Operando SXRD : a new view on catalysis

Ackermann, M.D.

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IV: SXRD study of Pd single crystal surfaces as model CO oxidation catalysts

CO oxidation catalysts are nowadays widely used in industrial and automotive applications. In the near future they will also play a very important role in fuel cell technology, which is very sensitive to CO contamination. Through the use of in-situ Surface X-Ray Diffraction (SXRD) we were able to unravel the atomic structure of the catalyst surface during CO oxidation, under realistic pressure and temperature conditions for different Pd single crystal surfaces. From our results we find that for all Pd surfaces the most efficient reaction path is the so-called Mars-Van Krevelen mechanism which involves the oxidation of only the outermost atomic layers of the catalyst surface. This effect is in clear contradiction with what has commonly been assumed in the field of catalysis for many years, namely that oxide formation poisons the catalyst. Combining our results on surface roughness during the oxidation of CO with results obtained with High Pressure STM [10], we can confirm several aspects of a new model for so-called self-sustained oscillations proposed by Hendriksen et al [70].

4.1: Introduction

Surface Science has for many years been dominated by experiments performed in Ultra High Vacuum (UHV) conditions. These conditions allow scientists to control very accurately which molecules, and how many molecules interact with a very clean surface. This is of course advantageous when trying to understand the fundamental interaction of molecules with crystalline surfaces. A second advantage of UHV conditions (compared to ambient pressure conditions) is that electrons and ions have a long mean free path, allowing one to use techniques that require these long mean free paths (e.g. LEED, RHEED, LEIS, LEEM, XPS). In ‘real life’ catalysis however, all important processes of molecules interacting with a surface take place at elevated temperatures and at pressures typically within two orders of magnitude around 1 bar. Although it is customary to extrapolate low-temperature UHV results to more relevant pressure and temperature regimes, this approach does not do justice to the dominant role of kinetic barriers that can completely distort the naïve, thermodynamic picture. Because of the role of these kinetic barriers, conclusions can only be drawn from experiments performed under true reaction conditions, i.e. high temperatures and high pressures. We have used a High Pressure *SXRD* setup [48] which allows us to investigate model catalyst surfaces in a relevant pressure and temperature regime, while maintaining the fully detailed, atomic information familiar from UHV *SXRD* experiments. With this technique we have investigated two, respectively low- and high-index Pd single crystal surfaces. These surfaces have been exposed to high pressures of both O_2 and CO, serving as model CO oxidation catalysts. We demonstrate that under relevant pressure and temperature conditions, the outermost atomic layers of all investigated Pd surfaces oxidize under formation of PdO, and that this ultra-thin oxide layer is typically one order of magnitude more reactive than the CO- or O-chemisorbed Pd metal surface.

4.2: Pd(001) oxidation

The experiments were performed at the ID03 beamline of the European Synchrotron Radiation Facility (ESRF) in a combined UHV - high pressure *SXRD* chamber (10^{-10} mbar – 2 bar), which had a volume of ~ 2 liter and was equipped with a 360° beryllium window for entrance and exit of the X-Rays [48]. The sample could be heated up to 1300 K in vacuum. Connected to the chamber were a gas manifold with four high-purity gasses (CO better than 99.998% pure, all other gases better than 99.9996%) and a quadrupole mass spectrometer (QMS) for online gas analysis. The chamber was mounted on a z-axis diffractometer with the crystal surface in a horizontal plane.

A focused beam of monochromatic, 17 keV X-Ray photons was impinging on the surface at an angle of 1° (~ $4x10^{12}$ photons/s). The fluorescence radiation in the scattered beam was filtered with a crystal analyzer. For the experiments performed on the Pd(001) crystal we describe the Pd lattice with two perpendicular unit vectors $\mathbf{A_1}$ and $\mathbf{A_2}$ in the surface plane along $[110]$ and $[1\bar{1}0]$ respectively and the third one, $\mathbf{A_3}$, along the [001] surface normal. $|\mathbf{A_1}| = |\mathbf{A_2}| = a_0 = 2.751$ Å is the Pd nearest-neighbor distance; $|\mathbf{A_3}| = \sqrt{2}a_0 = 3.891$. In reciprocal space **H** and **K** are the unit vectors in the surface plane (parallel to $\mathbf{A_1}$ and $\mathbf{A_2}$ respectively) and **L** is along the surface normal. Well-ordered, clean Pd surfaces were formed by Ar^+-ion sputtering and annealing cycles.

4.2.1: Low pressure structures

The clean Pd surface was first heated in vacuum to 600 K and then exposed to 10^{-4} mbar of O_2. New diffraction peaks appeared in reciprocal space along the axes $\mathbf{H} = 2\cdot\mathbf{K}$ and $\mathbf{K} = 2\cdot\mathbf{H}$. Along both these axes peaks appear at $(\mathbf{H}\ \mathbf{K}) = n\cdot(0.4\ 0.8)$ or equivalently $(\mathbf{H}\ \mathbf{K}) = n\cdot(0.8\ 0.4)$ with n = 1,2,3… . Peaks also appear along the axes in the perpendicular directions, respectively $\mathbf{K} = -2\cdot\mathbf{H}$ and $\mathbf{H} = -2\cdot\mathbf{K}$ (figure 1, top left panel). These axes, and the peaks that appear along these directions span two equivalent domains of square reciprocal unit cells of dimensions 2.04 by 2.04 $Å^{-1}$. This maps into real space unit cells of 3.08 by 3.08 Å. The orientation and size of this unit cell is very close to that of a Pd surface oxide layer [71,72]. This surface oxide forms a commensurate $\left(\sqrt{5}\cdot\sqrt{5}\right)-R26.5^{o}$ structure, or in short the $\sqrt{5}$-structure. This structure has already been observed and carefully characterized by several techniques recently [71,72,73]. It is called a "surface oxide" as it contains both O and Pd atoms in the correct stoichiometry and shares the same in-plane symmetry and unit cell size, but differs in structure from the bulk PdO oxide [36]. As more layers of Pd(100) oxidize, this surface oxide transforms into bulk PdO [46,47]. We have measured the diffraction intensities of several Crystal Truncation Rods

(CTR's) of the surface oxide, both in-plane (figure 1, top right) and out-of-plane (figure 1, bottom left). The slow variation of the diffracted intensity as a function of out-of-plane momentum transfer **L** confirms that this surface oxide is only 1 single monolayer (ML) thick.

