ESRF

| Experiment title: Study of nanostructural features of Pd/C and Pd-Au/C catalysts | Experiment number: 08-02-193 |
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| **Shifts:** 9 | **Local contact(s):** C. Meneghini |
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## Report:

Supported metal catalysts found large application in industrial processing. They are made by metals, often precious, dispersed as small particles (nanometer size) on inhert matrix by chemical procedures. The larger surface to volume ratio, in fact, improves the reactivity and efficiency of the catalyst and reduces the amount of active metal emploied.

The use of bimetallic compounds frequently improve the catalyst performances. Nevertheless the mechanisms by which the second metal improves the activity of the catalyst are often unclear: in some cases it seems to improve the dispersion of the metallic phases but the formation of metallic alloys could also play a relevant role [A. Balerna et al. Eur. Phys. J. B7, 89-97 (1999), A. Longo et al. Studies in Surface science and catalysis D 130, 3207-3212 (2000)].

The aim of this experiment was to evidence, quantify and characterize the metallic nano-phases on Pd/C and Pd-Au/C catalyst samples tailored as industrial ones, i.e. with very low metal content (Pd 1 wt/% Au 0.2 wt/%).

In particular we were interested in the evolution of these nano-phases under thermal treatment simulating industrial processes. To this aim in situ XRD experiments were performed on GILDA using the Translating Imaging Plate (TIP) detector system. Supported metal catalysts were obtained by impregnation of $Na_2PdCl_4$ aqueous solutions and then reduced with HCOOH at 352K. Bimetallic samples were obtained by successive impregnation of $Na_2PdCl_4$ and $HAuCl_4$ aqueous solutions and then reduced with HCOOH at 352 K.

In situ X-ray diffraction measurements with the TIP have been done using an heating gun and a catalytic cell developed at University of Venice. Diffractograms were collected during temperature scan from room temperature to 923 K (2 hours). The samples were taken under $N_2$ flux to prevent the oxidation of Pd.

The Pd/C sample behaved in an unusual way under annealing (fig. 1): the lattice parameter of the metallic phase expands with increasing temperature due to the thermal dilatation till about 553 K; but at 553 K there is a strong expansion of the lattice parameter that is too large to be related only to thermal expansion effect (fig. 2). We have interpreted this anomalous expansion as indicative of a reaction of Pd clusters with the carboninilic groups present on the carbon support that react with palladium forming PdC. Raising more the temperature the PdC phase is stable till 683 K then a contraction of the lattice is observed indicating that C is expulsed and Pd metallic is formed again (Fig. 2). An interesting effect is that the width of the Bragg peaks remains almost unchanged till about 683 K, indicating a particle size of about 10 nm. Raising T above 683 K the Bragg peaks become sharper pointing out the growth of metallic particles (to about 30nm).

These results suggest that the formation of the PdC phase prevents the growth of metallic particles that can only grow getting over 683 K, when PdC dissociates.

For bimetallic catalysts diffraction measurements evidenced that the "as received" Au-Pd/C sample is formed by pure Pd and by an alloy of Au-Pd very rich in gold and that during the thermal treatment there is a continuos transformation of the Pd and the initial alloy towards an alloy richer and richer in Pd (Figure 3). Comparing the X-ray diffraction patterns of the as received catalyst and the same sample after the thermal treatment are evident new diffraction peaks, marked with stars in figure 3, belonging to a new and unidentified phase.

The characterization of such new phase would be an interesting issue to understand the catalytic mechanisms on such materials and will be the subject of a new proposal.

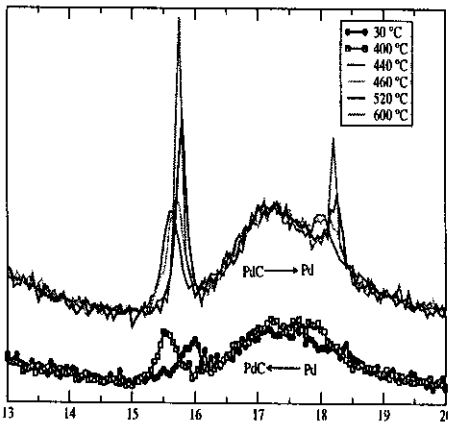


**Fig. 1** Diffractograms of Pd/C catalyst as a function of annealing temperature. Lower curves depict the expansion of lattice parameter, while the upper curves depict the lattice contraction and sharpening of Bragg peaks.

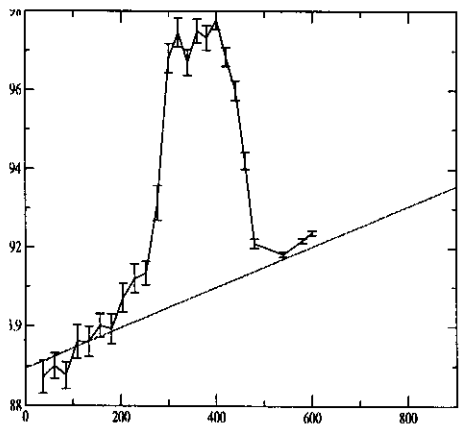


**Fig. 2** Lattice parameter of Pd(C) phase as a function of annealing temperature

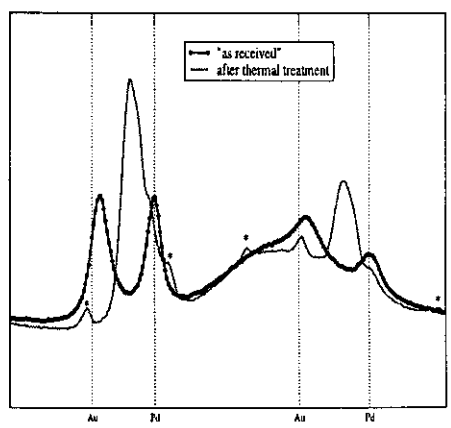


**Fig. 3** Right: [28]Diffractograms of Pd-Au/C catalyst "as received". Dot -lines indicates the expected positions of Bragg peaks for pure Au and pure Pd fcc.