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# Formation of surface oxides on Pt(100) during CO oxidation in the millibar pressure range

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## Abstract

CO oxidation on Pt(100) at oxygen pressures of  $9.0 \times 10^{-2}$  mbar was studied. An unusual decrease in catalytic activity with time was observed, which has not been observed at lower pressures. Post-reaction Auger and thermal desorption spectroscopy measurements showed the formation of a surface oxide species, which deactivated the catalyst. The surface oxide is compared to subsurface oxygen and to surface oxide studied previously on low index Pt single crystal surfaces. An adsorbate induced surface reconstruction is proposed as a possible driving force for oxide formation. © 2000 Elsevier Science B.V. All rights reserved.

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#### 1. Introduction

CO oxidation on Pt has been a model reaction for many years [1]. Under certain experimental conditions the catalytic activity of the surface can be oscillatory in time [2,3] and the formation of spatio-temporal adsorbate patterns has frequently been observed [4]. Several detailed studies have been performed by photoemission electron microscopy (PEEM) at oxygen pressures of  $4.0 \times 10^{-4}$  mbar on Pt(100) [5] and Pt(110) [6]. In contrast to low-pressure surface science experiments, industrial catalysis is typically performed at atmospheric pressures and above. Recently, increased efforts have been made to bridge this pressure gap [7,8]. In a step towards the understanding of non-linear phenomena during heterogeneously catalyzed reactions at higher pressures, CO oxidation on Pt(100) was carried out at oxygen pressures of  $9.0 \times 10^{-2}$  mbar and a surface temperature of 473 K. Surprisingly, the catalytic activity of the freshly cleaned Pt crystal decreased rapidly with time. Auger and thermal desorption spectroscopy (TDS) measurements showed the sample to be covered by a stable form of oxygen, which causes the surface to become non-catalytic.

In the literature the terms subsurface oxygen and surface oxide have been introduced [9–17] to distinguish oxygen species with behavior different from regular chemisorbed oxygen. Both names have been used interchangeably, while in this paper we want to clearly differentiate between subsurface oxygen and surface oxide. Subsurface oxygen is located directly underneath the first atomic layer of the surface, as deduced by Lauterbach et al. from spatially resolved work function measurements and TDS [9]. Surface oxide is also believed

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to be located underneath the surface [10], but might not necessarily be confined between the first and second layer of Pt atoms. Although the exact location of the different types of oxygen is very difficult to pinpoint, they can be distinguished using TDS due to their different properties of thermal decomposition. Adsorbed oxygen desorbs from Pt(100) at temperatures between 600 and 730 K [18]. Subsurface oxygen formed on Pt(100) is slightly more stable and decomposes between 650 and 770 K with a desorption maximum at 750 K [11]. Surface oxide is the strongest bound oxygen species and is stable below 1000 K [12]. Both adsorbed and subsurface oxygen can be reduced by CO exposure [9], whereas surface oxide is shown to be stable with respect to CO or  $H_2$ exposure [12].

The formation of subsurface oxygen on Pt(100)[9] and Pt(110) [14] was attributed to the restructuring of the surface. Low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) have shown that a clean Pt(100)reconstructs to a  $(5 \times 20)$  surface structure [19-21]. The adsorption of CO or oxygen can lift the reconstruction, after which the Pt(100) surface has a  $(1 \times 1)$  structure [22,23]. The restructuring of the surface from a  $(5 \times 20)$  to a  $(1 \times 1)$  surface allows oxygen to penetrate underneath the first layer of Pt atoms, producing subsurface oxygen. The formation of surface oxide on Pt(110) and Pt(111) was observed during oxygen exposure for surface temperatures above 800 K at oxygen pressures of  $1 \times 10^{-6}$  mbar [10,13,15–17]. Below 800 K oxygen could only chemisorb on the surface. The formation of surface oxide on Pt(111) and Pt(110)was attributed to Si impurities [15,24]. Si is difficult to detect in Auger electron spectroscopy (AES), because Pt masks its main peak located at 94 eV. The presence of Si impurities becomes visible through the chemical shift of the oxidized Si to 76 eV.

The formation of surface oxide during CO oxidation has only been reported for the Pt(111) surface [8]. Oscillatory reaction rates, observed at oxygen pressures of  $2.6 \times 10^{-3}$  mbar, were explained through the periodic formation and reduction of surface oxide. Because the observed oxygen species only existed during CO oxidation

and could be reduced by CO, it could fall more into the category of subsurface oxygen.

