

Catalytic Activity of Metallic vs. Oxidized Pt(110)

Lassi Linnala*

Lund University

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Catalysis plays an important role in many places, such as in the battle against climate change, and it has been extensively studied within surface science community. Despite of this extensive research, there has been a long disagreement on the active phase of Pt group metals for catalytic CO oxidation. In this paper, I try to resolve this disagreement, by studying the deactivation of catalytic CO oxidation instead of the activation, at realistic pressures on an oxidized Pt(110). My mass spectrometry and surface x-ray diffraction studies reveal that the oxide formed on Pt(110) single crystal is at least as active as its metallic surface, which paves the way towards more fundamental understanding of catalytic reactions.

INTRODUCTION

Catalysis plays an important role in many areas, for example, in reducing the emission of greenhouse gases. Therefore, gaining a fundamental understanding of catalytic reactions have been a major part of research within surface science for few decades. In catalysis, the rate of a certain chemical reaction is increased by introducing a catalyst, for example, using a platinum group metals to oxidize CO into CO₂, as commonly done in car catalytic converters. Furthermore, due to the simplicity and relevance for the industry, this CO oxidation has also been a very common model for catalysis research.

Typically, surface science studies have necessarily been performed in an ultra-high vacuum environment (UHV), but in recent years a lot of this research has shifted towards more realistic conditions. However, operating in an UHV has been studied to have a significant impact on the catalytic reactions [1], and therefore, being able to narrow down this pressure gap has been very important for real world applications of catalysis. Several studies of CO oxidation Pt group metals have already been reported at realistic pressures [2–4], but yet there still is no complete agreement on the active phase of this oxidation.

A high pressure surface x-ray diffraction (SXRD) study by Ackermann et al., [5] showed that the oxides formed on Pt(110) are significantly more active than the metallic surface. However, based on their experimental method of studying the activation of the catalytic CO oxidation, it is cannot be clearly distinguished whether the oxide is more active or if the oxide is actually formed as a result of the high activity of the metal. In a more recent SXRD study by Gustafson et al., [6], where the deactivation of the CO oxidations was studied instead of the activation, it could be distinguished that the metallic surface of Rh(111) is more active than the surface oxide, while for Pd(100) the different oxides formed varied in activity.

In this paper, I present a SXRD and mass spectrometry (MS) study of the catalytic oxidation of CO on Pt(110) single crystal surface under realistic pressures, with an aim to find out whether the metallic Pt(110) surface is more active than the oxide formed on it. The experimen-

tal methodology follows the deactivation of the catalytic reaction rather than the activation, very similar as in [6].

By studying the deactivation, the oxidized sample is initially at high temperature, with activity such that the reaction is limited by the transport of CO on to the surface, i.e., the reaction will be mass transfer limited (MTL). Slowly lowering the temperature decreases the activity, which then reduces the oxide coverage, exposing the metallic surface depending on its activity respect to the oxide. Going to low enough temperatures, the activity becomes so small that the surface will become covered by CO, which is inert, and therefore results in a sudden drop of the activity. This point is known as the extinction. From this deactivation experiment, two cases can be easily distinguished. If the oxide is less active than the metal, the oxide coverage will gradually decrease exposing more of the higher activity metal maintaining the reaction in MTL, until the temperature reaches the point of extinction. If the oxide is at least as active as the metal, the oxide coverage will remain almost unvaried until the extinction, where it abruptly disappears.

MATERIALS AND METHODS

All experiments were carried out at Lund University x-ray laboratory. A single crystal Pt(110) was placed in a high-vacuum (HV) environment. This HV was equipped with a gas flow system and a mass spectrometer, allowing for constant monitoring of the gasses. Prior to the experiment, the Pt(110) surface was cleaned by repeated cycles of sputtering with Ar⁺ ions and annealing, until no impurities could be detected with SXRD.

The clean bulk terminated Pt(110) surface exhibits a characteristic (1 × 2) missing-row reconstruction [7], which was removed by exposing the surface to 100 mbar of CO at 600 K [8]. The CO flow was then cut down and the (1 × 1) Pt(110) was oxidized by exposure of 500 mbar of O₂ at 673 K for 20 minutes. After the pure oxygen exposure, CO was re-injected to the HV chamber in a gas mixture of O₂ and CO with flows of 20 mL/min and 1 mL/min, respectively, while maintaining the constant

pressure at 500 mbar.

A monochromatic Molybdenum K_α laboratory x-ray source with wavelength of $\lambda = 0.71 \text{ \AA}$ and flux of $> 25 \times 10^6$ photons/s was aligned with the sample, such that the x-rays were incident on the Pt(110) surface with a small angle of $\mu = 0.2^\circ$ for surface sensitivity.

To study the active phases of the CO oxidation on the Pt(110) surface, the deactivation of the reaction, with the above gas flow and pressure, was studied by slowly lowering the sample temperature in steps of: 300 K, 267 K, 233 K, 200 K, 167 K. Each temperature step was maintained for 1800 s, during which an integrated SXRD intensity was recorded. Gas analysis was constantly monitored with the mass spectrometer.

