HAL
open science

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

Marie-Angélique Languille, Eric Ehret, Marie-Claire Saint-Lager, Aude Bailly, Bongjin Simon Mun, Jean-Jacques Gallet, Fabrice Bournel, Francisco Cadete Santos Aires

To cite this version:

Marie-Angélique Languille, Eric Ehret, Marie-Claire Saint-Lager, Aude Bailly, Bongjin Simon Mun, et al.. On Surface Oxidation Issues Arising during CO Oxidation on a PdAu(110) Surface. An In Situ Study by Complementary Environmental Methods (STM, SXRD, XPS). Microscopy and Microanalysis, 2021, 27 (S2), pp.53-54. 10.1017/S143192762101326X . hal-03846388

HAL Id: hal-03846388

https://hal.science/hal-03846388v1

Submitted on 10 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Marie-Angélique Languille[1,2], Eric Ehret[1], Marie-Claire Saint-Lager[3], Aude Bailly[3], Bongjin Simon Mun[4,5], Jean-Jacques Gallet[6], Fabrice Bournel[6], Francisco J. Cadete Santos Aires[1,7]

[1.] IRCELYON, UMR 5256 CNRS, Univ. Claude Bernard Lyon 1, 69626 Villeurbanne cedex, France.
[2.] *Present address:* CRCC/CRC, USR 3224, CNRS, MNHN, Ministère Culture, 75005 Paris, France.
[3.] Institut Néel, UPR 2940, CNRS, Sorbonne Univ., 38042 Grenoble cedex 9, France.
[4.] Department of Physics and Photon Science, GIST, Gwangju, 61005, Republic of Korea.
[5.] Center for Advanced X-ray Science, GIST, Gwangju, 61005, Republic of Korea.
[6.] LPCMR, UMR 7614, CNRS, Sorbonne Univ., 75252 Paris Cedex 05, France.
[7.] LCR, National Research Tomsk State University, Tomsk 634050, Russian Federation.

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 $Pd_{70}Au_{30}$(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 $Pd_{70}Au_{30}$(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 $P(O_2)/P(CO)\approx10$), 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 $P(O_2)/P(CO)>>10$, 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:

[1] Y Jugnet *et al*, Surface Science **521** (2002) L639.
[2] MA Languille *et al*, Catalysis Today **260** (2016) 39.
[3] MC Saint-Lager *et al*, Journal of Physical Chemistry C **122** (2019) 22588.
[4] MC Saint-Lager *et al*, ACS Catalysis **9** (2019) 4448.
[5] Y Jugnet *et al*, Journal of Physical Chemistry Letters **3** (2012) 3707.

[6] H Liu *et al*, ACS Catalysis **9** (2019) 10212.

