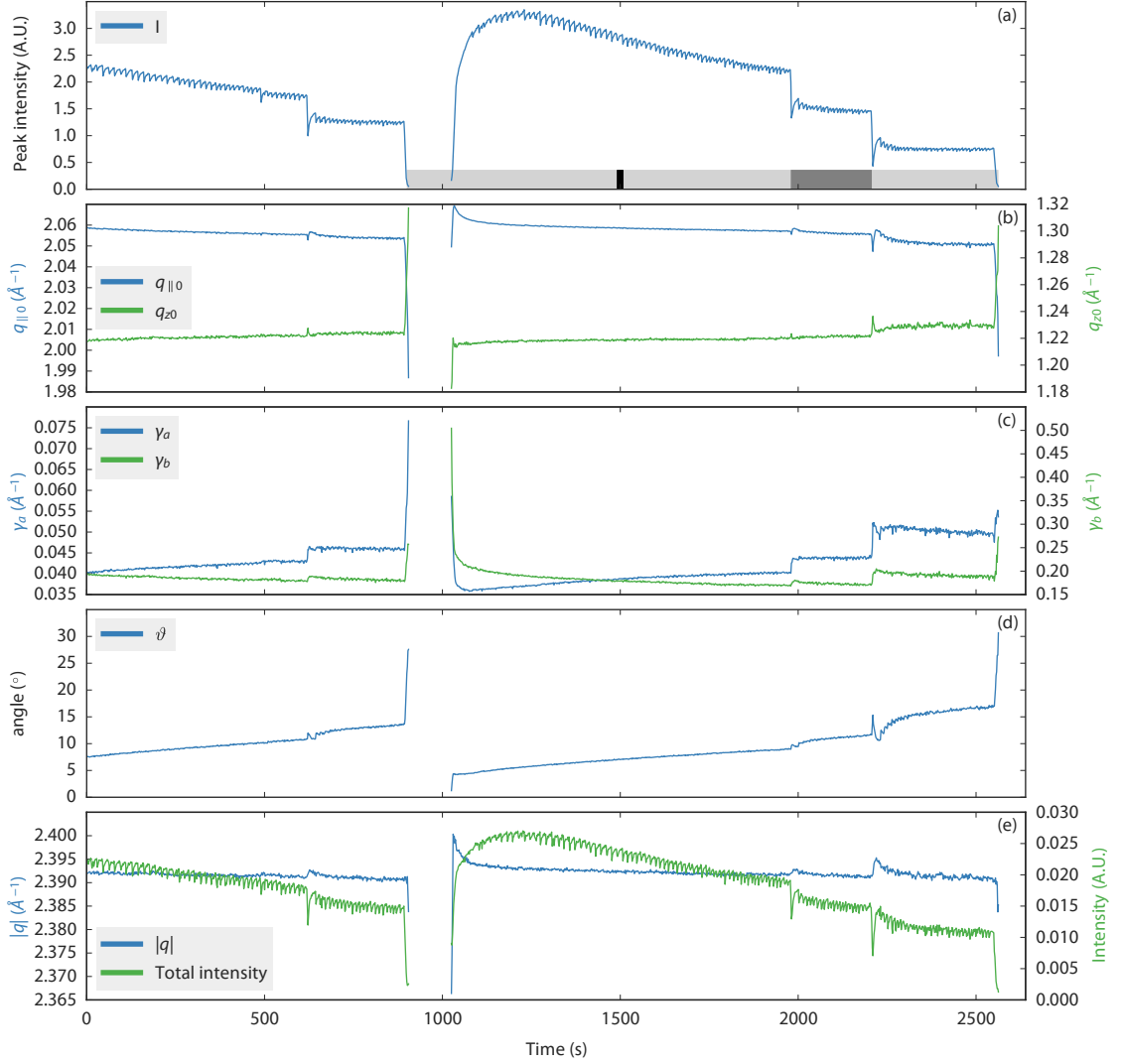


Figure 4.4. Best-fit values of the parameters used in the Lorentzian fit to the measured oxide Bragg peak on Pd(100) at $\text{HKL} = (0.81, 0.39, 0.75)$ as a function of time under conditions of spontaneous oscillations in the CO oxidation reaction. The conditions are specified in the text. (a) Intensity I . (b) Location of the peak centre. (c) Peak widths along the a and b directions. (d) Rotation angle ϑ . (e) Total momentum transfer at the peak centre and integrated Bragg peak intensity obtained from the fit (see text). The data points are removed where the fit failed, between $t = 900$ s and 1020 s and after 2556 s. The light grey area in panel (a) shows a full reaction oscillation. The dark grey area shows the duration of an oscillation on a faster timescale. The black area shows the duration of the fastest type of oscillations.

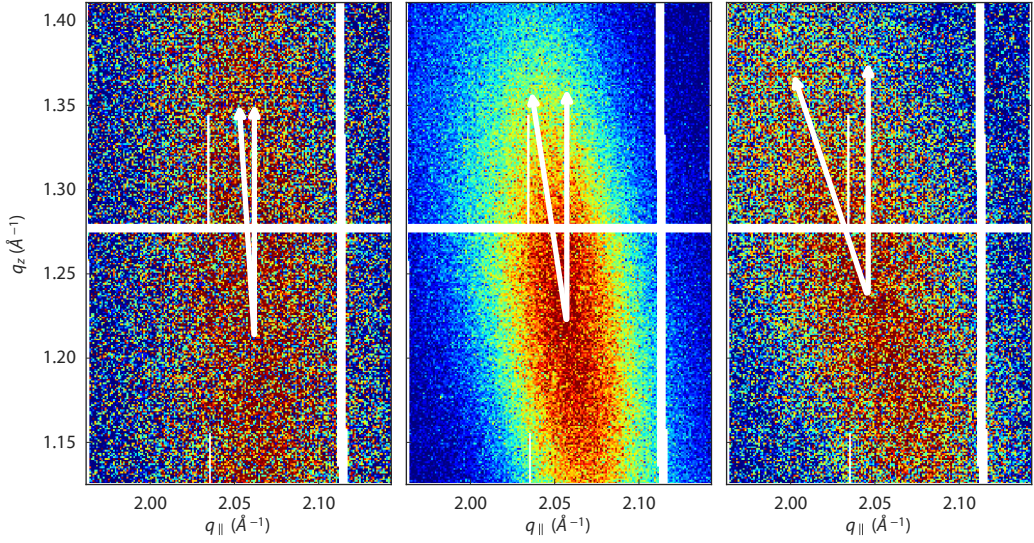


Figure 4.5. Three different types of observed surface structures. The three images show the transition of the Bragg peak from a crystal truncation rod, corresponding to a surface oxide (left) to a Bragg peak, corresponding to a bulk epitaxial oxide (middle) to a tilted Bragg peak, corresponding to an epitaxial oxide with a high degree of mosaicity (right). $t = 1030$ s for the left image, $t = 1870$ s for the middle image and $t = 2556$ s for the right image. The white stripes are inactive areas in the Maxipix detector. The colour scales vary for the three images. The left image is measured directly after oxidation and therefore shows a weak signal. The middle image is representative for the bulk oxide intensity throughout the oscillation. The right image shows the oxide Bragg peak after reduction of the oxide has started and is considerably reduced in intensity.

in order to understand these changes throughout a full cycle.

The central peak position q_{z0} and $q_{||0}$ indicates the lattice parameter of the palladium oxide. The changes of these values during the longest oscillation show how the palladium oxide layer is relaxing and expanding. γ_a and γ_b indicate the peak width of the Bragg peak (half width at half maximum). This combination of widths shows that the epitaxial layer consists of multiple small crystallites, all with different, minor misalignments of the crystallite with respect to the palladium(100) lattice. The total Bragg peak is a convolution of these separate signals. An increase of the two widths originates from either a decrease of the average crystallite size, or an increase of the mosaicity. The Lorentzian fit function does not take into account the crystal truncation rod, therefore γ_b will be an overestimate of the value.

Also the angle between q_b and q_z directly reflects the mosaicity of the palladium oxide layer. If all the crystallites in the palladium oxide were fully aligned with each other and the palladium surface, we would see a Bragg peak in the q_z direction since the intensity of the peak follows the crystal truncation rod. As the oxide becomes increasingly misorientated the Bragg peak smears out along the powder ring, which is orientated at an angle of 30° with respect to the q_z direction at this $|q|$ value. Therefore a change in angle between q_b and q_z indicates the ratio between the randomly orientated and epitaxial parts of the oxide. Figure 4.5 shows the transition of the oxide peak through a full cycle from crystal truncation rod to Bragg peak, to a tilted Bragg peak.

The complete disappearance of the Bragg peak at $t = 900$ s and $t = 2560$ s indicates that all palladium oxide is removed from the surface. These are the reduction transitions that were part of the oxidation-reduction cycles reported by Hendriksen et al. [11]. The total thickness of the oxide during the oscillation cycle cannot be calculated from this measurement. The epitaxial palladium oxide layer consists of 8 domains [29], i.e. a palladium oxide crystallite forms on the Pd(100) substrate in one of 8 possible orientations, and this peak shows only one domain. Secondly, if the thin oxide layer would be converted completely into a powder, the intensity of the resulting powder ring in the diffraction pattern would fall below the noise level in the pattern. Therefore, when the palladium oxide surface layer transforms from an epitaxial oxide to a powderous oxide the decrease in Bragg peak intensity resulting from the epitaxial intensity can be observed, but not the increase of intensity of the powder ring. We have measured the peak width γ_c in the in-plane direction perpendicular to γ_a and it showed the relationship $\gamma_c = 2\gamma_a$. If we generalise equation 4.1 to a Bragg peak in three

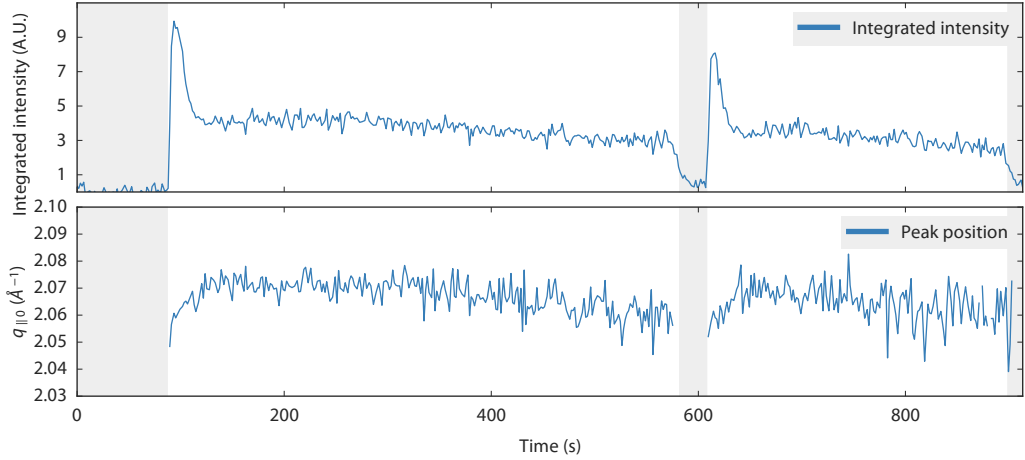


Figure 4.6. The top graph shows the integrated intensity of the oxide crystal truncation rod at $\text{HKL} = (0.81, 0.39, 0.2)$. The Maxipix images between 2.05 and $2.09 \text{ \AA}^{-1}$ in $q_{\parallel}$ and 0.37 and $0.38 \text{ \AA}^{-1}$ in q_z are integrated. A reference background is measured between $t = 33 \text{ s}$ and $t = 80 \text{ s}$ and subtracted from the integrated intensity. The second graph shows the peak position, $q_{\parallel}$, identified by a Lorentzian fit. The data points are shown only when the fit is successful. The grey bands indicate the metal phase, during which the surface is completely reduced. Note that this is a different episode than that of the reaction oscillations shown in previous figures (e.g. figure 4.4).

dimensions the total integrated intensity can be calculated with $4\pi^3 I \gamma_a^2 \gamma_b$. The resulting graph is shown in panel (e) in figure 4.4. From this we can see that almost all of the intensity that is lost at the points in time where the peak intensity I drops sharply, e.g. at $t = 1980 \text{ s}$ and $t = 2210 \text{ s}$, is recovered quickly, albeit in the form of a wider peak, i.e. with increased γ_a and γ_b . By contrast, the total intensity from the oxide displays a general reduction over the lifetime of the oxide.

Further information on the growth and reduction of the oxide can be obtained by investigating the crystal truncation rod at low L -values, at $\text{HKL} = (0.81, 0.39, 0.2)$. The crystal truncation rods originating from a surface superstructure such as a surface oxide are well defined when the oxide is thin. When the oxide thickness grows the truncation rods will make place for the Bragg peak we measured previously. To extract the peak position we have used a similar approach as we have done before for the Bragg peak. We have integrated a q_z range corresponding to 0.37 to $0.38 \text{ \AA}^{-1}$. The result was fitted by a (one-dimensional) Lorentzian line shape. In this way, again every detector image yielded one data point in figure 4.6. Note that this is a different oxidation-reduction sequence than

those in figure 4.4.

From the integrated intensity in figure 4.6 we can see the oxidation and reduction of the surface. For these L-values, the signal-to-noise ratio is too low to distinguish the rapid oscillations that were visible in the Bragg peak. We observe oxidation of the sample at $t = 90$ s and reduction around $t = 590$ s, and a re-oxidation at $t = 606$ s.

In figure 4.6 we see that each time the surface is oxidised, the intensity of the oxide peak at low L rises sharply to a high maximum. This was not observed at the L-value for the oxide’s Bragg peak (figure 4.4 panel (e)). We interpret this as evidence for the initial formation of a thin surface oxide, probably with the $\sqrt{5} \times \sqrt{5}$ periodicity [77]. After reaching its maximum, the peak intensity drops to a lower value. This happens on the same timescale that the oxide’s Bragg peak needed to reach its maximum intensity. We interpret this stage as the growth of a thicker surface oxide layer, using the initial thin oxide as a template. During this growth stage, the fitted value of the peak’s centre position shifts from 2.05 to 2.07 Å⁻¹. This indicates that the in-plane lattice parameter contracts slightly in this process. The rapid initial decrease of γ_a and γ_b (figure 4.4 panel (c)) when the surface is oxidised indicates that the crystal quality (average domain size) of the initial thin oxide is much poorer than that of the thicker oxide that soon forms.

Next we turn to the behaviour of the Bragg peak during the intensity variations on the intermediate time scale, e.g. that of the two rapid reductions in peak intensity at $t = 1980$ s and $t = 2210$ s in figure 4.4. The total integrated intensity at these points shows a sharp, but temporary reduction. We also see a jump in γ_a and γ_b . Furthermore, we see a shift in the location of the Bragg peak q_{z0} and $q_{\parallel 0}$, however $|q|$ remains constant. We also see a rotation of the Bragg peak in the detector plane, which is most pronounced at $t = 2210$ s. Our explanation that is consistent with these observations is that the oxide is partially reduced. The oxide crystallites decrease in size exposing part of the palladium metal below. The rotation of the peak towards a more powder-like pattern shows that during the rapid reduction the oxide layer becomes less epitaxial with respect to the Pd substrate. A possible explanation could be that the epitaxial crystallites are more susceptible to reduction than misaligned crystallites, an effect that could be related to epitaxy-induced stress.

Directly after this partial reduction we see a recovery of the total integrated intensity of the Bragg peak. γ_a and γ_b decrease, but without recovering completely. The Bragg peak rotates fully back and q_{z0} and $q_{\parallel 0}$ shift back, however $|q|$ starts to increase. We interpret this as regrowing

of the palladium oxide. However, the fact that γ_a and γ_b remain at higher values suggests that instead of restoring the lost oxide crystallites, new crystallites appear. This would also be consistent with the increase of length of the total scattering vector $|q|$. The new crystallites have, just like the freshly formed oxide at $t = 1025$ s in figure 4.4, a slightly smaller lattice parameter.

The behaviour of the oxide layer during the more rapid oscillations is hard to resolve because the subtle changes fall within the variance of the fit parameters, except for the intensity. The palladium oxide intensity shows a rapid, partial reduction, followed by a slower recovery. This follows the same path of rapid reduction of the old oxide followed by a slow growth of a new oxide that we just identified for the intermediate timescales. Directly after the partial reduction event at $t = 2210$ s discussed above, the rapid oscillations show noticeable variations not only in the peak intensity but also in the Bragg peak rotation. In these cases, we recognise the same behaviour as for the intermediate time scale events, namely that decreases in intensity correlate with increases in ϑ and vice versa. After every reduction, the intensity recovers, but only partly, while the Bragg peak angle rotates back, but not completely. The rotation of the peak follows the previously recognised behaviour that we interpreted as the preferential reduction of the epitaxial oxide and the regrowth of oxide that is less well-orientated.

