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Operando SXRD : a new view on catalysis

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II: Structure and Reactivity of Surface Oxides on Pt(110) during Catalytic CO Oxidation

We present the first structure determination by Surface X-ray Diffraction (SXRD) during the restructuring of a model catalyst under reaction conditions, i.e. at high pressure and high temperature, and correlate the restructuring with a change in catalytic activity. We have analyzed the Pt(110) surface during CO oxidation at pressures up to 0.5 bar and temperatures up to 625 K. Depending on the O_2/CO pressure ratio, we find three well-defined structures, namely (i) the bulk-terminated Pt(110) surface, (ii) a thin, commensurate oxide, and (iii) a thin, incommensurate oxide. The commensurate oxide only appears under reaction conditions, i.e. when both O_2 and CO are present and at sufficiently high temperatures. DFT calculations indicate that the commensurate oxide is stabilized by carbonate ions (CO_3^{2-}). Both oxides have a substantially higher catalytic activity than the bulk-terminated Pt surface.

2.1: Introduction

CO oxidation on Pt single crystal surfaces forms a favorite model system for heterogeneous catalysis. Most of our present-day understanding of this system is based on a large number of experiments that have been carried out under laboratory rather than industrial conditions, such as ultrahigh vacuum (UHV) and low temperatures. Presently, a growing number of experimental techniques is being adapted to bridge the so-called *pressure gap* and obtain atomic-scale insight in the structure, composition and other properties of model catalyst surfaces under (semi) realistic reaction conditions. Examples are scanning tunneling microscopy [9,20,22,44], surface X-ray diffraction [7,45-47], transmission electron microscopy [26], and photoelectron spectroscopy [25].

Previous high-pressure STM observations during CO oxidation on Pt(110) have demonstrated that at a sufficiently high O₂/CO pressure ratio this surface undergoes a structural phase transition, which has a dramatic effect on the reaction mechanism and strongly enhances the reaction rate [9]. The STM movies have been interpreted in terms of the formation of a thin platinum oxide film on the Pt(110) surface, on which the CO molecules oxidize through a Mars-Van Krevelen mechanism, and react with O atoms from the oxide. There is a growing body of evidence from experiments [6,9,10] as well as theory [28] strongly suggesting that similar scenarios are active for CO oxidation on other metal surfaces.

In this chapter we present the first observation by high-pressure Surface X-ray Diffraction (*SXRD*) of a correlation between the reactivity and the structure of a catalyst surface. The experiments performed during CO oxidation on Pt(110) show that the most active structures are, in fact, two thin oxide film configurations, one of which is stable only when the surface is in contact with *both* reactant gasses, CO and O₂, at elevated temperatures.

2.2: Crystal preparation

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 has a volume of ~2 liter and is 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 (N47 grade for CO, N55 for all other) 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° ($\sim 4 \times 10^{12}$ photons/s). The fluorescence radiation in the scattered beam was filtered with a crystal analyzer.

We describe the Pt crystal lattice with two perpendicular unit vectors $\mathbf{A}_1$ and $\mathbf{A}_2$ in the surface plane along $[1\bar{1}0]$ and $[001]$ respectively and the third one, $\mathbf{A}_3$, along the $[110]$ surface normal. $|\mathbf{A}_1| = a_0 = 2.774 \text{ \AA}$ is the Pt nearest-neighbor distance; $|\mathbf{A}_2| = \sqrt{2}a_0$ and $|\mathbf{A}_3| = a_0$. In reciprocal space $\mathbf{H}$ and $\mathbf{K}$ are the unit vectors in the surface plane (parallel to $\mathbf{A}_1$ and $\mathbf{A}_2$ respectively) and $\mathbf{L}$ is along the surface normal. Well-ordered, clean Pt(110) surfaces exhibiting the characteristic (1×2) missing-row reconstruction [33] were obtained after several ion bombardment (1 keV Ar^+) and annealing (1200 K) cycles. The full width at half maximum (*FWHM*) of a rocking scan around the $(0\ 0.5\ 0.2)$ reflection was typically 0.24° , which corresponds to ordered domain sizes of $\sim 1200 \text{ \AA}$.

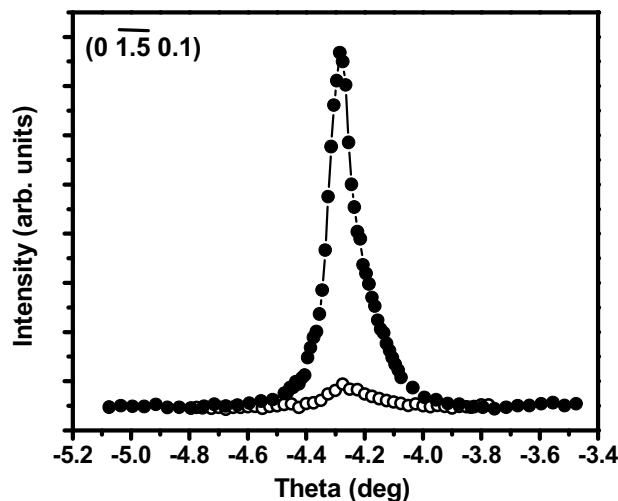


Figure 1: In-plane diffraction peak of the (1×2) missing-row reconstruction of the Pt(110) surface (black circles). The peak (and reconstruction) is almost gone after exposure to only 10^{-7} mbar of CO at 425 K for several minutes (hollow circles). After exposure to high pressures of CO (100 mbar) and higher temperatures (625 K) no peak of the missing row is detectable any more.

We then first expose the reconstructed Pt(110) surface to low pressures of CO, to lift the missing-row reconstruction [49]. By exposing the surface to 10^{-7} mbar of CO at 425 K the peaks of the missing row reconstruction have already almost disappeared. In figure 1, we can see the decrease in intensity of the (0 -1.5 0.1) during exposure to 10^{-7} mbar of CO for approximately 15 minutes (approximately 90 Langmuir). Due to the CO the intensity of the peak has dropped by more than 90%. We have learned from previous High Pressure STM experiments that in order to completely remove the missing row reconstruction, and completely reorder the surface to form large, smooth 1x1 (bulk terminated) terraces, we need to expose the surface to more elevated pressures of CO [9,50]. Our procedure to form a well-ordered bulk terminated surface was to expose the surface to 100 mbar of CO at 600 K for several minutes. The resulting surface shows no intensity at all any more at the position of the peaks of the missing row reconstruction. The width of the resulting surface diffraction peaks of the (1x1) bulk terminated surface correspond to a surface with smooth 1x1 terraces of ~ 3000 Å.

2.3: Exposure to high pressure of O₂

After lifting the (1x2) missing row reconstruction, the surface was cooled to room temperature under CO to preserve the (1x1) structure. Subsequently, the CO pressure was reduced to 10 mbar and 500 mbar of O₂ was admitted to the chamber, after which the sample was heated to 650 K. This procedure led to new diffraction peaks at non-integer **H** and **K** values (see figure 2) forming a regular, slightly distorted hexagonal pattern, exhibiting angles of 57.4° and 61.3°. As indicated in figure 2, the hexagons were aligned with respect to the substrate crystallographic directions. The intensities of the new reflections were similar to those of the surface reflections from the clean substrate, which immediately indicated that they arose from one or more layers of Pt atoms, rather than from an overlayer of merely O atoms or CO molecules. One diffraction peak of the hexagonal unit cell could not be measured due to instrumental limitations, and is missing in the figure. Higher order reflections of this structure have been measured up to 4th order but are not shown in this figure for clarity.

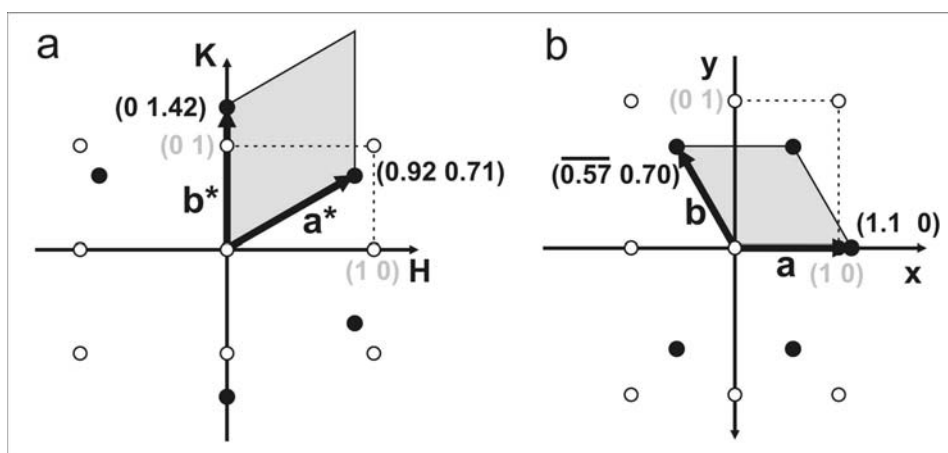


Figure 2: (a) In-plane reciprocal space map of the new unit cell formed on the surface of Pt(110) after exposure to 0.5 bar of O_2 at 625 K (black circles). The new unit cell is nearly hexagonal, and aligned along the H and K axes of the substrate (hollow circles). The reflection in the bottom left quadrant is missing, as it has not been measured due to spatial limitations of the diffractometer. (b) The unit cell in real space, as determined from (a).