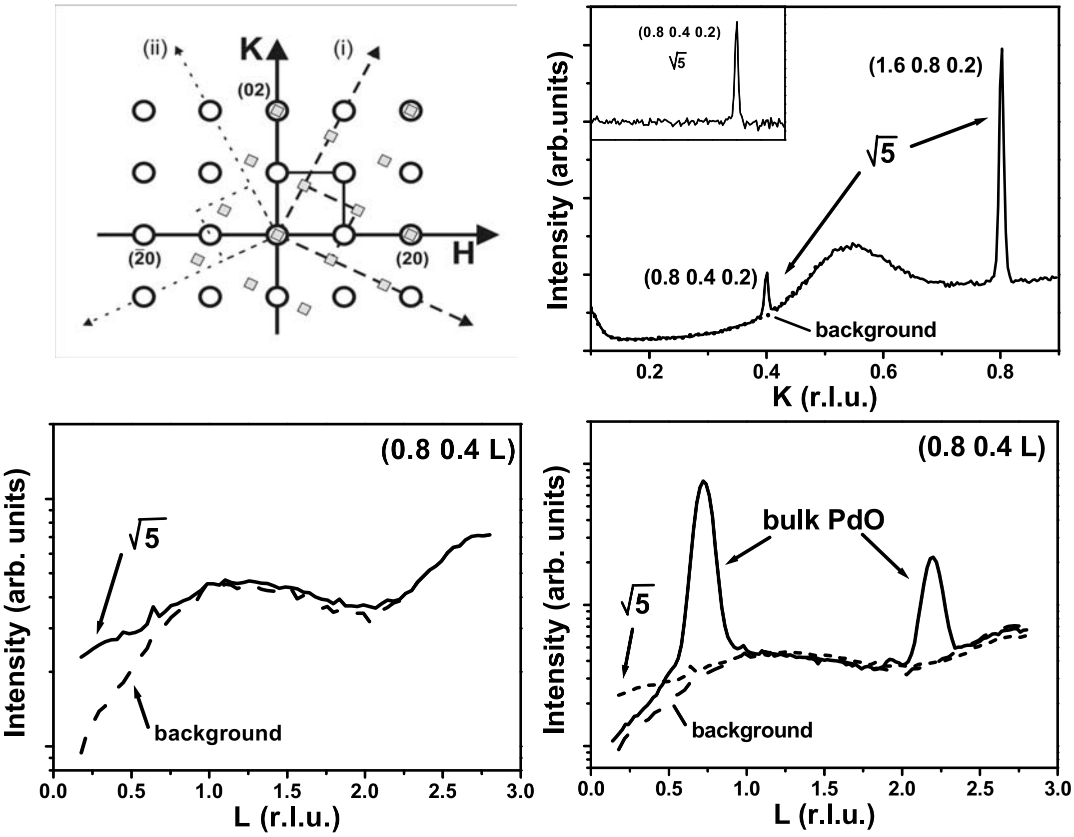

Figure 1: *left top: In-plane reciprocal space map of bulk terminated Pd(001) (circles, solid axes), and the* $\sqrt{5}$*-structure (grey squares, dashed axes for both possible rotations). The two equivalent domains are marked (i) and (ii). The axes are in reciprocal unit vectors of the Pd(001) substrate. Right top: In-plane diffraction peaks of the* $\sqrt{5}$*-structure. Top left insert is the same data from **K** = 0.1 to 0.5 with the background subtracted. Lower left panel: the out-of-plane diffraction intensity along (0.8 0.4 L) from the* $\sqrt{5}$*-structure at low pressure (*10^{-4} *mbar* O_2*, 600K) and the background intensity. Lower right panel: Out-of-plane intensity along (0.8 0.4 L) for the Pd(001) surface covered with a 6.4 monolayer thick slab of bulk-like PdO (500 mbar* O_2*, 600K). The* $\sqrt{5}$*-signal and background from the low pressure experiment have been added (to scale) to the right panel for comparison.*

4.2.2: Bulk-like PdO

The surface with the $\sqrt{5}$-structure, still heated to approximately 600 K, is then exposed to 500 mbar of pure O_2. The effect is that the intensities of the newly appeared crystal truncation rods of the surface oxide along the $\mathbf{H} = 2*\mathbf{K}$ and $\mathbf{K} = 2*\mathbf{H}$ axes change. The in-plane position of the reconstruction rods does not change in reciprocal space indicating that the size and orientation of the unit cell remains unchanged. The reconstruction rods however now show an increase in diffracted intensity and a strong variation of the intensity as a function of **L** (figure 1, bottom right panel). This shows that the superstructure has developed from the 1 ML-thick surface oxide to a thicker structure which comprises multiple atomic layers. The in-plane distance between the superstructure rods is still 2.04 $Å^{-1}$, mapping onto a real spaces a square unit cell of 3.08 x 3.08 Å. The strong variation of the diffracted intensity as a function of **L** of the superstructure rods. The distance between two peaks in the **L** direction is 1.16 $Å^{-1}$, which corresponds to a real distance of 5.4 Å. These dimensions are in very good agreement with the unit cell of PdO [74], with its c-axis parallel to the surface normal of Pd(001). We hence conclude that a layer of bulk-like PdO has formed on the surface under these circumstances, replacing the surface oxide structure. This is in accordance with earlier work of e.g. Lundgren *et al* [47]. The roughness, thickness and composition of this ultra-thin oxide film have been characterized by reflectivity measurements (figure 2, left and middle panel). From the fits to these reflectivity measurements we have determined that it is a very rough, 6.4 monolayer thick (~ 35 ± 3 Å) oxide film with the electronic density expected for bulk PdO. Using an approximated beta-roughness model [42], we find a value for beta of approximately 0.7, which is high but in good agreement with previous studies in these type of oxides [46, 75].

