

**Interaction of oxygen and carbon monoxide with Pt(111) at intermediate pressure and temperature : revisiting the fruit fly of surface science** Bashlakov, D.

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# Chapter 3

# Subsurface oxygen on Pt(111)<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>This chapter is based on: D.L. Bashlakov, L.B.F. Juurlink, M.T.M. Koper and A.I. Yanson, Catal. Lett. **142**, 1-6 (2011).

### **3.1 Introduction**

Platinum is a primary catalyst for many oxidation reactions from fuel cells to automotive exhausts. The industrial and technological importance is reflected in the efforts by the scientific community to understand the interaction between the platinum surface and gas phase oxygen over the last four decades [1-11]. Although this effort has yielded a wealth of information, we show in this chapter that even the most intensely studied system,  $O_2/Pt(111)$ , can still yield surprising results that affect our view of the catalytic action under realistic conditions.

Studies of the interaction of the Pt(111) surface with molecular oxygen under UHV conditions show that if dosed at temperatures below 100 K, O<sub>2</sub> adsorbs molecularly into the  $(\sqrt{3}/2x\sqrt{3}/2)R15^{\circ}$  structure and a 0.44 ML O<sub>2</sub> per Pt coverage. When temperature increases, adsorbed O<sub>2</sub> partially desorbs and partially dissociates into chemisorbed atomic oxygen. While the desorbing O<sub>2</sub> signal appears at 150 K during TPD measurements [1, 2, 4, 6], remaining atomic oxygen forms the p(2x2) structure on the surface, clearly visible by LEED [6]. This adsorbed atomic oxygen recombinatively desorbs at much higher temperatures with a maximum near 750 K on TPD spectra [1, 2, 4, 6].

The p(2x2) structure obtained by dissociating molecularly bound  $O_2$  can also be obtained by dosing  $O_2$  at room temperature [6, 8-10]. It has been shown that the dissociative adsorption of molecular oxygen on Pt(111) requires two next nearest unoccupied fcc threefold-hollow sites [11]. This limits the maximum coverage of a well-ordered overlayer to 0.25 ML of atomic oxygen, where O occupies every fourth fcc site [9, 10]. This overlayer has been extensively studied with UHV techniques and is often used as a starting point in studies of oxidation reactions on Pt(111) [3-5, 7-10, 12-14].

In contrast to  $O_2$ , other oxygen sources require only one fcc site for dissociation [15]. Therefore, coverages up to 0.75 ML of atomic oxygen can be achieved by dissociation of NO<sub>2</sub> on Pt(111) at 400 K [3, 16-18]. Even higher coverages (up to 2.5-2.9 ML) can be produced by exposure to more aggressive oxidants, such us ozone [19] and atomic oxygen [20, 21]. In combination with DFT calculations, it has been shown that oxygen adsorption on Pt(111) up to the coverage of 0.4-0.5 ML precedes the growth of a thicker platinum oxide layer [22-24].

Recently, a number of groups have combined preparation of single crystal or polycrystalline samples in UHV with reactivity studies at the

relatively high pressure of (up to) 1 atm. Under these conditions, a thin layer of platinum oxide forms on the surface in the temperature range of 450-600 K [25]. Furthermore, apparently the platinum oxide surface has a higher turnover rate for CO oxidation then the metallic surface [26]. This oxide has been identified by X-ray diffraction as  $\alpha$ -PtO<sub>2</sub> [27, 28] which decomposes at temperatures between 700 and 800 K [29]. These results differ from those obtained in UHV studies as no oxide formation has been observed on platinum in a similar temperature range [1, 4, 6, 30-32]. It is also opportune to note that the formation of platinum "oxide" state has been reported previously, albeit at considerably higher temperatures (900-1100 K) [33]. The same authors, however, had shortly thereafter re-assigned this effect to the oxidation of Si impurities in their platinum single crystals [34].