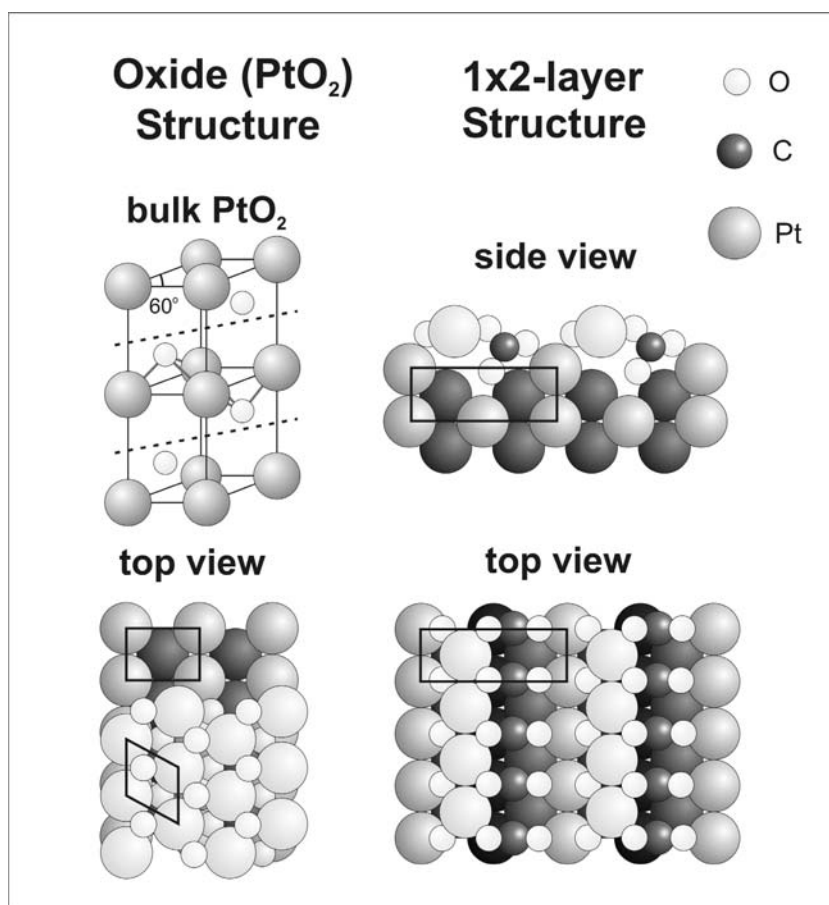


Figure 3: Ball models of both the incommensurate α - PtO_2 layer (left) and the (1x2) commensurate layer (right).

The reciprocal unit cell of this new structure is spanned by two unit vectors which point from the origin to the points $(h\ k\ l) = (0.92\ 0.71\ 0)$ and $(0\ 1.42\ 0)$. These two vectors, which we respectively name $\mathbf{a}^*$ and $\mathbf{b}^*$, span the near-hexagonal unit cell of the new surface structure in reciprocal space. For the transformation of this reciprocal unit cell to real space coordinates we use the formula found in many textbooks [30]:

$$\bar{\mathbf{a}} = \frac{2\pi \cdot (\bar{\mathbf{b}}^* \times \bar{\mathbf{c}}^*)}{\bar{\mathbf{a}}^* \cdot (\bar{\mathbf{b}}^* \times \bar{\mathbf{c}}^*)} \quad (1a)$$

and the cyclic permutations thereof. $\mathbf{c}$ is perpendicular to both $\mathbf{a}^*$ and $\mathbf{b}^*$, and hence also perpendicular to the surface, as both $\mathbf{a}^*$ and $\mathbf{b}^*$ lie in the surface plane. Equivalently, $\mathbf{a}$ and $\mathbf{b}$ are perpendicular to $\mathbf{c}^*$, and hence span the surface plane in real space. Using equation (1a) we can also calculate the length of all real space vectors. For vector $\mathbf{a}$ and $\mathbf{b}$ this results in (example give only for vector $\mathbf{a}$):

$$|\bar{\mathbf{a}}| = \frac{2\pi}{|\bar{\mathbf{a}}^*| \cdot \cos(\angle \bar{\mathbf{a}} \bar{\mathbf{a}}^*)} \quad (1b)$$

For $|\mathbf{c}|$ the equation simplifies to $2\pi/|\mathbf{c}^*|$ as the angle between $\mathbf{c}$ and $\mathbf{c}^*$ is zero. Figure 2 shows the unit cell of both the substrate and the newly formed hexagonal overlayer in both reciprocal (figure 2a) and real space (figure 2b). From these calculations and the resulting unit cell shown in figure 2, we conclude that the newly formed layer on the Pt(110) surface is a nearly hexagonal structure, with unit vectors of respectively 3.19 and 3.06 Å. The angle between the unit vectors is not exactly 60 degrees, hence breaking the 60 or even 120 degree symmetry. The new structure only exhibits mirror symmetry in both the **H** and **K** axes, reflecting the influence of the substrate on the overlayer structure. The unit mesh of this ‘nearly hexagonal’ layer is very close to that of α -PtO₂ (see figure 3), which is hexagonal and has unit vectors of 3.113 Å. This suggests that the overlayer is a distorted PtO₂ layer, azimuthally aligned with the substrate, and oriented with its $\mathbf{c}$ -axis parallel to the surface

normal [51]. Relative to the bulk lattice of α -PtO₂ our surface oxide exhibited compressive strain of 4% (± 1) along the $[1\bar{1}0]$ direction and tensile strain of 2% (± 1) along the $[001]$ direction. The combination of the electronic density of the layer and the stacking along the c-axis (see below) confirms that the overlayer is indeed a distorted α -PtO₂ layer. In different experiments we have also oxidized the (1x2)-reconstructed surface without pre-exposure to CO. The resulting oxide layers exhibited the same structure, but with very poor order [44], both in- and out-of-plane. Hence, all experiments discussed here were performed with oxide layers grown on the (1x1) bulk terminated surface. Although the structure of the oxide layer presented here is different from the structure observed in ref. [44] after exposure of Pt(110) to atomic oxygen at lower pressures, some of the structural elements seem to be similar. In particular, local configurations in figures 1b-d of ref. [44] resemble the geometry of the near hexagonal PtO₂ layer presented here.

A crystallographic data set consisting 22 in-plane reflections (up to 4th order, 10 non-equivalent) and 3 crystal truncation rods (2 non-equivalent, figure 4) was collected to determine the oxide structureⁱ. The oscillations in the diffraction

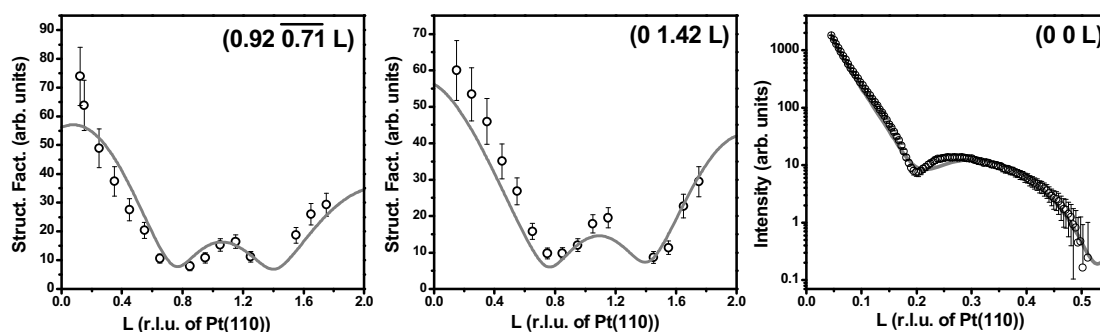


Figure 4: *left:* Structure factor as a function of L at $(H,K) = (0.92 \ -0.71)$. *Middle:* Structure factor as a function of L at $(H,K) = (0 \ 1.42)$. *Right:* Reflectivity curve $[(00L)\text{-rod}]$ (right), measured at 625 K and 0.5 bar of O₂ on Pt(110). L is expressed in reciprocal lattice units of Pt(110). The solid curves are a fit for an incommensurate, 2.6 ML, α -PtO₂ oxide film.

ⁱ The equivalence of the reflections is the one expected for a perfect hexagonal layer, exhibiting a 60 degree symmetry. Because of the distortion of the layer with respect to a perfect hexagonal layer, the equivalent data have not been averaged, but fitted separately.

intensity along **L** in the data in figure 4 show that several Pt layers were involved in the surface oxide. For a quantitative fit to the intensities [52], we started from a distorted α -PtO₂ film and had as free parameters (i) the thickness of the oxide, (ii) the lattice constant along **A**₃ and (iii) the distance between the oxide film and the bulk Pt(110). As the scattering of the X-Rays is largely dominated by the Pt atoms, the stoichiometry and the relative positions of the oxygen atoms were set to those for the bulk oxide. The continuous curves in figure 4 correspond to 2.6 ± 0.1 oxide monolayers (ML), i.e. a 40:60 mixture of 2- and 3-ML thick oxide film, an oxide monolayer being defined as an O-Pt-O triple layer. The fitted Pt-Pt distance is 2.8 Å along **A**₃, which is 36% shorter than the reported distance in bulk PtO₂. The fit to the (00L) rod (figure 4), confirms this rather high density of the oxide layer compared to reported values for bulk PtO₂. This strong contraction might be due to the very small thickness of the oxide film. The distance between the outermost Pt layer of the substrate and the innermost Pt layer of the oxide was found to be 3.3 ± 0.1 Å, which is very close to the Pt-PtO₂ distance calculated by Helveg *et al.* for a fully oxidized Pt atom row on the missing row reconstructed Pt(110) surface [54].

