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High Energy Surface X-ray Diffraction Applied to Catalytic CO Oxidation over Rh(100) and Rh(111)

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Acronym Page

CTR	Crystal Truncation Rod
RLU	Reciprocal Lattice Unit
UHV	Ultra High Vacuum
HESXRD	High Energy Surface X-Ray Diffraction
MTL	Mass Transfer Limit
SR	Super-structure rod

Abstract

We have studied the surface oxide created on Rh(100) and Rh(111) when exposed to a gas mixture of CO and O₂ at high pressures. The study of the oxide surface have been in comparison with already published result of the oxide surface created on the same surfaces but with only O₂ in the gas. The analysis has mainly been qualitative but some quantitative analysis have also been conducted.

The results for Rh(100) give a surface oxide structure of $c(8 \times 2)$. The surface oxide have a slightly distorted hexagonal pattern. The result for Rh(111) is a overlayer structure of (8×8) . The surface oxide is also hexagonal for Rh(111) with a lattice parameter of 3.07 Å. The oxide is then qualitatively the same as when the surface is exposed to pure O₂ for Rh(100). But the surface oxide is not the same for Rh(111) between the two cases. When Rh(111) is exposed to pure O₂ the surface oxide is (9×9) , a hexagonal pattern with a lattice parameter of 3.02 Å. The explanation of this is that when the surface is exposed to pure O₂ more oxygen is forced down on the surface which forces the surface oxide to shrink. The quantitative analysis has not been completed yet.

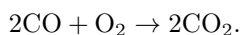
1 Introduction

This thesis work investigates the oxide layer created on two rhodium surfaces when exposed to a mixture of carbon monoxide, oxygen molecules and argon at near-atmospheric pressure. The main part of the work is a qualitative analysis of the surface oxide structures, but some quantitative analysis has also been done. The data that is analyzed was acquired at beamline P07, PETRA III, DESY in Hamburg using the recently developed High Energy Surface X-ray Diffraction (HESXRD) that makes it possible to collect enough data for a full surface structure determination in a few minutes [1].

1.1 Catalytic oxidation Of CO

In recent time society have become more aware of humanity's impact on the environment, especially the releases of the toxic gas carbon monoxide (CO). Combustion engines are one example of machines that release carbon monoxide, which can be a problem in densely populated areas. Therefore there is an interest to reduce the emissions of carbon monoxide.

Fortunately there is a chemical process that transforms the toxic carbon monoxide into the less harmful carbon dioxide (CO₂) with the loss of oxide molecules (O₂), i.e.



The process above is energetically favourable, but for it to happen the O₂ molecule has to dissociate into two separate oxygen atoms so the two CO molecules can be oxidized to form two CO₂ molecules. The problem is that the energy barrier, i.e. the energy needed, for the dissociation of the O₂ molecule is high in gas phase, and therefore the spontaneous reaction happens rarely. As a result the oxidation of CO molecules in a gas mixture with O₂ is a slow process.

If a catalyst, i.e. a substance that speeds up the chemical process without being consumed [12], is introduced the process described above will be accelerated. This can be understood as a process in which the catalysis lowers the energy barrier of the dissociation of O₂, which will give available single oxygen atoms to oxidize the CO. Because of the catalyst the oxidation of CO into CO₂ will be faster and therefore this is an interesting subject for industry.

Late transition metals, e.g. rhodium and palladium, have catalytic properties useful for oxidation of CO molecules [2]. More specifically, it is the surface that act as the catalysis. When the oxygen molecule is adsorbed, i.e. the oxygen molecule gets stuck on the surface (which should not be confused with absorbed, when the atoms enter the interior of the metal), the energy barrier for the dissociation of O₂ molecules will decrease making the molecules dissociate spontaneously during the adsorption process. When a CO molecule is adsorbed on the surface it can be oxidized easily with the now free oxygen atoms to create a CO₂ molecule, which then desorbs. This catalytic process is called the Langmuir-Hinshelwood mechanism. For rhodium the catalytic reactivity can be high enough such that under the conditions investigated in this thesis all the CO molecules that hit the surface are oxidized [3]. When the activity is this high, the CO₂ production is limited by the diffusion of CO molecules to the catalytic surface rather than the actual activity of the catalyst. This situation is often referred to as the mass transfer limit (MTL). Because all the CO molecules that reaches the surface are oxidized a thin layer of CO₂ and O₂ will be formed above the surface which will lower the production of CO₂ molecules. This makes it more difficult for CO molecules to reach the surface in order to react. In addition, the oxygen exposure may result in oxide formation.

The rhodium surface as a catalyst for oxidation of CO molecules have been studied in both ultra high vacuum (UHV) and under high pressure. UHV studies give important information about the interaction between the molecules and the surface, but in order to understand a real system, such as a catalytic converter in a car, studies under high pressure are of major importance. To conduct experiment in high pressure the experimental method have to give result independent of the gas above the surface. In this work HESXRD was used, which is suitable under high pressure since the X-rays interact weakly with matter and therefore the interaction with atmospheric gas pressures can be neglected. The weak interaction also means that the diffraction intensity from the surface, which is relevant for catalysis studies, is low. Therefore very intense synchrotron radiation is used.

Recently there have been several studies published about the catalytic activity of rhodium under high pressures. The problem is that these results contradict each other. Some papers report that under high activity, i.e. when the production of CO_2 molecules is high, the surface is metallic and therefore the active phase would be metallic, i.e. the rhodium atoms on the surface are unchanged and all the atoms adsorbed are found directly on the surface [4]. But other papers report that under high activity a thin oxide layer is formed on the surface [5-7]. This oxide layer is only be present when the catalytic activity has reached the MTL. This can mean either that the active phase is the surface oxide or that the oxide layer is a consequence of the high catalytic activity. The exact nature of the active phase is still unclear.

If the surface oxide is the active phase, the catalytic reaction will follow the so-called Mars-van Krevelen mechanism rather than Langmuir-Hinshelwood. In the Mars-van Krevelen mechanism the oxygen will form an oxide, and the CO molecules will react with O from this oxide rather than simply adsorbed O atoms, as illustrated in figure 1.

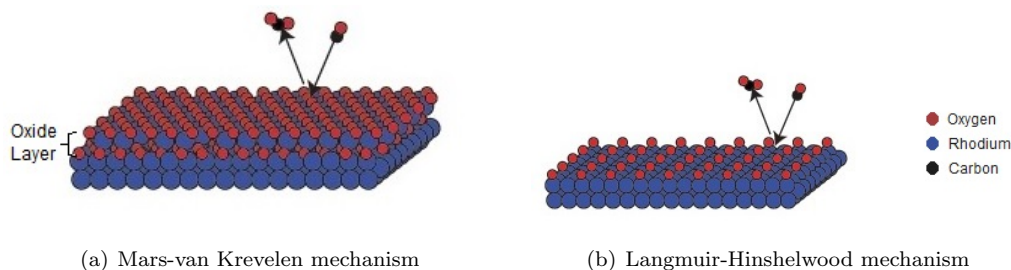


Figure 1: Illustration of (a) the Mars-van Krevelen mechanism and (b) the Langmuir-Hinshelwood mechanism.

1.2 Oxide structures on Rh(100) and Rh(111)

Surface oxide formed on both Rh(100) and Rh(111) surfaces when the sample is exposed by pure oxygen molecules, has been reported before and is known to be a RhO_2 layer with a $c(8 \times 2)$ and (9×9) surface structures respectively (for explanation of Wood's notation see the respective subsection in the section Method). Rhodium has a fcc crystal structure and therefore the (100) surface will have a square structure with in-plane lattice constant of 2.69 \AA and the (111) surface has a hexagonal structure with an in-plane lattice constant of 2.69 \AA . Note that both (100) and (111) have the same lattice constant despite being two different structures. The $c(8 \times 2)$ and (9×9) structures are illustrated in figure 2.

