

In-Situ Investigations Of The Initial Oxidation Of Some Late Transition Metals**E. Lundgren**

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The oxidation process is of fundamental importance in modern solid state physics research, and is often associated with corrosion. However, under the right conditions, oxidation can lead to oxide layers which can be applied e.g. as protective layers against corrosion, as insulating layers in microelectronic devices and as catalytic surfaces. On late transition metals, one reason for investigating oxygen induced structures has been due to the important role oxygen is believed to play in catalytic reactions, such as the CO conversion into CO₂ by a catalytic oxidation process on the metal surface. Lately however, it has been proposed in the literature that on Ru, Pt and Pd surfaces [1-3], it is not the chemisorbed atomic oxygen adsorbed on the surface, but rather the oxides formed on the surfaces under such conditions, that are the most efficient phases in oxidizing CO.

In this contribution, we present results using a multi-method approach from the oxygen interaction with Rh and Pd surfaces on the atomic scale at oxygen pressures in the 10⁻¹⁰ to 10³ mbar range and temperatures up to 1000 K. We will show that so-called surface oxides form [4-6] prior to the onset of thicker oxides, and that the presence of a surface oxide kinetically hinders the formation of the respective bulk oxide [6,7].

In Figure 1a is shown an example of such a surface oxide on Pd(001). At a sample temperature of 550 K and an oxygen partial pressure of 10⁻⁶ mbar a surface oxide is formed at the surface showing an oxygen induced surface periodicity corresponding to a ($\sqrt{5}\times\sqrt{5}$)R27° reconstruction. Using scanning tunneling microscopy, high resolution core level spectroscopy and density functional theory the structure could be determined to be a distorted PdO(101) layer, or a so-called tri-layer [5]. Increasing the oxygen partial pressure to 10⁻³ mbar does not induce any changes from the ($\sqrt{5}\times\sqrt{5}$)R27° structure, at these oxygen pressures no bulk oxide can be formed.

However, by the use of surface x-ray diffraction measurements, we are able to observe diffraction from the surface at oxygen partial pressures as high as 1000 mbar. Monitoring the oxidation of the Pd(100) surface over the pressure range from 10⁻⁶ to 10³ mbar and up to sample temperatures of 1000 K, we observe the formation of both the ($\sqrt{5}\times\sqrt{5}$)R27° surface oxide and the transform to three-dimensional bulk oxide films. In this way, we are able to study the oxygen interaction as well as the oxidation process on the Pd(100) surface on the atomic scale. In fact the ($\sqrt{5}\times\sqrt{5}$)R27° was found to inhibit the oxide formation at elevated temperatures even at ambient oxygen pressures. By comparing theory and experiment, we could show that the bulk oxide formation is kinetically limited by the ($\sqrt{5}\times\sqrt{5}$)R27° surface oxide [7].

Similar observations will be presented in the case of Rh(111). Here a thin surface oxide with a (9x9) periodicity can be observed in both LEED and STM. Again by comparing theory and experimental results, the structure of the (9x9) is found to be a tri-layer, O-Rh-O. The surface oxide is shown to prohibit the on-set of the bulk oxide growth, and the detailed reason for this behavior is unraveled by extensive DFT calculations [6].

References

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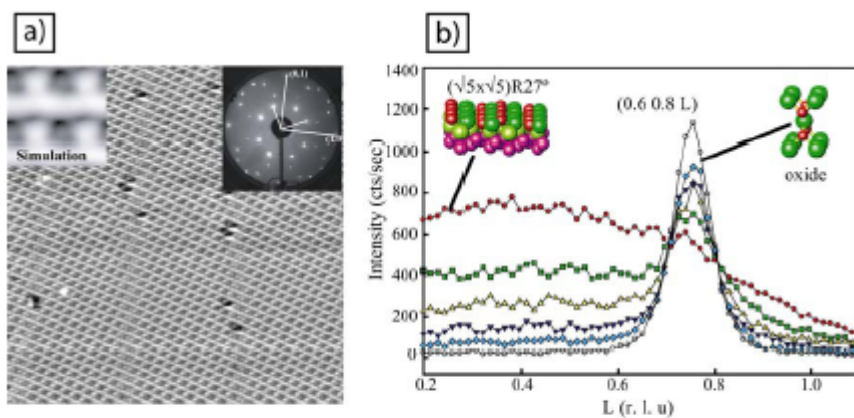


Figure 1) The oxidation of Pd(100). **a)** STM image from the surface oxide formed at 10^{-6} mbar and 550 K [5]. **b)** SXR measurements at elevated O pressures (50 mbar) showing the transition from the $(\sqrt{5}\times\sqrt{5})R27^\circ$ structure to the bulk PdO [7].