In this work we show that the 0.25 ML coverage limit for  $O_2$  dissociative adsorption on Pt(111) can be overcome even at high vacuum conditions, if oxygen exposure is conducted in the catalytically relevant temperature range 400-600 K. Our results indicate that oxygen adsorbs not only on the surface, but also migrates to the sub-surface region, so that additional oxygen is stored underneath the conventional 0.25 ML surface layer. While this subsurface oxygen has lower reactivity towards CO oxidation, its presence does not alter the reactivity of the surface-bound oxygen layer.

#### 3.2 Experimental section

Experiments were performed with two separate UHV systems using two Pt(111) single crystals. The detailed description of these systems and the procedures for Pt(111) surface preparation was given in the previous chapter. The Pt(111) samples were exposed to  $O_2$  (Messer 5.0) and CO (Air Liquide 4.7) by background dosing at 3-6x10<sup>-7</sup> and 1x10<sup>-8</sup> mbar, respectively. For every individual TPD measurement, Ar sputtering and annealing the crystal to 1200 K in vacuum preceded oxygen adsorption in the Lionfish UHV instrument. In the Omicron UHV system, the crystal surface was checked by STM in every experiment prior to  $O_2$  adsorption. Only when atomic resolution of a clean surface was achieved, the sample was transferred to the preparation chamber, exposed to  $O_2$  and placed back in the STM stage.

The quarter monolayer atomic O coverage at 300 K was used as a calibration for the amount of desorbed oxygen during the TPDs, and as a reference structure for the LEED and STM measurements. All results were

obtained by exposing a clean Pt(111) surface to 400 L of molecular  $O_2$  at various temperatures, and to 2.2 L of CO at 90 K unless noted otherwise (1 L=  $1 \times 10^{-6}$  Torr·s). In all measurements  $O_2$  dosing was stopped and system was pumped down before cooling the crystal.

#### 3.3 Results and discussion

3.3.1. Oxygen adsorption at various temperatures



Figure 3.1.  $O_2$  TPD spectra of Pt(111) exposed to 400 L  $O_2$  at various temperatures taken at 2 K/s heating rate. All spectra have been corrected for rising backgrounds at higher temperatures using formula (2.20).

Figure 3.1 shows TPD spectra obtained after exposing the Pt(111) surface to 400 L O<sub>2</sub> at different temperatures in the range 300-800 K. As the peak areas in these spectra are a direct measure of the amount of O adsorbed on the surface prior to the temperature ramp, it is clear that this amount depends non-linearly on the temperature at which the surface was exposed to O<sub>2</sub>. The TPD peak area increases with substrate temperature up to 500 K, and rapidly drops for higher dosing temperatures. Higher dosing temperatures induce an upward shift in the maximum desorption temperature. As the onset of O<sub>2</sub> recombinant desorption lies at ~600 K,

dosing oxygen at temperatures above 600 K simply leads to concomitant  $O_2$  desorption from the surface.

Figure 3.2a shows the integrated TPD peak areas versus adsorption temperature. The error bars reflect one standard deviation obtained from multiple TPD measurements convoluted with the estimated error resulting from background subtraction. The black line only serves to guide the eye.



Figure 3.2 a) Amount of adsorbed O as a function of adsorption temperature after the exposure of Pt(111) to 400 L of oxygen. b) The O uptake curve for dozing at 300 K (squares) and 500 K (circles).

The area of the TPD peaks is normalized to saturation coverage of atomic oxygen obtained at 300 K as shown in Figure 3.2b (black squares). The data points were fitted with an uptake curve calculated from the adsorption rate for Langmuirian dissociative adsorption:

$$\frac{d\delta}{dt} = s_0 f (1 - \delta)^2 \quad , (3.1)$$

where  $\delta$  equals the relative coverage,  $s_0$  is the initial sticking probability, and *f* is the normalized flux of molecules to the surface. Equation (3.1) can be transformed into a simple differential equation:

$$-\frac{d(1-\delta)}{dt} = fs_0(1-\delta)^2, (3.2)$$

which has a solution:

$$\delta = \frac{s_0 ft}{s_0 ft + 1} \,. \, (3.3)$$

By definition,  $\delta = \frac{\theta}{\theta_{SAT}}$  where  $\theta$  is absolute coverage and  $\theta_{SAT}$  is saturation

coverage of adsorbents in the ML, and product of flux f and time t gives the exposure L. Thereby, expression (3.3) transforms into:

$$\theta = \theta_{SAT} \frac{s_0 L}{s_0 L + 1} \cdot (3.4)$$

The black line in Figure 3.2b is calculated from (3.4) for an initial sticking probability  $s_0=0.05$  and  $\theta_{SAT}=0.25$  ML. It shows that exposure of Pt(111) to 400 L of O<sub>2</sub> results in (near) saturation for oxidation at 300K.