As mentioned above, a surface oxide may also form in a reactive mixture of CO and O_2 . The corresponding structure has not been studied in as much detail as when the surface is exposed to pure O_2 . Therefore there are some interest to see if there are some similarities or differences between the oxide layers in the two different cases. This is the purpose and goal for this thesis work.

2 Method

In this section the methods used for this thesis are presented. The section is divided into three subsections where one is about the concepts used and needed to understand and perform the analysis. The second subsection is the experimental method used to collect the data. The third subsection will deals with the analysis of the data.

2.1 Important concepts

2.1.1 The Bravais & reciprocal lattice

The Bravais lattice is a useful concept to describe a crystal. The definition of the Bravais lattice is an array of points in space, arranged such that any vector

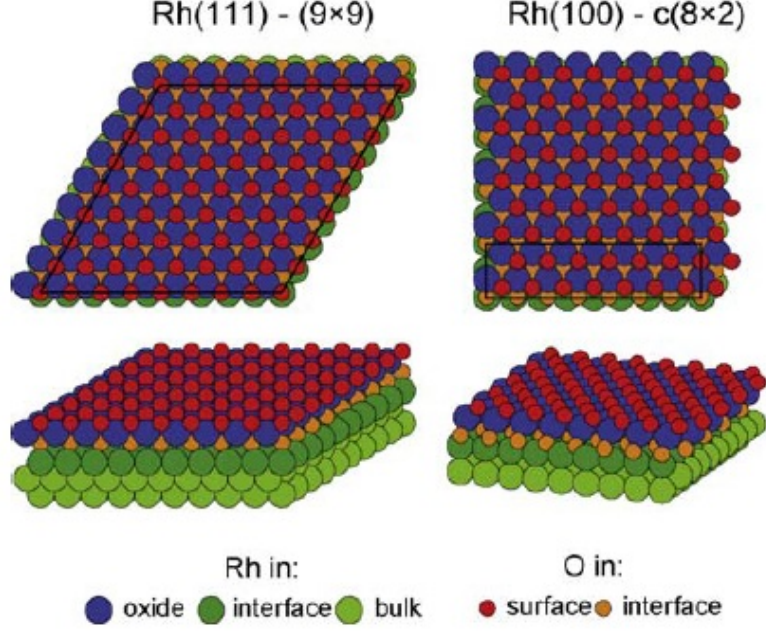


Figure 2: The structure of the surface oxide on Rh(111) and Rh(100). The black lines show the (9×9) and $c(8 \times 2)$ structure. Note the hexagonal structure of the surface oxide for both Rh(100) and Rh(111). The surface oxide in the Rh(100) is not exactly hexagonal but slightly stretched in order to fit the substrate. The figure is taken from ref. [2]

$$\vec{R} = m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3,$$

where m_1 , m_2 and m_3 are integers, connects two lattice points [8, 9]. \vec{a}_1 , \vec{a}_2 and \vec{a}_3 are the vectors spanning the Bravais lattice. In order to describe a crystal, each of these lattice points are connected to one or more atoms, arranged in a so-called basis. Note that to describe a crystals overall structures and periodicity, we only need to define the basis vectors (length and direction) and the basis. To describe a surface one often uses \vec{a}_1 and \vec{a}_2 as the in-plane vectors that span the surface lattice and \vec{a}_3 as the vector perpendicular to the surface.

Unit cells are is often used to describe the Bravais lattice. A unit cell is a region in the Bravais lattice that, if translated to a specific subset of Bravais lattice vectors, will fill up all the Bravais lattice, or surface. It is therefore convenient to talk only about the unit cell. The unit cell is chosen such that it reflects the periodicity of the crystal or surface that is studied.

Another useful concept in surface science is the reciprocal lattice, which will be used throughout this thesis. For a Bravais lattice the reciprocal lattice is defined as all points connected by vectors

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3,$$

with

$$\vec{a}_i \cdot \vec{b}_j = 2\pi\delta_{ij} \Leftrightarrow |\vec{a}_i| |\vec{b}_j| \cos\theta = 2\pi\delta_{ij}, \quad (1)$$

and h , k and l being integers [8, 9]. θ is the angle between the two vectors. An alternative way to describe it is that the reciprocal lattice is the Fourier transform of the Bravais lattice. For an infinite crystal, the reciprocal lattice will be defined as above. One often assumes that the crystal is infinite when constructing the reciprocal lattice.

Note the kronecken symbol in equation (1) above. If i and j are not the same the right-hand side of equation (1) will be zero. But the left-hand side has only one term that can be zero, the cosine function. This implies that the angle between the two vectors have to be 90° for equation (1) to make sense. If the direction of every vector in \vec{R} is known one can figure out the directions of all the vectors in

\vec{G} by using that the vectors with different i and j are perpendicular to each other. The same is also true for the opposite case, i.e. if one knows all the vectors in \vec{G} one knows the real space lattice vectors.

As an example the reciprocal lattice for the Rh(100) and Rh(111) surfaces (two dimensional Bravais lattices) are determined. Rh(100) has a square structure, i.e \vec{a}_1 and \vec{a}_2 are perpendicular to each other. As mentioned above equation 1 said that \vec{a}_1 and \vec{a}_2 respective reciprocal vectors, \vec{b}_1 and \vec{b}_2 , should be perpendicular to the other Bravais vector. But the Bravais vectors are already perpendicular to each other and therefore the reciprocal lattice vectors will be parallel to there corresponding Bravais vector. This will give a square reciprocal lattice. The length of the reciprocal lattice vector is then $b=2\pi/a$. Rh(111) is hexagonal, \vec{a}_1 and \vec{a}_2 is often chosen to have a 120° angle between them. One knows that \vec{b}_1 has to be perpendicular to \vec{a}_2 which will give a angle of 30° between \vec{b}_1 and \vec{a}_1 . The same is true for \vec{a}_2 . Note that the length of the reciprocal vectors are now $b=2\pi/a \cdot \cos 30^\circ$. This is illustrated in figure 3. The length of the reciprocal vectors is always proportional to the invers of the length of the real lattice vector. This gives that large distances in real space are small in reciprocal and vice versa.

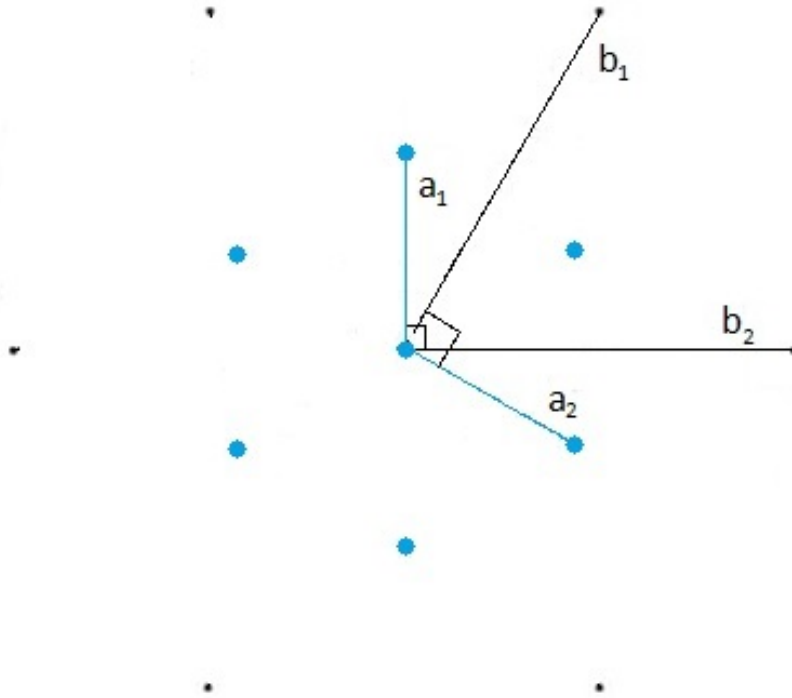


Figure 3: A two dimensional hexagonal Bravais lattice with its reciprocal lattice. The real Bravais lattice is in blue and the reciprocal lattice in black. Note that the reciprocal lattice is also hexagonal but rotated 90° . This is always the case for two-dimensional lattices.