2.4: Reactivity of the Pt surface in CO oxidation

When exposed to not only one single gas, but to a mixture of O₂ and CO, the Pt(110) acts as a CO oxidation catalyst. By leaking a small fraction of the gas mixture present in the reactor to a mass spectrometer, we can analyze the composition of the mixture of gasses inside the reactor. The reactor is used in the so-called batch mode, which means there is no flow through the reactor during the CO oxidation, and that all the CO₂ produced remains in the reactor. If the catalyst is working properly, the CO₂ pressure should rise as a function of time, and the O₂ and CO pressure should drop, as they are being consumed to form CO₂. We can determine the reactivity of the Pt(110) surface by measuring the CO₂ pressure as a function of time, or equivalently the CO pressure. The derivative of the CO₂ pressure as a function of time is directly equivalent to the reactivity of the surface.

By measuring simultaneously the diffraction intensities from the Pt(110) and the mass spectrometer signal, we can correlate the reactivity of the surface with the surface structure *in-situ*. With these reactivity experiments we can

determine the reactivity of both the bulk terminated metallic surface, and the oxidized surface described above.

2.4.1: Reactivity on the PtO₂ surface

All reactivity experiments were performed in the following way: the chamber was first filled with 500 mbar of O₂, with the Pt sample at a temperature in the range 425 - 625 K. The Surface X-Ray Diffraction signal showed that under these conditions the surface was covered with the α -PtO₂ structure discussed above. Pulses of pure CO were then introduced into the chamber (e.g. at point (a) in figure 5). The CO started reacting to CO₂ as soon as it entered the chamber. From the decrease in the CO and O₂ partial pressures, P_{CO} and P_{O_2} , and the increase in the CO₂ partial pressure, P_{CO_2} , the reactivity of the surface

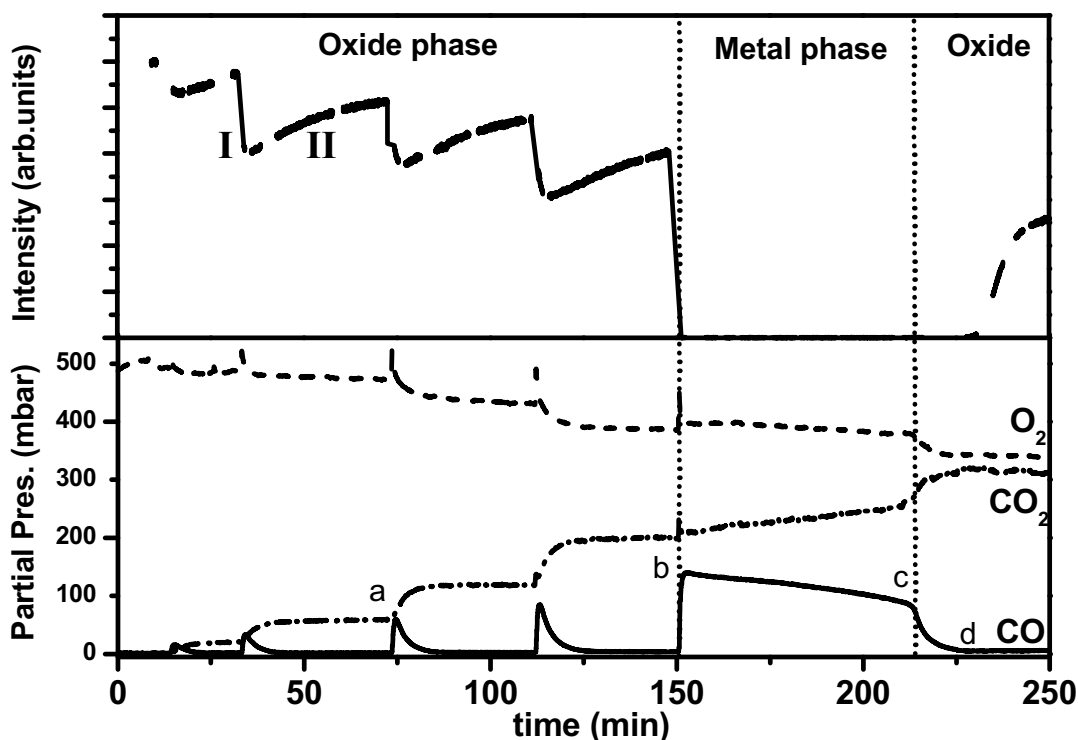


Figure 5: Simultaneously measured X-ray diffraction intensity at (0, 1.42, 0.5) from the quasi-hexagonal oxide (top panel) and partial pressures of CO, O₂, and CO₂ (bottom panel). Separate CO pulses were admitted to the reactor, which was initially filled with 500 mbar of O₂ at a temperature of 625 K. The sharp peaks in P_{O_2} are an artefact due to the sudden increase of total pressure at each CO pulse.

can be determined. We find that 3×10^3 molecules of CO react to CO_2 per site per second at 625 K in a mixture of 80 mbar CO and 500 mbar O_2 . The “turnover frequency” (number of CO_2 molecules produced per site per second) has been measured in experiments performed at different temperatures. The turnover frequency shows to be completely independent of temperature and oxygen pressure [10, 23], and depend linearly on the CO pressure. As CO oxidation is an activated process like any other catalytic reaction, it should exhibit an Arrhenius type behavior as function of temperature. The fact that the reaction rate is fully independent of temperature can only be explained in two ways. The first is that the energy barrier for this catalytic process is effectively 0, implying that every molecule that arrives at the catalysts surface has a probability of 1 to be converted to CO_2 . The other possibility is that not the catalytic reaction, but another process is the rate limiting step in the production of CO_2 . This would be the case if the reaction rate is limited by the diffusion of CO through the predominant O_2 atmosphere to the surface rather than by the oxidation reaction on the catalyst surface. In this case the probability for a CO molecule arriving at the surface to react is indeed 1, although the energetic barrier for the reaction does not need to be 0. A catalyst operates in this diffusion limited regime when the intrinsic turnover frequency of the catalyst is much higher than the flux of reactants to the catalyst surface. The observed turnover frequency then does not reflect the reaction kinetics of the surface, but is equal to the flux of reactants impinging on the catalyst surface. For our experiments we can calculate this flux assuming that the CO, O_2 and CO_2 molecules behave as an ideal gas, we can estimate the maximum flux of CO molecules to the catalyst surface in steady state conditions by using Fick’s first law:

$$J(\mathbf{r}) = -D \cdot \nabla \varphi(r) \quad (2a)$$

With $J(\mathbf{r})$ the flux of particles, D the diffusion coefficient and $\varphi(r)$ the particle concentration at point r . Due to the shape of our reactor (see appendix A), we assume that a gradient in the concentration can only build up in the radial direction, we can simplify equation (2a) to:

$$J(r) = -D \cdot \frac{d}{dr} \varphi(r) \quad (2b)$$

Furthermore, steady state conditions impose that the total number of particles diffusing through each sphere of radius r is constant, otherwise pressure would locally build up in the reactor. We can hence explicitly write $J(r)$ as:

$$J(r) = \frac{F}{4\pi r^2} \quad (3)$$

With F a constant which represents the total number of particles instead of the flux. Putting equation (3) into (2b) and integrating both sides to r gives:

$$\int_{r_1}^{r_2} \frac{F}{4\pi r^2} dr = -D \cdot \int_{r_1}^{r_2} \frac{d}{dr} \varphi(r) dr \quad (4)$$

Solving the integration, this means that the concentration difference between r_2 and r_1 equals:

$$\varphi(r_2) - \varphi(r_1) = \frac{F}{4\pi D r_2} - \frac{F}{4\pi D r_1} \quad (5)$$

From equation (5) we can calculate F_{max} , which represents the maximum number of CO molecules that can diffuse to the catalyst surface, and hence the maximum reaction rate for the diffusion limited case. As the diffusion limited regime implies that every single CO molecule which arrives at the surface is readily converted to CO_2 , the catalyst surface acts as a perfect CO trap. The local CO concentration at the catalyst surface, $\varphi(r_1)$, must hence be equal to 0. We determine $\varphi(r_2)$ from the partial pressure of CO measured at the wall of the reactor. At this position the local partial pressure of the gasses can accurately be determined as both the pressure gauge and the leak valve to the mass spectrometer are positioned there. In the specific case of diffusion limited reaction $\varphi(r_2) - \varphi(r_1)$ is hence equal to $\varphi(r_2)$ which itself corresponds to the

(measured) partial CO pressure in the reactor. With r_2 corresponding to a position at the wall of the reactor, and r_1 the radius of a small sphere with a surface area equal to that of our sample we can state that $r_2 \gg r_1$. Putting this in equation (5), and adding that $\varphi(r_2) - \varphi(r_1) \approx \varphi(r_2)$, equation (5) simplifies to:

$$\varphi(r_2) = -\frac{F_{\max}}{4\pi Dr_1} \quad (6)$$

or:

$$F_{\max} = -4\pi Dr_1 \cdot \varphi(r_2) \quad (7)$$

We note that $F_{\max}$ has a negative value, as it describes particle that are being removed from the system.