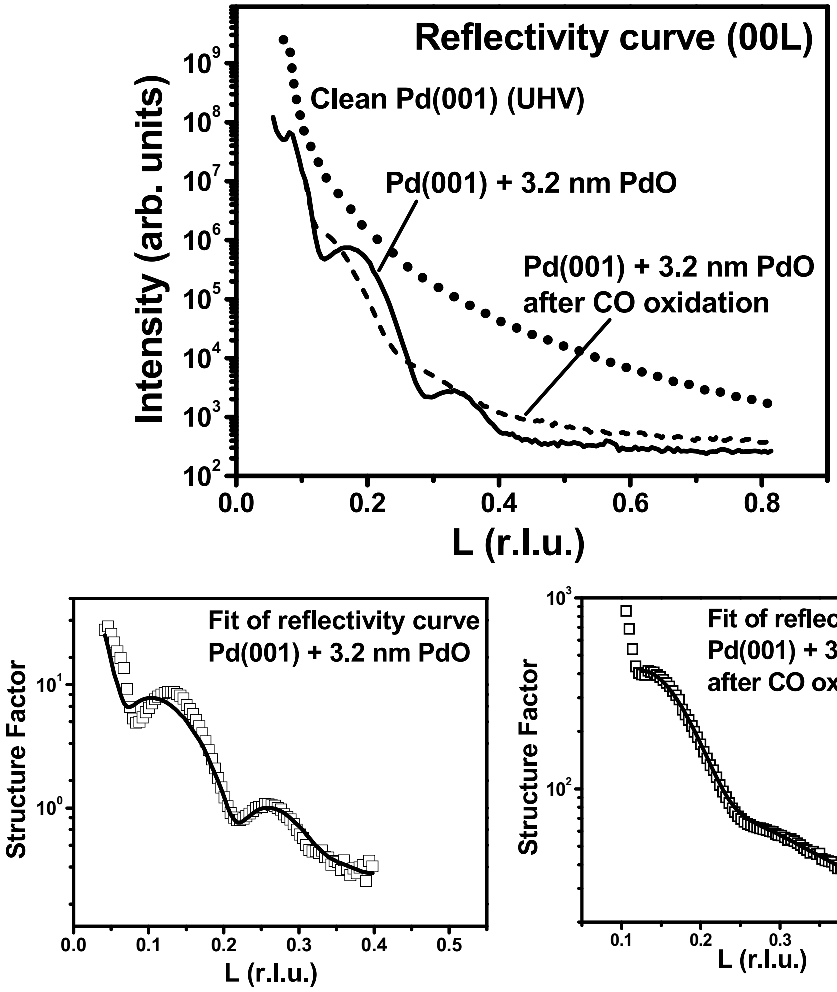

Figure 2: *Reflectivity measurements of the clean metallic surface in UHV conditions at room temperature after sputtering and annealing cycles (top panel, dotted line), and after exposure of the surface to 500 mbar of O_2 at 600K (solid line), forming an ultra-thin oxide layer on the surface. Finally the reflectivity is measured after the oxidized surface has been exposed to, and has oxidized 250 mbar of CO under formation of CO_2 (T = 475 K, V = 1L). The loss in intensity at higher L shows a clear roughening of the surface due to the initial oxidation step. The smaller intensity of the oscillations after the catalytic CO oxidation shows that the CO oxidation roughens the surface of the oxide layer even further (top and bottom right panel), whereas the thickness of the layer remains roughly constant.*

Next to these superstructure rods found along the **K = 2*H** axis, new rods appear along the same in-plane axes, but with a different in-plane unit cell. The in-plane vector of these different rods is very close to what would be the [001] or [011] cq. [101] vectors of PdO, corresponding to an out-of-plane orientation of the PdO layer of (100) cq. (010) or (1 0 0.32) cq. (0 1 0.32) respectively[i]. The presence of these rods implies that a certain fraction of the PdO layer is oriented differently than the orientation described before. The in-plane distances show that these other orientations within the PdO layer are incommensurate with respect to both the Pd(001) surface and the $\sqrt{5}$-superstructure. Although incommensurate, these new rods are only found aligned along the $\sqrt{5}$-axes.

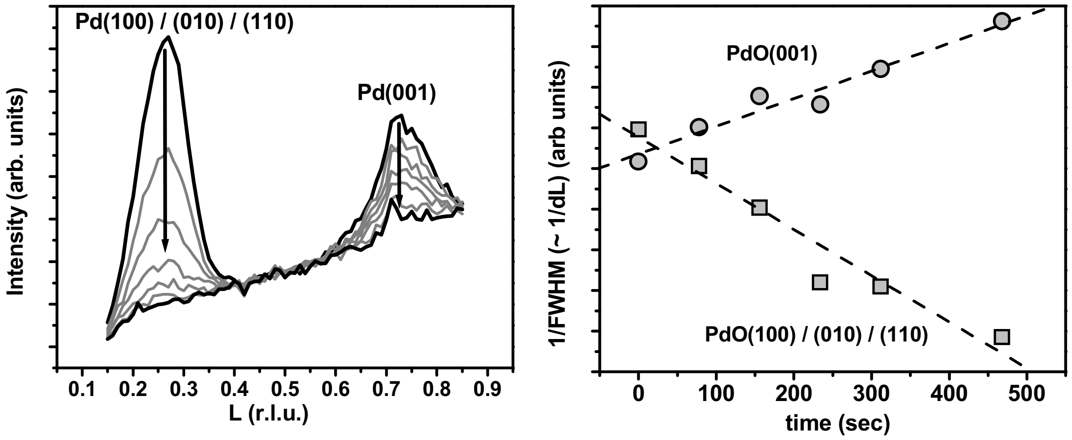

Figure 3: *left panel: Intensity as a function of time of the (001) orientation (right) and (110) / (100) / (010) orientations (left) during exposure to a single pulse of CO (P_{O2} = 500 mbar, T = 475K). Although both decrease in intensity, the diffraction peak of the (001) orientation grows smaller, but sharper, whereas the other peak widens and completely disappears. The width of the peaks is a measure for the ordered crystalline size of the different orientations. Right panel: Plotting this 1/FWHM as a function of time (and hence as a function of the total amount of CO oxidized on the surface) gives a clear view of the development of the different orientations during CO oxidation.*

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[i] *The value of 0.32 in the surface normal originates from the BCT structure of PdO. It corresponds to $(a/c)^2$ or $(b/c)^2$ with a, b and c the literature values for the unit cell of PdO [7].*

The mixture of the different orientations depends mainly on the preparation of the oxide layer. An oxide layer that has been grown at a higher temperature and higher O_2 pressure shows more mixing of the different orientations. When exposing the Pd(001) surface directly to 500 mbar of O_2 from UHV at temperatures above 500K, the oxide layer is a 50%-50% mixture of the (001) in-plane and out-of-plane. When the oxide layer is partially reduced by exposing it to a mixture of CO (< 20 mbar) and O_2 at 500K, we see that the diffraction intensity of both orientations diminishes (figure 3). But whereas the Full Width at Half Maximum (*FWHM*) of the (001) in-plane orientation increases, the *FWHM* of the peak from the (001) out-of-plane orientation decreases (figure 3). A lower intensity combined with a smaller *FWHM* means that less PdO is present on the surface, but that the PdO which is still present consists of larger ordered domains than before the exposure to CO. One way to explain this behavior of the PdO layer is to assume that larger 'crystallites' are more stable under reduction by CO than smaller ones. Secondly we conclude that the (001) out-of-plane orientation is more stable than the other orientations found after formation of PdO under pure O_2. When the PdO layer is fully reduced under these circumstances, and the Pd(001) surface is re-oxidized in a mixture of CO and O_2, only the (001)-oriented PdO appears on the surface. This confirms that PdO(001) is more stable than the other observed orientations. From these experiments we can not say whether this difference in stability is caused by a difference in the energetics or the kinetics of the different orientations of PdO.

4.3: Reactivity

When the Pd(001) surface is exposed to mixtures of O_2 and CO at elevated temperatures, the Pd surface catalyses the oxidation of CO according to:

$$CO + \tfrac{1}{2} O_2 \xrightarrow{Pd} CO_2 \qquad (1)$$

Previous experiments at elevated pressures and temperatures have shown that this CO oxidation reaction on Pd has two possible reaction mechanisms with distinct reaction kinetics and reaction rates [76,77]. The Pd surface can be made to change from one reaction mechanism to the other by changing either the gas composition or the temperature. Recent STM experiments [10] have proposed that in elevated pressure conditions the two different reaction mechanisms correspond to *a)* a metallic, adsorbate covered surface which exhibits a Langmuir-Hinshelwood type reaction [2,3], and *b)* an oxidized surface which exhibits a Mars-Van Krevelen type mechanism [4]. Probing the surface structure with *SXRD*, combined with on-line gas analysis at elevated pressures and temperatures allows us to unambiguously determine the surface structure and composition in both reactive phases. In order to link the surface structure to the reactivity of the Pd surface, we have exposed the surface mixtures of O_2 and CO, at a total pressure of approximately 500 mbar, and temperatures ranging from 460 to 625 K.

