



**Experiment title:**

**Etude *in situ* de la surface (NX2) de films ultra-minces de Pd en épitaxie sur Ni(110) en cours d'hydrogénation sélective du butadiène : Validation d'un dispositif pour la diffraction X dédié à l'étude *in situ* de catalyseurs modèles, préparés en UHV puis soumis aux conditions de réaction chimique.**

*In situ* study of the (NX2) surface of ultra-thin Pd films on Ni(110) during selective butadiene hydrogenation

Commissioning of a novel set-up for X-ray diffraction studies of model catalyst, elaborated in UHV, under chemical reaction conditions

**Experiment**

**number:**  
32-03-630

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As discussed in the proposal the aim of this experiment was the commissioning of the set, reactor for X-ray diffraction + UHV chamber, by studying the Pd strained in ultra-thin Pd films on Ni(110). The set up was described in RE n° 2-03-618, where we report on the commissioning of its first part, the x-ray reactor itself. We then worked on the alloy Au<sub>30</sub>Pd<sub>70</sub>(111) during butadiene hydrogenation and evidenced a strong effect due to hydrogen induced segregation ( see RE n° 32-03-631). However, there was no way to directly probe the chemical composition of the surface in the x-ray reactor and it was not possible to confirm this result.

This yields us to take the advantage of the new possibility offered by the connection of the UHV chamber equipped with an Auger spectrometer to verify segregation or not. As concern the reaction, we successfully already performed butadiene hydrogenation (see RE n° 32-03-618 and RE n° 32-03-631). Thus we thought that it was more relevant to test our set up for CO oxidation, which is also included in our scientific program (see accepted proposal 32-02-648 et SI 1459).

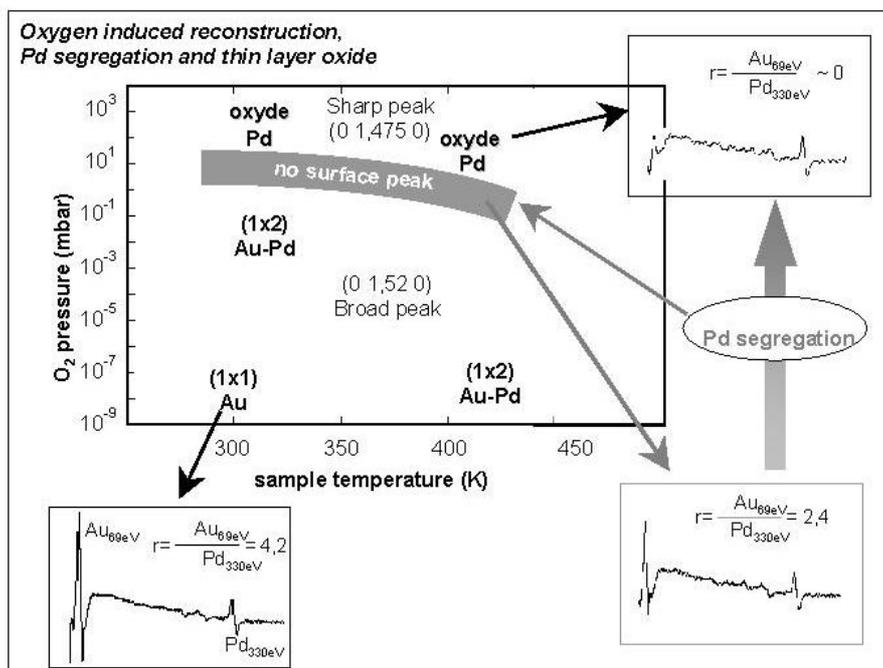
We thus checked our set up, by studying oxidation and CO oxidation on the alloy Au<sub>30</sub>Pd<sub>70</sub>(110).

In UHV, the Au<sub>30</sub>Pd<sub>70</sub>(110) surface is (1x1) and mainly composed by gold. Owing to the UHV chamber connected to the reactor, we performed AES spectra on this clean surface and found 4,2 for the ratio of the Gold signal at 69 eV over the Palladium signal at 330eV.

We exposed the surface to increasing pressure of oxygen at room temperature and at 420K.

The diagram summarises the observed surface reconstruction with the composition of the surface plane and the corresponding Auger spectra. The surface reconstruction was monitored by scanning the reciprocal space along the direction perpendicular to the dense rows of the (110) surface (Kscan) at L=0.

At low pressure, we saw that the surface peak at (0 1 0) decreased while rose a broad peak at around (0 1,52 0). At 300K, this effect was observed from 2 mbar of oxygen and soon from 5.10<sup>-6</sup> mbar at 420K.

