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On Surface Oxidation Issues Arising During CO Oxidation on a PdAu(110) Surface. An *In Situ* Study by Complementary Environmental Methods (STM, SXRD, XPS).

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CO oxidation is generally performed with an excess of oxygen in the reactive gas mixture. Whether this is a low excess (O_2/CO ratio in the 2 to 5 range often used in catalytic tests over realistic powder supported catalysts) or much higher excess (O_2/CO ratio in the 10 to 1000 range used in more model approaches) the question of surface oxidation and its role in the catalytic reaction is thus relevant. With these issue in mind, we have studied *in situ* the evolution and catalytic performance of the Pd₇₀Au₃₀(110) in CO oxidation by complementary surface science methods operating in quasi-realistic catalytic conditions (variable T and P_{gas}): NAP-XPS and Environmental STM and SXRD. The STM is a modified, gold-plated, OMICRON instrument operated within a home-made vacuum/pressure system [1,2]. The SXRD environmental system was developed by M.C. Saint-Lager *et al* to be operated in the ESRF BM32 beamline [3,4]. Both systems are capable of operating over 12 decades of gas pressure ($10^{-9} - 10^3$ mBar) and variable temperature. Two NAP-XPS systems were operated in gas pressures up to 20 mBar and variable temperature: one system is installed at ALS in beamline 9.3.2. [2,5], the other system is installed at SOLEIL in beamline TEMPO [6]. The Pd₇₀Au₃₀(110) (from SPL) is an unreconstructed Au-rich (~ 85-90%) surface under stable conditions after preparation cycles (ion bombardment followed by annealing). We have shown that upon exposure to CO, Pd segregates to the surface and the surface becomes rough (corrugation ~0.05 nm) [4]. In presence of oxygen, the surface reconstructs exhibiting a (nx2) structure ((1x2) with vacancies) and, as for CO, Pd segregates to the surface (Fig.1). Increasing the temperature and/or oxygen pressure eventually leads to oxidation of the Pd-rich surface. Under reaction conditions, for $P(O_2)/P(CO) \approx 10$, NAP-XPS reveals that the reaction occurs in the presence of adsorbed oxygen species at the surface but that the activity strongly decreases when oxidation of the surface appears at higher T (Fig.2). In the case of $P(O_2)/P(CO) \gg 10$, SXRD shows that an oxide strained layer (< 10 atomic layers) is formed (Fig.3) that is the active surface in such conditions [4]. Surface oxidation and its role in the CO oxidation strongly depend on the reaction conditions and for a same system surface oxidation can be either noxious or the best option to the reaction.

References:

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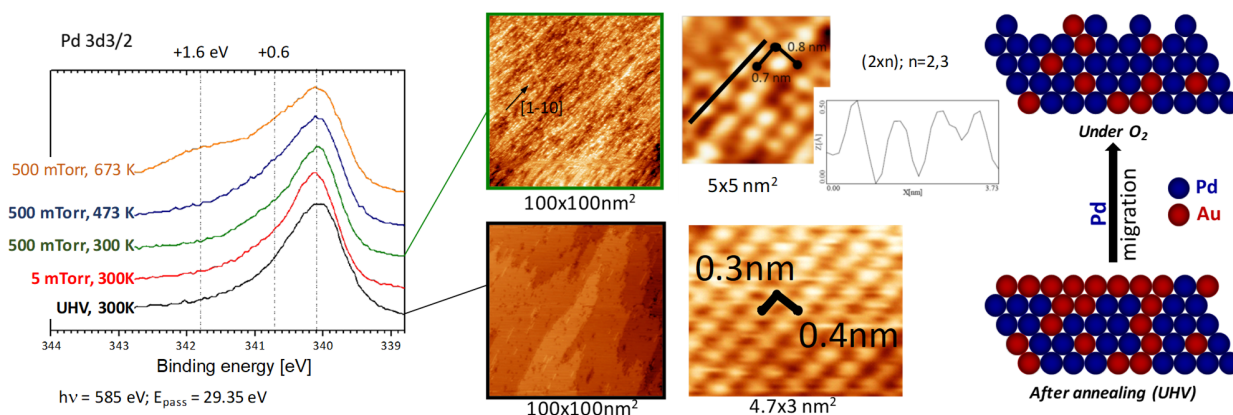


Figure 1. The PdAu(110) surface upon exposure to oxygen: (left) appearance of a high binding energy shoulder on Pd_{3d_{3/2}} XPS peak with increasing oxygen pressure and temperature; (center) reconstruction of the surface as seen by STM and Pd segregates to the surface; (right) schematics of the evolution.