The rapid fluctuations of the oxide peak intensity are an indication of reduction and re-oxidation of the surface oxide. Reduction of the surface oxide in the oscillation model by Hendriksen et al. [12] is the consequence of the increase of the step density above a certain threshold value. Above this critical step density the adsorbate structures on the metal surface are more stable than a surface oxide. This model, however, does not predict a short-lived metal phase, only a lengthy metal phase, during which the sample is sufficiently smoothened. We imagine the rapid re-oxidation to be caused by a fast partial smoothening of the metal surface. This partial smoothening removes roughness sufficiently fast, before the increase in CO pressure can stabilise the metal phase, which makes it easy for the surface to return to the oxide phase. A numerical model for these rapid oscillations that takes into account the slow response of the CO partial pressure is presented in the next chapter.

We summarise the behaviour of the oxide layer as follows.

1. Initially, a thin surface oxide is formed, probably with the $\sqrt{5} \times \sqrt{5}$ periodicity that is epitaxial with the substrate and forms a complete monolayer.
2. Soon after the formation of the thin surface oxide, a somewhat thicker

oxide develops, which is initially very well aligned with the Pd(100) substrate.

3. In each of the rapid and intermediate oscillations the oxide is partially reduced and the metal substrate is partly exposed.
4. In this reduction, epitaxial oxide grains are removed more quickly than misaligned grains, which we tentatively ascribe to the higher stress that the epitaxial grains experience.
5. When the exposed metal is smoothened sufficiently the surface reoxidises.
6. In the re-oxidation, new oxide grains are formed that are, on average, less aligned than the removed grains.
7. The net effect of the rapid and intermediate oscillations is to gradually turn the oxide layer from mostly epitaxial into misaligned and more powder-like.

4.3.2 Reflectivity

Figure 4.7 shows the integrated intensity of the specular rod ($q_{\parallel} = 0$) at $q_z = 0.12 \text{ \AA}^{-1}$ (incidence angle of 0.3°). This measurement is indicative of the total roughness of the sample. We perform an integration of the reflected beam for every detector image. The images are measured every 50 ms. This allows us to clearly capture all three timescales at which the oscillations are occurring.

Figure 4.7 shows that the specular intensity exhibits variations on all three oscillation timescales. For the rapid and intermediate timescales we need to inspect the data in more detail, as is done in the enlarged view in the inset of figure 4.7. We can see that all types of oscillations are accompanied by a fast increase in the specular intensity followed by a slower decrease.

We note that not only roughness can be responsible for a lowering of the integrated specular intensity. The presence of an oxide layer by itself can already lead to a change in reflectivity. In addition, the presence of an oxide replaces a single interface, that between the metal and the gas, by two interfaces, between the metal and the oxide and between the oxide and the gas. Both of these interfaces can be rough, each one contributing in its own way to a lowering of the specular intensity. This means that the sharp increases in specular intensity, accompanying all complete and partial reduction events, are caused either by a smoothening of the surface, a removal of the oxide, or both. In the metal phase, however, the increase of the reflected intensity will be mostly due to the smoothening of the surface.

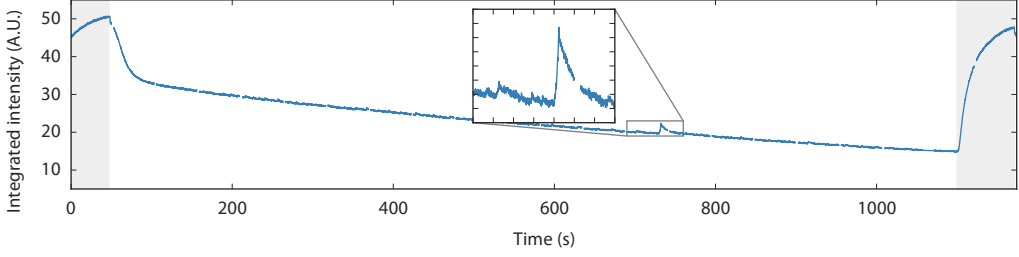


Figure 4.7. Integrated specular intensity at $q_z = 0.12 \text{ \AA}^{-1}$ during a complete period of the (long) oscillation. This intensity is indicative for the reflectivity and the root-mean-square roughness of the surface. The inset shows that rapid variations in the integrated specular intensity are superimposed on the gradual reduction over time. Each takes the form of a sharp increase, followed by a somewhat slower reduction. The grey bands indicate the metal phase, during which the surface is completely reduced. Note that this is again a different episode than the measurements in previous figures.

4.3.3 Metal oxide

The reflectivity curve of figure 4.7 shows that it is likely that the surface roughness is changing during the oscillations. We also have a look at one of the crystal truncation rods from the Pd(100) substrate. These crystal truncation rods originate only from the Pd substrate. They are sensitive to the roughness of its surface. This means that when the surface is oxidised, the Pd(100) crystal truncation rods inspect the roughness of the interface between the palladium oxide and the palladium substrate and that we can access this information even while the oscillations are occurring. The data points are measured every 50 ms.

Figure 4.8 shows the integrated intensity of the Pd(100) crystal truncation rod at $\text{HKL} = (1,1,1.6)$. All three oscillation timescales are visible in the graph.

The large increase in Pd intensity between $t = 657 \text{ s}$ and $t = 783 \text{ s}$ coincides with the part of the long oscillation in which the Pd surface is completely reduced. We recognise that the metal surface is smoothened significantly in this phase. Between $t = 783 \text{ s}$ and $t = 791 \text{ s}$ the intensity is reduced again. This stage coincides with the oxidation of the surface. The initial roughening is the direct consequence of the fact that even for the epitaxial oxide the areal density of Pd atoms does not correspond to an integer number of (100) layers of the Pd crystal. Therefore, oxidation immediately results in an island structure with a rough oxide surface and a rough metal-oxide interface. During the oxide phase, spikes are visible in the integrated Pd intensity, at timescales corresponding to both the rapid

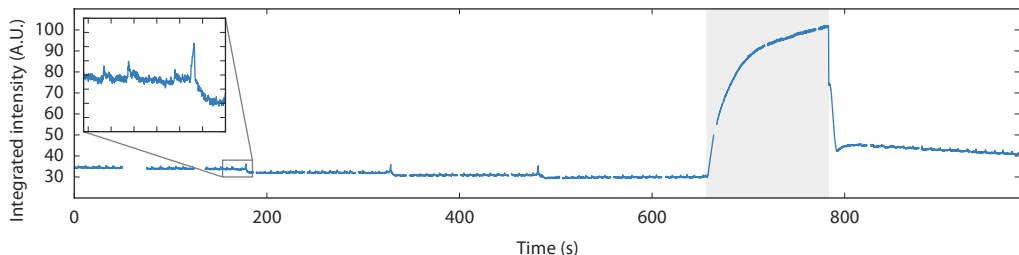


Figure 4.8. Integrated intensity of the Pd(100) crystal truncation rod at $\text{HKL} = (1,1,1.6)$. The inset shows that rapid variations in the integrated intensity are superimposed on the gradual reduction over time. Note that this is again a different episode than the measurements shown in previous figures.

and the intermediate oscillations. They take the shape of a sharp increase, followed by a slow decrease. In accordance with our earlier discussion, we associate each increase with a brief, partial reduction of the surface, during which part of the Pd becomes uncovered and smoothens, and each decrease with the re-oxidation of the surface and corresponding roughening of the interface. After each of the intermediate-scale spikes, such as the one at $t = 178$ s (see inset in figure 4.8), the intensity drops by more than the preceding increase, which indicates that the re-oxidation introduces more roughness than the brief smoothing during the preceding, partial reduction removes. For the rapid spikes, the increase and reduction in intensity are more or less equal, suggesting that in those cases the smoothing and roughening are approximately matched.

4.3.4 GISAXS

The palladium crystal truncation rod and the specular rod both provide information about the overall roughness of the surface. With GISAXS measurements we can examine the length scales of the scattering from the surface roughness. Figure 4.9 shows a typical detector image of the Yoneda peak in the GISAXS pattern. We have followed this pattern during multiple oscillations with a 1 second integration time, every 3.5 seconds.

The differential cross section for the incoherent scattering from the surface roughness is given by equation 120 in Ref. [15]:

$$\frac{d\sigma}{d\Omega} = \frac{k_0^4 A_i}{16\pi} |n_1^2 - 1|^2 |t_{0,1}^i|^2 |t_{0,1}^f|^2 S(q_z, q_{\parallel}) \quad (4.2)$$

Here k_0 is the incident wave vector and A_i is the total illuminated area. $|t_{0,1}^i|^2$ and $|t_{0,1}^f|^2$ are the transmission coefficient of the incoming x-rays in the

material and the transmission coefficient of x-rays exiting the material. n_1 is the refractive index of the substrate. For a detailed explanation see Sinha et al. [78]. All information about the roughness profile and the corresponding scattering as a function of momentum transfer is contained in $S(q_z, q_{\parallel})$. For our purpose, it will be sufficient to concentrate on $S(q_z, q_{\parallel})$ and to regard the product of the other factors as a constant scaling parameter. $S(q_z, q_{\parallel})$ is given by:

$$S(q_z, q_{\parallel}) = \frac{e^{-\frac{1}{2}(q_{z,1}^2 + q_{z,1}^{*2})\langle z^2 \rangle}}{|q_{z,1}|^2} \int_0^{\infty} dr_{\parallel} [e^{|q_{z,1}|^2 \langle z(r_{\parallel})z(0) \rangle} - 1] r_{\parallel} \mathbf{J}_0(q_{\parallel} r_{\parallel}) \quad (4.3)$$

Here $\mathbf{J}_0$ is the Bessel function of the first kind and $\langle z(r)z(0) \rangle$ is the height-height correlation function of the surface, with $z(\mathbf{r})$ the height function of the rough surface, defined such that $\langle z \rangle = 0$. All information of the in-plane length scales of the roughness is present in the height-height correlation function. We assume that the height correlations on the surface are isotropic, and only depend on the magnitude of the in-plane distance $r_{\parallel}$. We examine the mean square height difference function $g(r_{\parallel})$, which is connected to $\langle z(r_{\parallel})z(0) \rangle$ via:

$$\begin{aligned} g(r_{\parallel}) &= \langle [z(r_{\parallel}) - z(0)]^2 \rangle \\ &= \langle z(r_{\parallel})^2 \rangle + \langle z(0)^2 \rangle - 2\langle z(r_{\parallel})z(0) \rangle \\ &= 2\langle z(0)^2 \rangle - 2\langle z(r_{\parallel})z(0) \rangle \end{aligned} \quad (4.4)$$

This function starts out at a value of zero for short distances $r_{\parallel}$ and asymptotically reaches a plateau for large $r_{\parallel}$, in case of non-diverging height profiles. We obtain $g(r_{\parallel})$ by performing a Fourier transform on $S(q_{\parallel})$ [79]. We normalise $g(r_{\parallel})$ on the plateau value at large $r_{\parallel}$. The normalisation factor contains all the prefactors from equation 4.2 and is a convolution of the roughness and the reflectivity of the surface. Figure 4.9 shows $S(q_{\parallel})$ and $g(r_{\parallel})$ at various times during several oscillation cycles.

We analyse the progression of $g(r_{\parallel})$ through three of the long oscillation cycles shown in figure 4.10. During these oscillations the surface switches back and forth between a rough metal and a rough palladium oxide on the metal. In the second case the diffuse scattering can arise from both the palladium oxide surface and the oxide-to-metal interface. However, the magnitude of the density fluctuations at the oxide to metal interface is much lower due to the similarity in the index of refraction of the oxide and the metal. Therefore the dominating contribution to the diffuse scattering will be from the palladium oxide surface.

From the calculated $g(r_{\parallel})$ at the end of the oxide phase, at $t = 1074$ s we see that the length scale above which there are no correlations is 80 Å.

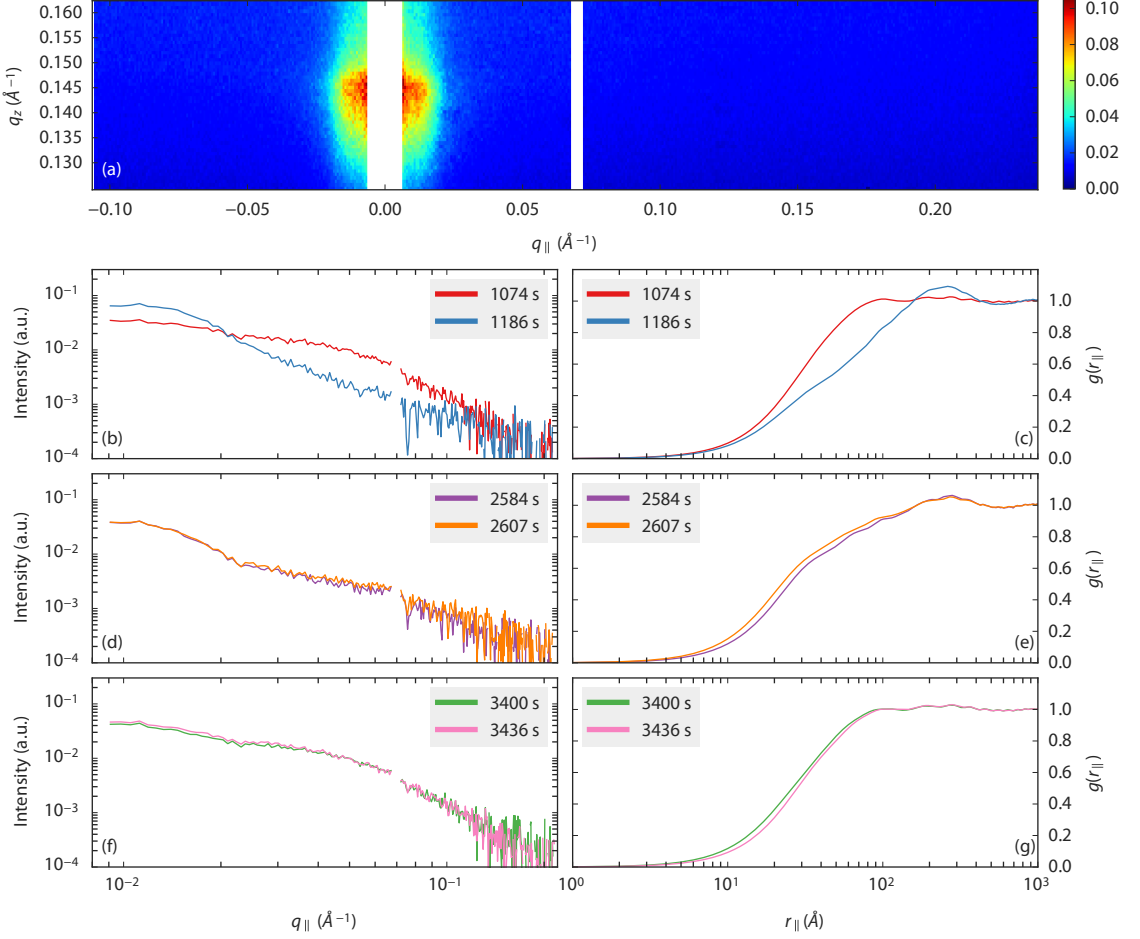


Figure 4.9. (a) GISAXS image of the Yoneda peak, for an incidence angle of the x-ray beam of 0.5° . Data is removed where the reflected beam on the sample is superimposed on the GISAXS signal. The white stripe on the right corresponds with an inactive area on the Maxipix detector. In panels (b), (d) and (f) the intensity $S(q_{\parallel}, q_z)$ integrated over q_z from 0.140 to 0.145 $\text{\AA}^{-1}$ in the q_z direction is shown for six points in time. Panels (c), (e) and (g) show the calculated and normalised mean square height difference $g(r_{\parallel})$, corresponding to the corresponding intensities in (b), (d) and (f). The six times are indicated by vertical bars in figure 4.10

By comparison, at the end of the metal phase, at $t = 1186$ s, correlations continue all the way up to $400 \text{ \AA}$ (panel (c) figure 4.9). During the metal phase the correlation length of the surface increases, while in the oxide phase the correlation length decreases. In figure 4.10 we follow for a few selected length scales how they are affected throughout an entire oscillation. While the mean square height difference $g(r_{\parallel})$ at $r_{\parallel} = 40 \text{ \AA}$ reaches a plateau already well before the surface switches from oxide to metal, $g(r_{\parallel})$ keeps increasing for the longer length scales, such as e.g. $80 \text{ \AA}$, until the transition.

In the metal phase the surface smoothenes. During this smoothening, roughness on short length scales disappears faster than roughness on longer length scales. Due to the limited duration of the metal phase, height variations on length scales above $400 \text{ \AA}$ do not have enough time to smoothen out. When the surface is reoxidised, the smoothening is stopped, and roughening starts again. The long-scale roughness accumulates over multiple oscillations. This scenario also applies for intermediate-scale oscillations, where between approximately $80 \text{ \AA}$ and $200 \text{ \AA}$ (panel (b) figure 4.10) is the longest length scale for which roughness is removed during the brief stages of reduction of the surface.

The continuous build-up of long-length-scale roughness throughout the rapid oscillations could be responsible for the observed hierarchy in oscillations. As roughness is increasingly dominated by long length scales, smoothening of the reduced surface becomes progressively slower. When the removal of the roughness is slow enough, the entire surface reduces and the CO pressure at the surface has time to increase and stabilise the metal phase. This is the complete oxide-to-metal phase transition that was at the heart of the model by Hendriksen et al. [12].