All reactivity experiments have been performed by first preparing a PdO layer on the Pd(001) surface as discussed above. In addition to the 500 mbar of O_2, ‘pulses’ of CO are added to the UHV / High pressure chamber [48], which then acts as a 1 liter batch reactor. A small portion of the gas in the reactor is leaked to a quadrupole mass spectrometer, to monitor the pressure of the different reactants and reaction products. This allows us to measure the reactivity of the Pd surface in real time, while probing the surface structure with *SXRD*.

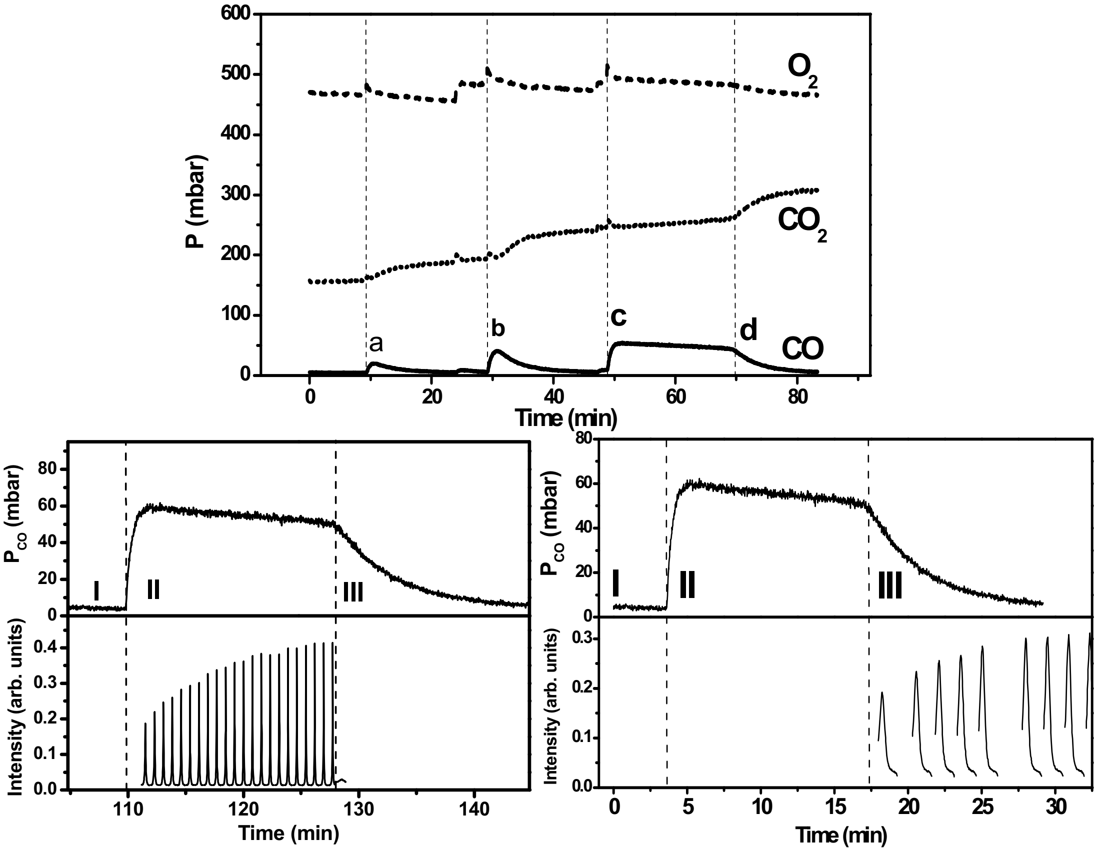

***Figure 4: Top panel**: Reactivity experiment at 475K, starting with approximately 500 mbar O_2 (dashed line) and adding CO pulses at a,b and c of respectively 20, 40 and 55 mbar. The reaction rate can be determined from the increase of P_{CO2} or decrease P_{CO}. The reaction rate at a and b is linear with the CO pressure. After c the reaction rate drops, and the dependence on the CO pressure changes. At d the reaction re-accelerates, and is again linear with the CO pressure. **Bottom left panel**: Repetitive rocking scans around the surface normal (1 deg wide) at (h k l) = (0 1 0.2) plotted as a function of time together with P_{CO}. They show the diffraction intensity from the metallic Pd(001) surface which coincides with the slow reaction rate (II). **Bottom right panel**: Repetitive scans crossing Bragg peaks of both PdO orientations (see figure 3, left panel). The signal from the Pd surface drops to 0 immediately after the transition from slow to fast reaction rate at 'III'. Simultaneously the PdO signal appears, showing that the surface is covered with PdO immediately after 'III'. Only one peak is visible in the PdO scans, indicating that only one orientation of oxide grows in the presence of both O_2 and CO (the (001) out-of-plane orientation). Although not shown here, the diffraction intensities show that also in the period from a to c (top panel) the Pd surface is oxidized. The two bottom panels are from two separate experiments, as the scans for the metallic surface and for the oxide layer are quite far apart in reciprocal space. Moving the detector from one to the other would strongly deteriorate the time resolution of the experiment.*

When a pulse of CO is added to the 500 mbar O_2, it readily reacts under formation of CO_2 (figure 4, top panel). The observed reaction rate is 2.2×10^3 molecules/site/sec[ii], at 460 K and 40 mbar CO. This is a high reaction rate for any catalyst surface, and is fully limited by the diffusion of CO to the catalyst surface through the predominant O_2 atmosphere (see this thesis, chapter 2). When exposed to sufficiently low doses of CO, the surface remains completely oxide-covered, and exhibits an exponential reaction rate as a function of time, which indicates a linear dependence on the CO pressure (figure 4, labels 'a' and 'b'). This is the expected behavior for the case in which CO diffusion to the surface is the rate limiting step.

When exposed to more than 40 mbar of CO, the catalyst is reduced to the metallic Pd(001) surface. The surface diffraction peak of Pd(001) at (0 1 0.2), that had completely disappeared in the oxidized state, reappears (figure 4, bottom left panel), and the oxide peaks, both from the bulk-like PdO, and from the surface oxide structure have disappeared. Simultaneously with the reappearance of the metallic surface the reaction rate dramatically decreases by more than a one order of magnitude (figure 4, bottom right panel) to approximately 160 molecules/site/second, and exhibits a constant reaction rate as a function of time, indicating that it no longer depends linearly on the CO pressure.

