Oxidation of CO on Pd(1 0 0): on the structural evolution of the PdO layer during the self sustained oscillation regime

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ABSTRACT
Under particular temperature and gas conditions the reactivity of the Pd(1 0 0) surface toward CO oxidation exhibits oscillatory behaviour. Here we examine the surface structure of this model catalyst and show that the periodic pattern is more complex than previously reported and that superimposed on the overall oscillation much faster structural variations are present. By examining the structure of the sample surface at high temporal resolution we conclude that the structure of the oxide layer present at the surface evolves continuously toward a more disordered phase in agreement with the Mars-Van Krevelen reaction mechanism.

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 [1–3]. Two competing reaction mechanisms have been proposed [4,5]. In the traditional Langmuir–Hinshelwood (LH) mechanism, oxygen molecules adsorb dissociatively on the metal surface and CO molecules are adsorbed molecularly. On the surface, they react to form CO$_2$ molecules that desorb to make room for new reactants. The observation of an increase in reaction rate, accompanying the formation of thin surface oxides under CO oxidation conditions [6,7] has been interpreted in terms of the Mars-Van Krevelen (MvK) mechanism: CO molecules adsorb on the oxide from which they extract O atoms to form CO$_2$. 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 its appearance is a consequence of the local decrease in the partial pressure ratio between CO and O$_2$ 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 activities of the metal and of the surface oxide separately. Mass spectrometry, the standard tool for measuring the turnover frequency of a reaction, measures the reactivity over the whole sample and does not allow for spatially resolving the active phase.

In order to circumvent this problem we have taken a different route. Here we focus on reaction oscillations of the CO oxidation reaction on the Pd(1 0 0) surface employing surface X-ray diffraction (SXRD).

Background
Reaction oscillations on Pd(1 0 0) at high pressure and temperature have been observed both with Scanning Tunnelling Microscopy (STM) and Surface X-ray Diffraction (SXRD) [6,7]. In the model of Hendriksen
sporadic and random drops of the intensity as at 600, 1970 and about 15 s is also present. This fast oscillation is interrupted by bands in the plot. A fast intensity oscillation with a period of surface PdO is absent. These regions are indicated by the grey in which the catalyst surface is completely reduced and the of about 1650 s, is composed by a short while, about 100 s, oscillatory behaviour. The main slow oscillation, with a period of CO. The time dependence of the intensity shows a complex time.

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Experiment

The X-ray experiments were carried out in the first hutch of the ID03 beamline of the ESRF [8] employing an incident X-ray energy of 24.3 keV. The beam was focused by the beamline optics to dimensions of 10 × 10 μm², using both the toroidal mirror in the optics hutch and the KB system in front of the diffractometer, which hosted the high-pressure Surface X-ray Diffraction (SXRD) flow reactor [9]. The beam footprint on the sample was about 10 × 300 μm². A 2 × 2 Maxipix detector [10] with a useful area of 28 × 28 mm² located at about 60 cm from the sample was used to detect the diffracted X-ray intensity.

Prior to the experiment, the Pd(1 0 0) sample was cleaned in UHV conditions by repeated cycles of Ar+ bombardment at an applied potential of 1000 V and annealing at 700 °C. Subsequently, the flow reactor around the sample was closed and the sample was investigated in situ by SXRD under realistic catalytic, high-pressure and high-temperature, conditions.

The self-sustained oscillation regime of the reactivity was observed at flow rates of 1.1 ml/min CO, 20 ml/min O₂, and 10 ml/min Ar at a total pressure of 1 bar, with a sample at approximately 170 °C.

The reciprocal coordinates that we use for representing our SXRD results are derived with respect to a surface unit cell of Pd(1 0 0) with two perpendicular surface vectors, a₁ and a₂, parallel to the [0 1 1] and [0 1 0] directions with magnitude |a₁| = |a₂| = a₀/√2, and a third vector a₃ perpendicular to the surface and with a magnitude |a₃| = a₀, where a₀ is the cubic lattice parameter of Pd and is equal to 3.89 Å.

Results and discussion

In order to follow the presence of PdO on the surface during the reaction oscillations, we have followed the intensity of the (0.81, 0.39, 0.75) peak at 170 °C in an atmosphere of 650 mbar O₂, and 30 mbar CO. The time dependence of the intensity shows a complex time oscillatory behaviour. The main slow oscillation, with a period of about 1650 s, is composed by a short while, about 100 s, oscillatory behaviour. The main slow oscillation, with a period of about 1650 s, is composed by a short while, about 100 s, oscillatory behaviour.
randomly oriented palladium oxide nano-crystallites would result in the powder ring indicated by the red band. The white stripes in the panel are intrinsic inactive areas of the Maxipix detector.

As the oxide becomes increasingly misoriented, the Bragg peak smears out along the powder ring. If all the crystallites in the palladium oxide were fully aligned with each other and with the palladium surface and terminated by the cation rod, therefore a change in the angle $\theta$ is a direct measure of the ratio between the randomly oriented and the epitaxial parts of the oxide.

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. The observed Bragg peak is three-dimensional in nature and we only observe a 2D view of it. If we assume the peak to have a 3D Lorentzian shape with two equal in-plane widths, we can estimate the total integrated intensity of the peak as $4\pi I_{\text{peak}}$. The resulting intensity graph is shown in Figure 3(e) and provides a direct volume measurement of the amount of PdO. From this plot, we can see that almost all of the intensity that is lost at the points in time where the peak intensity drops sharply, e.g. at $t = 1980\ s$ and $t = 2210\ s$, is recovered quickly, albeit in the form of a wider peak, i.e. with increased $\gamma_a$ and $\gamma_b$. By contrast, the total intensity from the oxide displays a general decrease over the lifetime of the oxide.