From the intensity profile in the out-of-plane direction we can obtain the critical angle of the surface through the transmission factor $|t_{0,1}^f|^2$ in equation 4.2. This transmission coefficient depends on the electron density difference between the ambient and the first layer. The oxide layer has a lower electron density than the metal, and therefore upon oxidation we should see a shift in the critical angle. This shift depends on the thickness of the oxide but not on the roughness of the surface. Therefore, the total shift will depend on the fraction of the surface, inspected by the x-ray beam, that is covered by oxide and the thickness of this oxide. The predicted maximum shift in q_z due to the change in the critical angle is $0.0042 \text{ \AA}^{-1}$, based on tabulated values for the oxide refractive index and density.

Both the slowest and the intermediate oscillations are visible in the total integrated intensity in figure 4.10. The rapid oscillations are not distinguishable. The increasing roughness throughout the oscillation is

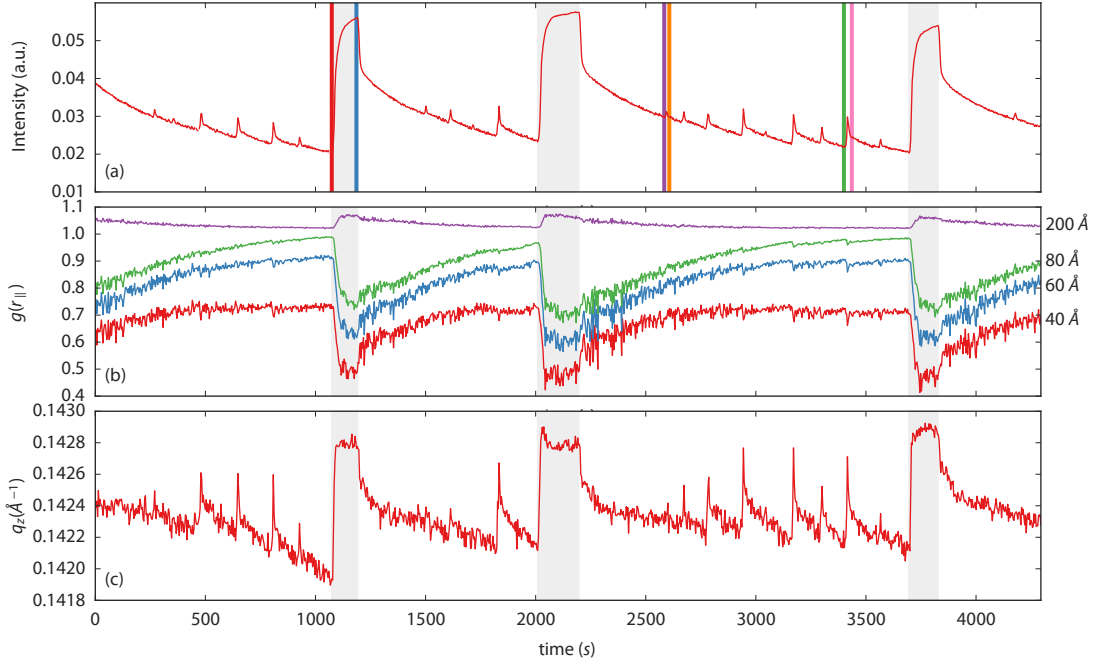


Figure 4.10. (a) Integrated intensity of the GISAXS image in figure 4.9. The integrated area ranges from 0.143 to $0.145 \text{ \AA}^{-1}$ in the q_z direction and from 0.009 to $0.21 \text{ \AA}^{-1}$ in the $q_{\parallel}$ direction. The six coloured, vertical lines indicate the points in time for which curves of $S(q_{\parallel})$ and $g(r_{\parallel})$ are shown in panels (b) to (g) of figure 4.9. The three grey bands indicate the metal phase, during which the surface is completely reduced. (b) Time evolution of the mean square height difference $g(r_{\parallel})$ for four distances $r_{\parallel}$. (c) q_z position of the maximum of the Yoneda peak, equivalent to the critical angle for scattering of the employed 24.3 keV x-rays. Note, that the position expected for the completely reduced Pd surface would be $0.137 \text{ \AA}^{-1}$, while the position observed here for the metallic phase (grey bands) is $0.143 \text{ \AA}^{-1}$. The shift is likely due to a misalignment of the sample of approximately 0.025° .

visible in a similar fashion as the reflectivity curve of figure 4.7: a slow buildup of roughness, interrupted by short bursts of smoothening.

The shift in the critical angle in figure 4.10 shows that the electron density at the surface decreases during the oxidation (immediately after the grey bands). This effect is a factor 10 lower than expected for full oxidation of the surface. This suggests either that in the oxide phase the surface still contains large regions that remain unoxidised, or that the initially formed oxide film is so thin, that the electron density at the surface is intermediate between that of a thick oxide and that of the underlying metal. During the oxide phase, the shift of the critical angle slowly increases, suggesting either that the oxide is gradually covering a larger fraction of the surface, or that the oxide grows in thickness. At the intermediate oscillations, the critical angle shifts back, often up to almost the metal value.

4.3.5 Locality and beam effects

These x-ray experiments are usually performed at low incidence angles. The consequence of this is that the beam footprint covers the entire length of the surface. During our analysis we assumed the area probed by the x-rays to be homogeneous, i.e. to show identical behaviour everywhere. This assumption is supported by local x-ray measurements that show that similar oscillation behaviour is present everywhere on the surface. A second supporting argument for this assumption is that with the optical set-up described in the previous chapter these synchronised oscillations have been observed everywhere on the sample surface.

The x-ray beam undoubtedly has an effect on the catalysis of surface. While the interaction between the x-rays and the gas might be small, the photoelectrons generated in the palladium surface ionise the gases above the surface and potentially alter reaction pathways. With the optical set-up mentioned in chapter 2 we have seen similar reaction oscillations using 625 nm light. Therefore we conclude that, even though the photoelectrons may change the timescale with which the oscillations occur, they do not change the oscillation dynamics.

4.4 Conclusion

We have experimentally observed reaction oscillations with three distinct timescales. The slowest is a full reduction of the palladium surface, the two shorter ones consist of partial reduction and re-oxidation of the surface. The oscillations of the oxide Bragg peak show that an epitaxial oxide disappears and reappears. The GISAXS experiments confirm the slow increase of

the long-length-scale roughness during one long oscillation, and the faster oscillations in the shorter length scales. These observations are consistent with the x-ray reflectivity measurements.

From the Bragg peak of the oxide we can extract more information than just the appearance and disappearance of the oxide peak. In particular, the shape and orientation of the peak also indicate the degree to which the oxide layer is epitaxial with respect to the Pd(100) substrate as well as the spread in orientation and the average oxide grain size. We observe that epitaxial palladium oxide reduces faster than a misaligned oxide. In this way, the oxide layer is gradually losing its epitaxy. We suggest that the cause for the increased reactivity of the epitaxial oxide and, hence, for the growing loss of epitaxy is the stress on the oxide film, induced by the epitaxy.

The mechanism that seems to drive the oscillations on all timescales, is the buildup of roughness during the oxide phase, due to the Mars-Van-Krevelen reaction mechanism, and the smoothening of the surface in the metal phase, in combination with the preferred adsorption of CO molecules on step sites of the metallic surface. The hierarchy of rapid, intermediate and long oscillations is associated with the distribution of the reaction-induced roughness over different length scales. Whereas the reaction on the oxide primarily generates roughness with a relatively short correlation length, the accumulation of such roughness over long timescales increasingly also introduces height variations with longer wavelengths. When the total step density, irrespective of its spectrum of wavelengths, exceeds a threshold level, the surface is reduced.

Our measurements add two new aspects to this scenario. The first is that there are fast and intermediate oscillations. During these, the oxide is removed only partly, with the epitaxial oxide regions being removed preferentially. The second is that during the rapid and intermediate oscillations, the metallised regions on the surface can only smoothen out their short-length-scale roughness. When this is sufficient to bring the total step density of the surface below the threshold level, the surface switches back to the fully oxidised state. In this way, memory is gradually built up over multiple fast and intermediate oscillations, with accumulating height variations with long wavelengths and with accumulating polycrystallinity of the oxide layer. After a sufficiently long time, including a number of the short and intermediate oscillations, the total step density at long wavelengths by itself exceeds the threshold level. That is the point at which short or intermediate oscillations, i.e. brief excursions in which only a certain fraction of the surface is reduced, cannot suffice to bring the step density below the

threshold level. Instead, at that point the oxide is removed completely, the CO partial pressure rises and stabilises the surface in the metallic state and steps are removed over much longer length scales. In this way, the metallic phase of each long oscillation 'resets' the surface and effectively wipes its memory, thus preparing it for the next episode of this scenario.

It is clear from this description, that there is an important distinction between the long oscillations on the one hand and the rapid plus intermediate oscillations on the other. Whereas the surface is completely reduced in the metallic phase of the former, the oxide is never removed completely during the rapid and intermediate oscillations. We have not found a clear, qualitative difference in behaviour between the rapid and intermediate oscillations. A statistical analysis of their amplitudes and periods would be required to establish whether such a distinction would be really appropriate.

A final remark is in place on the reactivity of the oxide. As was remarked above, the rapid removal of the strained, epitaxial grains suggests that the CO oxidation rate would be higher on these grains than on the unstrained, misaligned grains. This may explain the difference in reactivity observed in experiments on oxidised Pd(100) and the reactivity predicted theoretically for the surface of (unstrained) PdO(101) [80]. The mechanism in which the oxide becomes gradually less strained and therefore less reactive could naturally lead to an alternative scenario for reaction oscillations. We speculate that if strain would indeed be a necessary ingredient for a high reactivity of PdO, reaction oscillations might be a key mechanism for keeping the performance of Pd-based oxidation catalysts high.

Chapter 5

A model for slow and fast reaction oscillations during CO oxidation on metal surfaces

A new model is presented for reaction oscillations during CO oxidation on metal surfaces, such as Pd(100). During the reaction oscillations the surface switches between a metal configuration and an oxide configuration. Which of these two configurations is energetically favoured, is partly determined by the roughness, which is increasing during the oxide phase and decreasing during the metal phase. In our new model the rate of decrease of roughness depends on the Fourier transform of the surface height variations. We show that incorporating this dependence in our model, in addition to the role of the integrated roughness, leads to a new type of reaction oscillations.

5.1 Introduction

In the previous chapter we have shown that during the CO oxidation reaction on Pd(100), oscillations are visible at three distinct timescales. Central to our understanding of the hierarchy in timescales between the slow 'regular' oscillations and the rapid oscillations is the notion that the state of roughness of a surface is not defined fully by the step density, but that for a complete description also information is required about the height correlation function. The adsorption energetics of CO molecules on a rough metal surface may depend primarily on the step density, irrespective of whether the steps are upwards or downwards. On the other hand, the rate at which roughness decays and steps are removed also depends on the height correlation function, e.g. on the probability that an up-step is followed by a down-step and vice versa [81]. When this probability is high, the typical length scales of height fluctuations are short. Lower probabilities for up-down combinations correlate with height fluctuations on longer lateral length scales. Short-length-scale roughness decays faster than long-length-scale roughness. As a consequence, the decay rate of the steps, when the surface is in the metallic phase, depends on the distribution of length scales, composing the roughness profile of the surface.

If the roughness is characterised mostly by short length scales, the step density will decay fast, and with that the free energy difference between oxide configuration and the metal. If the roughness mostly reflects long length scales, longer diffusion lengths are required to even out the larger height differences over the longer distances, so that the step density will decay slowly. The relative contributions of different length scales to the step density depends on the history of the sample. When we start with a perfectly flat metal surface, which enters the oxide phase of the reaction (C in figure 4.1), the Mars-Van-Krevelen-type reaction creates roughness on the surface (D in figure 4.1). Initially, this roughness features mainly short distances, as new roughness is always added by the formation of local depressions and local protrusions. Later, during the Mars-Van-Krevelen process, depressions can grow and merge with other depressions, while similarly protrusions can grow. This will open the door to new depressions forming within existing depressions and new protrusions emerging on top of existing protrusions. In this way, the longer length scales are introduced progressively at longer timescales. After the phase boundary is crossed into the metal phase (A in figure 4.1), the surface smoothens again. This smoothing removes mainly roughness that is associated with short length scales. This roughness disappears fast, and the step density decays fast. When the step density is reduced sufficiently, the surface oxidises again (B-C in figure 4.1). At this

point, the long-range roughness is not removed completely yet. The starting point for the second oxidation-reduction cycle is now different than before where the sample was perfectly flat. This difference will have a consequence for the duration of the metal and the oxide phases.

5.2 Construction of the model

In our previous model of spontaneous reaction oscillations [12], the roughness was described by a single parameter, the step density. Here, we construct a new model to demonstrate how some of the major characteristics of the oscillations depend on the roughening and smoothening history of the surface. We assume that the roughness increases when the surface is in the oxide phase, and decreases when the surface is in the metal phase. In the oxide phase, we assume the surface to have a higher reactivity than in the metal phase. For simplicity we keep the sample temperature constant.

We only look at the length scale behaviour in one dimension. We follow the time evolution of a real-valued height function over time $z(x, t)$, with spatial frequencies k in the Fourier domain.

$$z(x, t) = \int z(k, t) e^{i2\pi x k} dk \quad (5.1)$$

We now turn to the differential equations governing the time dependence of the system.

5.2.1 Roughness generation

In the oxide phase, the roughness progressively increases via changes in the height profile $z(x, t)$ that we describe by:

$$\frac{\partial z(x, t)}{\partial t} = \eta(x, t).$$

We model $\eta(x, t)$ as random gaussian noise with zero mean and correlations given by [82]:

$$\langle \eta(x, t) \eta(x', t') \rangle = c_1 r(t) \delta(x - x') \delta(t - t'), \quad (5.2)$$

with r is the time dependent reaction rate of the surface that will be discussed later in this chapter. The assumption behind the gaussian-generated roughness is that the displacement of atoms is uncorrelated in time and space. This description fully neglects lateral correlations and will therefore result in a rougher surface than is to be expected from roughness generated according to a Langevin equation [82] or a KPZ [55] model.

We will evaluate the roughness in the Fourier domain. The fluctuations of the Fourier component k will satisfy:

$$\langle \eta(k, t) \eta(k', t') \rangle = c'_1 r(t) \delta(k + k') \delta(t - t') \quad (5.3)$$

The fluctuations on $\langle z(k, t) z(k', t) \rangle$ can now be expressed as:

$$\begin{aligned} \langle z(k, t) z(k', t) \rangle &= \int_0^t \int_0^t \langle \eta(k, t') \eta(k', t'') \rangle dt' dt'' \\ &= c'_1 \delta(k + k') \int_0^t \int_0^t r(t') \delta(t' - t'') dt' dt'' \\ &= c'_1 \delta(k + k') \int_0^t r(t') dt' \end{aligned} \quad (5.4)$$

The expectation value of the absolute value of the Fourier components increases proportionally to the square root of the integral of the reaction rate.

5.2.2 Smoothing

We describe the smoothing of the surface in the metal phase by Herring-Mullins theory [83]:

$$\frac{\partial z(x, t)}{\partial t} = -c_2 \frac{\partial^4 z(x, t)}{\partial x^4} \quad (5.5)$$

After Fourier transformation of $z(x, t)$, the differential equation leads to:

$$\frac{\partial z(k, t)}{\partial t} = -c_2 (2\pi)^4 k^4 z(k, t) \quad (5.6)$$

Solving this, we obtain:

$$z(k, t) = z(k, t_0) e^{-c_2 (2\pi)^4 k^4 (t - t_0)} \quad (5.7)$$

Here c_2 is a diffusion-related parameter that determines the decay rate of the Fourier components.

5.2.3 Gas flow

We have three gases, Ar, CO and O₂, flowing into the reactor with flow rates F_{Ar} , F_{CO} and F_{CO_2} . We assume that the surface is placed in a perfectly-mixed flow reactor. In the reactor CO and O₂ are converted into CO₂ according to:



The reactor volume v is pumped at the outlet of the reactor with a variable rate that is expressed in terms of a characteristic pumping time τ . The differential equations for the partial pressures inside the reactor are given by:

$$\begin{aligned}
\frac{dP_{\text{CO}}}{dt} &= \frac{F_{\text{CO}}}{v} - \frac{rk_bT}{v} - \frac{P_{\text{CO}}}{\tau} \\
\frac{dP_{\text{O}_2}}{dt} &= \frac{F_{\text{O}_2}}{v} - \frac{rk_bT}{2v} - \frac{P_{\text{O}_2}}{\tau} \\
\frac{dP_{\text{Ar}}}{dt} &= \frac{F_{\text{Ar}}}{v} - \frac{P_{\text{Ar}}}{\tau} \\
\frac{dP_{\text{CO}_2}}{dt} &= \frac{rk_bT}{v} - \frac{P_{\text{CO}_2}}{\tau}
\end{aligned} \tag{5.9}$$

with k_b is Boltzmann's constant. The pumping time τ at the reactor outlet is chosen such that the total pressure P_{tot} inside the reactor is constant. This condition is set in accordance with the experiment, in which a pressure controller at the reactor outlet is set such that it regulates the pressure in the reactor to a well-defined value.