In the closed batch reactor both the O_2 and CO pressures drop as a function of time, as they are consumed under formation of CO_2. The CO is consumed twice as fast as the O_2 under formation of CO_2 (see equation. 1) and hence the $CO:O_2$ ratio always changes towards a more oxidizing environment. When this ratio drops below a certain value (figure 5 d and lower left panel) the surface is re-oxidized and the PdO layer grows back to its full thickness within several minutes. Simultaneously with the moment of appearance of the oxide layer, the reaction rate increases, showing the typical exponential decay as a function of time again (and i.e. also the linear dependence of the reaction rate on the CO pressure). From the direct correlation between the presence of the ultra-thin PdO layer and the elevated catalytic activity we conclude that the oxide layer is much more reactive in CO oxidation than the metallic catalyst surface in this pressure and temperature regime. We have observed the same behavior for a

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[ii] *For the calculation of the reaction rate, the total reaction rate has been divided by the number of available sites on an unreconstructed, metallic Pd(001) surface, with each unit cell of the Pd surface counted as one site.*

both low- and high-index surfaces ((0 0 1), (5 5 3), (1 1 17)) of Pd single crystals in experiments performed with this high pressure *SXRD* setup, and with a high pressure STM [13]. We can state that this effect is general for Pd catalysts and should remain valid also for polycrystalline catalyst as their surface is nothing else than a combination of low and high index facets. Even though one should take more details into account as support-metal interaction and particle size effects, oxide-supported Pd-particles are also expected to behave similarly.

The higher reaction rate in CO oxidation of ultra thin oxide layers of late transition metals in comparison with metallic surfaces has recently been observed in several high pressures experiments [6,9,10,13,57,62,78,79]. Most authors propose a Mars - Van Krevelen type mechanism, as the oxidation of CO could be accelerated by the presence of relatively weakly bound O atoms in these ultra-thin oxide layers. This assumption is supported by the observation of a gradual roughening of the surface as a result of the CO oxidation. From the fits of the X-ray reflectivity measurements show in figure 2, we can confirm that the surface indeed is roughened by the oxidation of CO, although most of the roughness has been introduced by the initial oxidation step.

The roughness of the oxide surface can also be determined by measuring the Full Width at Half Maximum (*FWHM*) of the CTRs of the ultra thin oxide layer. According to kinematical diffraction theory the average domain size is inversely proportional to the *FWHM* of diffraction peaks [17,42]. We have measured the *FWHM* of the rocking scan around the surface normal of the PdO diffraction maximum at (0.4 0.8 0.72) as a function of the total amount of CO converted to CO_2 (figure 5, left panel). We find that the *FWHM* of the PdO diffraction peak depends linearly on the total amount of CO that has reacted with the PdO surface (figure 5, right panel). This is in agreement with a Mars-Van Krevelen type mechanism, in which CO reacts with oxygen atoms bound *in the oxide layer*. In most events the CO molecule reacts with, and hence extracts a single oxygen atom from the oxide layer, leaving behind a single reduced Pd atom. The Pd atom is immediately re-oxidized because by the oxygen present in the gas phase, exactly restoring the PdO layer. The oxide layer is, with respect to the Pd metal, rather static at this temperature, allowing little or no surface diffusion. But on rare occasions, a reduced Pd atom can diffuse away from its original position in the oxide layer, leaving behind a hole or defect in the oxide layer. It is then re-oxidized elsewhere, creating a PdO protrusion on top of the oxide layer (see this thesis, chapter 2, figure 6). This slowly creates roughness in the oxide layer as more and more CO is consumed. Similar scenarios have also been proposed by e.g Hendriksen *et al* [10] and Over *et al.* [6].

The PdO oxide layer appears to have a very low mobility, as at these temperatures none of the roughness created by the CO oxidation is annealed with time. Only once the surface is completely reduced, and reverts to the metallic state does the created roughness disappear. As soon as the surface is completely reduced, diffusion starts to smoothen the surface, as a rough surface is energetically less favorable than a smooth surface. We can follow the annealing of this surface by measuring the *FWHM* of a rocking scan around the surface normal of an in-plane diffraction peak of Pd(001). In figure 6, we show an experiment in which we oxidize and reduce the surface several times. In the top panel, the CO pressure is plotted. One can see the reactivity switch from the

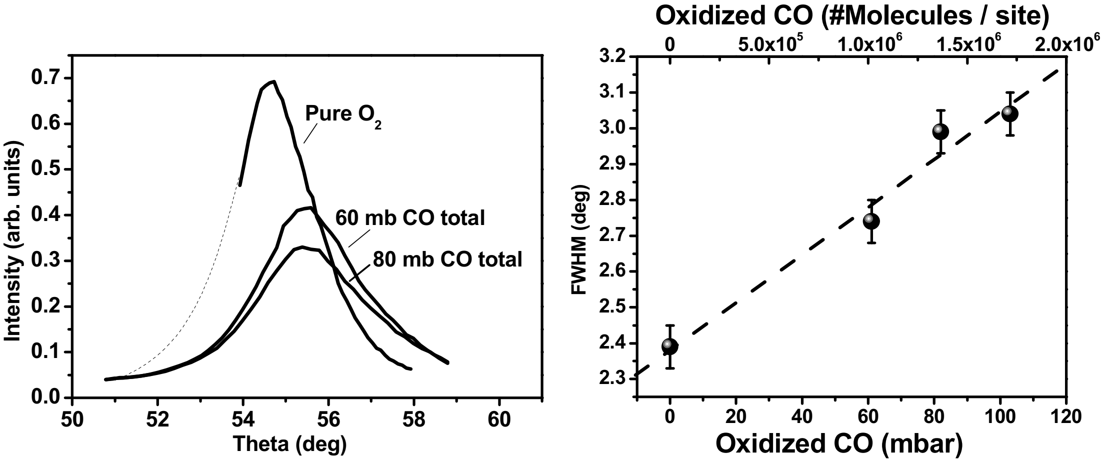

***Figure 5: left panel**: Rocking scans around the surface normal of a diffraction maximum of PdO at (0.4 0.8 0.72). The scan made directly after forming the PdO layer in pure O_2, exhibits the lowest FWHM, showing the best ordered PdO layer that we can prepare. After the surface has converted respectively 60 and 80 mbar of CO into CO_2, the rocking scans show a clear loss in height, and an increase in FWHM corresponding to a roughening of the oxide layer due to the catalytic conversion of CO to CO_2. This roughening as function of the total conversion of CO confirms the assumption of a Mars-van Krevelen type mechanism for this reaction on the ultra-thin PdO layer. **Right panel**: The FWHM as a function of the total amount of CO converted to CO_2 in mbar and in number of molecules per reaction site on the PdO surface. The dashed line is the lowest order fit for this measurement, showing a linear dependence of the roughness on the amount of oxidized CO.*

high reaction rate and exponential decay of the CO pressure, typical for the reaction on the oxide surface. No signal from the metal surface is present during this high reactive phase. When a large CO pulse is let into the reactor, the surface is reduced, and the signal from the Pd(001) surface reappears. We continuously measure rocking scans around the surface normal of the Pd surface at (0 1 0.2), and plot them along the same timeline as the CO pressure (figure 6, lower panel). One can see that the height of the diffraction peak grows as a function of time. When plotting this scan not as a function of time but in degrees, one can see that not only the height increases, but that also the *FWHM* decreases. The *FWHM* is a direct measure for the step density on this