The geometry in which our sample is mounted does not allow for direct diffusion from the bottom part of the reactor volume to the catalysts surface, due to the position of the sample on the ceramic heating plate. For this reason we only consider a half spherical solid angle for the impingement of CO onto the surface, diminishing the value for $F_{\max}$ found from equation (7) by a factor of 2. Our Pt single crystal sample has a surface of 1.13 cm², which corresponds to half a sphere with $r = 4.2$ mm. The dimensions of our reactor dictate that r_2 is equal to approximately 10 cm, confirming that $r_2 \gg r_1$. We take for D the *tracer diffusion coefficient* for CO in 500 mbar of air, which is approximately 1.25 cm²/second [53]. By putting these numbers into equation 7, we calculate $F_{\max}$. Dividing $F_{\max}$ by the number of available atomic sites on the sample surface, we then calculate the maximum number of CO molecules that will impinge on the catalyst surface in molecules per site per second. For the experimental conditions presented earlier, i.e. 80 mbar of CO in 500 mbar of oxygen and 625 K, we calculate a maximum flux of $3.0 \cdot 10^3$ molecules/site/sec. This value is in full agreement with the reaction rate found in those conditions, and confirms the hypothesis that the reaction rate in these conditions is diffusion limited. The intrinsic reactivity of the catalyst must hence be significantly higher than the number mentioned here. Although this is an unusually high reactivity, several other groups have found similarly high turnover frequencies in comparable conditions [55-58]. One of these reports

mentions that the reaction rate is indeed diffusion limited in similar conditions for Pt, Pd and Rh single crystals and polycrystalline wire catalysts. To overcome the diffusion limitation, they have diminished the total surface area of their catalysts. Although their results are inconclusive, a maximum reaction rate of $4 \cdot 10^4$ molecules/site/sec has been measured on a Pd(110) sample at 525K in 105 mbar of a 5:1 mixture of CO:O₂ [58]. These observations support the statement that the intrinsic reaction rate of the catalyst is much higher than the maximum flux of CO molecules in these conditions.

2.5: Surface morphology of the α -PtO₂ surface

In the top panel of figure 5 we show the diffracted intensity at (0 1.42 0.5), which corresponds to a diffraction maximum of the PtO₂ oxide layer. The introduction of CO causes a rapid $\sim 25\%$ drop in the intensity followed by a slow recuperation. This would seem to indicate a partial reduction of the oxide layer, resulting in a thinner oxide layer, and hence a lower diffraction intensity, followed by a slow re-growth of the oxide layer to its original thickness. However, we have measured the diffraction intensities as a function of L of the oxide layer during the recovery. They did not change significantly, indicating that the surface remained covered by an equally thick oxide layer throughout the reaction, contradicting this initial proposition. The intensity drop observed

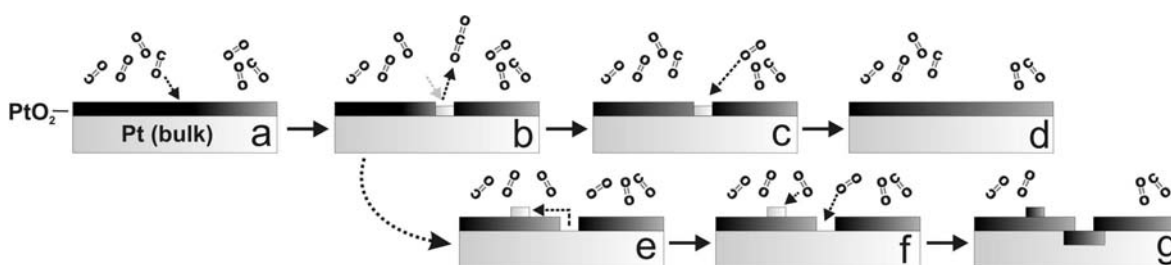


Figure 6: Roughening due to CO oxidation with the Mars-Van Krevelen mechanism. Most oxidation events will occur like depicted the images **a** to **d**. One CO molecule is oxidized, locally (partially) reducing a single Pt atom (**b**). The Pt atom is immediately re-oxidized (**c**), and the oxide layer is equal to the one at the start of the cycle (**d**). In very rare cases the reduced Pt atom can diffuse away from its original position (**e**) before being re-oxidized (**f**), forming a hole and a protrusion in the oxide layer (**g**), i.e. forming roughness.

in figure 5 after the introduction of each CO pulse is therefore ascribed to a *roughening of the oxide layer caused by the CO oxidation reaction*. Such a direct correlation between the surface morphology and the oxidation reaction can only be explained if the CO molecules react with one, or multiple atoms *within* the oxide layer.

We propose a model in which a CO molecule reacts with the oxygen atoms of the oxide layer, locally (partially) reducing the oxide layer, which we would describe as a Mars - Van Krevelen type mechanism [4]. This model is clearly different from the Langmuir-Hinshelwood type reaction, where the CO molecules would react with a molecule or atom adsorbed *on top of* the surface, which is commonly assumed to be responsible for the CO oxidation process on Pt surfaces [60]

Figure 6 shows the proposed process in schematic images. A single CO molecule interacts with the oxide layer, binding with an oxygen atom from the layer and hence (partially) reducing a single PtO_2 unit cell, leaving behind an under-coordinated Pt atom (figure 6 a,b). Normally, this partially reduced Pt atom is immediately re-oxidized by the oxygen from the gas phase (figure 6c), and the original oxide layer is restored (figure 6d). These ‘reduction-oxidation’ cycles have no effect on the structure of the oxide layer. Only rarely the partially (or fully) reduced Pt atom has time to diffuse away from its original position in the oxide layer, leaving behind a hole in the oxide layer (figure 6e). The Pt atom that has diffused away from its original position is re-oxidized on top of the original oxide layer, just as the Pt atoms ‘at the bottom of the hole’ (figure 6f). This process leads to a growing density of pits and protrusions in the oxide layer, i.e. roughness, which manifests itself as a drop in the out-of-plane diffraction intensity, as can be seen at every CO pulse in figure 5 at I. The sudden change in intensity can hence directly be correlated to this Mars-Van Krevelen type mechanism, in which the CO molecules react with the oxygen atoms within the oxide layer. We can also see that the recovery of diffracted intensity starts shortly *after* every CO pulse (figure 5 at II). Following the model for the roughening as proposed here above, the roughening of the surface is a function of the amount of CO oxidized by the PtO_2 layer. The formation rate of roughness is then directly dependent on the reaction rate, and hence on the CO pressure. Counteracting this roughening process we see an smoothening process: As soon as roughness is formed on the surface, the oxide surface will smoothen as a flat oxide surface is energetically more favorable than a rough

oxide surface [57]. The smoothening is a function of the temperature (annealing), the diffusion coefficient for the oxide layer, and the amount of roughness present on the surface [58].

The formation of roughness will start immediately after the introduction of the CO into the reactor. According to our model, the rate of roughness formation $f(t)$ is a function of the reaction rate, and in this diffusion limited situation i.e. a function of the CO partial pressure P_{CO} . If a single reduction event is responsible for a single roughening event, $f(t)$ will be linearly dependent on P_{CO} , with the probability c_0 of such an event happening. If two subsequent and locally coordinated reduction events are necessary, $f(t)$ will scale with $(P_{CO})^2$. In general, $f(t)$ will scale with $(P_{CO})^n$, with n the number of coordinated reduction events necessary for a roughening event. If several subsequent and locally coordinated events are indeed necessary for a Pt atom to diffuse out of the oxide layer, the rate of formation of roughness should also depend on the oxygen partial pressure P_{O_2} . Following the same arguments as here above, the probability for several reduction events taking place subsequently *without a re-oxidation event* in the meantime should scale with $c_0 \cdot (P_{CO})^n \cdot (1 - c_1 \cdot (P_{O_2})^m)^n$ with $c_1 \cdot (P_{O_2})^m$ the probability of re-oxidizing a locally reduced patch on the oxide layer. As we have not varied the oxygen partial pressure during our experiments, the whole term $1 - c_1 \cdot (P_{O_2})^m$ reduces to a constant, and we can effectively take $c_0 \cdot (P_{CO})^n$ as the probability of roughness formation, with c_0 now a function of P_{O_2} .

We see in figure 5 (lower panel) that the CO pressure drops exponentially as a function of time, after the introduction of each CO pulse. The roughening rate will hence have the same exponential time dependence, combined with the power law dependence mentioned here above:

$$f(t) = c_0 \cdot P_{co}(t)^n = c_0 \cdot \left(P_{co}(0) \cdot e^{-\alpha t} \right)^n = c_0 \cdot P_{co}(0)^n \cdot e^{-n\alpha t} \quad (8a)$$

With α the time constant for the drop in CO pressure. Renaming $c_0 \cdot P_{CO}(0)^n$ as a single constant c_1 the formula simplifies to:

$$f(t) = c_1 \cdot e^{-n\alpha t} \quad (8b)$$

If no smoothening would occur, the change in total roughness $R(t)$ as a function of time would be equal to $f(t)$:

$$\frac{dR(t)}{dt} = f(t) \quad (9a)$$

Or equivalently:

$$R(t) = \int_0^t f(t') dt' = -\frac{c_1}{n\alpha} \cdot e^{-n\alpha t} + \text{constant} \quad (9b)$$

Figure 7 (left panel) shows the roughness development as a function of time, if no annealing would occur. The smoothening rate $a(t)$ is the amount of roughness removed from the surface as a function of time. As smoothening due to annealing is a stochastic process, the smoothening rate $a(t)$ is linearly dependent on the amount of roughness present on the surface at time t [59]:

$$a(t) = c_2 \cdot R(t) \quad (10)$$

Taking the smoothening of the surface due to annealing into account, the amount of roughness is now determined by the sum of the formation of roughness, and the removal of it by the smoothening process:

$$\frac{dR(t)}{dt} = f(t) - a(t) \quad (11)$$

Putting equation (8b) and (10) in equation (11) we get:

$$\frac{dR(t)}{dt} = c_1 \cdot e^{-n\alpha t} - c_2 \cdot R(t) \quad (12)$$

Solving this differential equation gives:

$$R(t) = -\left(\frac{c_1}{\alpha - c_2}\right) \cdot e^{-\alpha t} + c^* \cdot e^{-c_2 t} \quad (13)$$

Where c^* is a constant that follows from the integration of equation (12), and which together with the factor $c_1/(\alpha - c_2)$ defines the starting value of the roughness. The value for $R(t)$ at $t \rightarrow \infty$ is 0 for all values of c^* according to equation (13). This means that the steady state condition for the surface is one with 0 roughness. Because of this, we also define the roughness at $t = 0$, i.e. *before* the first CO pulse is administered, as 0. In figures 5 and 8 we see that the intensity does not fully recover after each pulse. This means that each subsequent CO pulse, except the first one, starts roughening a surface which has a non-zero initial roughness. Because of this, we do not find the same value for c^* for all CO pulses. In an ideal experiment, the time in between each pulse would be long enough to allow the surface to fully smoothen, and each CO pulse would be administered to a surface with 0 roughness.