If the scalar product between the Bravais lattice vector and the reciprocal lattice vector is calculated it becomes

$$\vec{R} \cdot \vec{G} = (m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3) \cdot (h \vec{b}_1 + k \vec{b}_2 + l \vec{b}_3) = hm_1 \vec{a}_1 \cdot \vec{b}_1 + km_2 \vec{a}_2 \cdot \vec{b}_2 + lm_3 \vec{a}_3 \cdot \vec{b}_3 = 2hm_1\pi + 2km_2\pi + 2lm_3\pi = 2\pi(hm_1 + km_2 + lm_3) = 2\pi M.$$

Because h , k , l , m_1 , m_2 and m_3 are integers, M has to be an integer as well. This can be written equivalently as

$$e^{i\vec{R} \cdot \vec{G}} = 1. \quad (2)$$

The expression above will be useful in the discussion of X-ray diffraction below.

2.1.2 Surface Structures

In surface science one often deals with overlayers on a well defined substrate surface, as in the case with the surface oxide. Therefore it is convenient to have a notation to describe the overlayer unit cell, or periodicity, in a simple way. An often used notation is Wood's notation, which relates the unit cell of the overlayer to that of the substrate. Wood's notation in simple form is

$$p \left(\frac{|\vec{a}_{o1}|}{|\vec{a}_{s1}|} \times \frac{|\vec{a}_{o2}|}{|\vec{a}_{s2}|} \right) R\theta, \quad (3)$$

where p specifies if the overlayer lattice is primitive or centered, where c is centered and p primitive [10]. If the surface overlayer lattice is primitive the "p" is often not written. \vec{a}_{oi} and \vec{a}_{sj} are the surface lattice vectors for the overlayer and substrate respectively. $R\theta$ specifies if the overlayer unit cell is rotated with respect to the unit cell of the substrate. One should note that this notation works only if both the vectors spanning the unit cell of the overlayer are rotated by the same angle with respect to the vectors of the substrate. If there are no rotation it is often omitted from the notation. A more general way is a matrix notation where the vectors of the overlayer is written as a linear combination of the vectors spanning the substrate lattice. But the matrix notation is rarely used and therefore not considered in this thesis.

The unit cell of the substrate is often well known and therefore the vectors of the substrate is not any problem when constructing the Wood's notation. But the unit cell of the overlayer can be defined in several ways. It can even be defined so that Wood's notation does not work. Therefore the overlayer can be written in the Wood's notation in several ways. The most convenient way to write the overlayer such that it reflects the periodicity and that the fraction between the vectors of the overlayer and the substrate are integers, if possible.

To illustrate the Wood's notation the case of the surface oxide layer on Rh(100) is considered (see figure 2). The overlayer structure is denoted $c(8 \times 2)$. The surface oxide has a slightly distorted hexagonal structure and one of the oxygen atom at the interface between the oxide layer and the substrate is on-top a rhodium atom. One of the vectors for the overlayer is parallel with one of the lattice vector for the rhodium surface. In figure 2 the parallel vectors are in the horizontal direction. The overlayer will have a coincidence of every seven interface oxygen atoms and every eight substrate rhodium atoms. This will give a periodicity of seven oxygen atoms, or RhO_2 units. There will also be a coincidence in the vertical direction for every second rhodium atom. Therefore the overlayer unit cell will have the vectors $\vec{a}_{O1} = 8\vec{a}_{s1}$ and $\vec{a}_{O2} = 2\vec{a}_{s2}$. This is illustrated with a black line in figure 2. It is not clearly seen in figure 2 but the atoms in the corners of the black rectangle and the atom in the center of the rectangle are equivalent. Therefore the Wood's notation is $c(8 \times 2)$. Note that because of symmetry of the substrate, the overlayer can be rotated by 90 degrees to give a $c(2 \times 8)$ as well. This is referred as domains. Different domains on the surface will be taken into account in the quantitative analysis.

2.1.3 X-ray Diffraction

A widely used method to determine crystalline structures is X-ray diffraction. In basic principles the incoming X-rays scatter elastically in different directions from the atoms in the crystal and in some directions the scattered X-rays will interfere constructively and in others destructively, resulting in a diffraction pattern. The usability of X-ray diffraction lies in the conditions for the constructive interference, which connects the diffraction pattern to the crystal structure.

In order to find the conditions for constructive interference, we start by considering two atoms as in figure 3 [8]. The incoming X-rays are assumed to be plane waves, with wave vector \vec{k} and the detector which will observe the X-rays is far away, so that the detected x-rays are also plane waves. If the waves are scattered in the same direction and observed far away, the path difference between waves scattered by the two atoms will be

$$d' + d = R \cos \theta + R \cos \theta' = -\frac{\vec{R} \cdot \vec{k}}{k} + \frac{\vec{R} \cdot \vec{k}'}{k} = \frac{\vec{R} \cdot \Delta \vec{k}}{k}, \quad (4)$$

where $k = 2\pi/\lambda$ is the length of the wave vector (which is the same for \vec{k}' and \vec{k}). If the difference between the length travelled is equal to an integer times the wave length the two waves will be in phase and interfere constructively, which will give

$$\frac{\vec{R} \cdot \Delta \vec{k}}{k} = n\lambda \iff \vec{R} \cdot \Delta \vec{k} = nk\lambda = \frac{2n\pi\lambda}{\lambda} = 2\pi n, \quad (5)$$

where n is an integer and the relation $|\vec{k}| = \frac{2\pi}{\lambda}$ is used. This can be equivalently rewritten as

$$e^{i\vec{R} \cdot \Delta \vec{k}} = 1. \quad (6)$$

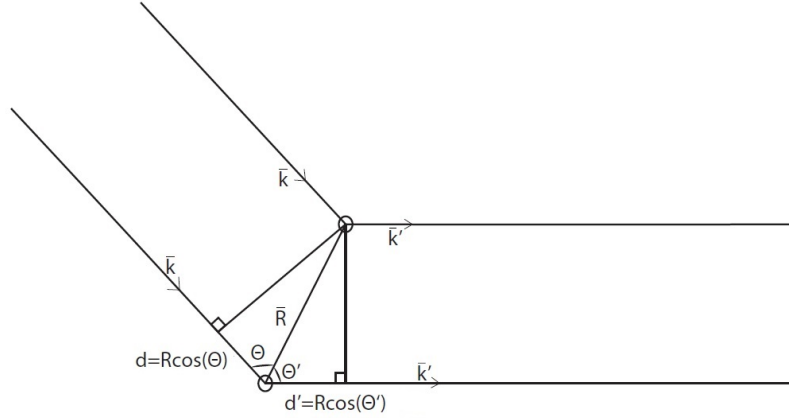


Figure 4: A plane wave scatters from two atoms in the same direction. The resulting plane wave will have a wave vector of \vec{k}' but with the same length as \vec{k} . The plane wave will hit one atom first and have to travel a distance of d to be scattered from the second atom. There will also be a distance difference, d' , between the two scattered waves to the detector.