5.2.4 Reactivity

The reactivity of the surface depends on the state of the surface. In our calculations, we employ two different reaction rates, one for the metal phase and one for the oxide phase. We assume that in both cases, the conversion at the surface is so rapid that the reaction rate is to a large extent limited by the mass transfer of CO through the gas phase [29] and therefore depends strongly on the CO pressure directly at the surface. The combination of the high CO consumption and the mass transfer limitation lowers the CO pressure at the surface. Therefore we make a distinction between the average CO pressure in the reactor P_{CO} and the CO pressure at the surface P_{CO}^* . The pressure at the surface depends on the reaction rate r .

$$P_{\text{CO}}^* = P_{\text{CO}} - c_3 rk_bT, \tag{5.10}$$

where c_3 is a constant that determines the decrease of the partial pressure at the surface due to the mass transfer limit and has the dimension of sm^{-3} . For simplicity, we now assume that the equilibrium partial pressure of CO at the surface is instantaneously reached for any given reaction rate and average CO pressure in the reactor. The reaction rate of the oxide is then given by:

$$r = \frac{P_{\text{CO}}^* A}{\sqrt{k_b T 2\pi m_{\text{CO}}}} \tag{5.11}$$

Here m_{CO} is the mass of the CO molecule, A is the surface area of the palladium crystal, T is the temperature. r is now connected to P_{CO} via:

$$r = \frac{P_{\text{CO}}}{\frac{\sqrt{k_b T 2\pi m_{\text{CO}}}}{A} + c_3 k_b T} \quad (5.12)$$

We know that the reaction rate is lower on the metal surface than on the oxide surface, but it is still dependent on the partial pressure of CO. Therefore, we adopt a reaction rate for the metal phase that is similar to that for the oxide phase, but reduced by a constant factor, following:

$$r = \frac{c_4 P_{\text{CO}}^* A}{\sqrt{k_b T 2\pi m_{\text{CO}}}}, \quad (5.13)$$

with c_4 smaller than one. We obtain a similar consistency equation as 5.12. The dependence of both reaction rates on only the CO partial pressure and not the O_2 partial pressure is justified by the high O_2 to CO ratio in the experiments, which is approximately 20 to 1.

5.2.5 Free energy contribution of roughness

The total surface free energy of the rough surface can be calculated with [84]:

$$\Gamma = \int \gamma(n) dS \quad (5.14)$$

We have written this free energy as an integral of the specific surface free energy $\gamma(n)$, which depends on the local orientation of the surface normal vector n , over the entire surface contour S . Because the height function of our simplified model only varies in one dimension, our free energy can be calculated with the integral

$$\Gamma = L \int \frac{\gamma(\theta(x))}{\cos(\theta(x))} dx \quad (5.15)$$

Where θ is the angle of the local normal vector n with the surface at position x and L is the length of the steps. If we presume that the angles are small, so that $\gamma(\theta) - \gamma(0) \propto |\theta|$, and that this difference is independent of temperature, the contribution to the specific free energy due to the surface roughness can be calculated with:

$$\Gamma^{\text{rough}} = L \int c_5 \left| \frac{dz(x)}{dx} \right| dx = c_5 A s \quad (5.16)$$

Here c_5 is equivalent to the step free energy per unit length and per height and s is the average step density.

5.2.6 Free energy contribution of adsorbates

The specific free energy of a surface in contact with a gas and with a coverage of atoms or molecules adsorbed from that gas is given by:

$$\gamma(T, \{P_i\}) = \frac{1}{A}(G^{\text{surf}} - \sum_i N_i \mu_i(T, P_i)) \quad (5.17)$$

Here G is the Gibbs free energy of the surface, including the adsorbates on that surface, and μ_i the chemical potential of the adsorbate species i , which is determined by the temperature and partial pressure of that species in the gas phase. N_i is the total number of adsorbates of type i present on the surface. In the present case, where we only consider CO molecules adsorbed on the Pd surface, we obtain:

$$\gamma_{\text{CO@Pd}} = \frac{1}{A}(G_{\text{CO@Pd}}^{\text{surf}} - N_{\text{CO}} \mu_{\text{CO}}(T, P_{\text{CO}})) \quad (5.18)$$

The chemical potential μ_{CO} is calculated as:

$$\mu_{\text{CO}}(T, P_{\text{CO}}) = E_{\text{CO}}^{\text{tot}} + \tilde{\mu}_{\text{CO}}(T, P^0) + k_b T \ln \left(\frac{P_{\text{CO}}}{P^0} \right), \quad (5.19)$$

where $\tilde{\mu}_{\text{CO}}(T, P^0)$ is the chemical potential at a reference pressure P^0 . $E_{\text{CO}}^{\text{tot}}$ is the value of the chemical potential at $T = 0$ K and is equal to the total energy of the isolated CO molecule. We have taken the values for $\tilde{\mu}_{\text{CO}}(T, P^0)$ from ref. [85]. The Gibbs free energy of adsorption is then given by:

$$\begin{aligned} \Delta G_{\text{CO}}^{\text{ads}} &= A(\gamma_{\text{CO@Pd}} - \gamma_{\text{Pd}}) \\ &= G_{\text{CO@Pd}}^{\text{surf}} - G_{\text{Pd}}^{\text{surf}} - N_{\text{CO}}(E_{\text{CO}}^{\text{tot}} + \Delta \mu_{\text{CO}}) \\ &= N_{\text{CO}}(E_{\text{CO@Pd}}^{\text{bind}} - \Delta \mu_{\text{CO}}) \end{aligned} \quad (5.20)$$

In $\Delta \mu_{\text{CO}}$ the pressure and temperature independent term is taken out of equation 5.19 such that $\mu_{\text{CO}}(T, P_{\text{CO}}) = E_{\text{CO}}^{\text{tot}} + \Delta \mu_{\text{CO}}$. The average binding energy per CO molecule is then:

$$E_{\text{CO@Pd}}^{\text{bind}} = \frac{1}{N_{\text{CO}}} \left(G_{\text{CO@Pd}}^{\text{surf}} - G_{\text{Pd}}^{\text{surf}} - N_{\text{CO}} E_{\text{CO}}^{\text{tot}} \right) \quad (5.21)$$

In our model the adsorption energy of CO at step sites of the metal surface differs from that on terraces. This makes that the total Gibbs free energy of adsorption of CO on the Pd surface in the metal phase depends on the roughness. Therefore, when the surface is not flat, the binding energy $E_{\text{CO@Pd}}^{\text{bind}}$ of the CO overlayer to the Pd substrate grows by an additional factor $(1 + c_6 s)$.

For the calculation of the free energy of the surface oxide we formally describe the configuration as an oxygen adsorbate structure and use an expression equivalent to that for CO in equation 5.20. However, since the O atoms form an intrinsic component of the surface oxide, we do not associate a preference in binding energy for the O atoms at the steps in the oxide, as we have introduced for the CO atoms binding at steps on the metallic Pd surface. The Gibbs free energy of adsorption in the oxide phase is given similarly to equation 5.20 and 5.21 by:

$$\Delta G_{\text{O}}^{\text{ads}} = N_{\text{O}} \left(E_{\text{O@Pd}}^{\text{bind}} - \frac{\Delta\mu_{\text{O}_2}}{2} \right) \quad (5.22)$$

and

$$E_{\text{O@Pd}}^{\text{bind}} = \frac{1}{N_{\text{O}}} \left(G_{\text{O@Pd}}^{\text{surf}} - G_{\text{Pd}}^{\text{surf}} - \frac{N_{\text{O}}}{2} E_{\text{O}_2}^{\text{tot}} \right) \quad (5.23)$$

The values for $\tilde{\mu}_{\text{O}_2}(T, P^0)$ are also from ref. [85]

5.2.7 Total free energy

For both phases, metal and oxide, the combined contribution from roughness and adsorbates can now be expressed in the quantities derived in equations 5.16 and 5.20:

$$\Delta\Gamma^{\text{metal}} = c_5 A s + N_{\text{CO}} (E_{\text{CO@Pd}}^{\text{bind}} (1 + c_6 s) - \Delta\mu_{\text{CO}}) \quad (5.24)$$

$$\Delta\Gamma^{\text{oxide}} = c_5 A s + N_{\text{O}} \left(E_{\text{O@Pd}}^{\text{bind}} - \frac{\Delta\mu_{\text{O}_2}}{2} \right) \quad (5.25)$$

With the difference calculated as:

$$\Delta\Gamma^{\text{m-o}} = \Delta\Gamma^{\text{metal}} - \Delta\Gamma^{\text{oxide}} \quad (5.26)$$

$$\begin{aligned} &= N_{\text{CO}} (E_{\text{CO@Pd}}^{\text{bind}} (1 + c_6 s) - \Delta\mu_{\text{CO}}) \\ &\quad - N_{\text{O}} \left(E_{\text{O@Pd}}^{\text{bind}} - \frac{\Delta\mu_{\text{O}_2}}{2} \right) \end{aligned} \quad (5.27)$$

where the adsorbate numbers refer to the amount of CO adsorbed on the metal surface and the amount of O incorporated in the surface oxide. Note, that for simplicity, we have assumed in equations 5.24 and 5.25 that the step free energy parameter c_5 is equal for the metal and oxide phases. Introducing a difference would be nearly equivalent to changing c_6 , so that equation 5.27 will still capture the correct qualitative response of the surface energetics to the presence of steps. If $\Delta\Gamma^{\text{m-o}}$ switches from negative to positive, for example by a decrease in step density s , the surface switches to the oxide

phase and the reaction rate changes accordingly. For the calculation of the free energy of the CO adsorbed on the surface we use an average binding energy for CO $E_{\text{CO@Pd}}^{\text{bind}}$ of -1.63 eV per molecule and a coverage of 0.75 monolayer. This corresponds to a $4(\sqrt{2} \times \sqrt{2})R45^\circ$ adsorbate structure, which has been calculated to be lowest in free energy at the chemical potential range we use [86]. For oxygen, we use as a binding energy -1.2 eV per O atom and a coverage of 0.8 monolayer [87], corresponding to the thin, $\sqrt{5}$ surface oxide structure that forms initially (see chapter 4).

5.3 Results

Figure 5.1 shows results of the numerical integration of the differential equations of our adapted oscillation model. Similarly to the measurements in figure 4.2, the numerical results show two types of oscillations. The labels (A),(B), (C) and (D) are the same as in figure 4.1. After reduction, a rough metal surface (A) relaxes into a smooth surface (B). When the step density is low enough the surface oxidises (C). The reaction mechanism that becomes active upon oxidation roughens the surface. When the step density is increased above a certain limit the oxide is reduced (D).

Whether the surface reoxidises (E) or remains reduced (F) immediately after it has switched from oxide to metal, depends on a competition between the rate at which the step density is reduced and the rate at which the CO partial pressure rises. When the surface switches from the oxide to the metal phase, the reaction rate r decreases and CO is consumed at a lower rate. As a result, the partial pressure of CO will increase to a higher level. While the rising CO partial pressure adds to the stability of the metal phase, the reducing step density undermines it. Their contributions in equation 5.27 determine whether the free energy difference between metal and oxide remains negative or turns to positive. If the step density change increases the free energy difference faster than the CO partial pressure decreases it, the surface returns to the oxide phase (E). In such cases, the metal phase does not last long enough for the long length scales to decay and long-length-scale roughness keeps building up throughout these rapid oscillations. As the number of rapid type-E oscillation cycles becomes larger, the roughness consists more and more of the long length scales and the step density necessarily decays more and more slowly after each oxide-metal switch. This gives the CO pressure increasingly more time to build up and change the free energy difference in favour of the metal (F). It now takes much longer to reach the free energy where the oxide is the favourable configuration again (A). The nonlinearities in the rates of pressure buildup

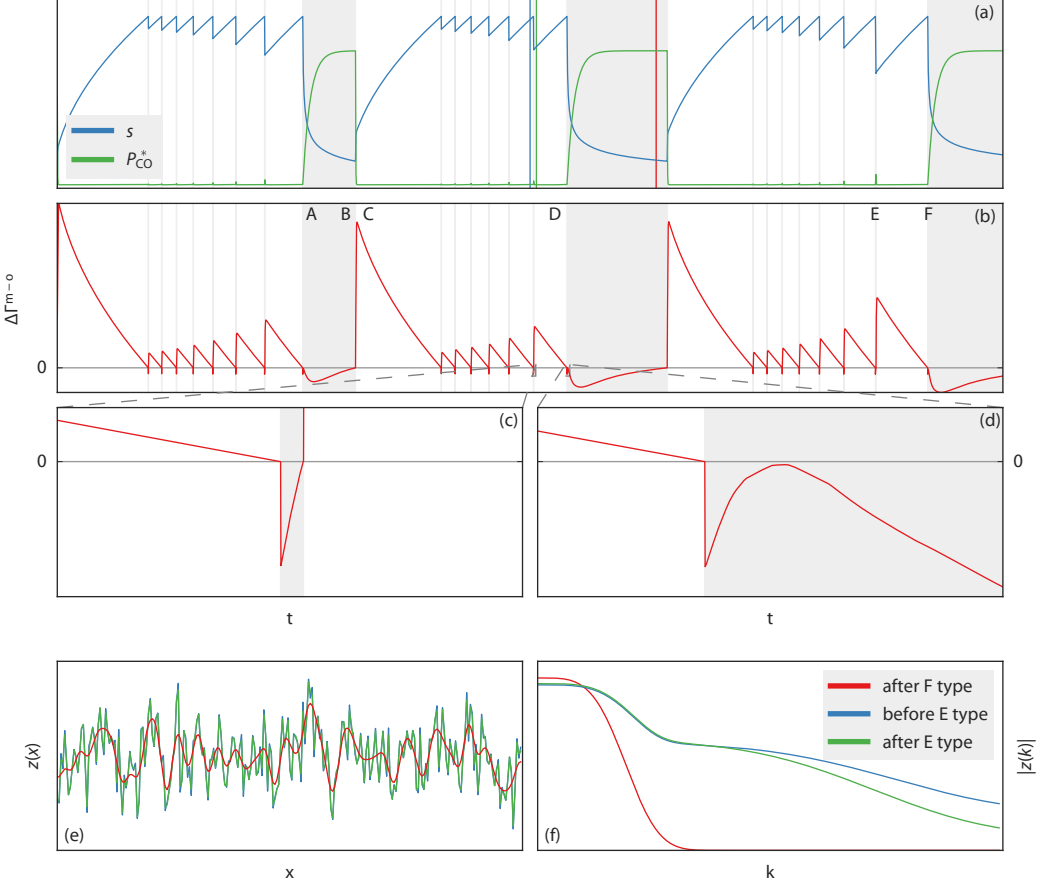


Figure 5.1. Spontaneous reaction oscillations, as computed with the refined model, discussed in the text. Graph (a) shows the step density and the partial pressure of CO at the sample surface in the reactor. Graph (b) shows the free energy difference between metal and oxide versus time. The grey areas indicate where the surface is in the metallic phase. The stages in the Hendriksen model (A, B, C and D) in figure 4.1 can be seen as well as additional, more rapid oscillations. Graphs (c) and (d) show a zoom-in of the free energy difference around an E- and an F-type switch. After an E-type switch the surface is only briefly in the metal phase due to the fast smoothening. After an F-type switch P_{CO}^* has time to increase due to the lower rate of smoothening and stabilise the metal surface. A lower roughness is needed at this P_{CO}^* for the oxide configuration to become favourable again. Graph (e) shows examples of the height function of the surface at three different stages in the oscillation model. They show the surface before oxidation (red) and before (blue) and after (green) a switch of type E, corresponding to the three vertical lines in graph (a). Graph (f) shows the roughness components $z(k)$ corresponding to the three height functions in Graph (e).

and step density decay can make the duration of the metal phase a very sensitive function of the roughness distribution with which the metal starts, directly after the oxide-metal transition. Small changes in this roughness distribution can make the difference between a short, type-E oscillation and a long one of type F. Panel (c) and Panel (d) in figure 5.1 show the free energy difference between metal and oxide for the two types of oscillations. It can be seen that the free energy difference for the E-type oscillation increases faster after reduction than for the F-type.

The Gibbs free energy for adsorption of CO (equation 5.20) increases faster with temperature than the Gibbs free energy for adsorption of O (equation 5.22). When $P_{\text{CO}} < P_{\text{O}_2}$, μ_{CO} decreases faster as a function of temperature than μ_{O_2} . In addition, O_2 dissociates upon adsorption. This adds a factor 1/2 to equation 5.22, which renders the Gibbs free energy of adsorption for O_2 even less sensitive to the temperature. Therefore an oxide structure is more favourable at high temperatures. The oscillatory behaviour can be found close to the transition point from the metallic to the surface oxide structure. The formation energy of the oxide and the binding energy of the CO atoms that we have used in our calculations for exploring the oscillation have been taken from a previous DFT study [87]. These numbers are such that they predict the oxide to be favourable at much lower temperatures than we have experimentally observed. However, this does not influence the qualitative behaviour of the result of our model.