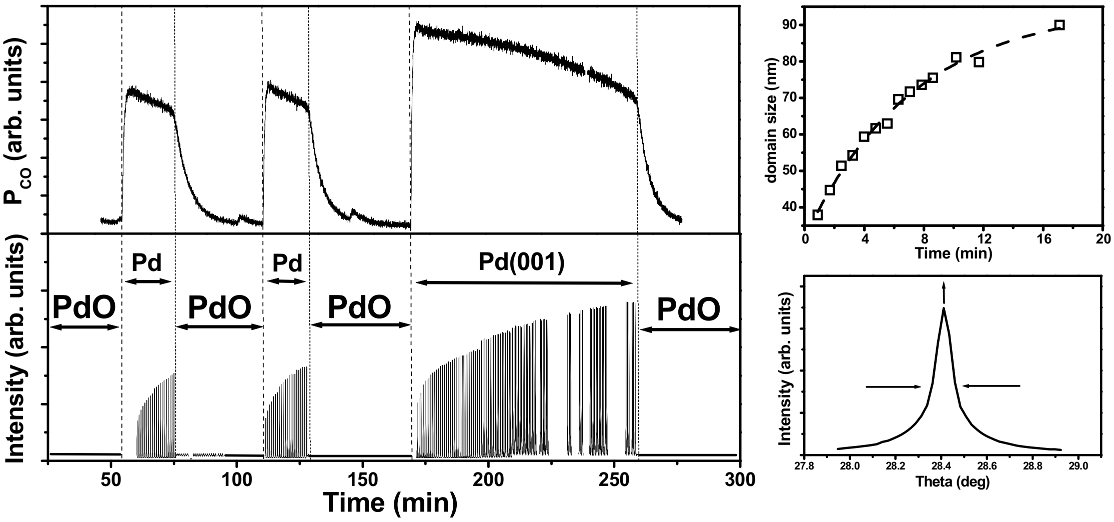

***Figure 6: Left panel**: Rocking scan around the surface normal at the anti-phase point of a Pd(001) CTR at (h k l) = (0 1 0.2). This scan is measured repetitively during an experiment, and plotted as a function of time. During the experiment shown here, the surface is alternately switched from the 'rough' oxide phase to the metallic phase by exposing it to 40 to 55 mbar of CO (P_{O2} = 480 mbar, T = 460 K). The surface is reduced back again by oxidizing the CO to CO_2, while the O_2 pressure remains almost constant. From the increasing height of the surface diffraction peak one can conclude that the metallic surface is annealing in the metallic phase. **Bottom right panel**: One of the surface diffraction peak from the left panel as a function of the rocking angle around the surface normal (Theta). **Top right panel**: Average terrace or ordered domain size as function of time calculated from the FWHM of the surface diffraction peaks of the Pd surface, assuming that the roughness on this metal surface is mainly due to single atomic steps. One can clearly see the smoothening of the surface in these circumstances. The smoothening behaves as expected for an unreconstructed, flat single crystal surface.*

surface and hence of the average terrace size of the surface as a function of time (figure 6, right top panel). From this we see that the annealing of this surface behaves as expected for a metal single crystal surface, with a constant diffusion coefficient at a constant temperature. This roughening and annealing behavior in the different branches of the reaction, combined with the difference in reactivity can be an explanation for spontaneous self sustained reaction oscillations to appear. A thorough description of the model which we propose for this mechanism causing self sustained oscillations is given in chapter 5 of this thesis.

4.4: Switching behavior and self sustained oscillations

In certain pressure and temperature conditions the Pd surface can, without change in the externally applied pressure and temperature conditions, spontaneously switch from one reaction mechanism to the other and back again in so-called *self sustained oscillations*. Many models have already been proposed to explain this spontaneous switching, based on both UHV- and elevated pressure experiments[76,77, 81-84].

A novel explanation for self sustained oscillations on Pd(001), based solely on *in-situ* observations has been proposed by Hendriksen *et al*. recently [70]. In the proposed model, a new but major role is played by the roughening of the oxide surface as a result of the Mars-Van Krevelen mechanism, and subsequent annealing in the metallic phase. Although no self-sustained oscillations have been observed in any of the reactivity experiments performed as described above, the experimental conditions in which oscillations occur can be recreated very accurately to measure specific parameters that play a role in the oscillation model as proposed by Hendriksen *et al.* [70].

For the roughness to play a role in self sustained oscillations, the roughness of the surface must have an influence on the stability of one, or both phases of the oscillations, i.e. on the stability of the metal and / or oxide phase. According to the model of Hendriksen *et al*, the increasing roughness caused by the reaction must destabilize the oxide phase. This would imply that at constant oxygen pressure and temperature, partial pressure of CO necessary to completely reduce an oxidized surface should diminish with increasing roughness. Inversely, this implies that the CO:O_2 ratio at which the metallic surface spontaneously oxidizes in the reactivity experiments described above should diminish with increasing roughness.

We have kept the O_2 pressure and temperature constant (variation < 1%) during an experiment, in which we let the surface switch several times from a metallic to an oxidized surface (figure 6, left panel). When the surface has been exposed to a large CO pulse, it will remain in the metallic state longer than with a smaller CO pulse, as it will take more time to oxidize enough CO to return to oxidizing conditions. By reducing the surface with small or lager pulses of CO, we can choose the amount of time which the surface will stay in the metallic state. As the annealing process at a fixed temperature only depends on time, the surface that has been exposed to the largest CO pulse, will be smoother at the moment it is re-oxidized. Using this mechanism we can control the roughness of the surface at the moment it switches from metal to oxide. Doing this for several different CO pulses, we can determine the CO pressure at which the surface spontaneously re-oxidizes for different surfaces. Figure 7 shows the

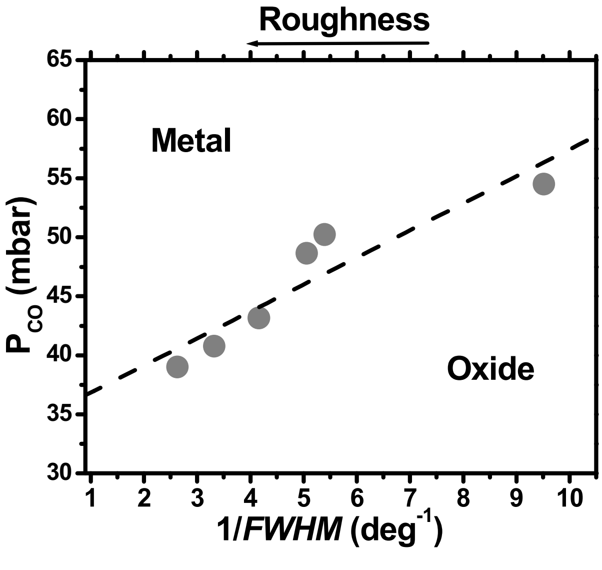

Figure 7: *CO pressure at which the surface switches from the metallic phase to the oxide phase as a function of (FWHM)$^{-1}$ of a rocking scan around the surface normal of the Pd(001) surface at (h k l) = (0 1 0.2). This value scales approximately with the roughness, where a high roughness corresponds to a high FWHM, and hence a low value of (FWHM)$^{-1}$. Data are taken from the experiment shown in Figure 6 (T = 460 K, P_{O2} = 480 mbar).*

variation in CO pressure as a function of the roughness of the Pd(001) surface. This measurement confirms that at higher roughness values, a lower CO pressure is needed to oxidize the surface. This proves that for a constant CO:O_2 ratio the metal surface can be destabilized by annealing (decreasing roughness, dotted arrow). Simultaneously this means that an oxide surface is destabilized by increasing roughness. Both these observations confirm the behavior of this surface necessary for oscillations, namely that the process occurring in each phase (annealing in the metal phase, roughening in the oxide phase) destabilize each phase.