In order to get constructive interference from the whole lattice relation (4) should hold for all Bravais vectors of the reciprocal lattice. Therefore relation (4) can be recognized as the same as relation (2), with $\Delta \vec{k} = \vec{G}$. In other words the change in the wave vector has to be equal to a reciprocal lattice vector for constructive interference to occur, which is called the Laue condition. The reciprocal lattice vector can from equation 2 be interpreted as a wave vector giving the periodicity of the Bravais lattice. Therefore the diffraction pattern gives the periodicity of the crystal.

The Laue condition gives the interpretation of the diffraction pattern. The intensity peaks in the diffraction pattern are the reciprocal lattice points. Therefore the reciprocal lattice can be determined by X-ray diffraction and thereby the structure of the crystal can be determined.

One important view of the Laue condition is the Ewald sphere. Because the scattering is elastic the length of the out-going wave vector is the same as that of the in-going wave vector. This will cause the change in wave vector to lie on a sphere with radius equal to the size of the wave vector. If this is imagined in reciprocal space the points that lie on the boundary of the sphere will fulfil the Laue condition and thereby appear in the diffraction pattern, see figure 5.

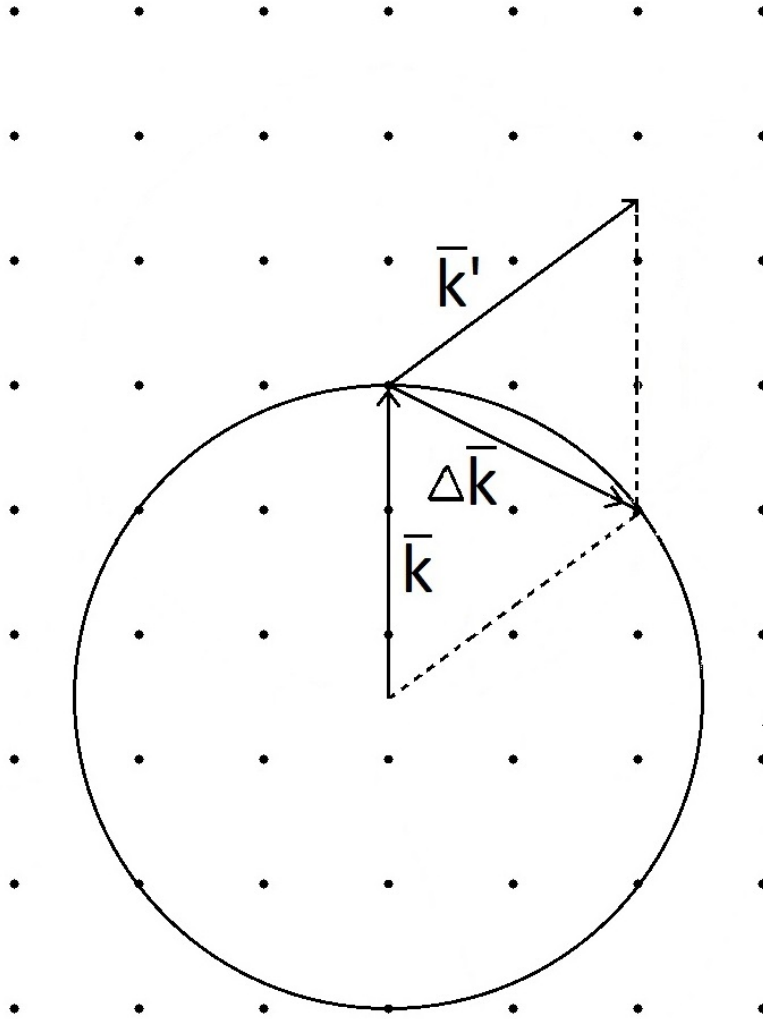


Figure 5: The grid is a reciprocal lattice with a quadratic structure. \vec{k} is the incoming X-ray. \vec{k}' is the out-going scattered X-ray, which is detected, and $\Delta\vec{k}$ is the change in momentum between the incoming and out-going X-ray. The circle is the Ewald sphere in two dimensions. Note that $\Delta\vec{k}$ is equal to a reciprocal lattice vector

2.1.4 Surface X-ray Diffraction

When a surface is studied the method used has to be sensitive to the uppermost layers. But X-rays interact weakly with matter and therefore most of the signal comes from the bulk. For X-ray diffraction to be useful for surface science the signal from the surface of the material has to be maximized so that it can be measured with good statistics.

To obtain the surface sensitivity the incoming X-ray is directed to hit the surface at a grazing angle. Therefore the bulk atoms will not contribute to the signal in any severe way. In this way the X-ray diffraction can be surface sensitive. This is referred to surface X-ray diffraction.

As mentioned above the diffraction pattern of a crystal is an image of the crystals reciprocal lattice. The reciprocal lattice can be seen as a Fourier transform of the crystal lattice and if the crystal lattice have an infinite number of lattice points the Fourier transform will consist of delta functions with peaks at the points of the reciprocal lattice. But if the number of lattice points are finite the reciprocal lattice will be smeared out between the points. This will correspond to finite intensity between the peaks in the diffraction pattern.

The surface of a crystal can be approximated as an infinite lattice and therefore give delta peaks

parallel to the surface of the crystal. Therefore the (h,k) plane in the reciprocal space will look like the reciprocal lattice of an infinite two dimensional crystal lattice. But because surface X-ray diffraction measures a finite number of layers the reciprocal lattice will have "rods" of continuous intensity between the Bragg reflections perpendicular to the surface, as seen in figure 6b. These rods are referred to as crystal truncation rods (CTR). So the measured diffraction will have delta peaks in the (h,k) plane and non-zero intensity in the l direction between these peaks.

For a perfect surface only the CTR will be present. When other structures appear on the surface, which have different periodicity, additional rods will appear, see figure 6c. These rods are called super-structure rods (SR) and will be perpendicular to the overlayer.