The parameters c_1 to c_6 have to be suitably chosen to produce the oscillation characteristics observed in the experiment. If we set a temperature just above the metal to oxide phase transition the system will oscillate spontaneously. The type of oscillations, however, depends on the values of the constants c_1 to c_6 . Both E-type and F-type oscillations occur if the CO pressure increases with a rate (dependent on the choice on c_4 and the flow rates) that lies between the decay times of short and long length scales. If a too slow decay time (c_2) is chosen, the slow increase in CO partial pressure near the surface, directly after the oxide-to-metal transition, is still rapid enough to keep the surface metallic for a long time (F-type), as in the original model by Hendriksen et al. [12]. However, if the decay time is too fast the surface always reoxidises immediately (E-type).

There are several additional elements that we have ignored in the model. The temperature can play a similar role as the CO partial pressure. The higher reactivity of the oxide phase increases the sample temperature due to the exothermicity of the reaction. Both a higher temperature and a lower CO partial pressure, resulting from the increased reaction rate, lower the chemical potential of CO at the surface more than the chemical potential

of O, thereby stabilising the oxide configuration. Therefore the reactivity difference of the two phases induces a positive feedback on the stability of the two phases.

We also assumed the step free energy to have the same value in the oxide and in the metal phase. This assumption is probably not justified in view of the large difference in composition and bonding characteristics between metals and oxides. However, the occurrence of oscillations only requires the net effect of roughness, the comparative change of surface free energy and the increase of adsorption energy of CO on the metal surface, to favour the metal phase. In the opposite case, when roughness were to favour the surface oxide, the system would be stabilised against the type of oscillations discussed here. It may well be that this is the case for CO oxidation on some specific surfaces, such as Pt(110), which seems to be robust against reaction oscillations, even though it exhibits a well-documented metal-oxide transition that results in a higher CO oxidation rate and a progressive surface roughening, similar to Pd(100).

Another element we have ignored is the 'communication' between roughness length scales; in reality, the Mars-Van-Krevelen mechanism cannot 'populate' the longer wavelengths directly, as we have assumed in the model. Instead, the amplitudes of height variations at longer wavelengths are growing by virtue of height variations with shorter wavelengths, while the Mars-Van-Krevelen mechanism typically adds roughness only on short wavelengths.

We notice that both the CO partial pressure and the local surface and gas temperature account for the synchronisation of the oscillations over macroscopic distances, forcing large, cm-scale areas to oscillate completely in phase. Transitions of the entire surface probably proceed by a nucleation-and-spreading mechanism. For example, when locally the conditions for reduction are met and a small region in the oxide is transformed into metal, the local CO pressure increases, which, in turn, pushes the free energy balance for the surrounding surface from oxide to metal, so that a transition wave emanates radially from the starting point of reduction. Thus the entire surface should be converted on a timescale that is determined to a large extent by the properties of the communicating gas phase.

Finally, this model assumes that the partial pressures of the gases in the reactor are distributed homogeneously, and only crudely models the mass transfer limit of CO by calculating a different CO pressure at the surface. In real reactors this perfect mixing is usually not achieved. This results in gradients in partial pressures over the catalyst surface and adds a spatial component to the differential equations for the gas flow and the roughening

of the surface. Exploring the roughening in such an extended model could be used to investigate the spatial behaviour of the surface observed with the optical microscope introduced in chapter 2.

5.4 Conclusion

In this chapter we have introduced a new model for spontaneous oscillations in the catalytic oxidation of CO over metal surfaces, such as Pd(100). Our model captures the essence of the interplay between the effects of roughness on short and long length scales. In spite of the crude nature of the model, it naturally leads to the combination of rapid oscillations with a partial removal of roughness and long oscillations that also affect height variations on long length scales.

Chapter 6

Oxide shell formation during spontaneous oscillations in the catalytic oxidation of CO on palladium nanoparticles

Spontaneous reaction oscillations on palladium nanoparticles during the catalytic oxidation of CO have been investigated by a combination of in situ microscopy techniques and x-ray scattering. The oscillations are identified as sequences of switches between a high- and a low-reactivity phase and vice versa. The high-reactivity phase is accompanied by the presence of a 1 nm thick palladium oxide shell that encapsulates the metallic core of each particle. Based on this observation, a mechanism is proposed for the oscillations that involves the catalytic activity and the stability of the palladium oxide.

The work presented in this chapter has been performed together with Dr. Sander Roobol.

6.1 Introduction

Spontaneous reaction oscillations have been observed for many heterogeneous catalytic systems, ranging from single-crystal model systems in ultrahigh vacuum [88], to thin films [89], supported nanoparticle systems [90], and even up to commercial reactors such as automotive catalytic converters [91]. Only for a few single-crystal model systems, atomic-scale mechanisms for reaction oscillations have been studied in detail [12, 92–95]. In this chapter, spontaneous oscillations during CO oxidation on Pd nanoparticles, supported on flat substrates, are investigated with a variety of techniques. The measurements suggest that the oscillation mechanism on the particles could be similar to that on Pd single-crystal surfaces.

In previous work on the Pd(100) surface [12], a high-pressure mechanism has been identified that features a refined interplay between variations in the step density or surface roughness, the stability of the PdO surface oxide (which depends on the surface roughness and the local gas composition), and the catalyst activity (which in turn depends on the state of the surface). A full cycle of the oscillation on Pd(100) proceeds as follows. The reaction takes place under conditions that are so oxygen-rich that the smooth metal surface is unstable with respect to oxidation. As a consequence, a thin surface oxide is formed. The oxidised surface is more reactive than the metal, causing a higher consumption of CO and thus a drop in CO partial pressure as soon as the formation of the surface oxide starts. This locally accelerates the oxidation and makes it synchronise across the whole surface. In the oxide phase, the reaction follows the Mars-Van Krevelen mechanism [96]: CO adsorbs on the surface oxide, and reacts with this oxide to form CO₂. In this process, some of the Pd atoms get reduced and become mobile, diffusing out on top of the oxide until they get re-oxidised, thereby increasing the surface roughness. Eventually, this roughness destabilises the surface oxide and the system switches back to a rough metallic surface. The reason for this is thought to be that the CO binds even more strongly to the step sites on the metal surface than to terrace sites. This increasingly favours the metal surface as roughening on the oxide progresses. The lower activity of the metal surface makes the CO partial pressure increase again, now further stabilizing the metal surface. The high surface mobility of the metal surface leads to a swift smoothening. This removes the binding advantage of CO to the step sites and makes the metal surface unstable again, causing the whole process to start over again.

Oscillating nanoparticle catalyst systems have been reported, but there have been few attempts to systematically investigate the precise oscillation mechanisms. Detailed mass spectrometry analysis of oscillations during CO

oxidation on platinum particles by Jensen and co-workers [97] suggested that the surface-transition mechanism described above for Pd(100) could also apply to these nanoparticles. However, the roughness of an extended surface is a property that is difficult to translate to a nanoparticle, and such a “translation” has not been performed in ref. [97]. Also on Pt particles, in an in situ Transmission Electron Microscopy (TEM) study [98], particle morphology variations have been observed that correlate with the oscillations. By employing mass transport simulations and DFT, the conclusion was drawn that the oscillations are the result of a bistability in the Langmuir-Hinshelwood kinetics.

The interaction of oxygen with palladium nanoparticles has been studied on Fe_3O_4 substrates [99–101], on Al_2O_3 [102, 103], and for epitaxially aligned particles on MgO [104], both at low and high O_2 pressures, and also in the context of CO oxidation. Nevertheless, oscillations in the CO oxidation rate on Pd nanoparticles have not been reported before.

6.2 Methods

In order to acquire as much structural information as possible, under actual, high-pressure, high-temperature conditions, we have employed a combination of four complementary structurally sensitive techniques, each under operando conditions.

High-pressure X-ray Diffraction (XRD) experiments have been conducted in the special, 17 ml flow-reactor setup that has been installed at the ID03 beamline of the European Synchrotron Radiation Facility (ESRF), especially for surface x-ray diffraction under catalytic conditions [21]. These experiments reveal which structural components, e.g. metal or oxide, are present. The same setup has been used to perform Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) measurements on the Pd particles, which provides information on the average spatial arrangement of individual particles and is sensitive to the presence of special structures, such as a core-shell structure [15].

A direct, real-space view of Pd nanoparticles under reaction conditions has been obtained with two in situ microscopy techniques. We have conducted in situ, non-contact Atomic Force Microscopy (AFM) experiments, using the new ReactorAFM setup with its 0.5 ml reactor volume, described in detail in ref. [9]. These observations give information on the irreversible changes, such as ripening or sintering, and on reversible changes in the shapes and heights of the nanoparticles during reaction oscillations. The AFM observations have been complemented by extensive high-pressure TEM

observations, where we have made use of the especially developed nanoreactors, which are described in refs. [5, 105]. The TEM experiments were performed at 300 keV using an FEI Titan microscope at Delft University of Technology.

For the x-ray and AFM experiments, the nanoparticles had to be supported on a flat substrate. Samples with well-defined densities, ($100/\mu\text{m}^2$ for the AFM, $700/\mu\text{m}^2$ for the x-ray experiments), of size-selected Pd particles, generated using a spark discharge method (average diameter of 6 nm for AFM and 15 nm for the x-rays) and supported on a flat $\alpha\text{-Al}_2\text{O}_3$ substrate, were kindly provided by Dr. M.E. Messing and Prof. K. Deppert and co-workers from Lund University in Sweden [106]. For the TEM experiments, the nanoreactor was loaded with palladium nitrate salt. After oxidation with O_2 at 300°C and reduction by H_2 at 500°C , Pd nanoparticles had formed with sizes ranging from 5 to 50 nm.

Like the x-ray flow-reactor setup, the ReactorAFM operates in flow mode using a combination of mass flow controllers and back pressure controllers, typically operating with residence times of the gas in the reactor volume of 5 to 20 seconds. The x-ray flow reactor has an adjustable leak to the UHV system which also contains the quadrupole mass spectrometer (QMS), resulting in gas composition measurement without any delay. For the ReactorAFM, the gas analysis is performed downstream by a (QMS-based) T100 analyser from LPM [40]. This configuration introduces a delay of a few seconds, but does not suffer from a loss in time resolution, thanks to the small volume of the input stage of the T100 analyser. However, the flow through a TEM nanoreactor is too small to be controlled with a commercial flow regulator, and the nanoreactors have been operated by defining a certain pressure of a gas mixture at the inlet and feeding the outlet directly into the differentially pumped ultra-high vacuum system (UHV) of a T100 analyser. Because of the micrometre-scaled dimensions of the nanoreactor, the pressure drops completely to zero over the length of the reactor, and the flow through the reactor can be handled directly by a turbomolecular pump. The second turbomolecular pump on the UHV system maintains the optimal working pressure for the QMS. The large volume of the capillary from the nanoreactor to the gas analyser compared to the flow results in a time resolution for gas detection of approximately 30 s.

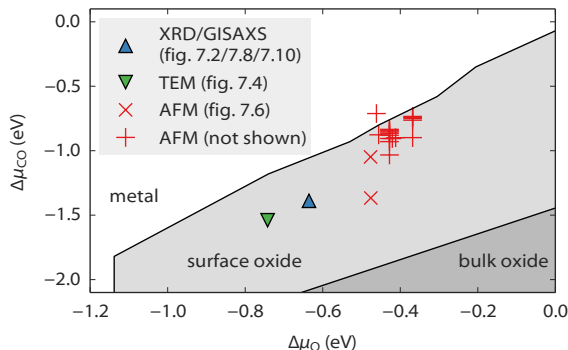


Figure 6.1. Experimental conditions of all experiments reported in this chapter, expressed in terms of the chemical potentials of carbon monoxide and oxygen. The three greylevels indicate three of the phases of a Pd(100) surface in contact with CO and O₂, as calculated using DFT by Rogal et al [107]. Since a nanoparticle exposes multiple different facets, it is to be expected that the phase boundaries for a nanoparticle system will be in slightly different positions. The phase boundaries will also shift and blur because of the CO oxidation reaction itself [108]. The two triangles correspond to observed reaction oscillations, indicating that these points are near a phase boundary, whereas only microscopy images but no reactivity data could be obtained for the cross markers.

6.3 Results and discussion

In this section the experimental results are presented. We start with the crystallographic information derived from the XRD experiments. After addressing the particle shapes with TEM and AFM, we analyse the GISAXS patterns to obtain a detailed view of the rearrangement of the Pd nanoparticles during the catalytic reaction oscillations.

Although the different experimental techniques have not been applied under identical conditions, all data have been obtained close to the metal/surface oxide boundary, as indicated in figure 6.1.

6.3.1 X-ray diffraction

The upper panel of figure 6.2 shows the periodic variations in the CO₂ and CO partial pressures during spontaneous reaction oscillations on size-selected 15 nm Pd particles on α -Al₂O₃ in the 17 ml XRD flow cell. The nanoparticles were exposed to a constant gas flow of 60 ml_n/min consisting of CO, O₂ and Ar, at partial pressures of 9, 210, and 281 mbar respectively. The sample was heated at constant power to a temperature of about 588 K. The XRD measurements that were taken simultaneously with the mass

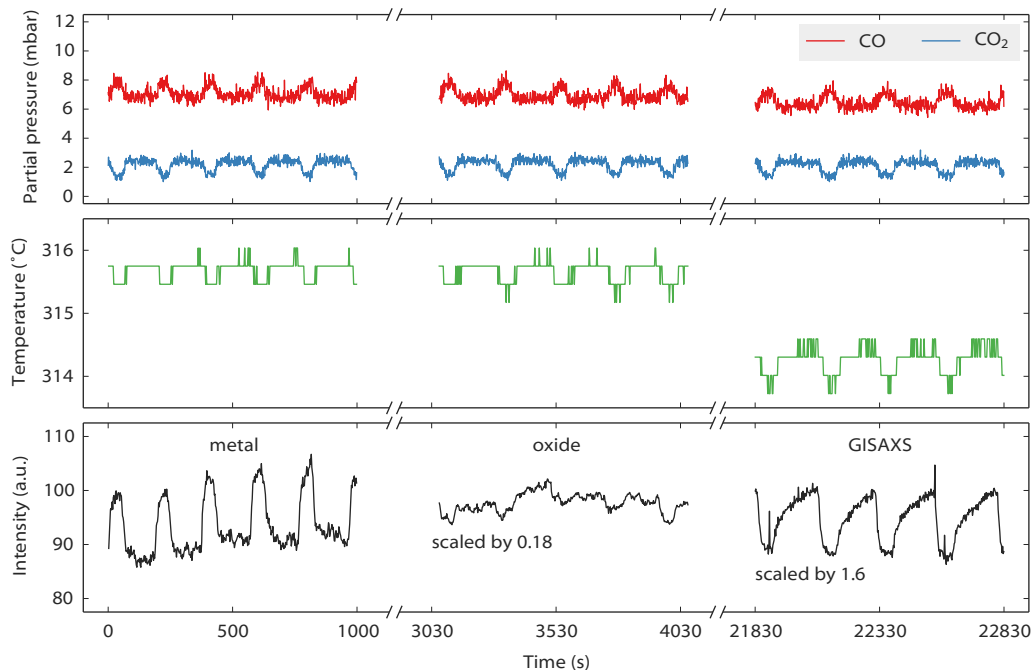


Figure 6.2. Spontaneous reaction oscillations observed using x-ray scattering. The upper panel shows the CO and CO₂ partial pressures as a function of time. The middle panel shows (a low resolution measurement of) the sample temperature. The gas feed was kept constant at 9 mbar CO, 210 mbar O₂, and 281 mbar Ar at a total flow of 60 ml_n/min, and the sample heater was operated at a constant power (its value was adjusted slightly around $t = 20\,000$ s). Note that the absolute value of the partial pressures of CO and CO₂ contains an error due to varying background levels for these gases in the mass spectrometer. The amplitude of the oscillations in these signals is not affected by this. The lower panel shows the periodic intensity variations in three different x-ray signals: the metal Pd peak at the $2\theta = 17.6^\circ$ diffraction angle, the oxide PdO peak at $2\theta = 15^\circ$ (see also figure 6.3), and the integrated intensity from a region in a series of GISAXS patterns (see figure 6.8). A high metal intensity is correlated with a low turnover rate, whereas a high oxide intensity correlates with a high turnover rate. Also the changes in the GISAXS signal are synchronised with the reaction oscillations.