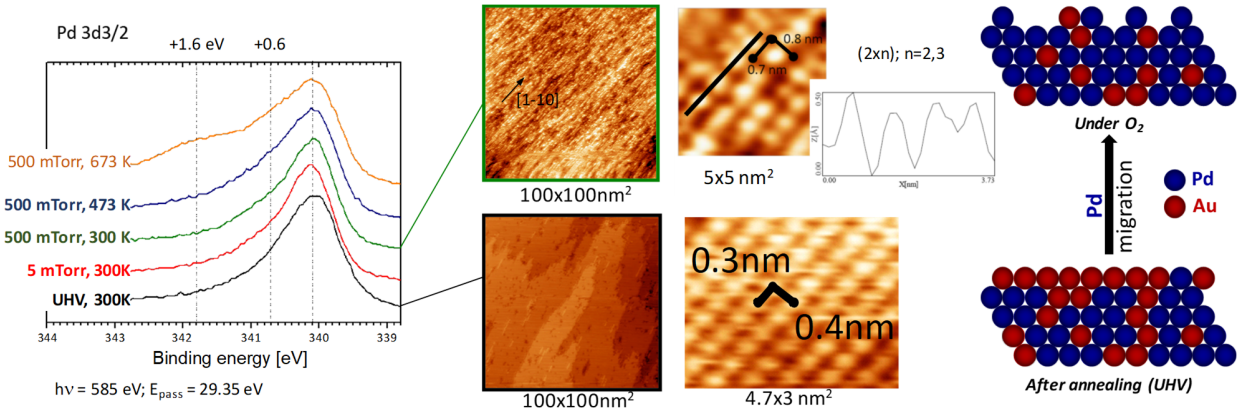

Figure 1. The PdAu(110) surface upon exposure to oxygen: (left) appearance of a high binding energy shoulder on Pd3d$_{3/2}$ XPS peak with increasing oxygen pressure and temperature; (center) reconstruction of the surface as seen by STM and Pd segregates to the surface; (right) schematics of the evolution.

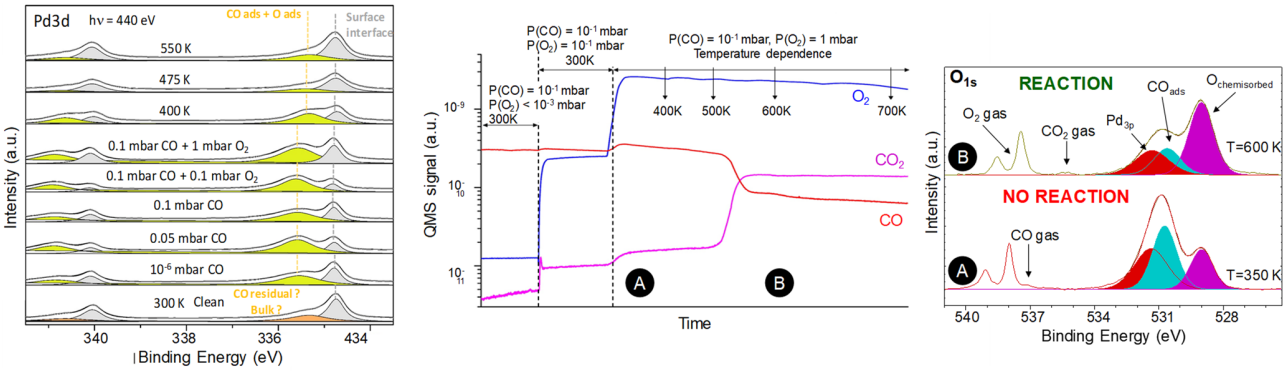

Figure 2. (left) XPS Pd3d peak evolution with gas mixture, pressure and temperature; (center) QMS and (right) corresponding XPS O1s peaks (solid and gas phases) for active and inactive conditions.

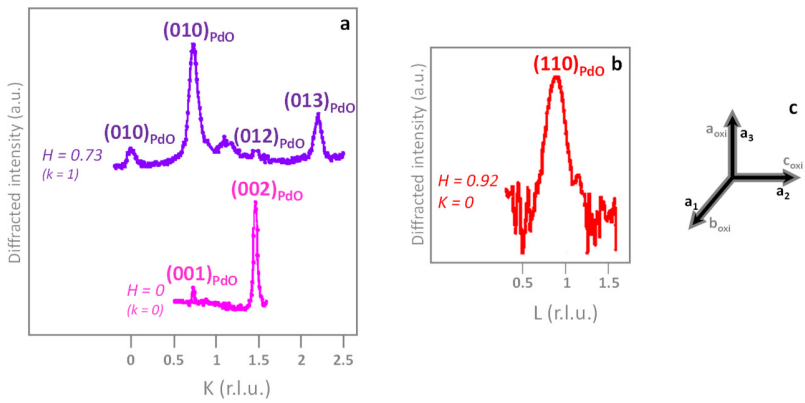

Figure 3. PdO peaks measured by SXRD along several directions of the reciprocal space (along *K* in with *L*=0 and *H*=0 and *H*=0.73, in **a**; along *L* with *H*=0.92 and *K*=0, in **b**) in the frame of the fcc PdAu(110) surface by (a_1, a_2, a_3) with the Miller indices (*H, K, L*) and the oxide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