Figure 3.2a demonstrates that by increasing the substrate temperature, the total amount of adsorbed O on Pt(111) can be at least twice as high as the 0.25 ML obtained for oxidation at 300K. This result seems to be at odds with most results from previous UHV experiments as 0.25 ML was considered the maximum coverage when dosing molecular oxygen on Pt(111) [8-10, 13, 14]. However, the result is simultaneously not surprising considering recent reports of formation of an oxide layer on platinum single crystals and polycrystalline platinum during oxidation at atmospheric pressures (0.1-1 bar) in the temperature range 420-650 K [27, 28, 35]. Also, Derry and Ross reported a similar observation for Pt(111) and Pt(100) surfaces [36]. In their studies, platinum surfaces were exposed to ~40 L and ~3000 L O<sub>2</sub> at 370 K and 570 K respectively. While in the former case they obtained a coverage of ~0.2 ML, in the latter the amount of adsorbed oxygen was reported 3-5 times higher, which is very similar to our observations for Pt(111). We must also note that if we significantly increase the dose of  $O_2$  at 500 K, the desorption signal will exceed the ~0.5 ML, as shown for the O uptake curve on Figure 3.2b (green circles). We conclude that even at UHV conditions oxygen dosing well above room temperature allows the Pt(111) surface to take up considerably more than the equivalent of 0.25 ML of atomic oxygen.

In this light it is interesting to note that the exposure of platinum to  $400 \text{ L} \text{ O}_2$  at 700 K leads to the adsorption of roughly the same amount of oxygen as exposure at 300 K, albeit with a significantly different desorption profile. In Figure 3.3, we show both TPD traces as red and green lines, respectively. However, unlike the 0.25 ML oxygen covered surface created at 300 K, the surface with the same coverage created at 700 K remains

active toward further oxygen adsorption when cooled back to room temperature. To demonstrate this, the surface was first exposed to 400 L of  $O_2$  at 700 K, then cooled to room temperature and exposed to the same amount of oxygen again at 300 K. The consecutively recorded TPD trace is shown as a black line in Figure 3.3. The TPD peak area for the 700+300 K dose corresponds to an O coverage of 0.48 (±0.04) ML. As 0.25 ML is the maximum coverage that can be obtained for dissociation of  $O_2$  at 300 K, we conclude that during the initial high-temperature exposure, oxygen is adsorbed in positions that do not block sites for consecutive dissociative adsorption of  $O_2$  at 300 K.



Figure 3.3 TPD spectra of oxygen adsorbed at 300K (green line) and 700K (red line) on clean Pt(111) and of oxygen dosed at 700 K and 300 K consecutively (black line). Heating rate is 4 K/s.

Enhanced oxygen coverage was previously obtained on Pt(111) in a number of TPD studies in which NO<sub>2</sub>, O<sub>3</sub> or O where used as the source of atomically adsorbed oxygen [19, 21, 37]. For low doses, oxygen adsorbs into the same p(2x2) structure as for O<sub>2</sub> dosing at room temperature [8, 17, 37]. Higher doses lead to the formation of p(2x1) domains with a local 0.5 ML coverage [17]. TPD traces from these higher coverages show an additional O<sub>2</sub> desorption peak at 500 K. The lower desorption temperature is suggested to result from repulsive interaction between oxygen atoms in the p(2x1) domains [21, 22, 37]. Our data in Figures 3.1 and 3.3 do not show an additional peak at 500 K, even at oxygen coverage corresponding to ~0.5 ML. Instead, we observe an increase in the peak intensity at 710 K. These observations indicate that the oxygen-loaded surface resulting from exposure to  $O_2$  at higher temperatures is different from the p(2x1) overlayers observed in the O/O<sub>3</sub>/NO<sub>2</sub> experiments.