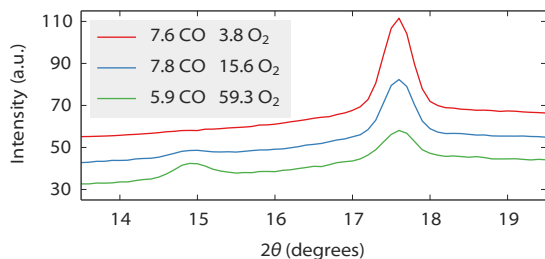


Figure 6.3. X-ray diffraction patterns of the Pd nanoparticles in three different mixtures of O_2 and CO at a total pressure of 200 mbar and a temperature of 375°C . The CO and O_2 partial pressures in mbar are indicated in the legend, the rest of the atmosphere consisted of argon. The patterns are offset by 10 a.u. for clarity. The peak at $2\theta = 17.6^\circ$ corresponds to the (111) reflection of metallic Pd, $2\theta = 15^\circ$ corresponds to the (101) reflection of the oxide PdO.

spectrometry data exhibited periodic variations in the diffraction intensities at angles corresponding to either the crystal structure of metallic Pd or that of PdO. These variations were out of phase with each other; when the Pd signal was high, the PdO signal was low and vice versa. These oscillations were fully synchronised with those in the CO and CO_2 partial pressures. Figure 6.2 shows that the high-reactivity phase coincided with the presence of the oxide. The sample temperature varied in response to the changes in the turnover rate, since CO oxidation is an exothermic reaction. The oscillations had a period of a few minutes, depending on the temperature, and could be sustained indefinitely within the time scale accessible in our synchrotron experiments. The presence of the x-ray beam only quantitatively affects the oscillations: without the beam the oscillation period is a factor 2 longer and the amplitude of the temperature variations increases by 50%.

In addition to XRD, GISAXS experiments have been performed. Figure 6.2 shows that also the GISAXS signal varied synchronously with the reaction oscillation. These variations will be addressed in more detail in section 6.3.4.

6.3.2 Transmission electron microscopy

in situ TEM has been used to obtain a direct view in real space of Pd nanoparticles during oscillations in CO oxidation at atmospheric pressures and elevated temperatures.

In the employed configuration of nanoreactor gas lines, QMS system and vacuum pumping, the residence time of gas in the 0.4 nl reactor was less than

1 ms, and the sensitivity of the reaction product detection was sufficient to measure CO conversion, although the time resolution was only about 30 s, due to diffusive mixing of the gases between the reactor and the mass spectrometer. In addition to reactivity measurements, the TEM nanoreactor allows sensitive calorimetric measurements with a time resolution of 0.5 s, and this was our primary detection method for the oscillations. The reactor was operated at constant temperature using an electronic feedback circuit, and since the CO oxidation reaction is exothermic, the high-reactivity regime corresponded to lower power input from the sample heater, while the low-activity regime corresponded to higher heating power.

When operating at elevated temperature, there were large temperature gradients in the region around the electron-transparent windows that need to be taken in consideration. Measurements on an earlier version of the nanoreactor [109] and simulations on the current version [98] showed that when operating the heater at a setpoint of 723 K, the center of the heated region was typically 50 K hotter, while the electron-transparent windows, which are situated near the edge of the heated zone, were typically 100 K colder than the value measured from the resistance of the heater.

The nanoreactor was loaded with 5 to 50 nm nanoparticles, as described in section 6.2. When exposing these particles to a mixture of 33 mbar CO and 217 mbar O₂ at temperatures near 400°C, spontaneous reaction oscillations occurred as can be seen in the time dependence of the heater power shown in figure 6.4.

In contrast to the x-ray experiments, the oscillations in the nanoreactor could not be sustained for prolonged times. After the oscillations started, either spontaneously or triggered by a small temperature increase in the order of 1 K, the system continued oscillating for at most several minutes. Typically, the period of the oscillations continuously increased from 2 to 15 seconds over the course of 10 to 100 periods, before coming to a halt in the low-reactivity regime. We attribute the shorter period and the reduced lifetime of the oscillations compared to those in the SXRD reactor to the higher temperature in the TEM experiments, as the processes that determine the time scale of the oscillations (for the Pd(100) surface these were the roughening and smoothening), are likely to take place at a faster rate at the higher temperature. Also the wider particle size distribution could play a role, as these processes might come to a halt earlier on small particles causing the system to switch to the other regime.

Figure 6.4 shows two TEM images of Pd particles in a downstream window, taken in consecutive low- and high-reactivity phases. The difference image shows absolutely no features above the noise. This shows that the

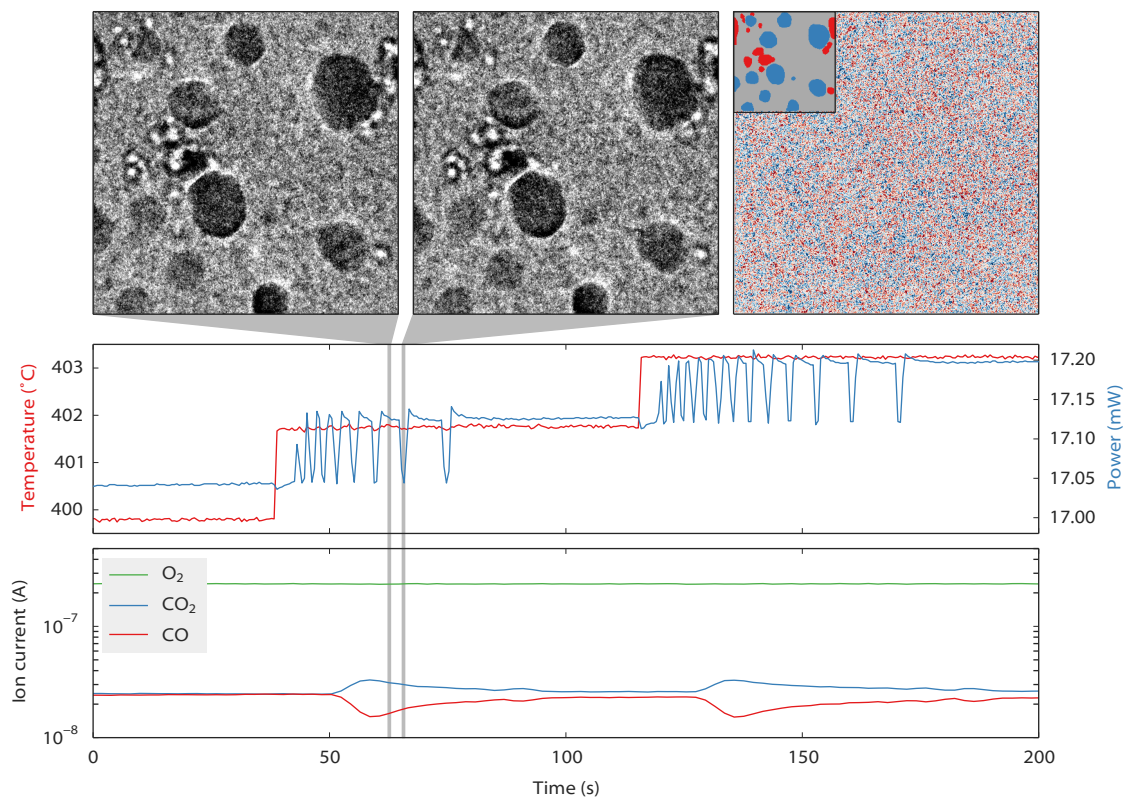


Figure 6.4. (Upper panels) TEM observations during reaction oscillations, $98 \times 98 \text{ nm}^2$ field of view. The first image was taken in the low-reactivity regime, and the second image, which was taken 3 s later than the first, was taken in the high-reactivity regime. The third image shows the difference image (after drift correction) between the first and second image, with the inset indicating in blue the particles that were in focus, and in red the particles on the other window of the nanoreactor that were out of focus. (Middle panel) Sample temperature and required heating power. After both temperature steps, the system exhibited a finite number of reaction oscillations, as can be read off from the heating power variations. (Lower panel) Mass spectrometry signals. The time resolution of the gas detection system was not good enough to resolve the oscillations, even though the partial pressures of CO and CO_2 do reflect the average effect of a burst of oscillations, at $t = 40$ and $t = 120$ s.

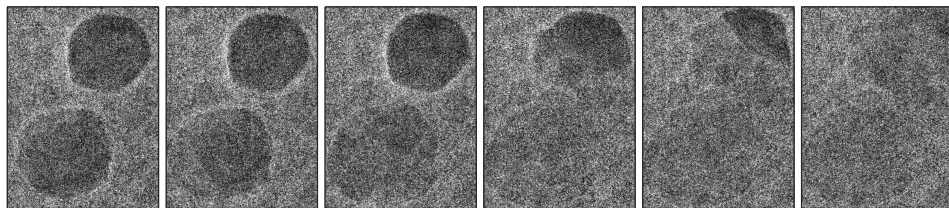


Figure 6.5. Bulk oxidation of Pd particles in 250 mbar O_2 at 400°C , imaged with $30 \text{ e}/\text{\AA}^2 \text{ s}$. A single oxidation front passed through both particles. Note the reduced contrast after oxidation due to the lower density of PdO with respect to that of pure Pd. Each image measures $33 \times 44 \text{ nm}^2$.

TEM images cannot resolve any changes in the particle morphology. Due to the low signal-to-noise ratio of the particles on the speckled background (from the amorphous SiN nanoreactor windows), and due to the Fresnel scattering halo around each particle perimeter, the effective resolution in our images was limited to values not better than 0.5 nm for metallic Pd, and 1 nm for PdO, due to its lower density.

The images in figure 6.4 have been taken with an electron flux of $30 \text{ e}/\text{\AA}^2 \text{ s}$. Higher current densities have been observed to inhibit bulk oxidation of Pd, but we have verified that at the current density of our experiment the Pd particles could oxidise completely in pure oxygen (figure 6.5).

Due to the existence of large temperature gradients in the reactor, it is possible that the region imaged in these experiments was actually not participating in the reaction oscillations. The central hot region might have been oscillating, while the particles downstream of the hot zone and (which experience nearly the same gas conditions but are at $100\text{-}150^\circ\text{C}$ lower temperature), might have behaved differently. Unfortunately, there were no electron-transparent windows in the hot zone. Also, no difference has been observed between particles in windows upstream and downstream of the hot zone.

6.3.3 Atomic force microscopy

Whereas TEM gives high-resolution cross-sectional information on the nanoparticles, height information is mostly inaccessible. In addition, the Pd particles in the nanoreactor were supported on the SiN windows, while Al_2O_3 has been used as the support for the Pd particles in the XRD and GISAXS measurements. We have used the ReactorAFM [9], to obtain in situ real-space observations on a sample of Pd particles similar to the one used for the XRD and GISAXS measurements, but with a smaller average particle

diameter of 6 nm and a lower coverage of 100 particles/ μm^2 . Unfortunately, due to this low Pd coverage it was not possible to measure the turnover rate with mass spectrometry. Calorimetry was also not possible because of the large thermal mass of the sample and sample mounting structure compared to the heat of reaction. Therefore, we cannot be sure whether the reaction was oscillating under the conditions of our AFM observations.

Figure 6.6 shows an ensemble of Pd particles imaged by non-contact AFM in two different atmospheres and at high temperatures, in both cases close to the phase boundary between metal and surface oxide (figure 6.1). For these images, the rms-roughness of the line profiles on the Al_2O_3 substrate was taken as a measure for the vertical resolution, and this was found to be 0.2 nm. Within this margin, the particle heights did not change when the atmosphere was changed. The horizontal resolution was limited due to convolution of the particle contours with the tip shape, therefore a systematic analysis of the lateral particle shape has not been attempted.

Summarizing the real-space observations of TEM and AFM, it can be concluded that the particles remained largely unchanged. In particular, we can conclude that the particles did not get fully oxidised under reaction conditions. Neither have other effects such as fragmentation, clustering, or particle migration been observed as a direct consequence of the switch from one gas composition regime to the other.

6.3.4 Grazing incidence small angle x-ray scattering

The GISAXS data have been obtained at the ID03 beamline of the ESRF operating at 18 keV using a Maxipix 2D-detector. To optimise the signal-to-noise ratio the GISAXS data have been averaged in the following way. GISAXS patterns have been acquired continuously during several consecutive periods of the reaction oscillation. Each period has been manually segmented into 12 sections, based on the phase of the oscillation using the CO_2 signal as reference and on the intensity in a 20-pixel region close to the center of the Yoneda peak in the GISAXS pattern. This segmentation is illustrated in figure 6.7. All data within each segment (irrespective of the period it belonged to) was taken together and averaged. Two horizontal lines from the 2D-detector (each line has a width of 0.05 mrad) that cut through the Yoneda peak (as indicated in figure 6.8) were used for a detailed analysis as described below.

The GISAXS pattern showed an intensity that was oscillating along $q_{\parallel}$ in the low-reactivity phase, and a more monotonic profile in the high-reactivity phase (figure 6.8). This change in profile can be interpreted as a change in the abruptness of the electron density profile as a function of radius

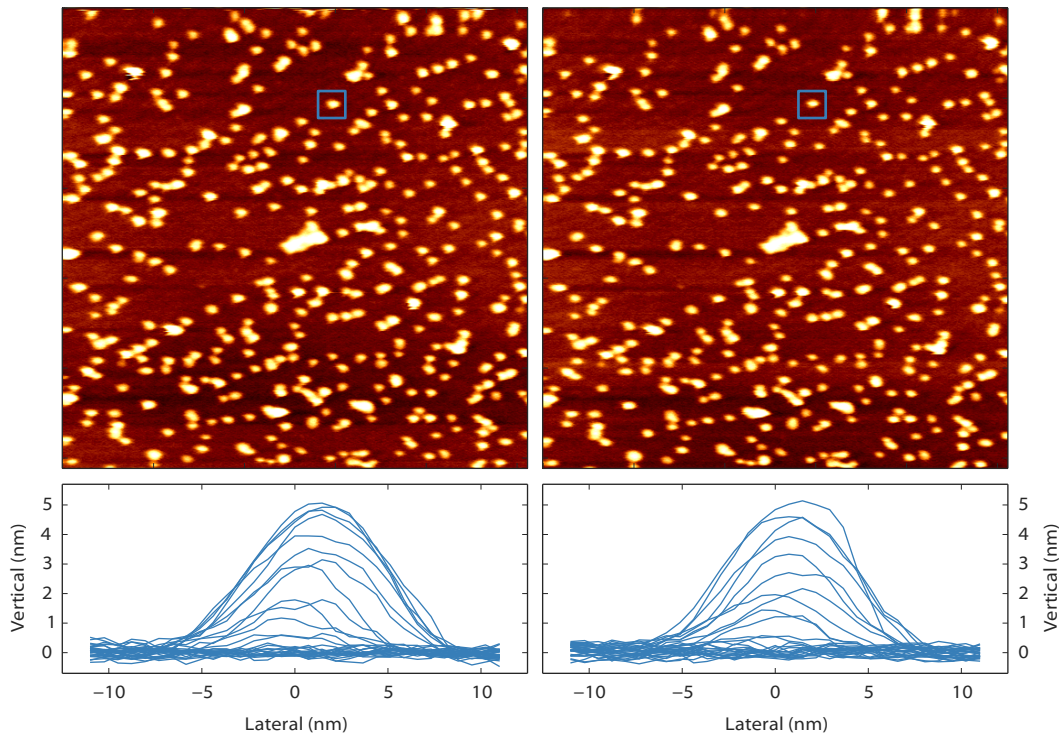


Figure 6.6. The upper panels show $700 \times 700 \text{ nm}^2$ non-contact AFM images on size-selected Pd particles supported on $\alpha\text{-Al}_2\text{O}_3$, obtained at 475 K and a total pressure of 1 bar. The coverage is about 100 particles/ μm^2 , but the particles are distributed inhomogeneously over the surface, giving rise to a higher coverage in the region imaged here. The left panels have been obtained in a 1:3 Ar:O₂ mixture, the right panels in a 10:1:30 Ar:CO:O₂ mixture. The AFM was operating in frequency modulation mode with a frequency shift setpoint of +5 Hz and an oscillation amplitude of 5 nm. The lower panels each show 30 horizontal line profiles from the regions indicated by the blue rectangles in the images, proving that the particle height did not change. The cross-sectional particle shape has not been analysed in detail, as it is formed by the convolution of the tip shape with the particle shape.

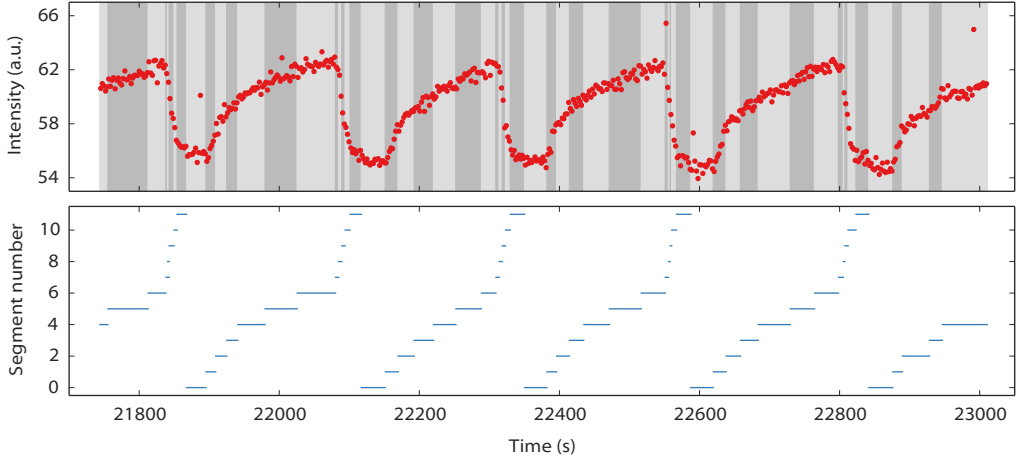


Figure 6.7. The upper panel shows the GISAXS intensity integrated from a small region near the Yoneda peak (see figure 6.8 for details) versus time during five full oscillation cycles. The lower panel and the grey bands in the upper panel show how we have manually classified all GISAXS data into 12 epochs, 6 for the parts of the oscillation cycle during which the GISAXS intensity increased, and 6 for the decreasing parts. In this way, the full data set with multiple oscillations was averaged into a combination of 12 GISAXS patterns, with good signal-to-noise characteristics, together covering the complete oscillation cycle. These 12 patterns were used for the subsequent analysis.