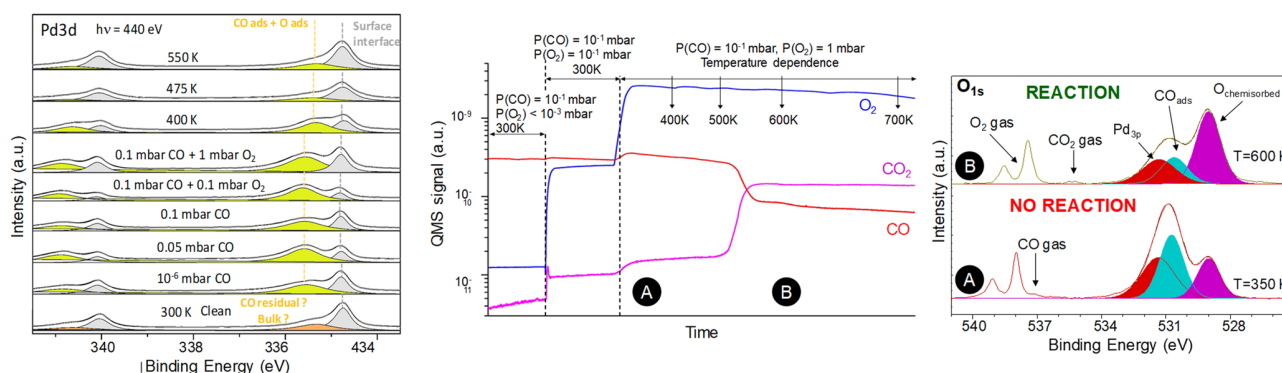


Figure 2. (left) XPS Pd_{3d} peak evolution with gas mixture, pressure and temperature; (center) QMS and (right) corresponding XPS O_{1s} peaks (solid and gas phases) for active and inactive conditions.

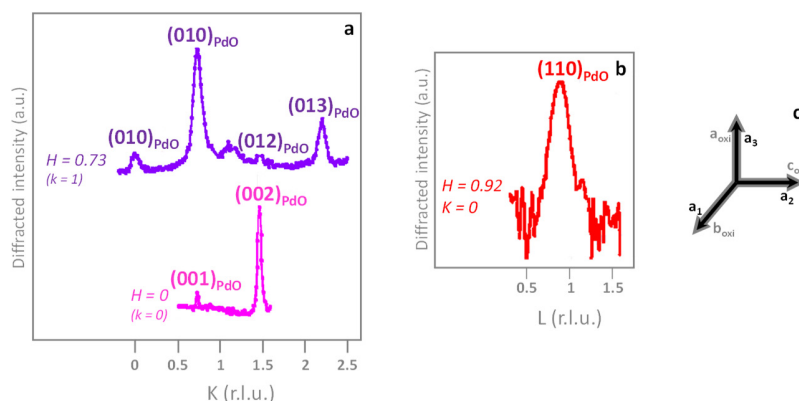


Figure 3. PdO peaks measured by SXR D along several directions of the reciprocal space (along K in with $L=0$ and $H=0$ and $H=0.73$, in **a**; along L with $H=0.92$ and $K=0$, in **b**) in the frame of the fcc PdAu(110) surface by (a_1, a_2, a_3) with the Miller indices (H, K, L) and the oxide peaks are labeled with the Miller indices (h, k, l) in the PdO frame $(a_{\text{oxi}}, b_{\text{oxi}}, c_{\text{oxi}})$ defined in **c**.