

## SI-821: The initial oxidation of Rh(111)

Recently the formation and reactivity of oxides on late transition metals in oxidizing environments such as in an automotive catalytic converter has been recognized [1,2]. This has triggered an effort to understand the details of the oxide formation and reaction pathways on such materials and under such conditions on the atomic scale. In particular it has been discovered that thin so-called surface oxides are formed before the onset of the growth of a thicker oxide film. Since most of the more traditional UHV methods are based on the detection of electrons, such as Low Energy Electron Diffraction (LEED) or Photo Electron Spectroscopy (PES), which suffers from the strong interaction of the electrons with the surrounding gas phase at elevated O partial pressure, a method of choice is Surface X-ray Diffraction (SXR). At beamline ID3 an excellent experimental setup has been constructed to perform in-situ investigations of the interaction of a gas with a solid surface at ambient pressures.

We have used this setup to investigate the initial oxidation of Rh(111) and in particular the surface oxide formed on this surface. The surface oxide forms at an O pressure of  $1 \times 10^{-3}$  mbar and a sample temperature of 450 C. The resulting surface oxide is stable under UHV conditions. It adapts a hexagonal structure and forms a coincidence lattice with the underlying Rh(111) surface, resulting in a (9x9) reconstruction as observed by SXR and LEED. The structure and composition can be deduced by a combination of SXR (see Fig 1a), High Resolution Core Level Spectroscopy and Density Functional Theory (DFT, See Fig 1b). It consists basically of a so-called tri-layer, two oxygen layers with one Rh layer in between (Fig 1b) [3].

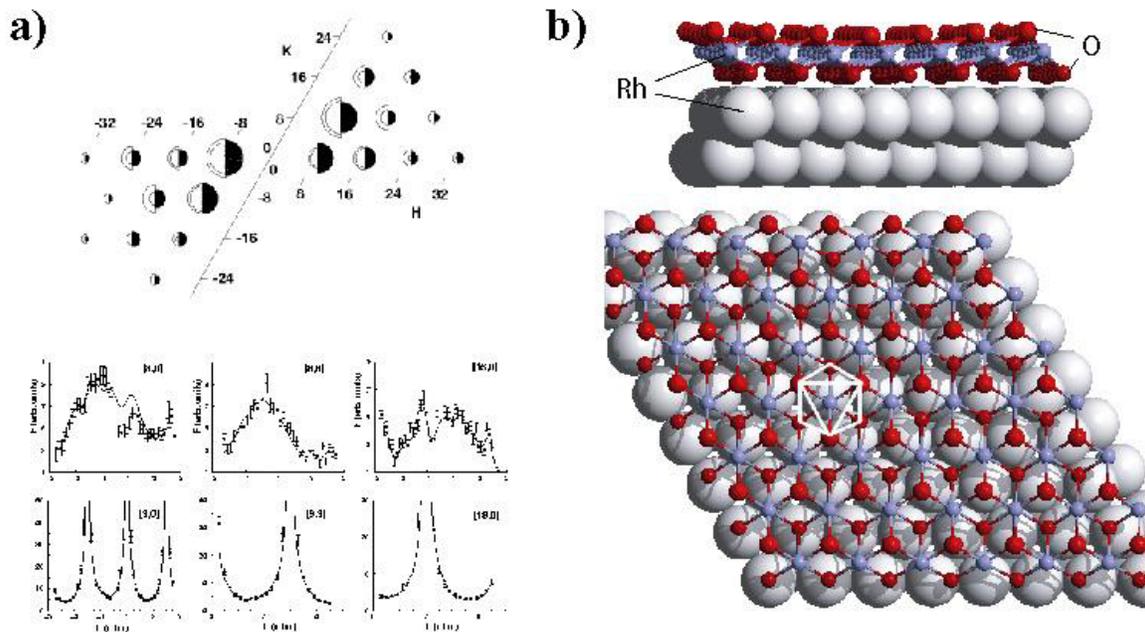


Figure 1 **a)** Calculated and experimental in-plane (top) and out-of-plane (bottom) structure factors obtained from the (9x9) oxygen induced surface oxide on Rh(111). **b)** Best model obtained from SXR and DFT.

- [1] H. Over et al Science **287** (2000) 1474.
- [2] B. Hendriksen et al Phys. Rev. Lett. **89**, 046101 (2002).
- [3] J. Gustafson et al Submitted to Phys. Rev. Lett.