The scattered x-rays were detected using a 2D detector that covers a large portion of the reciprocal space, which allows for simultaneous monitoring of the diffraction from both the substrate crystal truncation rod (CTR) and the oxide at $(h, k, l) = (0, -1, l)$ and $(0, -1.42, l)$, respectively.

RESULTS

Figure 1 shows the mass spectrometry and SXRD measurements during the cooling down of the oxidized Pt(110) single crystal, in a flow of 20 mL/min and 1 mL/min of O_2 and CO at 500 mbar, respectively. 1a shows the measured CO_2 mass spectrometer signal as a result of CO oxidation. At high temperatures, the reaction is MTL and the observed slight decrease of the signal with decreasing temperature is only due to degassing of the filament. Around 235°C the CO_2 mass spectrometer signal drops abruptly. This is the point of extinction, which occurs due to the surface becoming covered by CO, stopping the dissociative adsorption of O_2 .

Figure 1b shows the corresponding SXRD measurements of both the CTR (orange) and the oxide (blue). At high temperatures, the Pt(110) surface is largely oxidized, but after the extinction, diffraction from the oxide disappears and the intensity of the CTR is increased in turn, i.e., the surface is now metallic. Because of the few data points, the decrease of the oxide seems gradual, but in reality is abrupt. As described in the introduction, since the CO oxidation activity, shown in a, does not increase when the surface becomes metallic and the drop of the oxide at the extinction is abrupt, the oxide is, therefore, at least as active as the metal.

DISCUSSION

My results show that the oxide formed on Pt(110) stays until the activity drops, suggesting that the oxide is at least as active as the metallic surface. The present study,

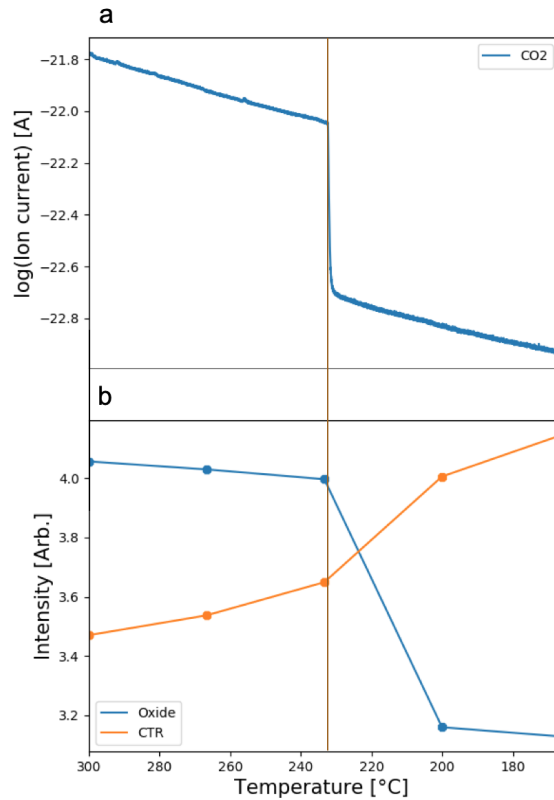


FIG. 1. **Mass spectrometer and SXRD measurement of deactivation of the CO oxidation.** (a) Measured CO_2 signal in the mass spectrometer. Activity declines steadily as a function of the sample temperature until extinction at around 235°C . (b) SXRD intensity for both the oxide and the CTR with exposure time 1800 s between the data points. The oxide disappears abruptly from the surface at the extinction. The abrupt drop of the oxide at the extinction indicates that the oxide is at least as active as the metallic surface.

studying the deactivation, is not, however, able to distinguish whether the oxide is more active than the metal.

At first sight, as already mentioned in the introduction, the SXRD study of the activation of the catalytic CO oxidation on Pt(110) in Ref.[5] showed that the oxides on Pt(110) have significantly higher activity than the metal. However, as a consequence of studying the activation, it could not be clearly determined whether the oxides are more active, or if they rather are formed on Pt(110) as a result when the catalyst becomes active.

In a similar SXRD study to Ref.[5] for CO oxidation on Pt group metals, it could be distinguished that the Rh(111) surface is more active than the oxide, and for Pd(100), the thin oxide films are at least as active as the metal whereas thicker oxide films become less active [6]. This distinction could easily be achieved by studying the deactivation instead of the activation, as also done in this paper. Therefore on this note, it can be argued and verified that the oxide is at least as active as the metallic surface.

CONCLUSIONS

In summary, this paper studied the active phase of Pt(110) single crystal for catalytic oxidation of CO with SXRD and MS. It was found that the oxides formed on Pt(110) are at least as active as the metallic surface. For Pt(110), this result resolves one of the long-standing debates concerning whether the oxides formed on Pt group metals are actually active, or if they are just formed as a result of the high activity. Furthermore, by studying the deactivation catalyst reaction instead of the activation, a better understanding of catalytic reactions under realistic pressures can be achieved. This information can be of use for the further development of important catalyst applications even outside CO oxidation, such as oxidizing methane.

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* lassi.linnala.515@student.lu.se

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