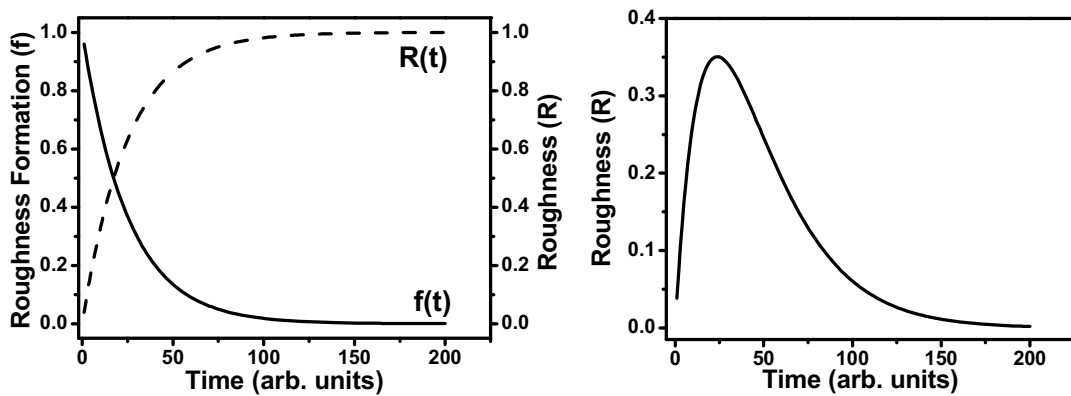


Figure 7: Left panel: Calculated roughness formation rate ($f(t)$, solid line), and corresponding total built up roughness ($R(t)$, dashed line) as a function of time for an exponential decay of the reaction rate in time. **Right panel:** Calculated total roughness as a function of time for roughness formation, and competing annealing process.

Equation 13 could then be simplified to:

$$R(t) = -\frac{c_1}{\alpha - c_2} \cdot (e^{-\alpha t} + e^{-c_2 t}) \quad (14)$$

Figure 7 (right panel) shows the development of the roughness as a function of time, taking the annealing process into account. We can see that the total roughness is determined by the sum of both processes. This means that the surface will roughen when the CO pressure and reactivity are high, i.e. shortly after the introduction of a CO pulse. As roughness is formed and the roughness formation rate drops due to the drop in CO pressure, the smoothing rate will quickly catch up with the roughening. The surface will start smoothing back

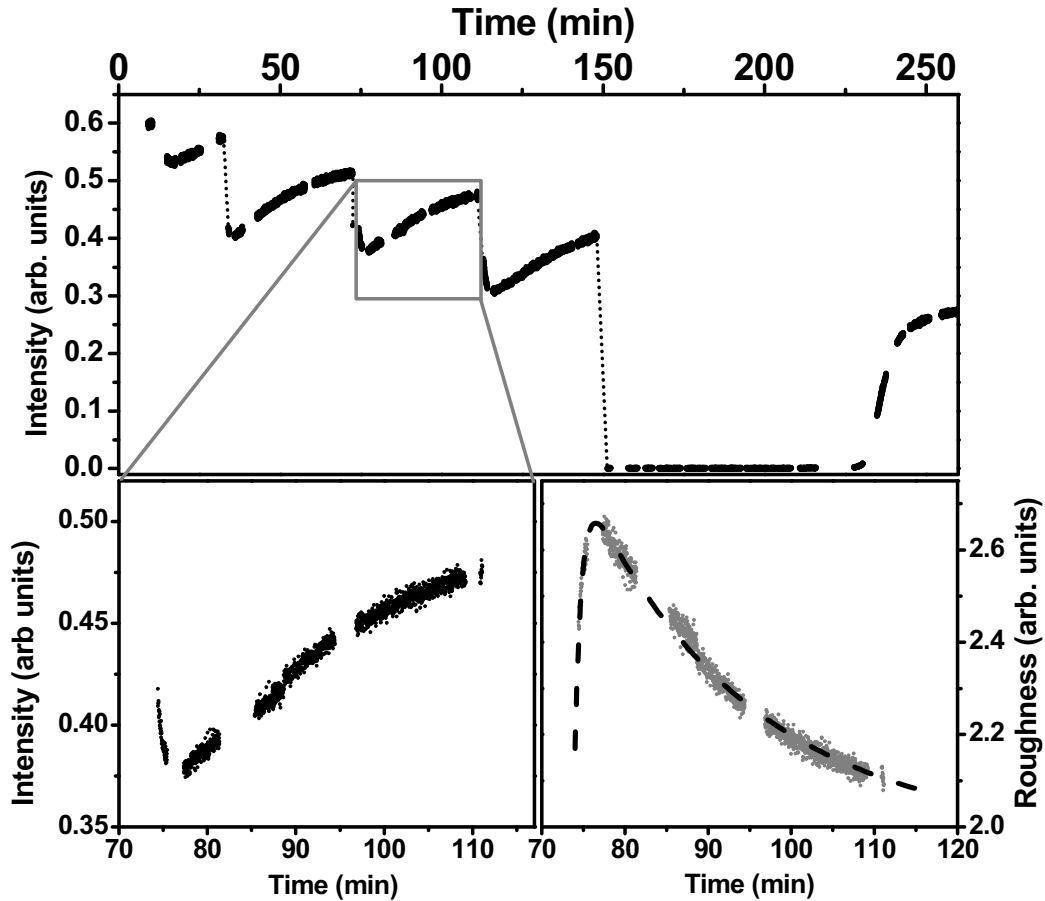


Figure 8: *Top panel:* Peak height of PtO₂ diffraction maximum as function of time, during catalytic CO oxidation (see fig 3); $P \sim 500$ mbar, $T = 625$ K. **Bottom left:** Zoom on peak height during one single CO “pulse”. **Bottom right:** Peak height converted to roughness. Dashed line is the fit to this data using equation 14.

to a flat surface soon after the introduction of the CO pulse (figure 8). Although the correct method for measuring the roughness of this surface would be to measure the reflectivity, we find that in our experiments the inverse of the peak height of the diffraction maxima of the oxide layer scales very well with the roughness of that layer. From the peak height shown in figure 8, we can get a good *qualitative* measure for the roughness of the surface. After converting the peak height to a roughness value (figure 8, lower right panel), we can fit the roughness development as a function of time using equation (14). From the quality of the fit, we see that the surface roughness indeed behaves as described here above. We get an excellent fit for a very short typical time for the roughening α of about 1 minute, and an annealing process at this temperature which is approximately 20 times slower.

This roughening of the surface during CO oxidation through a Mars-Van Krevelen mechanism on Pt has already been proposed by Hendriksen *et al.* from High Pressure STM under similar conditions [9]. Our experiments are in full agreement with their findings.

We also note that during the different CO pulses the *FWHM* of the different in-plane reflections remains almost unchanged. Due to the incommensurability of the oxide layer, the in-plane domain size is already very small ($\sim 7 - 20$ nm depending on growth conditions) in the oxide layer grown on the unreconstructed Pt(110) surface, and it does not reduce further during the roughening.

2.6: Switch from oxide to metal induced by CO pulse

At the fifth CO pulse (figure 5, point (b)), the peak in CO pressure was so large that the oxide layer was reduced completely: the diffracted intensity from the oxide layer dropped to zero and the surface reverted to the bulk-terminated (1x1) periodicity, found before in pure CO. A simultaneous decrease was observed in the reactivity. The turnover number at (b) as calculated from the decay rate of P_{CO} is approximately $1.5 \cdot 10^2$ molecules/site/sec which is roughly a factor 30 lower than the reactivity would have been if the surface would have behaved like at the preceding pulses. The reaction order has also clearly changed, since between the points (b) and (c), P_{CO} varied roughly linearly as a function of time, whereas it decayed exponentially during the preceding pulses.

From this we conclude that the reaction rate on the reduced, metallic surface is almost independent of the CO pressure, whereas the reaction rate found for the oxide surface depends linearly on P_{CO} . The O_2 partial pressure is itself, like the reaction rate, almost constant as a function of time during this metallic branch, making it difficult to make any statement about the dependence of the reaction rate with respect to the O_2 pressure. We assume that the oxidation of CO on the metallic surface occurs through a Langmuir-Hinshelwood reaction mechanism, as proposed in literature [2,3,60]. For the reactivity to be independent of the CO pressure in a LH reaction mechanism, the surface needs to be completely CO saturated.