It has become clear that the differentiation between adsorbed oxygen, subsurface oxygen, and surface oxide is difficult, if one wants to categorize the different types of oxygen reported on Pt single crystals. In this paper, we report a stable surface oxide formed exclusively under reaction conditions on Pt(100) at elevated pressures.

## 2. Experimental

All experiments were carried out in an ultrahigh vacuum system consisting of a main chamber and a reaction chamber, in which a base pressure below  $2 \times 10^{-10}$  mbar could be achieved. The sample can be transferred between chambers via a transfer line [25]. The Pt(100) crystal was spotwelded to two tungsten wires, through which it could be heated resistively. It was cleaned in the main chamber by alternating sputtering and annealing cycles. AES measurements were performed using a cylindrical mirror analyzer (Perkin-Elmer) and were recorded as differentiated spectra. TDS measurements were performed using a mass spectrometer (Stanford Research Systems) by heating the sample in the line of sight of the mass spectrometer at a controlled rate of 4 K/s.

The reaction chamber can be closed off from the main chamber by a gate valve. It allows for ellipsomicroscopy for surface imaging (EMSI) of the sample [26]. The reactants ( $O_2$  and CO) are fed into the reaction chambers with mass flow controllers (MKS). Reaction products can be detected with the mass spectrometer through a leak valve connecting the reaction chamber to the main chamber.

## 3. Results and discussion

Before each experiment the sample was cleaned in the main chamber until no impurities could be detected in the Auger spectrum (see Fig. 2a). The numbers shown in the spectra indicate the energy of the peak position. They all are characteristic for Pt and are in agreement within 3 eV with the literature [27]. TD spectra were recorded for saturated adsorbate layers of CO and O on the Pt(100) crystal. The measured spectra were in accordance with the literature [18].

For CO oxidation experiments the sample was transferred into the reaction chamber, where it was heated to 473 K. Oxygen was fed into the reaction chamber at a partial pressure of  $9.0 \times 10^{-2}$  mbar. CO was dosed at a CO/O<sub>2</sub> ratio of 0.1 and was cycled via the flow controller with a period of 1 min. The signal from the CO flow controller was recorded as an indication of the CO pressure in the reaction chamber (see Fig. 1a). The CO<sub>2</sub> partial pressure in the reaction chamber was measured with the mass spectrometer (see Fig. 1b). Fig. 1c and d show the data for the first two periods of forced oscillations. After 17 min, O<sub>2</sub> and CO were turned off and the reaction chamber was evacuated.

At the beginning of the time series and with increasing CO pressure  $CO_2$  is being produced as expected, indicating that the sample is catalytically active. Above a certain CO pressure the  $CO_2$ 

pressure decreases abruptly, and the sample becomes catalytically inactive. From low-pressure studies [28], we conclude that above a critical  $CO/O_2$  ratio the sample is transformed from a catalytically active, predominantly oxygen covered state, to a solely CO covered surface. Because the dense CO adlayer inhibits oxygen adsorption, the surface is called CO poisoned. As CO is turned off for the first time at 0.5 min (see Fig. 1c and d), the CO<sub>2</sub> pressure at first remains low and then quickly increases. After reaching a maximum it shows a gradual decay. The peak height of the second maximum is clearly lower than that of the first. Because of the hysteresis observed for the reactivity of Pt, the sample stays CO poisoned until the CO pressure falls below a second critical  $CO/O_2$  ratio. At this point the surface makes a transition to a catalytically active surface, causing the  $CO_2$  pressure to quickly rise. Meanwhile, the CO pressure continually decreases, which causes the CO<sub>2</sub> pressure to also decrease after reaching its maximum value. Because the reactivity of the sample is linear in the CO pressure and because



Fig. 1. Pt(100) was heated to 473 K and oxygen and CO were introduced at pressures of  $9.0 \times 10^{-2}$  mbar and  $9.0 \times 10^{-3}$  mbar, respectively. CO was cycled with a period of 1 min. (a) The CO signal from the flow controller; (b) the partial CO<sub>2</sub> pressure inside the reaction chamber. (c, d) The expanded region of (a) and (b) between 2 and 4 min.

the first critical ratio has a higher value than the second, the maximum reactivity observed for the first transition also shows a higher value than that observed for the second transition. The maximum value of the  $CO_2$  pressure observed when CO is switched on in the cycle clearly decreases with each period. On the contrary, the maximum  $CO_2$  pressure observed whenever CO is switched off at first increases with each period. Only after both peaks reach a similar height do both decrease similarly.

With EMSI the spreading of CO or O fronts can be observed whenever CO is switched on or off, which is characteristic for Pt(100) [29]. With each cycle, the front velocity observed increased whereas the image contrast decreased. After the seventh CO cycle, the fronts were becoming too fast to be distinguished from uniform global transitions. After the 12th period finally no change could be observed.