#### 3.3.2. Surface structure

To investigate the surface structure of these high oxygen-covered platinum surfaces, we use LEED and STM. Figure 3.4 shows LEED patterns for Pt(111) exposed to  $O_2$  at 300 (a), 500 (b) and 700 K (c). Diffraction spots resulting from the clean Pt(111) surface are encircled. Although considerably weaker in Figure 3.4c, all three images show an additional diffraction pattern that corresponds to a (2x2) structure [8]. We note that the Pt(111) surface covered mostly with p(2x1) oxygen domains yields a similar LEED pattern, while having twice the amount of oxygen on the surface [20, 21, 37]. Therefore, using LEED alone we cannot unambiguously identify the structure.



Figure 3.4. LEED images for the Pt (111) surface exposed to 400 L of  $O_2$  at (a) 300 K, (b) 500 K and (c) 700 K. All images were recorded at 100 eV incident electron beam energy and a sample temperature of 85 K. Image in panel (c) was digitally enhanced to reveal the weak (2x2)diffraction oxygen spots.

To visualize the surface structure locally, we have performed STM topography measurements. Images in Figure 3.5 were obtained for oxygen adsorbed on Pt(111) at 300 K (a) and 500±50 K (b). Figures 3.5a and 3.5b both show the same p(2x2) structure of 0.25 ML of adsorbed atomic oxygen known from previous STM studies [13, 14]. This means that, although TPD data in Figure 3.2 show that the amount of oxygen adsorbed at 500 K is twice that for 300 K, it is not found in the top layer. Therefore we are left to conclude that additional oxygen created by exposure to  $O_2$  at elevated temperatures is stored *below* the surface of the metal. We note that contrary to the reported step-edge facilitated oxidation on Rh(111) at elevated temperatures [38], our STM study did not reveal surface buckling near the step edges corresponding to oxide growth [39]. We would like to emphasize that by using the term "subsurface oxygen" we refer only to the location of this additional oxygen. We prefer to avoid the terms "subsurface oxide" or "bulk oxide" prior the additional studies of a surface structure, despite that oxides exist for most of the transition metals [40, 41]. Finally, we note that the strongly faded (2x2) diffraction pattern observed after dosing oxygen at elevated temperatures (Figure 3.4c) may result from small amounts of O remaining at the surface or from a (2x2) structure of O in subsurface sites.



Figure 3.5  $17x17 \text{ nm}^2$  STM topography images with fast Fourier transformation (FFT) insets for Pt(111) exposed to 400 L of O<sub>2</sub> at room temperature (a, 0.13 nA, 0.18 V) and at 500±50 K (b, 0.12nA, 0.1 V). Distortion in the hexagonal order, which appears as a difference in the inter-atomic distance in the FFT insets, is due to drift always present in our STM.

#### 3.3.3. Oxygen reactivity towards CO oxidation

An unusual reactivity of the additional adsorbed atomic oxygen would support the subsurface oxygen hypothesis. To this end we have carried temperature programmed reaction (TPR) measurements to check how oxygen adsorbed on Pt(111) at various temperatures reacts with carbon monoxide. From previous studies it is known that the 0.25 ML of atomic oxygen on Pt(111) does not react with CO at temperatures below 150 K [5, 7]. CO and O co-adsorb in a 1:1 [42, 43] ratio and an increase in surface temperature activates the reaction that produces  $CO_2$ . It has also been shown that covering the Pt(111) surface with atomic oxygen above 0.25 ML blocks adsorption of carbon monoxide [12, 44].

