# Transient surface structures of PdO on Pd(100)

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Apart from being an excellent oxidation catalyst, Pd surfaces have been used extensively as a prototype model system for CO oxidation [1-6]. In particular, it has been demonstrated that under semi-realistic reaction conditions, a thin oxide may form on Pd surfaces [7], which has also been observed under Ultra-High Vacuum (UHV) conditions [8]. The exact role of the oxides during a catalytic reaction is not yet clear. A recent UHV study found significantly less activity of an epitaxial PdO(101) film as compared to the metallic Pd(100) film [5], and a study performed during semi-realistic conditions found that the same PdO(101) film is at least as active as the metallic Pd(100) [6]. In fact, the active phase of Pd has been debated for a long time, and it is clear that a thin film of PdO(101) is an active phase in CO oxidation [5, 6].

However, it has previously been concluded that the most stable surface of PdO is the PdO(100) [9] based on theoretical calculations, a phase that has so far not been observed experimentally. The formation of a PdO(100) could affect the catalytic activity since the surface is oxygen terminated, which could therefore inhibit adsorption and dissociation, and possibly explain previously observed oxygen-poisoning during CO oxidation over Pd [10].

In this contribution, we present experimental evidence for the formation of a PdO(100) surface grown on Pd(100) under UHV conditions, by a combination of Temperature Programmed Desorption (TPD) and Low Energy Electron Diffraction (LEED). Additional support that the PdO(100) surface can also form under reaction conditions comes from so-called Transmission Surface Diffraction (TSD) [11, 12] measurements recorded under semi-realistic reaction conditions. The UHV experiments were conducted in a UHV chamber with a typical base pressure of $2\times10^{-10}$ mbar. The UHV chamber is equipped with a four-grid retarding field analyzer for low energy electron diffraction (LEED), a quadrupole mass spectrometer (QMS) used for TPD and TPRS experiments [5]. A single-stage differentially pumped chamber is attached to the main UHV chamber which houses an inductively coupled RF plasma source used to generate atomic oxygen beams. The TSD measurements were performed at ID31 at the ESRF, using a 71 keV X-ray beam and a specially constructed sample holder and sample to facilitate X-ray transmission and reduce background from the thermal diffuse bulk scattering.

In Fig. 1, we show the surface models of the (√5×√5)R27°, the PdO(101) and the PdO(100), the corresponding calculated LEED patterns and the experimentally observed patterns for oxygen coverages of 0.8, 6.6 and 16.1 ML as determined by TPD and using the well-known (√5×√5)R27° (top-most panel) as coverage calibration. The PdO(101) (middle panel) growing in a Stranski-Krastanov growth mode surface has been reported previously in UHV [5] as well

as under semi-realistic conditions [7]. At even higher oxygen coverages, the LEED pattern becomes streaky indicating the formation of grain boundaries and domain walls. However, weak spots along the streaks as well as elsewhere in the LEED pattern can be observed corresponding to spots from the calculated PdO(100) pattern. Further, evidence for the PdO(100) formation is found in TSD, which will be presented in this contribution. The implications of the formation of a PdO(100) surface in oxygen rich environments and the role of this surface in oxygen-poisoning will be discussed.

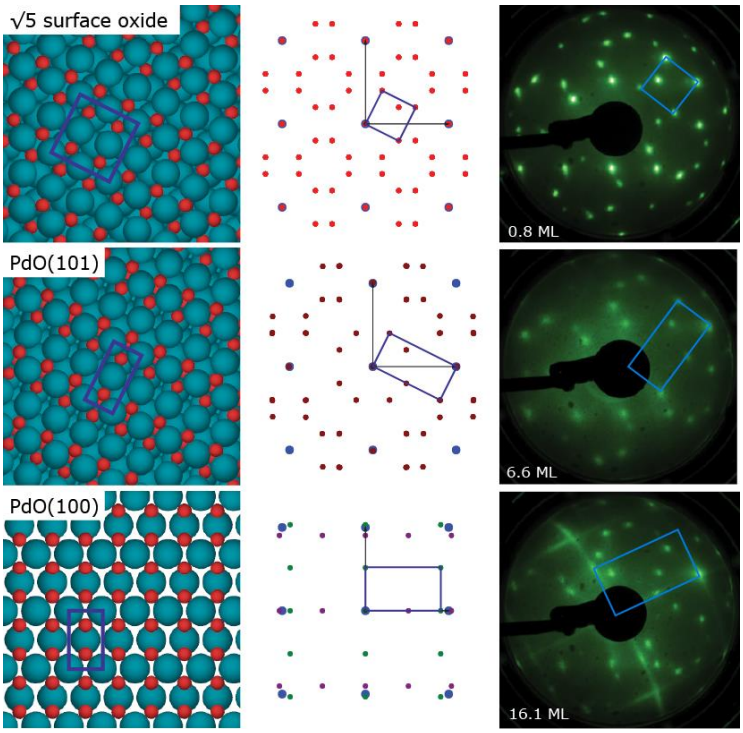


Figure 1 a) Models of the structures of the (√5×√5)R27°, the PdO(101) and the PdO(100) surfaces (left), their calculated LEED patterns including rotational domains (middle), and the observed LEED patterns (right) with indicated unit cells and oxygen coverages as obtained from TPD.

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