2.6.1: Rate Limiting step on the metallic surface

The reaction rate found on the metallic surface varies between $1.5 \cdot 10^2$ and $6.0 \cdot 10^2$ molecules/site/second at respectively 100 and 65 mbar of CO in 500 mbar of O_2 at 625 K. These values are clearly below the maximum diffusion maximum for CO molecules in these pressure and temperature conditions. Putting these turnover frequencies into equation (5), we calculate that the pressure drop between the measured CO partial pressure at the wall of the reactor and the local CO partial pressure at the catalyst surface is only in the order of 10 mbar. At these reaction rates the catalyst is hence *not* in the diffusion limited regime, and the observed reaction rate indeed reflects the intrinsic turnover frequency of the catalyst.

2.7: ‘Spontaneous’ switch to high reactivity

For each CO_2 molecule formed, 1 molecule of CO but only half a molecule of O_2 is consumed. This means that in this closed reactor (batch) configuration, twice more CO than O_2 is consumed during the formation of CO_2 . The CO oxidation reaction will hence always push the balance of the gasses towards a more oxidizing environment. The only exception to this is if at any moment *all* the oxygen is consumed and the CO is not. This means that due to the reaction, the conditions in the reaction chamber will slowly shift towards more oxidizing conditions as a function of time, and when enough CO is consumed, the surface will ‘spontaneously’ re-oxidize. This is what happens at point (c) of figure 5. At this point in figure 5 the partial pressure ratio P_{CO}/P_{O_2} reaches approximately

0.2 . The CO_2 formation rate spontaneously accelerates, and the variation in all partial pressures exhibits an exponential behavior again. From this we conclude that the catalyst had reverted to its ‘high-reactivity’ phase, i.e. the oxide phase.

Interestingly, the diffraction intensity associated with the PtO_2 incommensurate oxide layer only comes back after approximately 20 minutes after (c), at point (d). At this point, almost all CO has already been consumed and transformed into CO_2 . The reaction rate, which scales linearly with the CO pressure is at that point almost 0. Because of this delay, the high reactivity found at point (d), cannot be linked with the presence of the PtO_2 , as is the case for the first part of the experiment, before (c).

2.8: Intermediate structure: commensurate (1x2)

In figure 5 the X-Ray detector is placed at $(h\ k\ l) = (0\ 1.42\ 0.5)$, which corresponds to the diffraction maximum of one of the crystal truncation rods of the hexagonal PtO_2 layer. The intensities plotted in figure 5 have been recorded *only* as a function of time, with the detector at a fixed position. This means that we are only sensitive to structures that exhibit a diffraction maximum at that specific position. We remain insensitive to any structure with diffraction maxima at different positions in reciprocal space, or even this very structure, but with a slightly contracted or expanded lattice constant. By measuring more than one single point in reciprocal space, i.e. scanning a small area (line) repetitively we can be sensitive to different structures as a function of time. By then plotting a series of these scans as a function of time (figure 9, top panel), we get a clear picture of the development of different structures on the surface, instead of being sensitive to just one structure. Each of the scans plotted in figure 9 takes approximately 40 seconds, and consists of 40 points, 0.5 sec counting time per point. Our time resolution for structural changes on the surface is hence in the order of 40 seconds in the worst case, or less than 1 second in the case the detector is exactly at the peak position when the surface structure changes.

We see from figure 9 that simultaneously with the moment the reaction speeds up, a new diffraction peak appears in reciprocal space. This new peak, which exhibits no time delay with respect to the acceleration of the reaction rate appears at integer **H**-values and half-integer **K**-values. The new peaks

correspond to a commensurate (1x2)-structure (Ball model see figure 3, in-plane diffraction map see figure 10).

The intensities of the new diffraction peaks are high, indicating that also these are due to a structure involving Pt atoms. As discussed earlier in this chapter, the Pt(110) surface exhibits a so-called missing-row reconstruction after cleaning in UHV conditions, which has exactly the same in-plane symmetry as the one exhibited by this new structure [33]. One could think that the (1x2)-structure measured here is this already known structure. Figure 10 shows **L**-scans of the crystal truncation rods of two of the new (1x2)-structure diffraction maxima. They clearly differ from the calculated values expected for the (1x2) missing-row reconstruction, indicating that the structure differed strongly from the known missing-row reconstruction. We have found this

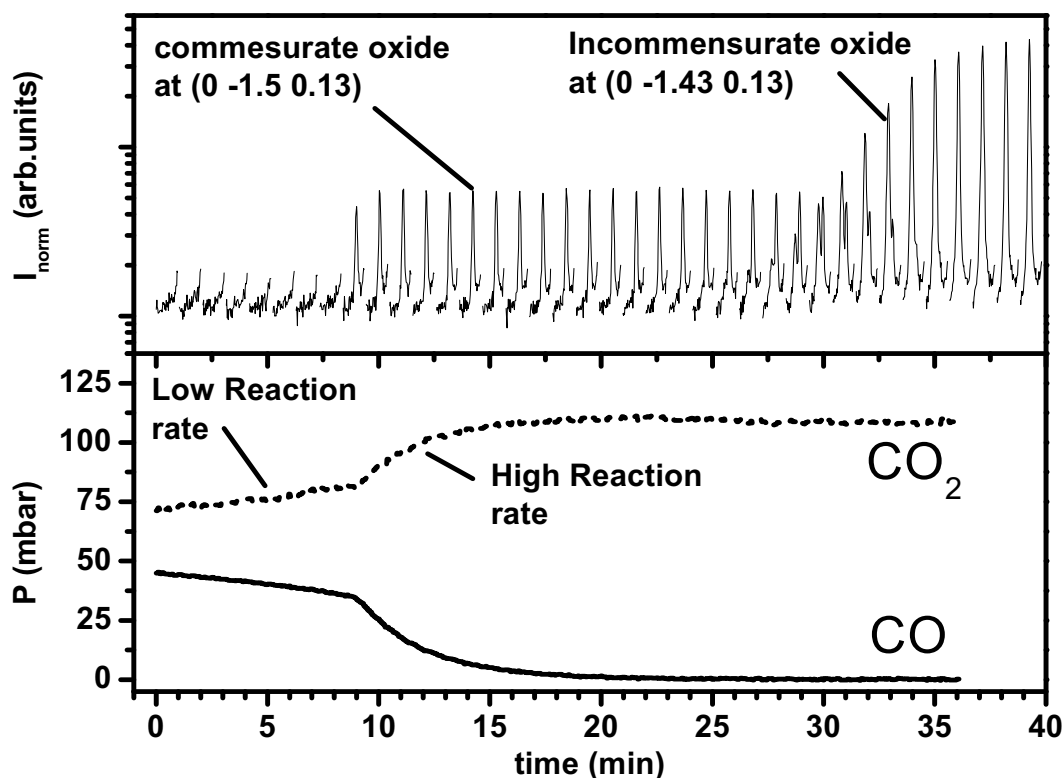


Figure 9: top panel: Diffraction scans in a narrow range from $K = -1.30$ to -1.65 and at $(H = 0, L = 0.13)$. **Bottom panel:** Partial pressures of CO and CO₂, simultaneously measured at $P_{O_2} = 500$ mbar and $T = 530$ K. Together with the increase in the reaction rate, at $t = 9$ min, a half-order diffraction peak appeared at $K = -1.50$. When nearly all CO had been consumed, at $t \approx 30$ min, this diffraction peak decreased to zero while the peak of α -PtO₂, at $K = -1.43$, appeared.

commensurate (1x2)-structure to only be stable under reaction conditions. Efforts to evacuate the present gasses, to study the new structure under UHV, or attempts to quench the surface with the (1x2)-structure present all failed. Even during reaction conditions the time during which the (1x2)-structure is stable is very limited.

The solid curves in figure 10 show the fit of the L-scans, based on a simple structural model in which every second close-packed $[1\bar{1}0]$ row of surface Pt atoms was strongly displaced both in- and out-of-plane. In addition to this large displacement, small relaxations of all other atoms in the two topmost layers of Pt were considered. Relaxations beyond this second layer did not add any accuracy to the fit, and were hence neglected, as were the C and O atom positions. In the best-fit structure every second Pt surface atom row was displaced by $(0.5\ -0.38\ 0.67)$, expressed in unit vectors of the (1x1) unit cell, while the relaxations of the other atoms were modest (figure 3). With the low-symmetry position of the shifted Pt atom rows, two equivalent mirror versions can be formed, and the best fit was obtained for nearly equal proportions of these.

2.8.1: The (1x2)-structure: DFT calculations

The observation that the (1x2)-structure was only stable under reaction conditions, when both CO and O₂ were present, strongly suggests that the (1x2)-layer was stabilized by the presence of CO or a CO-related species, adsorbed on or in the (1x2)-structure. In order to further substantiate this notion Density Functional Theory (DFT) calculations have been performed by B. Hammer and T.M. Pedersen [61, 62], following the methods described in ref. [44]. They have investigated structures with the Pt atom density of Pt(110)-(1x1) and at most one first layer row shifted half a lattice spacing along the A_1 direction, as found in the experiment, and with adjustable displacements along A_2 and A_3 . Only one structure was identified that involved a high-lying Pt row, consistent with the experiment (figure 3), and its free energy per surface unit cell was within 0.27 eV from the most stable structure found. Since this energy difference is comparable to the accuracy of DFT [63] for these specific calculations, the DFT results seem to support the presence of a surface structure with such a high-lying Pt-row.

An essential feature of the proposed structure is the presence of one carbonate ion (CO_3^{2-}) per unit cell, which stabilizes the high Pt row and thus the commensurate (1x2)-layer. The most stable structure found was incompatible with the structural data from the X-ray experiments, and is hence not presented here.