For the TPR traces shown in Figure 3.6, CO was adsorbed at  $\leq 90$  K onto the Pt(111) surface pre-exposed to  $O_2$  at different temperatures. Subsequently, the sample temperature was ramped up while recording the partial pressures of m/e = 32 (O<sub>2</sub>), 28 (CO) and 44 (CO<sub>2</sub>). In line with previous studies [5, 7, 42, 43], we observe that for the surface saturated with O at 300 K, all CO as well as most of the oxygen react to form CO<sub>2</sub>. However, when the surface is initially oxidized at 500 K, some amount of CO as well as  $O_2$  are left on the surface after the same amount of  $CO_2$  has been formed. At 700 K, even more CO desorbs at the expense of the CO<sub>2</sub> formation. This is most unusual: we seem to have both O and CO on platinum surface, vet they refuse to react even at elevated temperatures! Similar to our observation, Xu et. al. [45] reported the presence of unreactive isolated oxygen on the Pt(111) surface exposed to  $O_2$  at 600 K. This clearly indicates that part of the atomic O created by high temperature adsorption is not available for CO oxidation. Considering that unreacted CO desorbs at lower temperatures than unreacted O, these findings support our claim that the additional oxygen is absorbed in subsurface sites.

The observation that some oxygen remains unreacted even when CO is available on the surface and the temperature favors the oxidation reaction, suggests that sub-surface oxygen is thermodynamically quite stable even in the absence of oxygen in the top layer. Rotermund *et al.* [46] already suggested thermodynamically stable subsurface oxygen to explain a change in work function for Pt(100) when the oxygen-covered surface was heated from 360 to 600 K. Furthermore, they observed desorption of the subsurface oxygen at 760 K, which is lower but comparable to what we observe for Pt(111), and the reactivity of subsurface O towards CO oxidation similar to ours [47].



Figure 3.6 TPR spectra for a)  $O_2$  b)  $CO_2$  and c) CO recorded after CO adsorption on Pt(111), pre-exposed to  $O_2$  at different temperatures. Figure 6a contains TPD traces of  $O_2$  for comparison. Heating rate is 4 K/s. Graphs are offset vertically for clarity.

### 3.3.4. $^{16}O/^{18}O$ isotope exchange

Finally, we have carried out initial experiments with isotopically labeled O<sub>2</sub>, to investigate the exchange between subsurface and surface oxygen. Experiments were performed as described for the data presented in Figure 3.3, with the difference that  ${}^{18}O_2$  was dosed at 700 K and  ${}^{16}O_2$  was used for subsequent dosing at 300 K. The results of the subsequent TPD are shown in Figure 3.7. It is obvious from the  ${}^{16}O{}^{18}O$  (mass 34) TPD trace that there is significant exchange between subsurface <sup>18</sup>O (adsorbed at 700K) and overlayer <sup>16</sup>O during desorption. At the same time, desorption for mass 36 starts at slightly higher temperature. This suggests that there is a lack of <sup>18</sup>O in the p(2x2) layer for the associative desorption at the beginning. Apparently,  ${}^{18}O_2$  only desorbs when enough subsurface  ${}^{18}O$  has migrated up to the surface to occupy next nearest fcc sites. This also supports the idea that subsurface oxygen is stable without a p(2x2) overlayer present during cooling under UHV conditions. As only some exchange between the top and the subsurface oxygen layers is observed, this appears not to be a very fast process.



Figure 3.7. TPD spectra for 400L of  ${}^{16}O_2$  adsorbed at 300K on Pt (111) pre-exposed to 400L of  ${}^{18}O_2$  at 700 K. The heating rate is 2 K/s.

#### **3.4 Conclusions**

The Pt(111) surface, when exposed to molecular oxygen at elevated temperatures (400-600 K), can dissociatively adsorb more oxygen than the previously assumed limit of 0.25 ML. While we show that this total amount can significantly exceed 1/4 of a monolayer, we find only 0.25 ML present on the surface. This makes us conclude that excess oxygen is stored below the surface of platinum. Its desorption temperature is equal to or higher than that of surface-bound oxygen, making it quite stable even in the absence of the latter. While non-reactive on its own, this sub-surface oxygen layer has no negative effect on the catalytic surface reactivity of platinum towards CO oxidation under conditions studied. This sub-surface oxygen is likely the precursor of the stoichiometric  $\alpha$ -PtO<sub>2</sub> formed in catalytic reactors [27, 28] and as such provides an extra link between our understanding of catalytic oxidation reactions in UHV and in high pressure conditions.

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