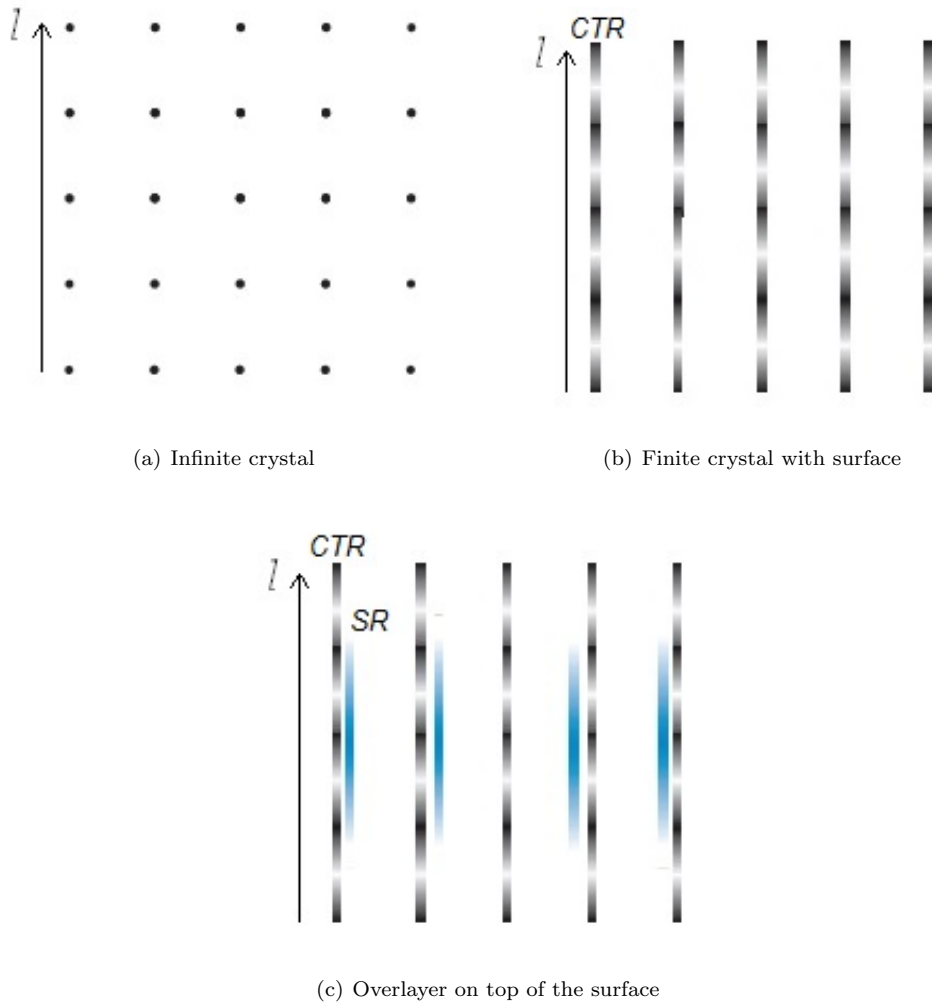


Figure 6: (a) is the diffraction from an infinite crystal, (b) is the diffraction with a surface and (c) is when a overlayer is on top of the surface. The vertical line indicates the direction of l . SR stands for Super-structure Rods.

2.2 Experimental Method

In this subsection the experimental method will be introduced briefly. The sample is first mounted in the chamber. Often there are unwanted contaminations at the surface, which are removed by so-called Ar^+ sputtering, i.e., bombarding of the surface with Ar ions [10]. The sputtering causes the surface to become rough. This is fixed by annealing (heating) the sample. With the higher temperature the atoms have more energy to rearrange themselves and form a smooth surface [10]. The process of sputtering and

annealing is repeated several times. The sample is further cleaned by running the CO oxidation reaction under varying conditions, such that the surface switches between low and high activity.

The X-ray beam is then directed to hit the surface at a grazing angle. The sample is then rotated to find the Bragg reflections. Where the Bragg reflections appear on the detector lead pieces are placed. This is because the Bragg reflections are too intense and would finally break the detector.

The surface oxide is created by adjusting the gas flow such that it is rich in O₂ and increasing the temperature such that the surface is catalytically active. When the surface oxide appears the sample is rotated around its z -axis (the axis normal to the surface) while continuously recording detector images, see figure 7. In conventional surface X-ray diffraction experiments, only a small part of reciprocal space is measured simultaneously, and in order to probe a certain point one has to rotate the sample and move the detector to the corresponding direction for the outgoing beam. With high energy X-rays, as used in this work, the diffraction angles shrink and can be detected using a stationary two-dimensional detector [1]. In this case a large part of reciprocal space can be explored by only rotating the sample.

A reference measurement of a metallic surface is performed by changing to a CO rich gas flow. The measurement of the reciprocal lattice will be similar to the case of the oxide surface.

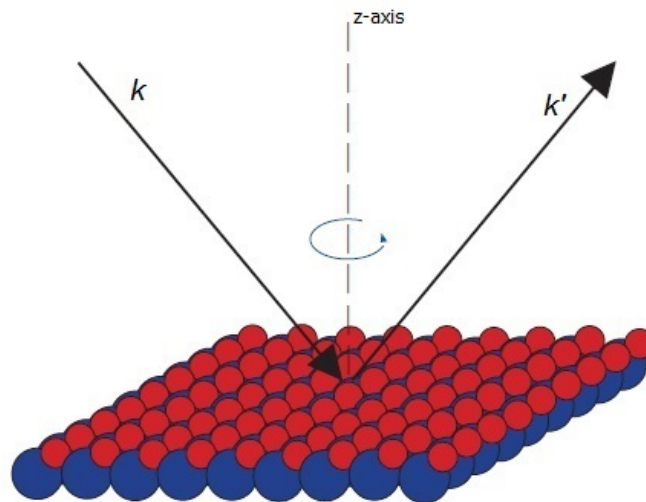


Figure 7: An X-ray is diffracted on the surface and detected by a two dimensional detector(not shown in the figure). The surface is rotated around its normal (z -axis).

2.3 Analysis method

In this subsection the method for analyzing the data is presented. As mentioned before, the main part of this project is a qualitative analysis of the surface oxide structure, but an attempt with quantitative analysis was made as well. The qualitative analysis is done by a visual inspection of the images collected by the detector, or combined detector images. The quantitative analysis has been done by comparing the measured rods with theoretically calculated rods.

2.3.1 Qualitative Analysis

In the qualitative analysis, a program called ImageJ with a plugin for High Energy Surface X-ray Diffraction analysis (HESXRD), written by M. Shipilin, is used [16]. The main usage of the program in the qualitative analysis mode is the creation of combined detector images and in-plane projections of the data.

The combined detector image is a combination of all the images taken during a rotation of the sample, such that each pixel is represented by its highest intensity throughout the rotation. An example is shown in figure 8. The horizontal direction will be the distance from the axis around which the sample is rotated. The vertical direction will be the perpendicular to the surface. From the image one cannot distinguish between the rods that have the same distance to the origin in the (h,k) plane and therefore some of the CTR:s and superstructure rods can overlap each other in the image. But when the superstructure rods are found at another distance from the origin than the CTRs the combined detector image can be a quick and simple way to determine the length of the lattice parameter of the overlayer, if the structure is already known.

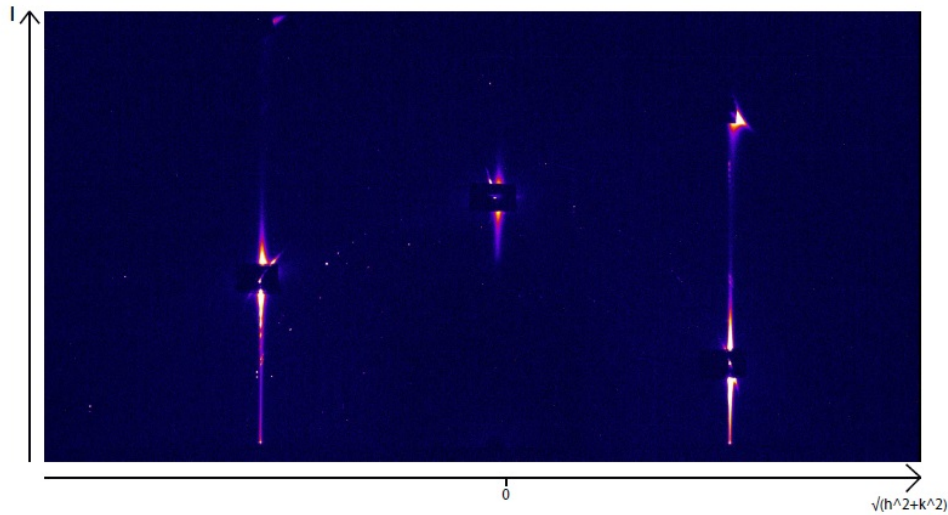


Figure 8: Stack to total image of a Rh(111) surface. The x -axis is the distance from origo in the plane (h,k) . Note that the left-hand side of the origo in the x -axis are the mirror image of the right-hand side. The vertical axis is the l -axis. The scale of the l -axis can be determined by knowing where the Bragg peaks occur. Note that the CTR:s that cuts the Bragg reflections are perpendicular to the (h,k) plane.

Most important for the qualitative analysis are the in-plane projection images. To create the in-plane projection images the program adds the nearby rows at a specific l -value from the detector images. It then assembles all the added rows from the different images, at different angles, such that the (h,k) plane is created at a specific l -value, see figure 9. In this figure and the following ones, the Reciprocal Lattice Unit (RLU), i.e. the units of the reciprocal vector, is used.