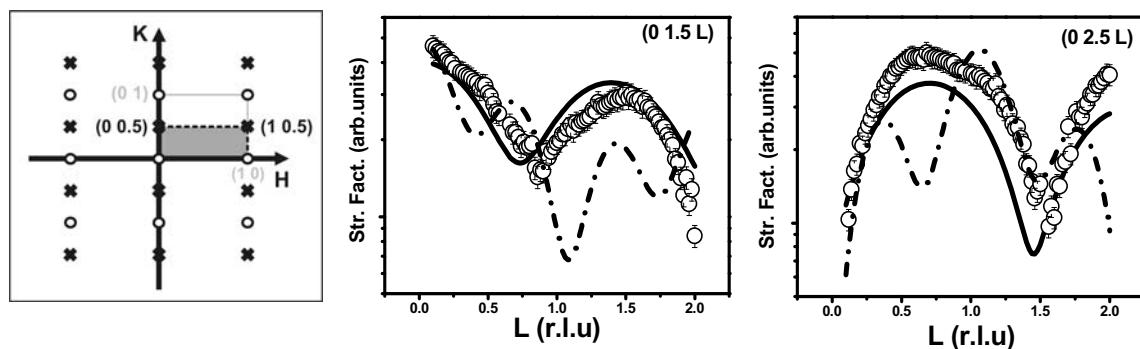


Figure 10: left: in-plane reciprocal space map of the commensurate (1x2)-structure. Middle and right: The (0 1.5 L) and (0 2.5 L) rods of the (1x2)-structure, formed at 625 K and 0.5 bar of O_2 and approximately 35 mbar of CO on Pt(110). The solid curves are fits for the carbonate-stabilized commensurate oxide film, as discussed in the text. The dash-dot lines are calculated curves for the (1x2) missing row reconstruction [14].

2.8.2: Mixed coverage and stability of (1x2)-structure

Looking further down the timeline in figure 9 we see that the incommensurate, quasi-hexagonal oxide structure starts gaining intensity only after approximately 30 minutes. The appearance of the incommensurate oxide layer coincides with the disappearance of the (1x2)-layer. By normalizing the total intensity of the incommensurate oxide layer to 1, we get a crude number for the “coverage” of the surface with respect to the incommensurate oxide. We can do the same for the (1x2)-layer. The result of the intensities normalized for every scan of figure 9, and plotted as a function of time is shown in figure 11. The average of both normalized intensities has also been plotted. We can interpret this averaged value as a “total coverage” of the surface. From the constant value of this total coverage, we conclude that the surface is *fully covered* by either the (1x2)-layer or the incommensurate oxide, or a mixture of both at any time during this reaction. This excludes the possibility that a small fraction of the surface would e.g. still be in the metallic state and responsible for a part of the reactivity measured during the experiment. From this graph we can also conclude several things about the growth rate, the rate limiting step for the oxide growth, and whether the surface is in thermodynamic equilibrium with the gas phase or not.

The fact that the normalized curve of the oxide is exactly complementary with the normalized curve of the (1x2)-layer means that the bulk-like oxide layer grows to its full thickness already while it is competing with the (1x2)-layer on the surface. If the thickness of the oxide layer would continue to grow after the (1x2)-layer has disappeared, the normalized sum of both would not add up to 1 during the growth of the oxide peak, but to a lower value until the oxide would have reached its full thickness. The fact that the ‘average’ curve in figure 11b does not show a dip in intensity during the mixed (1x2) and oxide phase shows that the growth of the oxide layer is *not* the rate limiting step for the process of going from the (1x2)-layer to the oxide covered surface. Figure 11c shows the normalized intensity of the oxide layer at respectively 530 K and 510 K as a function of time. The oxide growth rate, which can be derived from this graph, is equal for both temperatures. We can therefore either conclude that the growth of the oxide layer, which replaces the (1x2)-layer, is a process which is *not* thermally activated, or that the switch from the (1x2)-layer to the oxide is *not* limited by the oxide growth rate. In this latter case, the surface structure corresponds to the real thermodynamic equilibrium structure at all times during

the experiment, and only depends on the partial pressures of the different gasses present at a specific time. As the growth rates are much slower than the exchange of molecules between the gas phase and the surface, we can rule out a process with 0 activation energy. The rate of such a process should be in the order of the impingement rate of molecules on the surface (i.e. the ‘attempt frequency’) which is between 10^3 (for CO) and 10^6 monolayers per second. The process observed here is much slower; the (1x2)-layer decays at a rate of 0.1 monolayer per minute, the oxide grows at about 3 times that rate. A process with 0 activation energy is hence excluded and we conclude that during these experiments the (mixed) surface structure and composition is always in thermodynamic equilibrium with respect the gas phase. The mixed coverage of the (1x2)-layer and the oxide at any moment during the experiment is hence the correct equilibrium structure for the present gas mixture, and not an unstable or transient structure. Whether this is a static or dynamic equilibrium cannot be concluded from our experimental observations, but in view of the proposed Mars - Van Krevelen mechanism and the high reaction rate, a dynamic equilibrium is the most probable.

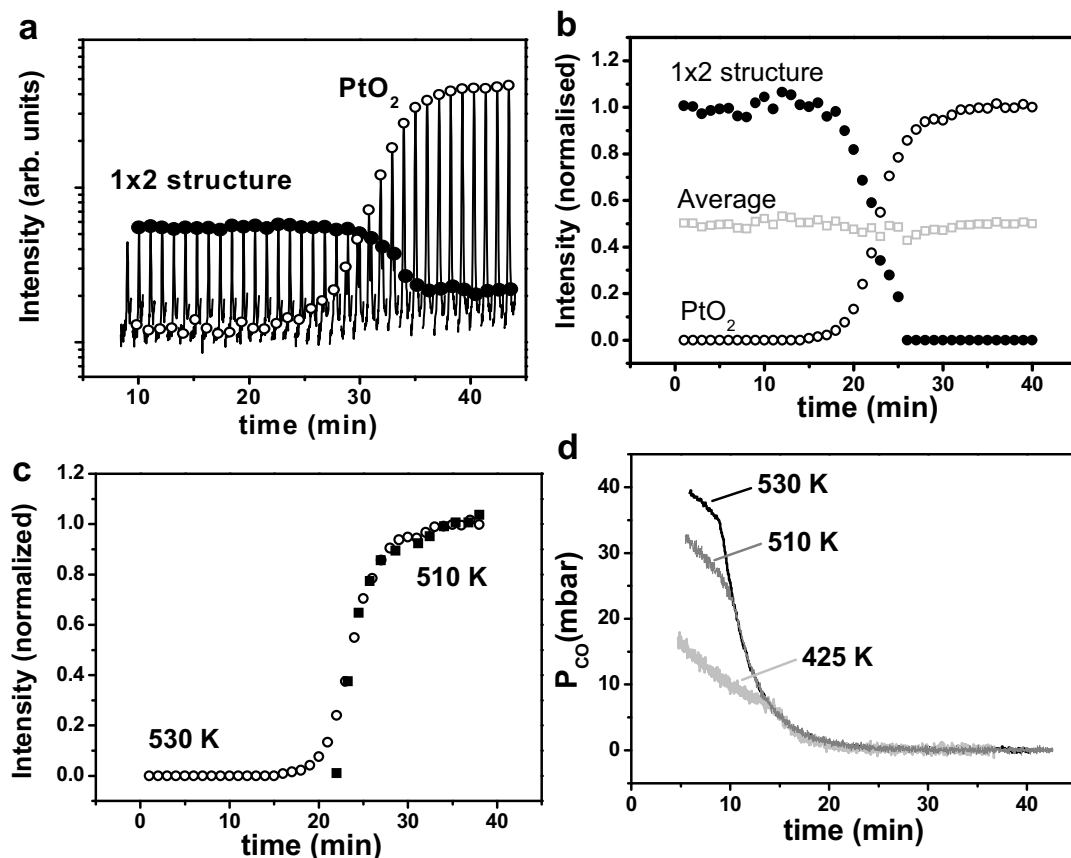


Figure 11: **a)** The intensities of the (1x2) layer (black circles), and of the bulk oxide (hollow circles) from the dataset shown in figure 9. **b)** The average of both normalized intensities $((I_{1x2} + I_{PtO_2})/2$, grey hollow squares) The constant value of this average shows there is no variation in total coverage, and that hence the surface is continuously covered by either the (1x2) structure or the bulk-like PtO₂ structure, or a combination of both. ($T = 530$ K, $P_{total} \sim 0.5$ bar). **c)** Comparison of the growth of the oxide layer upon switching from (1x2) to oxide at 530 (hollow circles) and 510 K (black squares). From the similarity of both curves we conclude that this is not governed by the energy barrier of the process and the growth rate of the oxide, but rather that the coverage of oxide at any time t reflects the true thermodynamic equilibrium state of the system. **d)** The reaction rate as a function of temperature in the low (metallic) branch and high (1x2 / oxide) branch. The reaction rate in the high reactive is the same for all temperatures, indicating that the reaction rate is diffusion limited as it does not exhibit the expected Arrhenius type behavior.

If the structure of the surface indeed only depends on the chemical potential of the different gasses present, the same structure (or mixture of structures) in the different experiments must be dictated by the chemical potential. It does not need to be equal for the exact same gas composition of each experiment, as the temperature of each experiment is different and the chemical potential changes with temperature. But the *rate* at which the surface structure changes is determined by the *rate of change in gas composition*. This rate is the same for different experiments, because the change in gas composition is determined by the reaction rate, and this value is limited by the diffusion of the CO through the predominant O₂ atmosphere. The rate at which the gas pressures change during the different experiments must be equal (figure 11, bottom right panel), and the rate of change of the surface structure also will be. This is clear evidence in support of the statement made here above that the surface structure, even when composed of a mixture of the (1x2) and α -PtO₂ oxide layer, reflects the true, thermodynamic equilibrium situation in which the sum of surface free energy and chemical potentials has been minimized.