4.5: Pd(553): structure and reactivity

4.5.1: Introduction

One major difference between highly dispersed, small-particle catalysts and low index, single crystal catalyst is the average step density and terrace size of the catalyst surface after preparation in a UHV system. One option to overcome this difference, while still working with single crystal model catalysts, is to use high index surfaces, where after preparation with sputter and anneal cycles (as described above), one can prepare a surface with a high step density, and short terraces. For our experiments on such high index surfaces, we chose the Pd(553) surface orientation. This surface has a 12.3° degree miscut with respect to the (111) surface. To accommodate this miscut, it consists of (111) facets or terraces of 10.32 Å long, separated by single $\left(1\,\overline{1}\,1\right)$ steps (figure 8c). The surface has been prepared in UHV by the same methods described above for the Pd(001) surface. The experimental setup is the same as for the Pd(001) experiment described earlier, using the same photon source for the *SXRD* experiments, and the same UHV / High Pressure setup [48]. The in-plane unit cell is chosen as shown in figure 8a. The vectors **a** and **b** span the surface unit cell, with **c** the out-of-plane vector perpendicular to the (553) surface (not shown). Because of this particular choice of **a** and **b**, the **H** vector is oriented in the direction perpendicular to the steps (i.e. perpendicular to **a**), and 0.59 $Å^{-1}$ long. The **K** vector is *not* parallel to the step direction, but perpendicular to **a**, with a length of 2.30$Å^{-1}$. The vector parallel to the steps is with this choice of **a** and **b** the $\left[\overline{1}20\right]$ direction.

Diffraction from the surface after UHV preparation shows a diffraction pattern as expected for a (553) oriented surface as described above. No faceting, reconstruction or relaxation of the surface atoms is observed under UHV conditions.

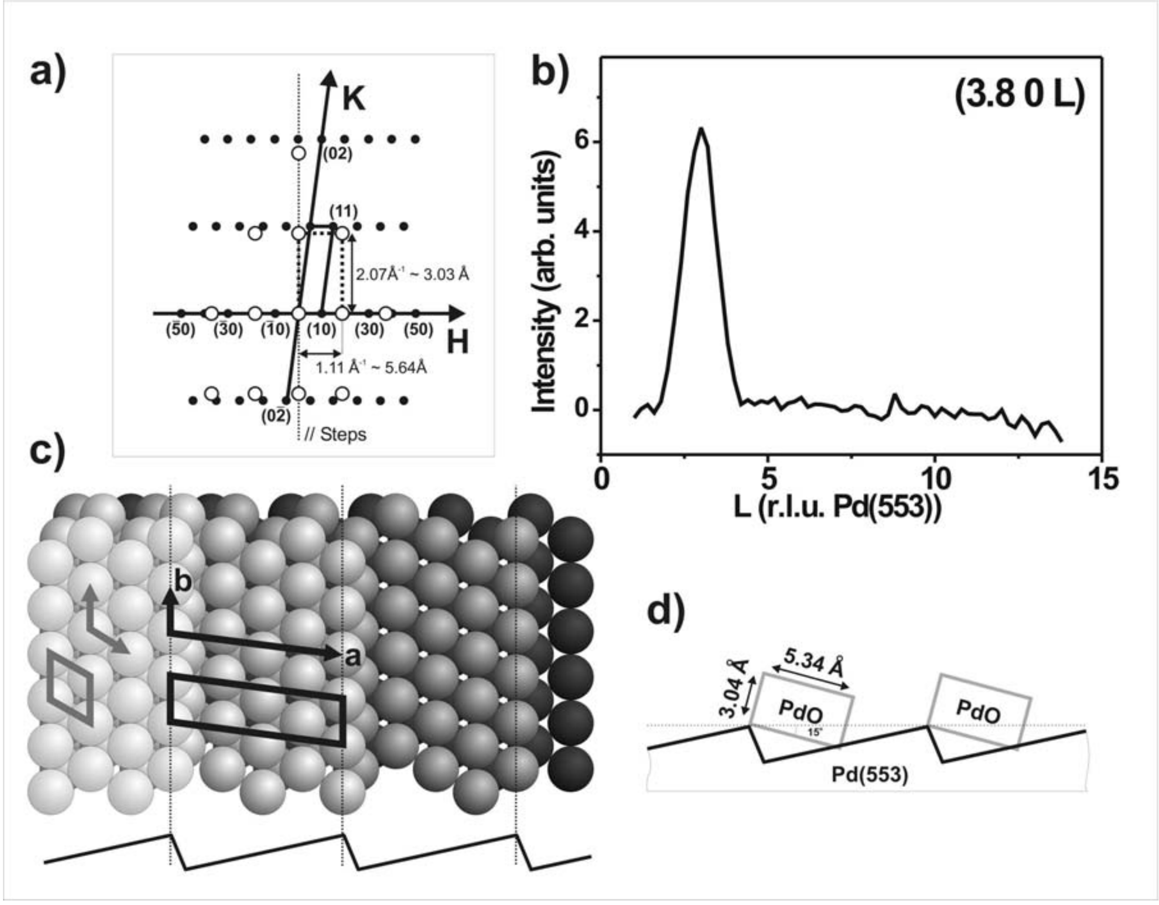

***Figure 8: a)**: In-plane reciprocal space map of the Pd(553) (black dots) and the bulk-like PdO layer (hollow circles). All coordinates are given in reciprocal unit vectors of Pd(553) as described in this chapter. The PdO layer is incommensurate, but aligned along **H** (the direction perpendicular to the step lattice), and along the steps. Due to the choice of the unit cell, the direction parallel to the steps is not **K** but is given by the vector (2**K**-**H**), and is marked by the dotted line. **b)**: The diffraction intensity distribution along a rod of the PdO layer as a function of **L** at **H** = 3.8 and **K** = 0. **c)** A ball model of the Pd(553) surface, and a schematic side view showing the height variation in the direction perpendicular to the step lattice. **d)** The model for the growth of the incommensurate bulk-like PdO, giving the dimensions of the PdO unit cells and the tilt angle with respect to the Pd(553)*

4.5.2: Experimental

When exposing the surface to 10^{-4} mbar of O_2 at 475 K, the X-Rays shows new diffraction intensities along **H** at **K** = ...-1,0,1,2… . The intensity distribution of these new spots in the out-of-plane direction does not exactly follow the [553] (i.e. **L)** direction. Close analysis of the direction of the intensity distribution by Westerstrom *et al*. show that they are probably due to a faceting of the (553) surface to (332) facets. To compensate for the longer terraces of the (332) orientation with respect to the (553), the surface must form double steps once every 4 terraces. The formation of facets and double steps has been confirmed by STM measurements [80].