The importance of the in-plane projection images is that reciprocal lattice in the (h,k) plane for the overlayer can easily be determined. One can easily distinguish the rods with the same distance to the center. Because the plane that is seen is parallel to the surface, the in-plane projection can be directly compared to LEED patterns.

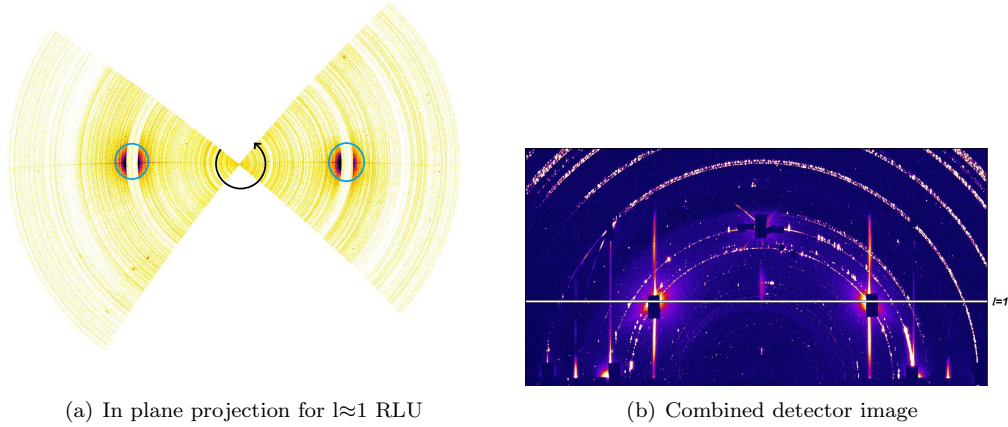


Figure 9: (a) In plane projection at $l=1$ RLU. The blue circles are the Bragg reflections in. (b) shows a combined detector image for the metallic Rh(100) surface. The white line in indicates where $l=1$ RLU.

2.3.2 Quantitative Analysis

The qualitative analysis only gives information about the overall surface structures. But it does not give the exact positions of the atoms in the unit cell. Neither will the qualitative analysis give information about the compositions of the overlayer. To get a detailed description of the surface one has to analyze the rods. The rods are sensitive to the positions of the atoms and the type of atoms, e.g. rhodium or oxygen atoms. Therefore the rods will be sensitive to any relaxations of the atoms from the perfect periodic surface [11].

In diffraction theory the fundamental property that will determine the diffraction intensity from an investigated crystal, is structure factor, F . The integrated intensity from the experiment is proportional to the square of the structure factor [11]. The relation between the structure factor and integrated intensity is described in ref [1] as

$$I = a | F_{jkl} |^2 C_{tot},$$

where a is a constant dependent on the material. C_{tot} is a correction factor and is written as

$$C_{tot} = C_{hp} C_L C_{rod} C_d C_i.$$

Here C_{hp} is the horizontal polarization correction factor and can be set to one for synchrotron light. C_L is the Lorentz correction factor, C_{rod} is the interception factor, C_d is the in-plane detector acceptance and C_i is the beam inclination factor. The derivation and description of all the corrections factors can be found in [13].

To extract the structure factors from the experimental data the program ImageJ is used together with the HESXRD plugin mentioned above. The program extracts the intensity from the rods and calculates the structure factors with taking the corrections into account.

As mentioned above the qualitative analysis is performed by comparing the measured rods with theoretically calculated rods. The theoretical rods are calculated in the program ANA-ROD [15]. For the program to be able to calculate the structure functions of the rods a model of the surface has to be created as a in-pup file. From the qualitative analysis and previous knowledge about the system one can create a model to begin with. One often creates several layers of atoms in the input file and the program translates it to create a "infinite" system. The atomic positions in the model have to be written in the terms of a appropriate unit cell.

There are many unit cells that can be used to create the surface but some will work better for ANA-ROD compared to others. This is because of the calculations work better with rods in integer positions in reciprocal space, i.e. h and k are integers. The unit cell can be defined such that all the rods will be placed at integer h and k . There are several such unit cells but it is convenient to choose the smallest possible unit cell, which satisfies the requirement.

Often the atoms in the perfect model of the surface are moved/relaxed into a new position to minimize the energy. Therefore the rods calculated from a perfect model will not match the experimental rods. The atoms can be moved by the program in order for the calculated and experimental rods to match. For such a fit to be successful, it is important to minimize the number of free parameters. Depending on the system, certain atoms will have similar environments, which make them move in a similar way. Hence, their movements can be described by a single parameter. The symmetry can be different for the x , y and z direction, which has to be considered.

Different domains can be present on the surface. This has to be taken in consideration when calculating the rods. One should note that domains can change the smallest possible unit cell that gives rods at integer positions. Therefore when constructing the unit cell for the input files the domains have to be considered.

3 Result

3.1 Qualitative Analysis

3.1.1 Rh(100)

The sample is cleaned as described in the method section. A highly active surface oxide is then prepared by exposing the sample to a gas flow with 5 ml/min O₂, 0.5 ml/min CO and 44.5 ml/min Ar at a sample temperature of about 300°C. A HESXRD measurement is performed with a rotation of the sample over 90° in steps of 0.1°. The surface is then cleaned from the surface oxide by changing the gas flow to 2 ml/min O₂, 4.5 ml/min CO and 40.5 ml/min Ar, which also resulted in a drop in activity. Another measurement is done as above and the results of both measurements are shown in figure 10.

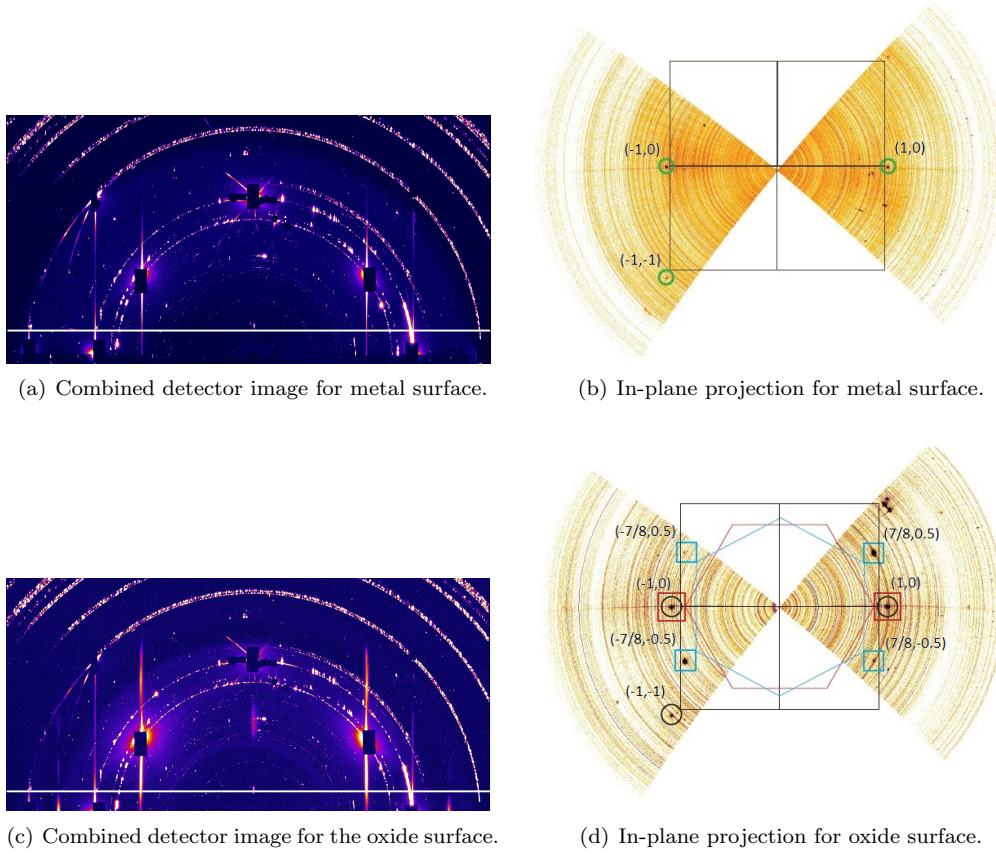


Figure 10: (a) and (b) refer to the (inactive) metallic surface and (c),(d) to the oxide surface. The white line at $l=0.4$ in (a) and (c) show where the cut was performed. In (b) the black squares show the structure of the substrate and the green circles show the CTR:s from the substrate. In (d) the black squares and circles originate from the substrate, while the blue and red hexagons arise from the structure of the overlayer. The red and blue small squares are SR:s from the overlayer.