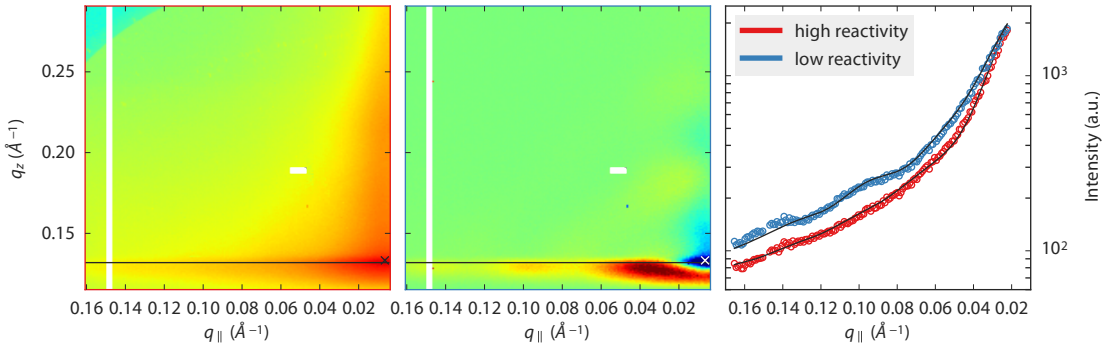


Figure 6.8. GISAXS data after averaging, (left panel) in the high-reactivity regime (logarithmic colour scale), (middle panel) difference signal between the intensity in the low-reactivity regime and that in the left panel, (right panel) linescans through the GISAXS data in the high- and low-reactivity regimes at the location indicated in the left and middle panels. The blue and red curves are the theoretical fits discussed in the text and explained in figure 6.9. The crosses in the lower right of the two GISAXS patterns indicate the location of a 20 pixel ($5 \cdot 10^{-5}$ steradian) region that was integrated to obtain the signal that is shown in figures 6.2 and 6.7.

(figure 6.9). The intensity oscillations are the result of a sharp transition in electron density from metal to vacuum, whereas a broadening of this transition blurs these oscillations. The broadening can be caused by a less compact particle shape (i.e. facets rather than sphere), a wider particle size distribution, or by the formation of a surface layer with a lower electron density. From the GISAXS patterns alone it cannot be concluded which of these three scenarios is at work.

6.4 Model and interpretation

Having discussed the four sets of experimental data (section 6.3), we now combine all evidence into a consistent model and test this model with numerical fits to the GISAXS data in figure 6.8. There were three competing scenarios for the changing electron density profile. A changing particle distribution can be ruled out because the changes were fully reversible (hence the oscillations), and the particle distributions remained also unchanged in the TEM and AFM images. Also faceting is not observed in TEM or AFM. On the other hand, the presence of PdO was observed in the high-reactivity phase with XRD, in combination with a reduced amount of metallic Pd. The only configuration that is consistent with all these pieces of evidence is one in which an ensemble of relatively compact, metallic Pd nanoparticles is changed into core-shell structures with a Pd core and a thin palladium oxide shell, both under the influence of the deliberate changes in the gas atmosphere (from reducing to oxidizing), and repeatedly during spontaneous reaction oscillations. The electron density of the oxide is lower than that of the metal, hence the blurring of the electron-density profile at the particle-gas interface. When the oxide shell is sufficiently thin, it should be hard to distinguish it in the TEM and AFM images under reaction conditions.

For our numerical fits, we modelled the Pd particles as truncated core-shell spheres on a flat substrate. The core was taken to be metallic (Pd), the shell to be PdO, and the substrate was set to alumina (Al_2O_3). Only three degrees of freedom were left in the fit, namely the oxide shell thickness, the total number of Pd atoms per particle, and the parameter quantifying the truncation of the sphere (figure 6.9).

The GISAXS patterns were computed using a formalism for dilute core-shell nanoparticles on a substrate, based on the Distorted-Wave Born Approximation [15]. In this approach, particles are treated individually, i.e. there is no scattering process involving multiple particles. To verify that this approximation is appropriate, scanning electron microscopy (SEM) images have been taken of a sample treated similarly to the one analysed here, but

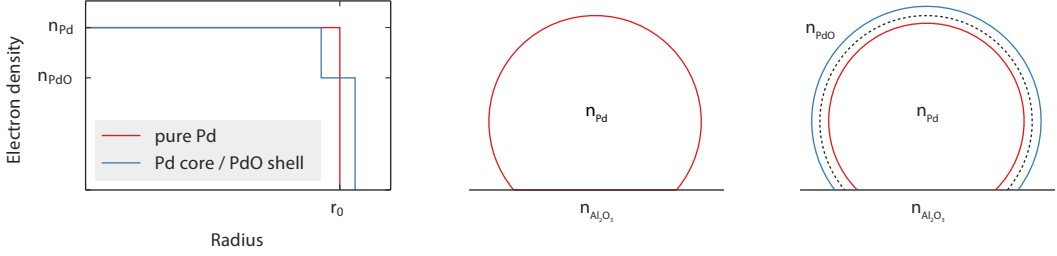


Figure 6.9. The presence of the oscillations along $q_{\parallel}$ in the line profiles in figure 6.8 correspond to sharp transitions of electron density n from metal to vacuum (as sketched for the pure Pd particle in the left panel). The blurring of these oscillations corresponds to a broader electron density profile. The electron density transition is influenced by particle morphology (e.g. faceted versus spherical shape), particle size distribution, and chemical composition (e.g. $n_{\text{PdO}} < n_{\text{Pd}}$). The model used to fit the GISAXS patterns is that of a spherical core-shell particle on a flat Al_2O_3 substrate having a Pd metal core and a PdO shell (middle, right panels). The fits have been made assuming all variations in the electron density profile can be attributed to changes in the thickness of the oxide shell, while all other parameters (number of Pd atoms per particle, particle size distribution, truncation of sphere) have been forced to adopt constant values throughout the entire oscillation period.

with a SiO_2/Si substrate. From these SEM images, the interference function was calculated and this was found to be sufficiently uniform to treat the particles independently in the GISAXS analysis. The Si substrate is not expected to give rise to a significantly different interference function than an Al_2O_3 substrate, and the latter is difficult to image with SEM.

We have developed special Python code in order to fit multiple GISAXS patterns simultaneously, with several shared parameters. This has enabled us to fit the 12 epochs in the average oscillation period in a single step, in which we only allowed the thickness of the oxide shell to vary from epoch to epoch, while forcing the number of Pd atoms per particle and the truncation of the sphere to adopt constant values throughout the entire oscillation period. In this way, internal consistency was ensured and convergence was facilitated, something that could not be done with previously existing software such as IsGISAXS [110].

Since the nanoparticles were not identical but varied slightly in size, each of the three fit parameters was assumed to follow a Gaussian distribution. These distributions were approximated by seven points linearly distributed from $\mu - 2\sigma$ to $\mu + 2\sigma$ and weighted by their relative values of the probability density function. In this way, each simulated GISAXS pattern was constructed as the incoherent sum of 7^3 patterns. A least-squares optimization was then performed on the 28 free parameters (the number of Pd atoms

and a sphere truncation parameter, which are kept constant during the 12 phase segments, and a shell thickness for each of the 12 phase segments; all parameters have a mean and standard deviation).

Figure 6.8 shows that the simulated GISAXS patterns obtained with this optimization procedure gave a good fit of the raw data. Figure 6.10 combines the XRD and GISAXS data for an entire period of the spontaneous reaction oscillation. The GISAXS fits are in excellent agreement with the XRD data. Both data sets show that the high-reactivity phase coincides with the presence of an oxide shell of approximately 1 nm thickness. The corresponding decrease in metal core size, demanded by the fit constraints, matches the decrease in scattering volume corresponding to the reduction in Pd diffraction intensity, while the increase in PdO volume matches the growth in PdO diffraction intensity. Independent confirmation for the reduction of the size of the Pd core during the high-reactivity phase comes from the increase in angular width of the XRD peak from the Pd, which is a direct, inverse measure of the average size over which the metallic component of each nanoparticle extends (figure 6.10, middle panel).

We were unable to get a good fit for the out-of-plane intensity profile of the GISAXS patterns. This could be due to an interface layer between the Pd particle and the Al_2O_3 substrate [103].

6.5 Oscillation mechanism

The periodic formation of the oxide shell seems to indicate a direct analogy to the oscillations observed on the single-crystal surfaces of Pd. However, the observations presented in this chapter provide no information on the feedback mechanism that drives the oscillation on the nanoparticles. Surface roughness played the role of “hidden parameter” on the single crystals, and the roughness-dependent stability of the PdO was the non-linear component required for oscillation. By contrast, TEM and AFM images showed no morphology variations on the nanoparticles. However, roughness on a sub-nm scale, which should be the scale for a nm-thick oxide, would be very difficult to observe, given the resolution of the microscopy images under high-pressure, high-temperature conditions. In addition, roughness can take several forms, ranging from steps on nanoparticle facets (the direct analogue of roughness on single-crystal surfaces), to intermediate surface orientations appearing between the dominant (100) and (111) facets, up to a complete rounding of the particles and a disappearance of the facets. Again, the TEM and AFM images can only be consistent with very modest changes in particle morphology.

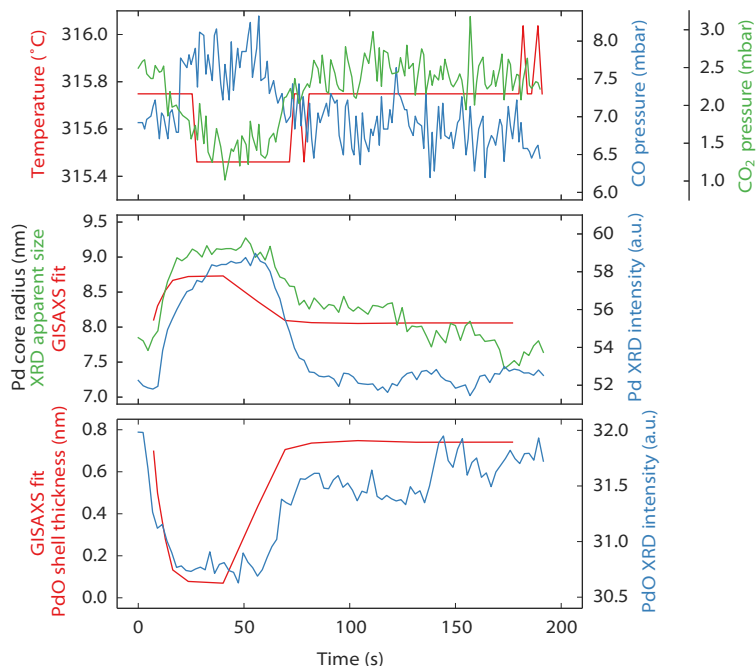


Figure 6.10. Reactivity, GISAXS and XRD data presented over a single oscillation period. Since it was not possible to acquire this complete dataset simultaneously, some curves derive from different periods while the system was oscillating. In particular, the gas composition and sample temperature were measured simultaneously with the Pd metal XRD peak, while the oxide XRD peak and the GISAXS signal were obtained separately. For the GISAXS fit procedure, data from multiple oscillations have been averaged to increase the signal-to-noise ratio (see figure 6.7). To compensate for the slightly different lengths of the periods, the oxide signal has been scaled by a factor 0.978 along the time axis, the GISAXS signal was scaled by a factor 0.789. The apparent particle size from XRD was estimated from the Full Width at Half Maximum (FWHM) of the Pd peak [111], assuming a perfect spherical shape.

Apart from the scenario where roughness is the hidden parameter, we can think of two other candidates for this parameter, although in both cases it is unclear what the non-linear component would be. The first scenario relates to the ongoing discussion about the activity of the PdO, as it is well established that the presence of the palladium oxide correlates with the high-reactivity phase [12, 29], but it is still under debate whether the increased activity should be attributed to the oxide or the oxide should be regarded as a mere consequence of the lower CO partial pressure due to the increased turnover of CO by the metal phase [80, 102, 107, 108, 112–114]. In the latter case, the poisoning of the palladium particles could be the hidden parameter. What speaks somewhat against this scenario is the observation in figure 6.10 that during the high-reactivity phase neither the thickness of the oxide layer, nor the total amount of PdO seems to increase, which is to be expected for this layer in the self-poisoning scenario. The second possibility for an alternative scenario could be related to the formation of an interfacial PdO layer between the metal particle and the Al_2O_3 substrate [103], which could have a large influence on the activity of the system.

6.6 Conclusion and outlook

Spontaneous reaction oscillations occur during CO oxidation over Pd nanoparticles. These oscillations are accompanied by the periodic formation and reduction of a thin oxide shell on these particles. Further research is required to establish the mechanism of the reaction oscillations. Improved resolution of the in situ microscopy techniques would be helpful, as this is required to reveal the small morphology variations that probably occur and influence the stability of the oxide. This would establish a key piece of evidence in support of the nanoparticle analogue of the mechanism found for single crystals [12]. Better resolution could be achieved by more stable and sharper tips for the ReactorAFM, e.g. made from diamond [115], and by better windows for the TEM nanoreactors, causing less electron scattering, e.g. in the form of 2D-materials such as graphene [116].

Even though this work adds to the debate on the activity of PdO, it cannot pinpoint the cause of the high activity during the presence of the oxide. Recent theoretical work is close to addressing this question for the flat surfaces [80, 108]. The observations presented in this chapter show that this issue is also relevant for nanoparticles, and thus for more realistic catalytic systems.

Samenvatting

Wanneer een koolmonoxide molecuul en een zuurstof molecuul in een gas-omgeving bij tweehonderd graden Celcius in aanraking komen, gebeurt er niets. Wanneer deze ontmoeting plaatst vindt op een stukje metaal gemaakt van palladium of platina, begint een chemische reactie te verlopen. Dit stukje metaal fungeert nu als katalysator. De energie in de moleculen is bij tweehonderd graden Celcius te laag om de verbinding tussen de twee zuurstofatomen in het zuurstofmolecuul te verbreken. De katalysator kan dit echter wel. Bij aanwezigheid van de katalysator adsorberen de moleculen eerst op het metaaloppervlak. Het zuurstofmolecuul valt uiteen in twee atomen die aan op het oppervlak blijven plakken. Wanneer nu een koolmonoxide molecuul in de buurt komt van een zuurstofatoom, reageren de twee met elkaar. Het product, kooldioxide, verlaat hierop het oppervlak, waarop het oppervlak opnieuw de ruimte biedt aan andere moleculen om te adsorberen. Dankzij de katalysator is de energie die nodig is om de verbinding tussen de zuurstofatomen te verbreken een stuk lager dan in de gasfase. Dit zorgt ervoor dat de oxidatiereactie bij een veel lagere temperatuur kan verlopen.

Katalyse speelt een belangrijke rol in de chemische industrie. Om efficiënt chemicaliën te kunnen produceren, zijn vaak katalysatoren nodig. Katalysatoren zorgen ervoor dat de omstandigheden voor de productie van deze chemicaliën veel gunstiger zijn, dat er minder warmte verloren gaat en dat er vaak ook minder ongewenste bijproducten worden gevormd. Als gevolg hiervan wordt het proces ecologisch minder belastend en kunnen de productiekosten omlaag. Dit betekent vaak dat grootschalige productie van bepaalde chemicaliën pas met behulp van katalyse economisch haalbaar wordt. Voorbeelden hiervan zijn het Haber-Bosch proces voor het produceren van kunstmest uit stikstof en aardgas en het Fischer-Tropsch proces voor het produceren van benzine uit aardgas. Zonder efficiënte katalysatoren is grootschalige productie hiervan onmogelijk.

Gezien de essentiële rol die katalysatoren spelen voor onze maatschappij is het van belang de werking van katalysatoren goed te begrijpen. Enerzijds

kan goed begrip van katalysatoren ons helpen om de bestaande productiemethoden te verbeteren, anderzijds zou dit kunnen leiden tot nieuwe ontdekkingen op basis waarvan compleet nieuwe katalysatoren kunnen worden ontwikkeld en nieuwe productiemethodes mogelijk gemaakt kunnen worden. De grote schaal van de chemische industrie brengt met zich mee dat zelfs een kleine verbetering al een grote kostenbesparing kan opleveren.