When exposing the surface to 500 mbar of O_2 at 475 K, the diffraction intensities that appeared as a result of faceting disappear, and new intensities appear along **H**, at **K =** n · 0.92, with n = …-1,0,1,2… (figure 8a, hollow circles). From the symmetry of the newly appeared diffraction intensities, we conclude that this new structure has a rectangular in-plane unit cell (figure 8a, dotted line) which is aligned along the perpendicular *and* parallel direction of the steps, but is incommensurate with respect to the Pd lattice. From the value of 0.92 in the **K** direction we can calculate that the lattice constant along the steps of this new structure is 3.03 Å, which is equal to the length of the [100] or [010] vector of PdO. In the direction perpendicular to the steps of the Pd(553) surface, new diffraction rods appear at **H** = n · 1.9 (at **K** = 0). This length does not correspond to any simple combination of vectors of the PdO unit cell. The PdO CTR at **H** = 3.8 has a maximum in diffraction intensity at **L** = 3. The total diffraction angle (2θ) of this peak show that this must be the (002) peak of PdO. This peak should have been at **L** = 0 if the (001) vector of PdO would have been in-plane, pointing perpendicularly to the Pd(553) steps. As it clearly is not at **L** = 0, we can conclude that the (001) vector of the PdO unit cell is tilted out-of-plane by ~15° degrees. The (004) peak of PdO is found at (7.6 0 6). The observation that position of the diffraction maxima along **L** increase as the order of the rod increases supports the suggestion that the PdO crystal is tilted with respect to the Pd(553) surface. The tilt angle as calculated from the position of this second diffraction maximum would again be ~15° degrees with respect to the Pd(553) surface plane. This perfectly confirms the first tilt angle calculated here above for the (001) peak.

The thickness of the oxide layer can similarly as for the Pd(001) surface, be estimated by oscillations in the reflectivity curve taken from this surface, or from the *FWHM* along **L** of the diffraction maxima of the PdO. Both methods show that the thickness of the oxide layer is 6 to 7 nm. Taking into account the tilt angle of the oxide slab, this thickness corresponds very well with to one found for the oxide layer on Pd(001). The thickness of the oxide layer depends slightly on the temperature and O_2 pressure the surface has been exposed to in the preparation stages of each experiment.

By exposing this oxidized surface to pulses of CO, we can reduce it back to a metallic state. When the surface is reduced in such a way, the optical orientation of the surface does not change, but it is strongly facetted in (111) and $\left(1\,\overline{1}\,1\right)$ facets. We can estimate the size of the facets from the width of the rocking scans of the (111) and $\left(1\,\overline{1}\,1\right)$ crystal truncation rods near **L** = 1. From oscillation along the (111)-rod (figure 9) we can also get an estimate for the amount of step bunching, i.e. the $\left(1\,\overline{1}\,1\right)$ facets. Both methods are in agreement with each other and show (111)-facets ranging from 2 to 8 nm, depending on the thickness of the original oxide layer covering the Pd surface. The size of the facets seems to scale with the thickness of the reduced PdO layer.

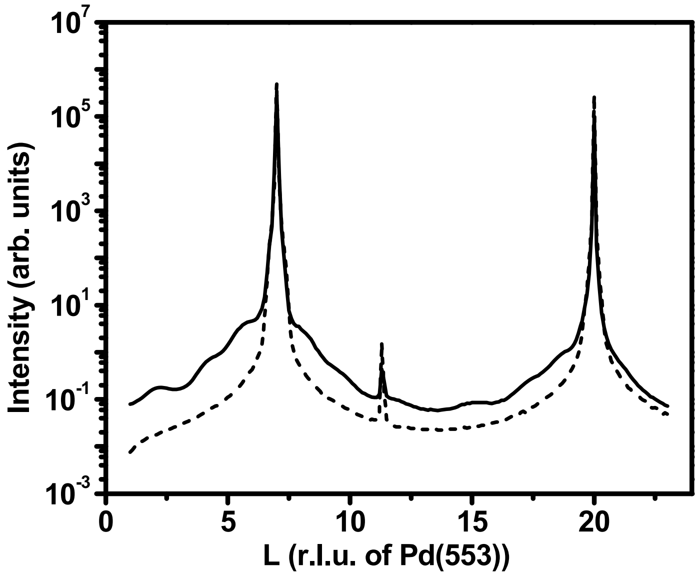

Figure 9: *Crystal truncation rod of the (111) facets of the (553) surface. The dashed line is the background value, measured on a clean (553) surface after preparation in vacuum. The solid line is after 1 oxidation and subsequent reduction cycle. Next to a clear rise in intensity in between the Bragg peaks, one can also clearly see oscillation as a function of **L** on the solid line.*

Reactivity measurements on this surface have been performed in the exact same way as described here above for the Pd(001) surface. After pre-covering the surface with an oxide layer in 500 mbar of O_2 at 475 K, it was then exposed to pulses of CO. The CO in relatively small pulses was reacted to CO_2, with the reaction rate depending linearly on the CO pressure. The measured reactivity of the PdO layer on Pd(553) is 2.7×10^3 molecules/site/sec at 40 mbar CO, and 490K. This value is, within the experimental error bars and taking the slightly higher temperature into account, equal to the one found for the PdO layer on Pd(001). The reactivity on the metallic surface is again found to be lower than on the oxide surface, by more than 1 order of magnitude. This confirms that our observations are also valid for surfaces with a step density and terrace size similar to nanometer-sized particles.

4.6: Conclusions

SXRD experiments on the different Pd surfaces show that an ultra thin PdO-layer forms on these surface when exposed to elevated pressures of O_2. The orientation of the PdO layer depends on the orientation of the substrate. The *SXRD* measurements also provide information about the morphology of this layer. All experiments show that at elevated pressures and temperature the oxide layer is more reactive in CO oxidation than the metallic Pd surface.

We find that there is a direct correlation between the amount of CO molecules that have reacted to form CO_2 and the surface morphology (i.e. the surface roughness). From the change in *FWHM* of the PdO peaks during oxidation experiments we find that the CO oxidation process roughens the oxide layer. This strongly suggests that the CO reacts with a component *inside* the PdO layer. The most likely reaction path to explain this is one in which the CO reacts with an oxygen atom within the PdO layer in a so-called Mars-Van Krevelen mechanism. As long as the $CO:O_2$ ratio is low enough, the locally reduced Pd atoms will quickly re-oxidize, and the outermost Pd layers of the catalyst will remain fully oxidized. The Mars-Van Krevelen reaction path on the oxide is apparently much more efficient than the Langmuir-Hinshelwood reaction path observed on the metallic surface. Our experiments also show that the surface roughness plays a key role in self sustained reaction oscillations, as the formation of roughness in the oxide phase, and the annealing of the surface in the metal phase each destabilize their own phase.