Figure 10a and b show the combined detector images and the in-plane projection at $l = 0.4$ respectively. The Rh(100) surface has a square surface structure, which will give a square reciprocal surface lattice as discussed in section 2.1.1. Therefore the CTR:s should be oriented in a square pattern in the (h,k) plane (in-plane projection). It is then straight-forward to identify the different CTRs, which define the basis for further analysis of the surface oxide. The reciprocal surface lattice of Rh(100) is shown on top of the experimental data in figure 10b.

As mentioned in the introduction, the surface oxide on Rh(100), when the surface is exposed to pure oxygen, is a hexagonal structure that gets a $c(8 \times 2)$ coincidence with the square substrate. The reciprocal lattice of the overlayer is then also hexagonal. The $c(8 \times 2)$ structure will have two superstructure rods coinciding with the $(1,0)$ and $(-1,0)$ CTRs [6]. In addition, the hexagonal structure can be rotated by 90° on the four-fold rotation symmetric substrate, so that the corresponding rods of this second domain will coincide with the $(0,1)$ and $(0,-1)$ CTRs. This is shown in figure 10d, where the blue and red hexagons show the orientation of the two oxide domains. Because the substrate has a square structure and the surface layer has a hexagonal structure the ratio between the in plane lattice parameters of the two structures are

$$\frac{a_{oxide}}{a_R} = \frac{b_R}{\cos 30 * b_{oxide}} = \frac{2}{\sqrt{3}} \iff a_{oxide} = \frac{2a_R}{\sqrt{3}},$$

where a_{oxide} and a_R is the lattice parameter for the oxide overlayer and substrate respectively. The b_{oxide} and b_R are the length of the reciprocal lattice vectors for the overlayer oxide and substrate respectively. Because there are a coincidence at $(-1,0)$ and $(1,0)$ both b_{oxide} and b_R can be defined as the half distance between the two points. The ratio between the reciprocal lattice vectors is therefore one. Note that

the angle between a_{oxide} and its respective reciprocal lattice vector is 30° to satisfy eq. 1. With $a_R = 3.80/\sqrt{2} \approx 2.69 \text{ \AA}$ the surface oxide lattice parameter is $a_{Oxide} \approx 3.10 \text{ \AA}$.

A lattice parameter of 3.10 \AA will agree well, but not perfectly, with the $c(8 \times 2)$ surface structure. For a perfect agreement, the hexagon has to be distorted slightly as mentioned in figure 2. If the surface oxide would have been perfectly hexagonal, the line between the rods at $(7/8, 1/2)$ and $(-7/8, -1/2)$ should be aligned with the line between the rods of the other domain at $(3/2, 7/8)$ and $(-3/2, -7/8)$, but they differ by an angle of about 0.5° . Although the accuracy is not great, Figure 11 indicates that there is a distortion, in good agreement with a structure of $c(8 \times 2)$ as expected. The change of the hexagonal pattern cannot be directly determined by figure 11 alone because of low accuracy, but one can assume that it adopts the $c(8 \times 2)$ structure.

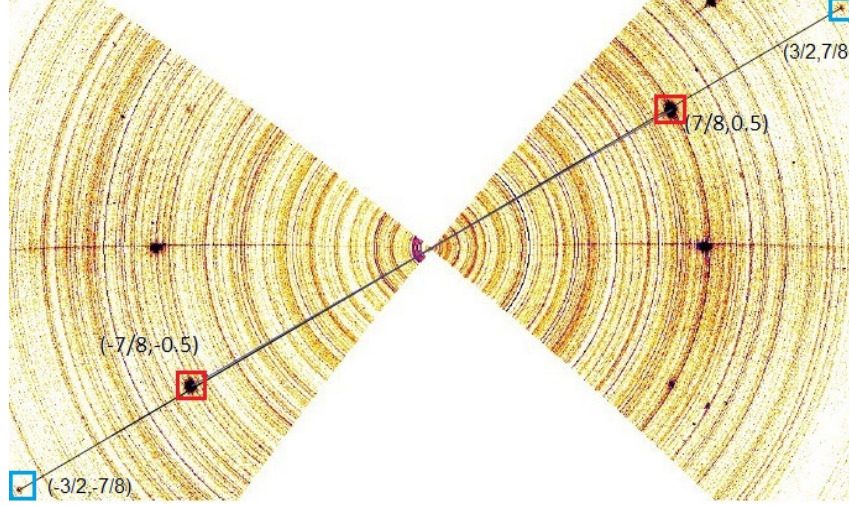


Figure 11: The figure shows two lines drawn between the points at $(3/2, 7/8)$ and $(-3/2, -7/8)$ and the points at $(7/8, 1/2)$ and $(-7/8, -1/2)$ respectively. If the two lines would coincide we would have a perfect hexagonal overlayer structure.

3.1.2 Rh(111)

As for Rh(100), measurements of the metallic Rh(111) was done in a CO rich gas flow (1.5 ml/min O_2 , 4 ml/min CO and 44.5 ml/min Ar at about $325^\circ C$), and of the surface oxide after increasing the O_2 flow to 3 ml/min, making the flow O_2 rich. Also as before the activity was high for the oxidized surface and lower for the metallic surface. This time the measurements were performed over a very short range of angles, just covering two CTRs as shown in figure 12.

The surface oxide shows up as the superstructure rods just inside the CTRs in figures 12c and d. In figure 12d the oxide hexagonal is smaller than the substrate in reciprocal space which would mean the opposite in real space. From the figures it is straight-forward to measure the ratio between the reciprocal lattice vectors b_O (of the oxide) and b_R (of the Rh substrate). b_O and b_R can be defined as the half distance between the two STs rods and the two CTRs rods respectively. The ratio between them then becomes $b_R/b_O = 1.14 \approx 8/7$. Since both the surface oxide and the substrate, in this case, are hexagonal, this directly shows that there is a coincidence between eight Rh cells and seven oxide cell, which gives an (8×8) structure. The corresponding in-plane lattice constant for the surface oxide is $a_O = 1.14 \times a_R = 1.14 \times 3.80 = 3.07 \text{ \AA}$.