Een katalytisch proces kunnen we onderverdelen in een aantal basiselementen die allemaal goed begrepen moeten worden om het geheel te kunnen doorgronden. Op het allerkleinste niveau moeten we identificeren wat de individuele stappen zijn die een reactie doorloopt. Daaronder vallen bijvoorbeeld de adsorptie en de desorptie, het breken van bindingen binnen en tussen moleculen en het aangaan van nieuwe bindingen. Als de afzonderlijke stappen bekend zijn willen we graag de energieniveaus en barrières te weten komen. Dit vereist een uitgebreide combinatie van geavanceerde experimenten in combinatie met theoretische modellen en computerberekeningen. Voor een volledig begrip van de werking van een katalysator zijn ook diverse praktische aspecten van belang. Zo zijn bijvoorbeeld de vorm van de reactor en de locatie en vorm van de katalysatoren deels bepalend voor de concentratieverschillen in de reactor, hetgeen weer van doorslaggevende invloed kan zijn op de uiteindelijke reactiesnelheid.

Onderzoek naar heterogene katalyse bevindt zich op het snijvlak van natuurkunde en scheikunde. De verscheidenheid aan verbindingen die moleculen met elkaar aan kunnen gaan is bij uitstek het domein van de scheikunde. De studie van de mogelijke structuren van het oppervlak waarop de chemie plaats heeft, is van oudsher een onderwerp waar de natuurkunde zich mee bezig houdt. De oppervlaktenatuurkunde onderzoekt het letterlijke raakvlak van twee verschillende fasen of twee verschillende materialen. Dit raakvlak is van belang omdat, alhoewel de katalysator geen deel uitmaakt van het eindproduct van de chemische reactie, de aanwezigheid van de geadsorbeerde moleculen een cruciale invloed kan hebben op de samenstelling en structuur van de katalysator. Op atomaire schaal kunnen nieuwe stapelingen van atomen ontstaan, dus nieuwe kristalstructuren. Op grotere schaal kunnen stappen worden gevormd, waardoor het katalysatoroppervlak ruw wordt. Natuurkundigen hebben een groot aantal analysetechnieken ontwikkeld om een oppervlak in kaart te kunnen brengen. Zo kan men met röntgen-diffractie de kristalstructuur aan het oppervlak bepalen en met andere röntgenverstrooiingstechnieken eigenschappen van de katalysator afleiden zoals de ruwheid van het oppervlak. Met scanning tunnelling microscopie (STM) kunnen individuele atomen en andere morfologische kenmerken van het oppervlak in kaart worden gebracht. Ook geavanceerde elektron-

microscopen kunnen oppervlaktestructuren atoom voor atoom zichtbaar maken.

Een van de uitdagingen van dit type onderzoek is om de wisselwerking tussen alle essentiële aspecten van de katalyse goed te begrijpen. Hiervoor is het noodzakelijk om ook experimenten uit te voeren onder de omstandigheden waarbij de katalysatoren in de chemische industrie worden gebruikt, dus bij hoge druk en bij hoge temperatuur. De technologische stappen die hiervoor noodzakelijk zijn, werden pas in de laatste twee decennia gezet. Voorheen werden katalyse-experimenten voornamelijk uitgevoerd onder een veel lagere druk dan gebruikelijk is in de chemische industrie. Dit was noodzakelijk omdat vrijwel alle, gebruikte experimentele technieken uitsluitend werken onder deze ultralage drukken. Ten tweede was dit noodzakelijk omdat de preparatie van model-katalysatoren vaak wordt uitgevoerd in ultrahoog vacuüm (UHV). De model-katalysator mag na preparatie niet meer bloot worden gesteld aan lucht om de invloed van lucht op de katalysator uit te sluiten. Daarom moeten de preparatiekamer en de reactor geïntegreerd worden. In Leiden zijn in de loop der jaren meerdere meetopstellingen ontwikkeld die een reactor integreren met een preparatiekamer en een geavanceerde meetmethode om zo onderzoek naar katalytische reacties te kunnen doen. Daaronder vallen een scanning tunnelling microscoop, een atoomkrachtmicroscoop (AFM) en een opstelling voor röntgentechnieken. De laatste opstelling vereist de aanwezigheid van een zeer intense röntgenbundel zoals die alleen in een synchrotron kan worden geproduceerd. Daarom staat deze meetopstelling bij de European Synchrotron Radiation Facility (ESRF) in Grenoble.

Geavanceerde experimentele technieken zijn vaak geoptimaliseerd voor één specifieke taak. Om deze taak zo goed mogelijk uit te voeren wordt veelzijdigheid opgeofferd waar deze de prestatie van die taak kan verminderen. Een voorbeeld hiervan is de reikwijdte van de scanning tunnelling microscoop. Wanneer het van belang is dat de laterale resolutie van de microscoop groot is, moet het gezichtsveld van de microscoop klein worden gehouden. Zo heeft elke techniek vaak één echte specialiteit. Omdat bij katalyse vaak enorm veel verschillende aspecten gelijktijdig een rol spelen, is één techniek meestal niet toereikend om het complexe samenspel volledig te doorgronden. Alleen een combinatie van technieken kan de informatie vergaren die nodig is om alles te begrijpen. Hierdoor zullen meetresultaten van meerdere opstellingen met elkaar vergeleken moeten worden. Een vraag die daarbij komt kijken is in hoeverre de omstandigheden waarin elk van die afzonderlijke resultaten zijn gemeten wel identiek zijn. Om verschillen in de omstandigheden uit te sluiten, wordt in hoofdstuk 1 een

scanning probe microscoop geïntroduceerd die kan worden geïnstalleerd op de eerder in Leiden ontwikkelde röntgendiffractiekamer. Het doel is om zowel röntgenexperimenten uit te kunnen voeren als het oppervlak in kaart te brengen door middel van scanning probe microscopie.

Bij katalyse, zowel in de industrie als in het laboratorium wordt vaak gebruik gemaakt van een gasstroom. Een mengsel van een aantal gassen stroomt met een vaste snelheid aan de ene kant de reactor binnen, terwijl aan de andere kant gas de reactor weer uitstroomt. Voor de druk wordt een vaste waarde gekozen met behulp van een drukregelaar achter de uitlaat van de reactor. Tijdens veel reacties, zoals de oxidatie van koolmonoxide, kan de reactiesnelheid zo hoog zijn dat de interne menging van het gas in de reactor niet snel genoeg gaat om het mengsel in de reactor homogeen te houden. Hierdoor treden gradiënten op in de partiële drukken van de gassen. Door deze gradiënten worden verschillende delen van het oppervlak aan verschillende gascondities blootgesteld. Zoals hierboven beschreven, kunnen de verschillen in condities aanleiding geven tot verschillende oppervlaktestructuren, verschillende reactiemechanismen en verschillende reactiesnelheden. Voor de reactor die wordt beschreven in hoofdstuk 2 introduceren we een techniek die bedoeld is om het oppervlak van een modelkatalysator met een diameter van 1 cm te volgen tijdens een katalytische reactie. Hiermee kunnen we zien of er optische verschillen optreden tussen de verschillende delen van het oppervlak. Dat oxidatie van koolmonoxide daadwerkelijk een optisch spoor achterlaat op een palladium modelkatalysator, wordt aangetoond in dit hoofdstuk. We zien dat de reflectie van het oppervlak afneemt wanneer de reactiviteit van het oppervlak is verhoogd. Dit wordt toegeschreven aan de aanwezigheid van een dunne oxidelaag op het oppervlak, die tijdens het katalytische proces gaandeweg steeds ruwer wordt.

Tot nieuwe technologische ontwikkelingen moet ook software worden gerekend. De versnelling van inname van meetresultaten heeft zich ook bij de bundellijnen aan het ESRF voltrokken. Dit is met name een gevolg van de ingebruikname van een tweedimensionale detector. Efficiënte software die de meetresultaten kan analyseren aan de bundellijnen is niet altijd aanwezig omdat elke bundellijn anders is en daarom vraagt om een eigen analysemethode. Om het onderste uit de kan te kunnen halen hebben we het in hoofdstuk 3 beschreven programma BINoculars ontwikkeld. Deze software is geschreven samen met Dr. Sander Roobol. BINoculars verzamelt de tweedimensionale röntgenplaatjes en 'plakt' deze aan elkaar als vormden ze tezamen een driedimensionale panoramafoto. Op deze manier is het eenvoudig voor gebruikers van het programma om grote hoeveelheden aan meetresultaten te verzamelen en op een overzichtelijke manier weer te geven.

Dit leidt ertoe dat wetenschappers op bezoek bij het ESRF efficiënter gebruik kunnen maken van de ID03 bundellijn.

Tijdens de eerdergenoemde oxidatie van koolmonoxide zijn reactieoscillaties waargenomen. Deze oscillaties zijn een gevolg van de wisselwerking tussen de partieldrukken van de gassen en de structuur van het oppervlak, hetgeen op zijn beurt weer een sterk effect heeft op de reactiviteit van het oppervlak. Deze wisselwerking levert enorm complex gedrag van de katalysator op, waarbij agressieve verruwing wordt afgewisseld met snelle vervlakking. Deze verruwing gaat gepaard met de aanwezigheid van een oxidelaag op het palladiumoppervlak en een hoge reactiviteit. De vervlakking treedt op als de oxidelaag verdwijnt. Kort gezegd worden deze oscillaties veroorzaakt door het feit dat koolmonoxide zich sterker aan een ruw oppervlak bindt dan aan een glad oppervlak. Wanneer de ruwheid van de oxidelaag te groot is, wordt de oxidelaag daarom onstabiel. Als de oxidelaag verdwenen is, verlaagt de reactiesnelheid, waardoor de partieldruk van koolmonoxide in de reactor kan toenemen. De toegenomen partieldruk van koolmonoxide voorkomt dat de oxidelaag weer terug groeit, totdat de ruwheid zodanig is afgenomen, dat de vorming van een oxidelaag weer energetisch voordelig is. Met behulp van een aantal röntgentechnieken beschrijven we in hoofdstuk 4 de precieze toestand van het oppervlak en de oxidelaag. Uit deze waarnemingen ontstaat het vermoeden dat de ruimtelijke eigenschappen van de ruwheid bepalend zijn voor het oscillatiegedrag van de katalysator.

Of deze ruwheidseigenschappen daadwerkelijk de waargenomen oscillaties kunnen verklaren wordt onderzocht in hoofdstuk 5. Er wordt een model opgesteld waarmee de verruwing en vervlakking van het oppervlak tijdens de reactie worden doorgerekend. Dit model bevestigt het vermoeden dat de karakteristieke lengteschaal van de ruwheid op het oppervlak een belangrijke parameter is in het gedrag van het oppervlak.

Reactieoscillaties zijn ook waargenomen op nanodeeltjes van palladium. Het belang van het onderzoeken van katalytische reacties op extreem kleine nanodeeltjes is dat in industriële toepassingen voornamelijk gebruik wordt gemaakt van deze vorm. Een groot kristal is namelijk niet efficiënt. Voor de nanodeeltjes is de verhouding van het oppervlak tot de totale massa maximaal. Zo zit een groot deel van de katalysator 'aan de buitenkant' en speelt actief mee in het katalytische proces. Het gedrag van de nanodeeltjes is echter nog moeilijker om te ontrafelen dan dat van grote kristallen. In hoofdstuk 6 wordt beschreven hoe drie technieken worden gebruikt om het gedrag van nanodeeltjes te ontcijferen. Deze drie technieken zijn allemaal speciaal ontwikkeld voor om de katalyse op nanodeeltjes te bestuderen. Zo maken we gebruik van de in Leiden ontwikkelde atoomkrachtmicroscop, de

aan de TU Delft ontwikkelde, extreem kleine chemische reactoren die in een elektronenmicroscop passen, en de eerdergenoemde röntgendiffractiekamer in Grenoble. Met deze combinatie aan technieken is het gelukt om aan te tonen dat de dunne oxidelaag ook verschijnt en verdwijnt tijdens de reactieoscillaties op deze nanodeeltjes.

De diversiteit aan technieken die zijn toegepast bij het in dit proefschrift beschreven onderzoek, illustreert dat het onderzoek naar katalyse expertise vereist op een combinatie van terreinen binnen de scheikunde en natuurkunde. Alleen met de combinatie van inzichten op elk van deze terreinen zal het uiteindelijk mogelijk zijn om tot volledig begrip te komen van het complexe verschijnsel katalyse.

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Curriculum vitae

Willem George Onderwaater was born on September 28, 1984 in Guildford in the UK. He got his highschool degree from the Gymnasium Haganum in The Hague in 2002, and went to Leiden to study physics. After obtaining his Bachelor's degree he continued with a Master's track in experimental physics. He arrived in the surface science group of Prof. Dr. J. W. M. Frenken to work in the field of heterogeneous catalysis and instrumental development. His first Master's thesis concerned the central components of the ReactorAFM, which he worked on under the supervision of Dr. M. E. Cañas Ventura. For his second Master's thesis he moved to Grenoble to work at the European Synchrotron Radiation Facility (ESRF) with Dr. R. van Rijn and Dr. R. Felici on shape changes of Pd nanoparticles during the CO oxidation reaction. In 2011 he received his Master's degree from Leiden University.

Under the supervision of Prof. Dr. J. W. M. Frenken and Dr. R. Felici he continued at Leiden University and the ESRF to pursue a PhD project, which is described in this thesis. He used a wide variety of experimental techniques to investigate the complex behaviour of the model CO oxidation reaction.

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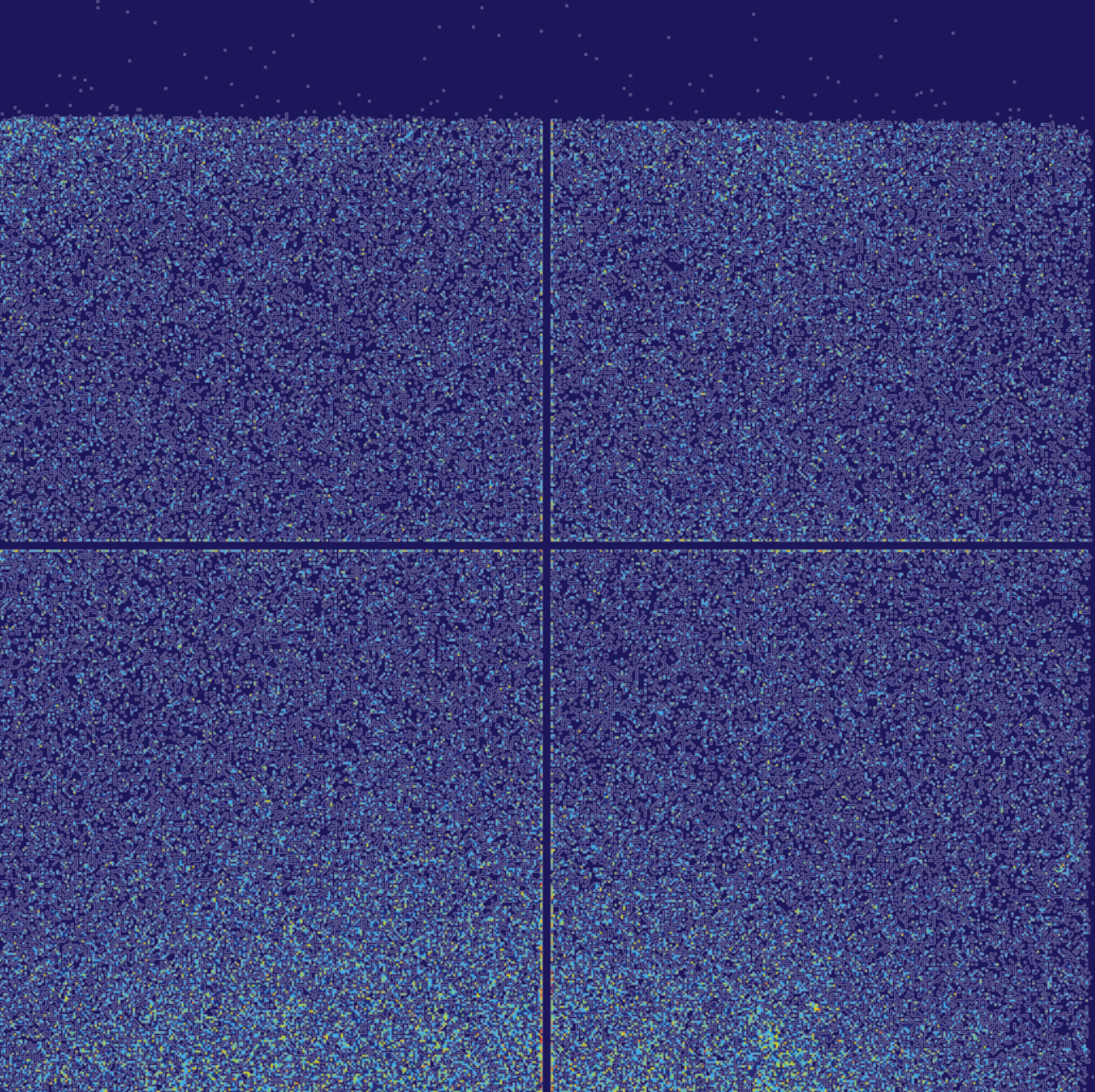
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