Next we turn our attention 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 3. The observed Bragg peak is three-dimensional in nature and we only observe a 2D view of it. If we assume the peak to have a 3D Lorentzian shape with two equal in-plane widths, we can estimate the total integrated intensity of the peak as $4\pi I_{\text{peak}}$. The resulting intensity graph is shown in Figure 3(e) and provides a direct volume measurement of the amount of PdO. From this plot, we can see that almost all of the intensity that is lost at the points in time where the peak intensity drops sharply, e.g. at $t = 1980\ s$ and $t = 2210\ s$, is recovered quickly, albeit in the form of a wider peak, i.e. with increased $\gamma_a$ and $\gamma_b$. By contrast, the total intensity from the oxide displays a general decrease over the lifetime of the oxide. Furthermore, we observe a shift in the location of the Bragg peak, $q_a$ and $q_b$, however the magnitude $|q|$ remains constant. We also see a rotation of the Bragg peak in the detector plane, which is most pronounced at $t = 2210\ s$. All these signs are consistent in indicating that the oxide is partially

![Figure 2](image-url) **Figure 2.** (a) Image of the PdO peak measured at $(0.81, 0.39, 0.75)$ in reciprocal space. $q_a$ and $q_z$ are the exchanged wave-vectors along directions parallel and perpendicular to the sample surface. (b) Lorentzian fit of the peak shown in panel a. The main axes of the fit, indicated by $q_a$ and $q_z$, are rotated over an angle $\theta$ with respect to the surface coordinate system and (c) The limiting behaviour we expect for an epitaxial PdO film is a Lorentzian perfectly aligned along $q_z$ as indicated by the grey ellipse, while an ensemble of randomly oriented palladium oxide nano-crystallites would result in the powder ring indicated by the red band. The white stripes in the a panel are intrinsic inactive areas of the Maxipix detector.

The central peak position $q_a$ and $q_b$ provides a direct measurement of 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. $\gamma_a$ and $\gamma_b$ are the peak widths of the Bragg peak (half width at half maximum). An increase of the two widths originates from either a decrease of the average crystallite size, or an increase of the PdO film mosaicity. However we have to keep in mind that in order to properly calculate the shape of the peak along the $\gamma_z$ direction the contribution of the crystal truncation rod should be properly evaluated. This contribution will be maximum when the sample surface is smooth and minimum in the case of a rough surface. The Lorentzian fit function does not take into account the crystal truncation rod, therefore $\gamma_z$ will be an overestimate of the value.

Also the angle $\theta$ 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 with the palladium surface and terminated by well-defined surfaces parallel to the substrate, we would see a Bragg peak elongated along the $q_z$ direction since the intensity of the peak would follow the crystal truncation rod. As the oxide becomes increasingly misoriented, the Bragg peak smears out along the powder ring.
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 oxide followed by a slow growth of a new oxide that we just identified for the intermediate timescales.

Immediately 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 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.

Directly after this partial reduction we see a recovery of the total integrated intensity of the Bragg peak. $\gamma_a$ and $\gamma_b$ decrease slightly indicating that the crystallites increase in size to a certain extent. All the plotted parameters in Figure 3 seem to indicate a re-growth of the palladium oxide. However, the fact that $\gamma_a$ and $\gamma_b$ remain at higher values suggests that instead of restoring the lost oxide crystallites, new crystallites with reduced dimensions appear.
with increases in $\vartheta$ 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 re-growth of oxide that is less well-oriented.

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. [7] 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.

From the experimental observations reported in Figure 3, we can summarise the behaviour of the oxide layer as follows:

1. Initially, a thin surface oxide is formed. It is epitaxial with respect to the substrate and its lattice parameter indicates that it is strained with respect to bulk PdO.
2. Soon after the formation of the thin surface oxide, a somewhat thicker and structurally relaxed oxide develops, which is initially very well aligned with the Pd(1 0 0) 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.
5. This leaves exposed a fraction of the metal surface, which is able to smoothen, after which it re-oxidises.
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.
8. In the process roughness builds up finally preventing the formation of PdO.

Conclusions

We have experimentally observed reaction oscillations with three distinct timescales. The slowest is a full reduction of the palladium surface, already studied in the past [7], while 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.

From the fit of 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 of the peak is a sign of the degree to which the oxide layer is epitaxial with respect to the Pd(1 0 0) substrate, and provides information about its spread in orientation and its average oxide grain size. This analysis also shows that epitaxial palladium oxide reduces faster than misaligned oxide. During the “active” phase, the oxide layer is gradually losing its epitaxy. The mechanism that seems to drive the oscillations on all timescales is the build-up 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.

Our measurements add a new aspect to this scenario, namely that there are fast and intermediate oscillations. During these, the oxide is removed only partly, with the epitaxial oxide regions being removed preferentially. Here, we speculate that during the rapid and intermediate oscillations, the metallic regions on the surface can most likely smoothen out roughness on a local level. This may be sufficient to bring the total step density of the surface below the threshold level at which point the surface should switch back to the fully oxidised state even though the oxide presents smaller domain sizes and an increase in disorder. In order to better understand the interplay of the local and long-range correlations of the roughness during this process we have performed additional grazing-incidence small-angle X-ray scattering and X-ray reflectivity measurements that will be reported in a future publication.

A final remark concerns 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(1 0 0) and the reactivity predicted theoretically for the surface of (unstrained) PdO(1 0 1) [14]. 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.

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