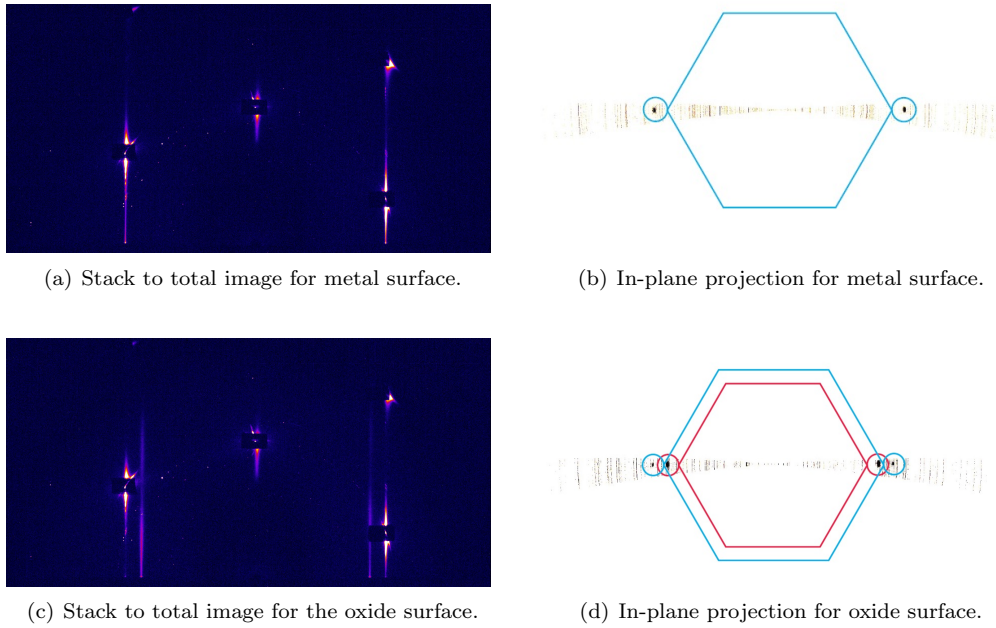


Figure 12: (a) and (b) represent the (inactive) metallic surface and (c),(d) the oxide surface. (b) shows the hexagonal substrate. The blue hexagon is the metallic surface and the red hexagon is the surface oxide. In (d) the oxide overlayer appears which is consistent with a hexagonal pattern.

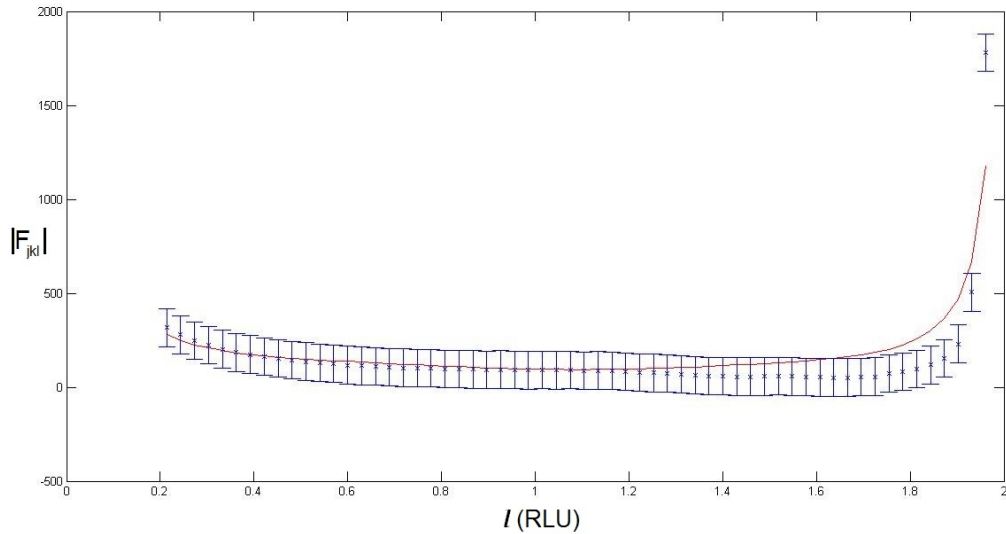
When the Rh(111) surface is exposed to pure oxygen the surface oxide has a (9×9) coincidence structure with a lattice parameter of 3.02 \AA [5]. The surface oxide on Rh(111) is then different when the surface is exposed to a reactive mixture of CO and O_2 or pure O_2 . Note that there was no difference in the case of Rh(100).

3.2 Quantitative Analysis

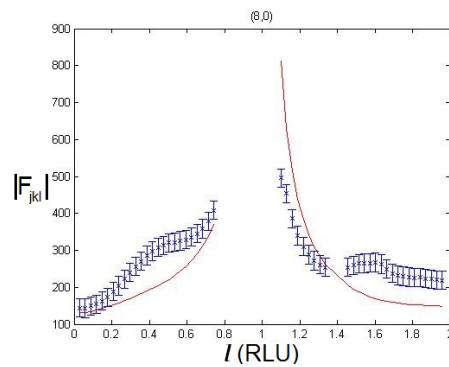
3.2.1 Rh(100)

The model used for the calculations is a square (8×8) unit cell. The $c(8 \times 2)$ unit cell in ref. [6] is used to create the (8×8) unit cell. The (8×8) unit cell is just four $c(8 \times 2)$ unit cells. This is done because different domains exist on the surface. There are four domains present rotated 90° to each other. Because of this the smallest unit cell which will give rods at interger h and k is the (8×8) . The positions of the atoms in the model can be seen in ref. [6].

The quantitative analysis is not finished yet. The calculated rods do not fit yet with the data as seen in figure 13.



(a) (8,8)



(b) (8,0)

Figure 13: (a) shows the calculated rod with the data for (8,8). (b) shows the calculated rod with the data for (8,0). The y -axes are the structure factors of the rods and the x -axes are l in RLU. The solid lines are the calculated rods and the x are the data. The error bars do not give the real error but are there for calculation reasons.

4 Discussion

A surface oxide has been found to form on rhodium surfaces during high catalytic activity for CO oxidation. In this thesis work, the structure of the surface oxides formed on Rh(100) and Rh(111) in a mixture of CO and O₂ has been investigated. More specifically, high-energy surface X-ray diffraction data acquired at beamline P07, PETRA III, DESY in Hamburg have been analyzed, and the results have been compared to the surface oxide structures formed in pure O₂.

4.1 Rh(100)

In contrast to the result of Rh(111), the results from Rh(100) are in good agreement with the surface oxide formed to pure O₂. In both cases a surface oxide with a $c(8 \times 2)$ structure is formed and most probably they both have the structure of a trilayer RhO₂. In order to say for sure, however, a quantitative analysis is needed. Within this work, quite an effort has been put in to do this, but there have been a few problems and the final result is not there yet.

As support for the above interpretation, however, Pd(100) has been studied in detail both in pure O₂ and a reaction mixture of O₂ and CO, and it has been found that the same surface oxide is found in

both cases [1, 14]. It is therefore likely that the surface oxide is similar on Rh(100) in a mixture of CO and O₂ as in pure O₂

4.2 Rh(111)

The surface oxide created on Rh(111) under exposure of CO and O₂ differs from the surface oxide when only the surface formed in pure O₂. The surface oxide is (8 × 8) for the gas mixture instead of (9 × 9) in O₂. DFT calculations are consistent with the (8 × 8) surface oxide [5]. For both cases the surface oxide has a hexagonal pattern but the lattice constant for the gas mixture is slightly larger (3.07 Å) than for pure oxygen (3.02 Å). The lattice parameter for the gas mixture is more similar to that lattice constant of the surface oxide on Rh(100) and also agrees with previous DFT calculations. This could mean that the optimal hexagonal pattern has a lattice parameter around (3.07 Å).

The (9 × 9) surface oxide could exist because the smaller lattice parameter fits better with the substrate. Alternatively, the explanation can be that under pure oxygen more oxygen can be forced down when the hexagonal pattern shrinks. For the gas mixture defects are likely to exist on the surface. These defects would take away the need for more oxygen on the surface, and the oxide structure can adopt the optimal size.

5 Outlook

As discussed before the quantitative analysis has not been finished because of lack of time. Therefore a quantitative analysis of the surface oxide would be appropriate to continue with. There can be a difference between the surface oxide created on Rh(100) for the two gas contents. This difference would only be seen from a quantitative analysis but the description of the system is not complete. The same is true for Rh(111).

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