Changing the temperature at which the experiment is performed has strong influence on the stability of both the oxide and (1x2) phases. In figure 12 I show consecutive experiments performed at respectively 530 K (top panel), 510 K (middle panel) and 425 K (lower panel). The lifetime of the (1x2) phase is clearly longer at more elevated temperatures. At 425 K the lifetime shortens to a point where the (1x2)-layer is only visible in the very first scan, and then is already gone in the second one. To get a clear value for the lifetime of the (1x2)-layer at this temperature, we have repeated the experiment, with the detector at one single position (no scan), which allows for a time resolution well below 1 second. The result of this is shown in the inset (bottom right). The typical lifetime for the (1x2)-layer has been fitted with a single exponential decay. From this fit we find a typical time τ of 45 seconds. The counting time for each point in this scan is 0.2 seconds. Even in this faster scan, not a single point has been measured showing an intermediate intensity, i.e. showing the growth process of the (1x2)-layer. We can conclude from this that the switching from the metal surface to the (1x2)-layer is much faster than a single measurement point, i.e. much faster than 0.2 seconds.

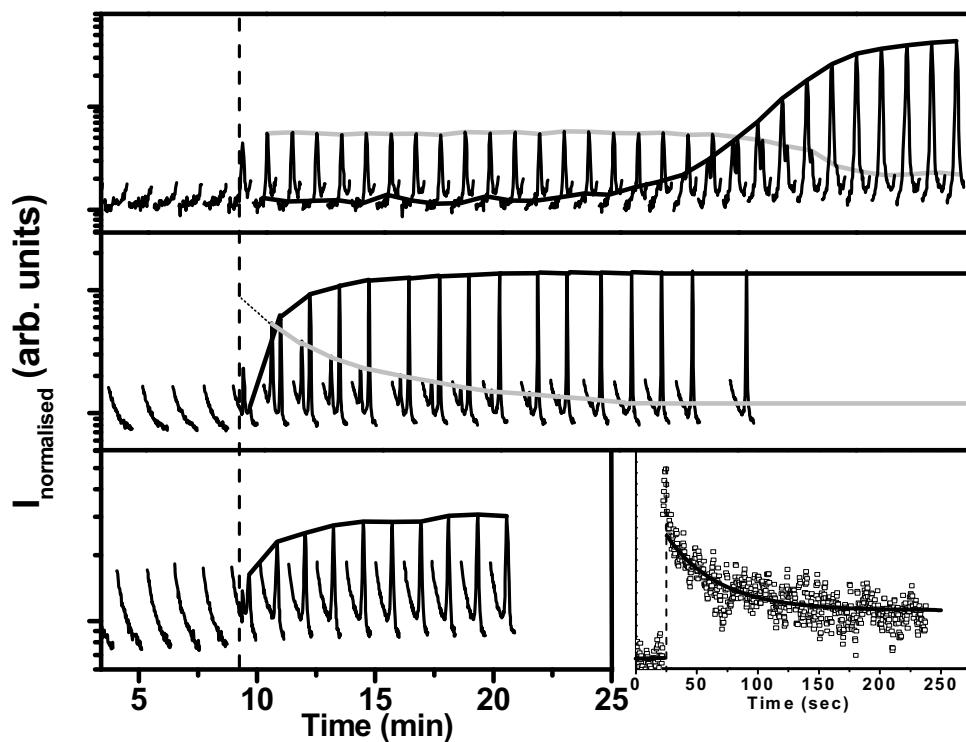


Figure 12: Behavior of the (1x2)-structure and PtO_2 layer as a function of time for respectively 530 K (top panel), 510 K (middle panel) and 425 K (bottom panel). The dashed line gives the exact switching moment from low to high reactivity. The solid line are just lines to guide the eye along the intensity maxima of both the (1x2)-structure and the oxide layer. At 425 K the (1x2)-structure appears and is removed in a time of the order of a single scan. It can be seen only as a small, asymmetric peak in the scan starting at minute 9 of the bottom panel, exactly at the dashed line. The inset on the right (bottom panel) shows the behavior as a function of time of the (1x2) structure with the detector at a fixed position. The intensity has been fitted with a simple exponential decay function (solid line). The typical time for the structure to disappear is 45 seconds. This is indeed in the same order as a single line scan.

The change in lifetime is caused by the varying CO pressure, or more accurately the CO/O₂ ratio at which the surface switches from the metal surface to the high reactive, (1x2)-layer *or* oxide layer. This change in the CO/O₂ ratio at which the surface switches is caused by the change in chemical potentials of the different gasses with respect to the surface free energy of the different structures. We can gain more insight into the behavior of the surface by plotting the CO/O₂ ratio at which the surface switches from the metallic phase to the (1x2)-layer, and then from (1x2)-layer to the incommensurate oxide as a function of the temperature at which the experiments were performed instead of the time. This is plotted in figure 13. The transition from the (1x2) layer to the oxide is a gradual one, allowing for mixed (1x2) and oxide coverage. This gradual change is not expressed in this phase diagram. Within the whole area named ‘mixed (1x2) / oxide’ the surface exhibits all coverages from 100%

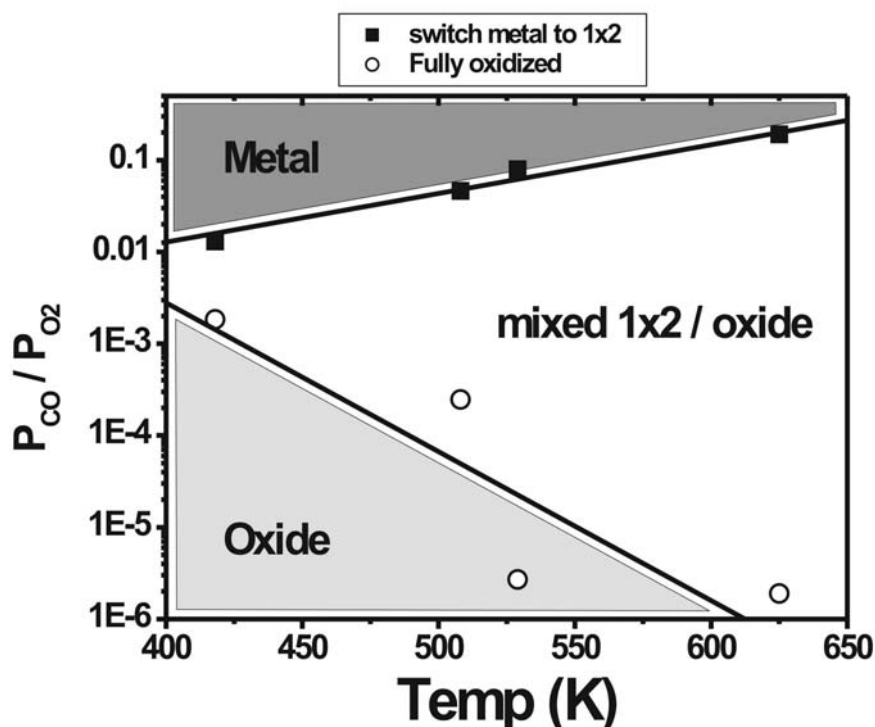


Figure 13: Phase diagram showing the stable regions for the metal phase (dark grey), the (1x2) or mixed (1x2) and oxide phase (white) and the PtO₂ phase (light grey). The solid line and black squares show the CO / O₂ ratio at the transition from metal to the (1x2) or oxide phase, i.e. the switch from low to high reactivity, as a function of temperature. The hollow circles (and solid line) depict the CO / O₂ ratio at which no (1x2) structure could be detected any more as a function of temperature.

(1x2) to 100% oxide. The line delimiting the transition from this phase to the pure ‘oxide’ phase represents the CO / O₂ ratio at which no (1x2) signal is detectable any more with the X-Rays. This boundary has a large (relative) error bar, as the removal of the (1x2)-layer is a gradual process showing no ‘sharp’ transition, and the exact diffracted intensity at which no signal from the (1x2)-layer is detectable any more depends strongly on the noise and background levels of our detector.

The graph shows that the pressure (ratio) window inside which the (1x2) layer is stable increases with temperature. By extrapolating this trend to conditions of higher temperatures and higher CO / O₂ ratios, we can predict the state of an automotive catalyst under real working conditions. A typical automotive CO oxidation catalyst runs at temperatures up to 1200 K, and in a CO / O₂ ratio of approximately 1 [64]. Our measurements indicate that at those temperatures and mixture, one should expect the (1x2)-layer to be the only phase present on the surface. Obviously, real conclusions can only be drawn from experiments actually performed under the real temperature and pressure conditions. Furthermore one has to take into account the fact that a “real” automotive catalyst is exposed to a wider mixture of reactive gasses next to O₂ and CO, including mainly NO_x species and (partially oxidized) carbohydrate chains.

2.9: Conclusions

In this chapter we have explicitly demonstrated the influence of the formation of a surface oxide in a catalytic process under realistic pressure and temperature conditions. The surface oxide and (1x2)-layer found here on Pt(110) have a much higher reaction rate than the original metallic surface, and are hence a ‘better’ catalyst for CO oxidation. Our observations show that *in-situ* measurements under actual reaction conditions are an absolute necessity for a meaningful investigation of the surface structure and chemical behavior of this model catalyst. The presence and role of the (1x2)-layer, which is obviously of great importance when the reaction mechanism and reactivity of a real catalyst, could not have been found either in experiments under UHV or in so-called pre- and post-reaction experiments.