Both the change in  $CO_2$  peaks and the increase in front speeds indicate a marked change in the sample's catalytic behavior. Clearly the change in the surface is gradual, but continuous with each cycle. The change in reactivity can be understood in terms of the hysteresis measured with respect to the CO pressure. In the low-pressure region, the reactivity remains linear in the CO pressure, but has a decreasing slope due to the deactivation of the surface, causing the first maximum to decrease. Simultaneously the CO pressure difference between the two transition points of the hysteresis decreases, causing the second maximum to increase. After the seventh cycle this difference has decreased to zero and both transition points show the same maximum reactivity. It is interesting to note that after the seventh period the  $CO_2$  production stays finite while CO is switched on. Consequently the surface cannot be CO poisoned any longer.

After the reaction measurements, we performed AES and TDS in order to study the surface composition of the deactivated sample. AE spectra showed two additional peaks at 490 eV and 510 eV, which were identified as oxygen (see Fig. 2b). Oxygen TDS showed two desorption maxima located at approximately 1020 K and 1160 K (see Fig. 3b). The formed oxygen could not be removed by exposure to  $9.0 \times 10^{-3}$  mbar of CO at 473 K



Fig. 2. Auger spectrum of a clean Pt(100) surface after sputtering and annealing (a) and after 20 min of cyclic CO oxidation at 473 K (b). The numbers indicate the exact location of the minimum peak position of clean Pt (a) and inactive oxide covered surface (b).



Fig. 3. Oxygen TD spectra of the Pt(100) crystal after 20 min of cyclic CO oxidation at 473 K. The individual curves show the spectra of different runs.

over 30 min. Due to the high thermal stability of the new oxygen species, we believe to have formed a surface oxide.

The amount of surface oxide formed after CO oxidation revealed a rather poor reproducibility, which also has been noted in the literature [30,31]. The peak-to-peak  $O_{510}/Pt_{233}$  ratio varied between values of 2 and 8. The integrated areas of the oxygen TDS curves, which were normalized to the

amount of adsorbed oxygen, varied between values of 1.5 and 4. No measurable amounts of impurities could be detected in the Auger spectra either before or after the reactions. On the other hand, minute concentrations of impurities, which were below the detection limit of AES, have been shown to alter the surface's behavior towards oxygen adsorption [15,24]. Therefore we cannot completely rule out the presence of any impurities and purposely called the oxygen species surface oxide.

By changing the experimental conditions, we tried to further elucidate the formation conditions of the surface oxide. For example exposing the clean surface at 473 K to oxygen and CO without cycling of the reactant feed produced no measurable amounts of surface oxide. Since the surface is predominantly CO poisoned under these conditions, obviously oxygen cannot adsorb in order to form the surface oxide. Prolonged exposure to oxygen pressure of  $9.0 \times 10^{-2}$  mbar at 473 K, as well as at temperatures up to 900 K, also produced no detectable surface oxide. The formation of surface oxide during CO oxidation hence must be caused by the transition from the catalytically active to the CO poisoned surface and vice versa. Since these transitions induce the  $1 \times 1 \leftrightarrow 5 \times 20$  restructuring of the surface [22], we believe that the formation of surface oxide follows a similar process as was proposed for the formation of subsurface oxygen on Pt(100) [9]. In comparison to the surface oxides observed on the low index Pt single crystals so far, the surface oxide reported here is formed at much lower temperatures, namely 473 K. Therefore, surface reconstruction acts as a promoter towards the formation of the surface oxide.

The formation of a stable surface oxide at intermediate pressures, and its lack of formation at pressures only two orders of magnitude lower [9], indicates that the total reaction pressure can indeed have a significant influence on the basic surface mechanisms in heterogeneous catalysis. The presented measurements are therefore only one step towards building a bridge between surface science and industrial catalysis.

#### 4. Summary

During CO oxidation with cycled CO feed, a rapid decrease of the surface's catalytic activity of

Pt(100) was observed. AES proved the presence of large amounts of oxygen on the deactivated catalyst. TD spectra with two desorption maxima at 1020 K and 1160 K showed the oxygen to be strongly bound to the surface. The oxygen was stable towards CO exposure, but could be decomposed by annealing up to 1200 K. Due to its high temperature stability it is believed to be a surface oxide, which is in strong contrast to subsurface oxide could not be formed by simply exposing the surface to oxygen, but was formed only during CO oxidation. To explain this, restructuring of the surface is proposed as a possible mechanism, which allows oxygen to penetrate underneath the surface.

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