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## **Oxidation catalysis on Pt and Au : complexity of simple chemistry**

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### **Citation**

Spronsen, M. A. van. (2016, June 29). *Oxidation catalysis on Pt and Au : complexity of simple chemistry*. *Casimir PhD Series*. Retrieved from <https://hdl.handle.net/1887/41415>

Version: Not Applicable (or Unknown)

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**Issue Date:** 2016-06-29

# Summary

## Oxidation of Pt(111)

The oxidation of Pt(111) by O<sub>2</sub> was studied in situ with the ReactorSTM. This unique system houses a small-volume flow cell incorporated within a STM. The combined reactor with STM is housed inside a conventional vacuum system to allow for traditional surface science preparation and analysis techniques. Under the experimentally probed conditions, we did not observe the formation of  $\alpha$ -PtO<sub>2</sub>. This observation contradicts both previous in situ experiments and theoretical predictions. Instead, we discovered the formation of two different surface oxides, between 1.0–5.0 bar O<sub>2</sub> and 437–538 K. The first observed structure consists of small triangles forming a spoked-wheel superstructure. The STM results show an  $\sim 8\%$  expanded lattice constant of  $0.30 \pm 0.1$  nm within the spokes. We propose that the driving force for this expansion is the tendency to match the lattice constant of  $\alpha$ -PtO<sub>2</sub>. Prior to the formation of the spoked-wheel oxide, we observed a structure with a distorted, hexagonal lattice. This oxidic intermediate was not stable and transformed into the spoked-wheel oxide. When the O<sub>2</sub> pressure was increased to 5.0 bar, a second, stable structure was formed. It is proposed that it shared identical structural building blocks with the spoked-wheel oxide, namely the expanded oxide rows. However, instead of triangles, it formed a row pattern, which could be described as a lifted-row oxide with possibly a  $c(4 \times 8)$  unit cell.

This discrepancy with the SXRD studies can be explained by the fact that the surface oxides observed in this study give rise to similar in-plane diffraction peaks as  $\alpha$ -PtO<sub>2</sub>. A second possibility is that X-ray beam-induced formation of O<sub>3</sub> was responsible for oxidizing the surface into  $\alpha$ -PtO<sub>2</sub>, during the SXRD measurements.

High-pressure exposure (1.0 bar O<sub>2</sub>) at lower temperatures did not result in well-ordered structures. However, STM images hint on the formation of both triangles and rows. The surface oxides were only fully stable at high O<sub>2</sub> pressure. After evacuating the reactor, STM images show that the structure faded, which we ascribed to O<sub>2</sub> desorption or reaction with residual gases. While O<sub>2</sub> was disappearing, the order was lost and mobility was very high. Even in high vacuum, some triangles and rows remained visible. XPS measurements (in vacuum, without exposure to ambient conditions) gave a lower estimate for the O coverage, which was 0.88 ML. This is higher than the previously observed surface oxide and supports a model of a single-layer surface oxides of expanded Pt oxide stripes.

## CO oxidation and NO reduction over Pt(110)

Two catalytic systems have been studied at high pressures on the Pt(110) surface on an atomic level. The first system was the oxidation of CO by O<sub>2</sub> towards CO<sub>2</sub>. In the framework of the second reaction, namely NO reduction, the effect of room temperature exposure of the surface to NO and H<sub>2</sub> was investigated. To study these reaction systems at relevant pressures, the ReactorSTM has been used. The STM images obtained with the ReactorSTM under reaction conditions show the lifting of the  $(1 \times 2)$  missing row reconstruction by high-pressure CO exposure. The lifting is followed by the formation of the  $(1 \times 1)$  metallic Pt(110) structure for high CO/O<sub>2</sub> ratios and a  $(1 \times 2)$  lifted-row

type surface oxide for more O<sub>2</sub>-rich conditions. Interestingly, the surface oxide shows a higher reactivity towards CO oxidation. The second study on this surface under a reducing environment shows different reconstructions. The room temperature exposure to H<sub>2</sub> results in the formation of a (1×4) missing-row structure and deeper, nested missing rows. The exposure to high-pressure NO removes these missing-row structures.

## Hydrophilic interaction between low-coordinated Au and water

In this work, we study the relatively weak H<sub>2</sub>O-Au interaction on the highly stepped and anisotropic (310) surface with TPD and XPS. Compared to Au(111), we report an enhanced adsorption energy of H<sub>2</sub>O/Au(310) as observed from the (sub)monolayer desorption peak. This peak shows zero-order desorption kinetics, which we do not explain with a typical two-phase coexistence model, but rather by desorption from the ends of one-dimensional structures. These could cover both the steps and (part of) the terraces. We do not observe crystallization of ice clusters as observed on Au(111). This leads to the conclusion that this stepped surface forms a hydrophilic template for H<sub>2</sub>O adsorption. We also notice that the precise orientation of the steps determines the H<sub>2</sub>O binding strength. Despite the surface's enhanced H<sub>2</sub>O interaction, we do not observe any significant H<sub>2</sub>O dissociation. This indicates that the presence of low-coordinated Au atoms is not enough to explain the role of H<sub>2</sub>O in Au catalysis.

## The role of water in Au-catalyzed CO oxidation at low-coordination sites

We have studied catalytic CO oxidation at low-coordinated Au atoms using a single-crystal approach. We use electron irradiation to activate an otherwise unreactive overlayer of undissociated D<sub>2</sub>O on Au(310). A low-coverage mixture of D<sub>2</sub>O:O is subsequently allowed to react at surface temperatures from 105 K upward with CO supplied from the gas phase. XPS shows the absence of Au oxides and quantifies various O-containing species during the reaction. The dependency of the reaction rate on the surface temperature yields an activation energy for the Langmuir-Hinshelwood (LH) reaction of O<sub>ad</sub> and CO between 26±4 and 42±5 kJ/mol. Our results provide evidence that atomic O and not OH is the active reactant on small Au nanoparticles. Importantly, we observe that water has a negative effect on the reactivity of O. We conclude that the beneficial contribution of H<sub>2</sub>O to catalytic CO oxidation by small Au nanoparticles could rely on the reactive species being provided by spillover from the support.

