Au – Pd surfaces for catalysis studied by Surface X-Ray Diffraction

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In many reactions, the combination of several metals leads to better catalytic properties than in the case of pure metals. This explains why supported bimetallic particles are widely used in a broad range of catalytic reactions such as hydrogenation and oxidation processes. Palladium is a good catalyst for many hydrogenation reactions. Whereas gold is known to be a poor catalyst in its bulk state, it appears to be very promising when used, for instance, as oxide-supported nanoparticles for low-temperature CO oxidation [1]. The explanation for such an excellent activity is still an open question. Recently, it has been shown for several reactions that activity [2] and selectivity [3] could be both considerably increased by the simultaneous presence of gold and palladium, compared to conventional gold or palladium catalysts. This is to better understand this "synergetic" effect in bimetallic catalysts that we started a study on model catalysts in real conditions of pressure. One of the most powerful tools to perform such *in situ* experiments is the Surface X-Ray Diffraction (SXRD) as it is a non destructive technique and it will not be disrupted by the ambient pressure (i.e. pressure about 10^9 times larger than in conventional surface chemistry experiments).

Our work concerning gold-palladium model catalysts includes the study of Au thin films on Pd(110) as well as (110) and (111) surfaces of a Pd-rich alloy ($Au_{30}Pd_{70}$), from UHV to reaction conditions. This approach should permit to identify the respective influence of segregation, strain ($a_{Au} \sim 1.05\ a_{Pd}$) and local chemical environment on catalytic activity.

We present here the results concerning the structural evolution of 2.5 monolayer (ML) thick deposit of gold strained on Pd(110) with the annealing temperature. The structure has been studied by SXRD in UHV. According to the annealing temperature, 3 or 4 atomic planes different from those of the substrate are necessary for a good description of the structure. This information is given by the diffracted intensity modulations along the crystal truncation rods (see figure 1). The surface plane exhibits a (1x2) missing row reconstruction constituted exclusively by gold atoms (see figure 2 and references [4,5]). Underneath, a well-defined interfacial alloy is present. Its composition profile and thickness are dependent upon the film annealing temperature. It is thus possible to tune the composition profile by adjusting the annealing procedure. We have then the possibility to check which structure influences the catalytic activity in the most favourable way in order to put light on the relevant parameters.

We will also present the first results of the structural changes induced by the presence of reactive molecules (H_2 and O_2) on both the (110) and (111) $Au_{30}Pd_{70}$ surfaces since we are interested in two reactions: the butadiene selective hydrogenation and the CO selective oxidation. For the (111) $Au_{30}Pd_{70}$ surface, almost no gold segregation is predicted so that the outermost layer should be composed of gold atoms mainly surrounded by palladium ones [6]. Conversely, the (110) open face should favour a large gold surface segregation and a (1x2) missing row reconstruction of gold surface atoms according to our results on the annealed film.
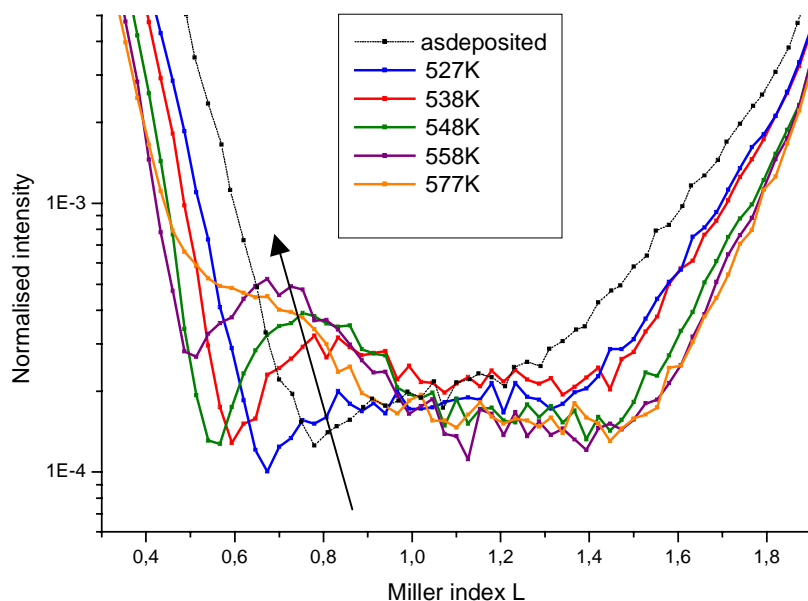
Figure 1 – Evolution of the specular rod intensity during an annealing series of 2.5 ML Au / Pd(110)
The Miller index L (abscissa) is oriented perpendicular to the sample surface. The intensity is normalised by the photon incident flux. The film thickness can be deduced from the modulations of the diffracted intensity. It is slightly moving from 3 to 4 atomic planes when the annealing temperature is increased. Changes already occur with the first annealing at 473 K (curve not showed here).

Figure 2 – Evolution of the superstructure peak intensity during an annealing series of 2.5 ML Au / Pd(110)
The intensity is followed at the (0 3/2 0.15) reciprocal point. The half-order value of the Miller index K indicates a (1x2) reconstruction which appears already at 473 K and becomes more and more pronounced when the annealing temperature is increased. The intensity is maximised for T = 558 K.
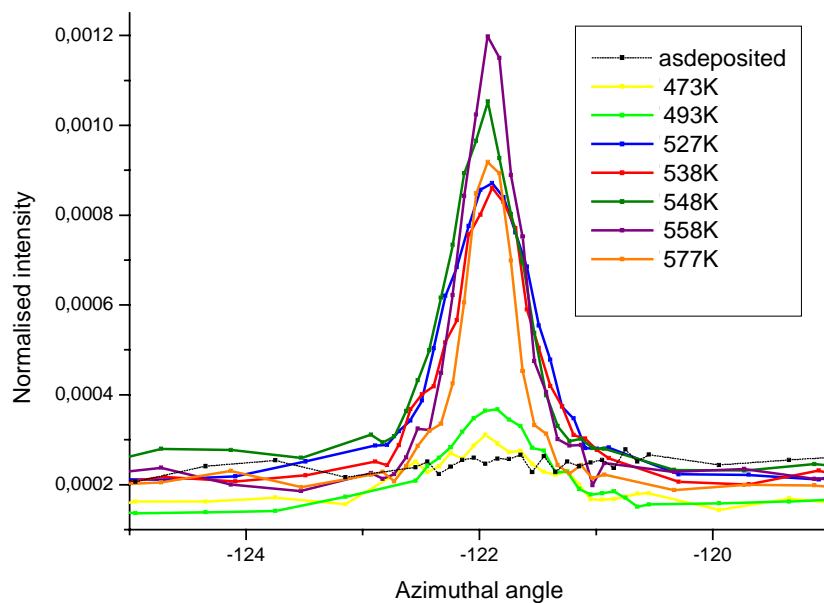
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