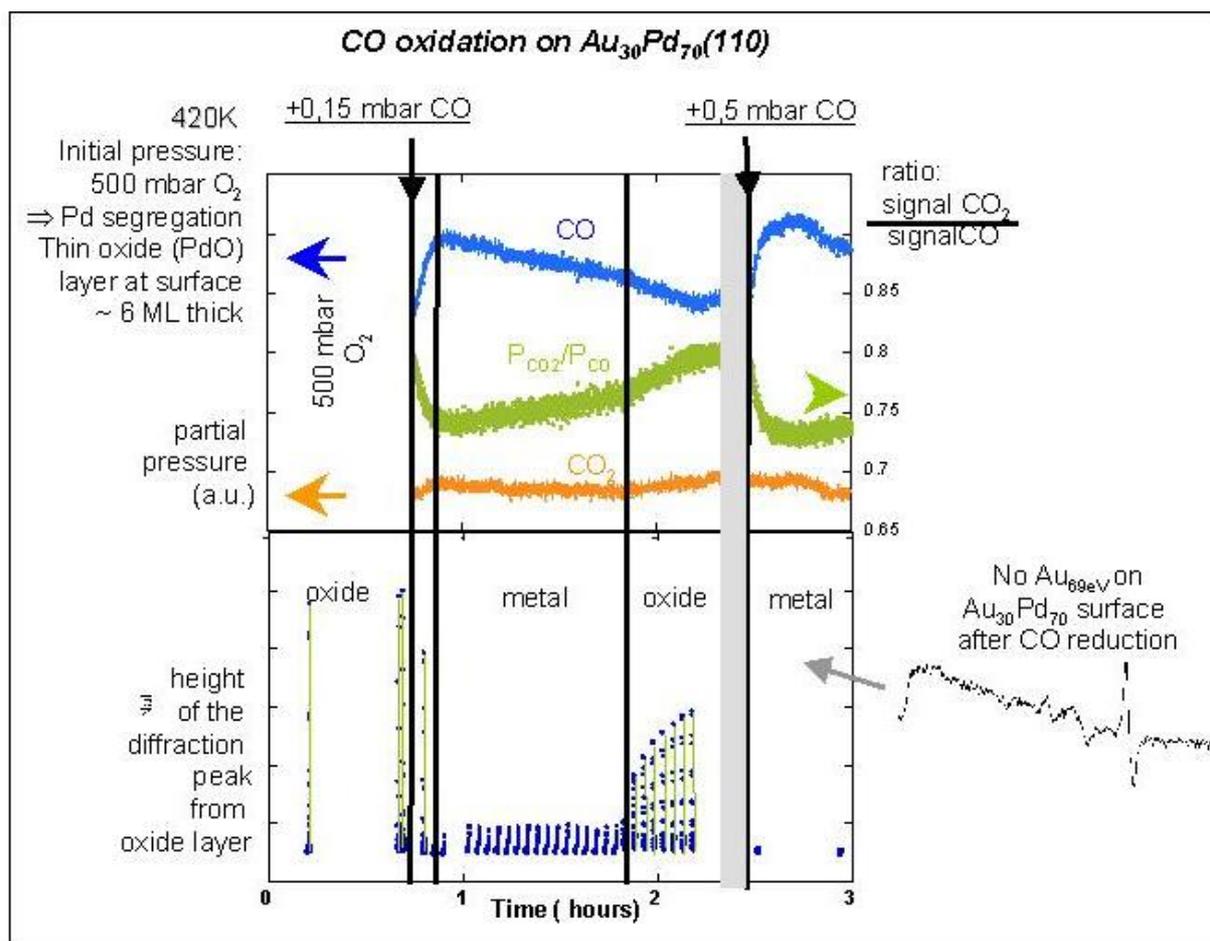


Just after the vanishing of the (1x2) LP (low pressure) reconstruction, the Auger ratio is equal to 2.4 showing a mixture of gold and palladium at surface. We also recorded data along several rods to analyse the (1x2) LP reconstruction. The quantitative analysis is under progress.

When increasing the pressure, there is a domain where all surface peaks disappeared.

At higher pressure, around 100 mbar at 300K, a new sharp peak appears at (0 1.475 0). Auger spectra showed that, at this moment, there is lonely Palladium at surface. The X-ray diffraction data clearly indicate that the surface is covered by a thin layer of palladium oxide, PdO, with the  $c$  axis perpendicular to the dense rows of the (110) surface.

We then performed CO oxidation on this surface. The hereunder figure illustrate the observed behaviour versus time: the top curve shows the signal recorded through a leak valve by the mass spectrometer and on the below one the evolution of the diffracted intensity at (0 1,475 0), which is characteristic of the surface PdO oxide.



The sample is heated at 420K and at the beginning it is exposed to 500 mbar of oxygen, we thus measured the oxide signal. When 0,15 mbar of CO is added, the oxide signal is vanished. As shown by the ratio of the CO<sub>2</sub> signal over the CO signal, the CO<sub>2</sub> rate production is negligible. About one hour latter the oxide peak reappears and the reaction rate increases. A new CO introduction reduced again the oxide and stops the reaction. An Auger spectra performed on this reduced surface shows clearly that there is still lonely palladium at surface. To recover the UHV gold composition at surface we have to clean again the sample (Ar sputtering + annealing at 720K). By the way we checked that there was no sample contamination problem such as Nickel carbonyl, which strongly interact with gold surface when it is present.

To summarise this work, as planned, we checked successfully our set up; the connection between the two chambers, x-rays reactor and UHV chamber, allowed us to combine surface x-ray diffraction and Auger spectroscopy. We thus clearly evidenced that oxygen induced Pd segregation, which pay a great role during the reaction: the whole behaviour of this surface looks close to that of pure palladium bulk. Deeper analysis of our data is under progress and would yield a more complete understanding of the process especially the influence of gold.