ESRF	**Experiment title:** How do the size, structure and morphology of supported gold-palladium nanoparticles influence their catalytic performance for butadiene hydrogenation ?	**Experiment number:** **32-02-764**
Beamline: BM32	**Date of experiment:** from: June 10, 2014 to: June 17, 2014	**Date of report:** March 1, 2017
Shifts: 24	**Local contact(s):** Dr Odile Robach	*Received at ESRF:*

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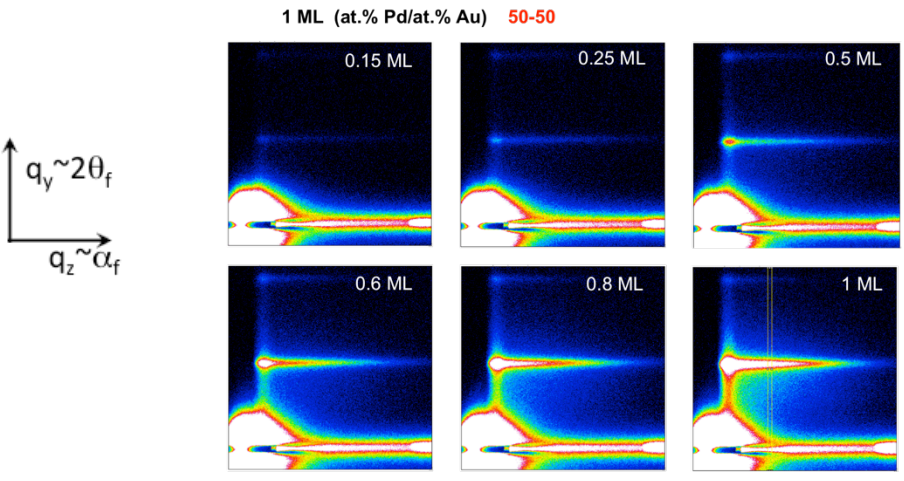
Report:

Note: Due to serious technical problems encountered with the experimental setup supposed to be installed on the GMT diffractometer at ESRF, we finally performed the experiment using the INS instrumental setup. This means we had to change a little bit the experimental schedule with regard to the submitted proposal.

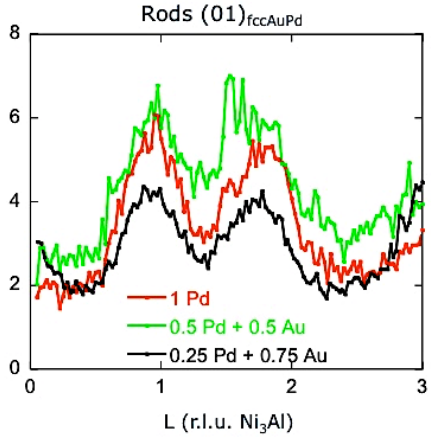
By combining Grazing Incidence X-Ray Diffraction (GIXRD) and Grazing Incidence Small-Angle X-ray Scattering (GISAXS), we analyzed the growth of organized arrays consisting of bimetallic palladium-gold nanoparticles (NPs). The NPs were grown *in situ* on an ultrathin nanostructured alumina film obtained by the direct oxidation of a $Ni_3Al(111)$ single crystal. This Al_2O_3 film acts as a template promoting the self-organized growth of either mono- (Pd) or bimetallic (AuPd) nanoparticles. Several Pd/Au atomic compositions have been explored: 10/90, 25/75, 50/50 and 100/0 for a total (Pd+Au) amount equal to 1 ML. In each case, GISAXS was performed in situ during the sequential growth of each metallic species. As an example, the following figure shows the images obtained in the case of the 50/50 deposit. Pd was deposited first until the completion of 0.5 ML and then, 0.5 ML of Au was added. In this case, the ordered character of the 2D NPs array gives rise to the sharp diffraction rods (1st and 2d order) of which intensity increases with the total deposited amount.



While increasing the relative gold amount in the deposits, we noticed a progressive disordering of the NPs arrays with the appearance of an additionnal diffuse component peaking at the position of the first-order scattering rod. A quantitative analysis has been done based on the GISAXS images acquired during deposition. For each deposit, the intensity of the first-order rod has been estimated as a function of the total (Pd+Au) amount. It turns out that the disorder phenomenon intervenes more rapidly for the Au-richest deposits (25/75 and 10/90) compared to the Pd-richer ones. And it is much more pronounced for the 10/90 sample.

Thanks to GISAXS, we've been thus able to determine the Au thickness above which the arrays start to disorder. For a given size of the Pd cluster, we estimated that Au grows in an ordered manner until the completion of an 1 atomic layer-thick shell. The mean morphological parameters of the ordered nanoparticles (in-plane diameter, aspect ratio and correlation length) were also obtained from the quantitative GISAXS analysis. The typical diameter was estimated to ~2 nm with a correlation length of ~75 nm.

After the completion of each deposit (i.e. at a total Pd+Au amount equal to 1ML), we acquired GIXRD data in order to determine the structural parameters characteristics of the ordered part of the NPs arrays. The diffracted intensity was in perfect agreement with the disordering phenomenon evidenced by GISAXS. We showed that the NPs have a *fcc* structure with a preferential (111) epitaxial relationship (see figure below). The in-plane interatomic distances obtained by GIXRD were very close from the one of pure bulk Pd (2.75 Å), arguing in favor of the scenario drawn from the GISAXS analysis (i.e. only one Au atomic plane on the Pd clusters).



Intensity (in a.u.) of the (0 1) rod obtained for three different compositions: pure Pd, 50 at. % Pd and 25 at. % Pd. The total Pd+Au deposited amount was equal to 1 ML.

In conclusion, we have investigated by GISAXS and GIXRD the growth of Pd-Au arrays of NPs for different Pd/Au compositions, ranging from pure Pd to almost pure Au. We've been able to characterize the disordering phenomenon occuring when the relative Au amount increases. For each composition, the main structural and morphological parameters have been obtained from a quantitative analysis of either the GISAXS images (using the IsGISAXS software) or the GIXRD spectra. For a given size of the initial Pd clusters, we were finally able to precisely determine the maximum Au amount which could be deposited before the appearance of disorder. This information is of primary importance for further applications of this type of organized arrays, since it will set the size and the composition of the bimetallic NPs.

N.B.: The results briefly described above are part of a paper intended to be submitted soon (under review by the co-authors).