

**Experiment title:**

Supported gold-palladium nanoparticles for butadiene hydrogenation: how do their size, structure and morphology influence their catalytic performance ?

**Experiment number:**

SI 2569

**Beamline:**

BM32

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By combining *operando* Grazing Incidence X-Ray Diffraction (GIXRD), Grazing Incidence Small-Angle X-ray Scattering (GISAXS) and mass spectrometry measurements, we initially aimed at analyzing the effect of different Pd compositions on the efficiency of bimetallic gold-palladium nanoparticles (AuPd NPs) during the 1,3-butadiene hydrogenation. The NPs were grown *in situ* (in the preparation chamber) on a ultrathin nanostructured alumina film obtained by the direct oxidation of a Ni<sub>3</sub>Al(111) single crystal. This Al<sub>2</sub>O<sub>3</sub> film acts as a template promoting the self-organized growth of either mono- (Pd) or bimetallic (AuPd) nanoparticles.

These experiments have been carried out on the GMT diffractometer using the specific equipment developed at the Institut Néel which allows to correlate the structure and the morphology of model catalysts to their catalytic activity in the course of a given reaction. Before the synchrotron beamtime, a lot of time was devoted to the sample preparation. Actually we used a new Ni<sub>3</sub>Al(111) single-crystal and we were already aware that some steps of the preparation procedure were quite delicate. Indeed some features are really crucial in order to obtain a good alumina thin film such as the ion bombardment parameters and the quality of the vacuum just before oxidation, for instance. Thanks to several discussions with colleagues who already worked with this Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) surface, we've been able to significantly improve the sample surface preparation procedure according to the LEED diffraction patterns quality (not shown here). Unfortunately the GISAXS patterns acquired during beamtime still exhibit broad diffuse peaks around the reciprocal space origin in addition to the thin correlation peaks characteristics of the long-range order of the NPs array (see figure 1). These broad peaks have already been observed before (see ER 20100524) and their origin was not quite clear.

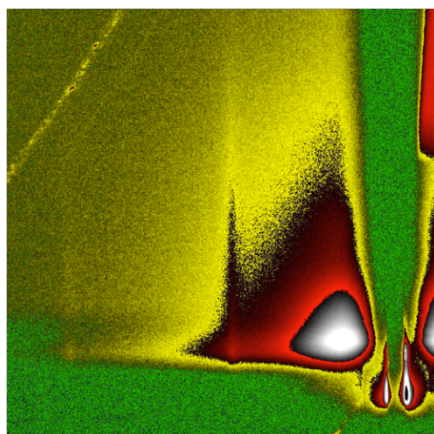


Figure 1 - GISAXS pattern for a 0.5 ML deposit of Pd on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111) showing the two first order peaks characteristic of the long-range order of the Pd NPs array. The broad diffuse peak is attributed to random crystallites, as explained in the text.

Thanks to additional experiments led back in laboratory, we have finally found that the  $\text{Ni}_3\text{Al}(111)$  bulk alloy surface was undergoing some kind of transition, probably due to too long and repeated argon ion bombardments (cleaning procedure). The Scanning Electron Microscopy (SEM) images in Figure 2 show the appearance of micrometer-square areas constituted by "hills and valleys" finally leading to the growth of some kind of crystallites. The areas nucleated randomly almost everywhere at the surface and could explain the GISAXS diffuse signal previously mentioned. We also performed an Energy Dispersive X-ray analysis (see Figure 3). The spectra evidence some trace of tungsten contamination, probably coming from the sample mounting system.

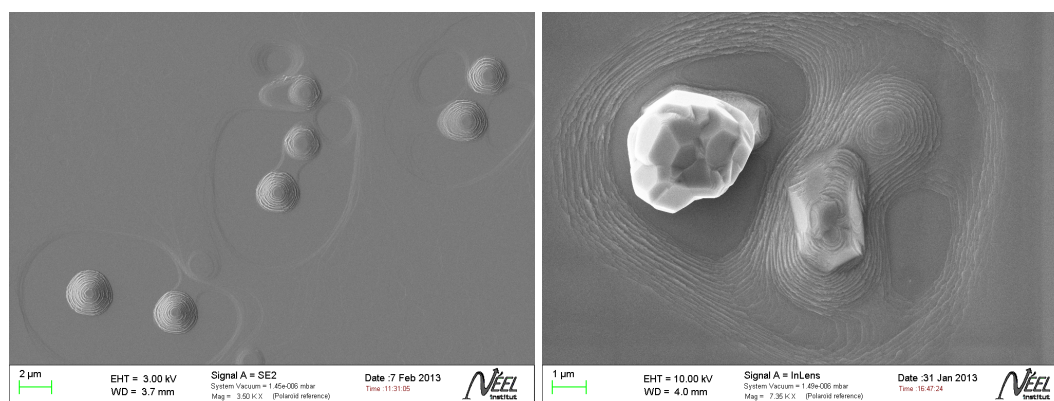


Figure 2 – SEM images obtained after the present experiment at ESRF. Micron-sized crystallites have nucleated everywhere on the surface of the  $\text{Ni}_3\text{Al}(111)$  single-crystal.

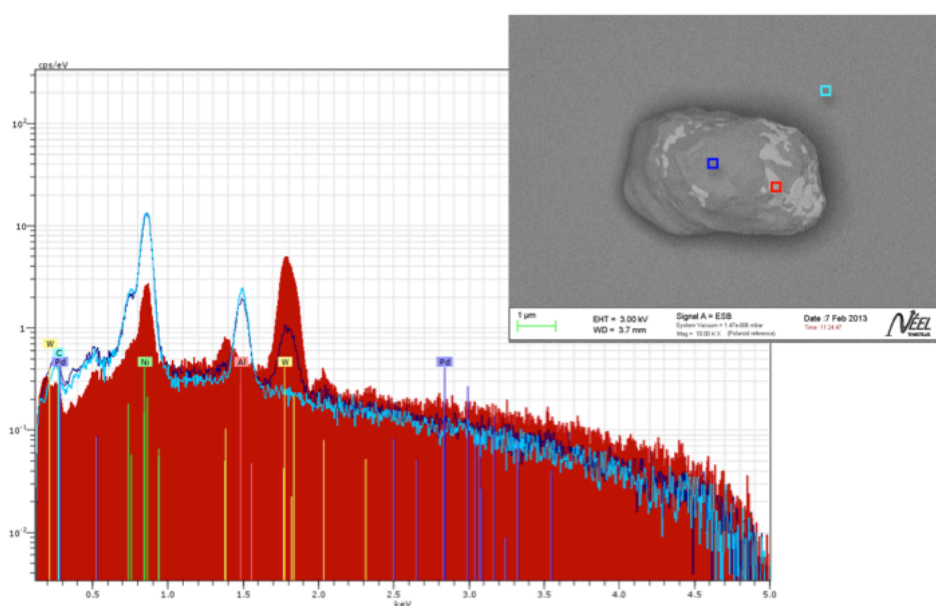


Figure 3 – EDX spectra obtained in three different areas on the crystallite shown in the inset. The colour of the spectra corresponds to the coloured boxes identified on the crystallite. Except on the substrate, a tungsten contamination is found probably due to the sample mounting system used.

As we were not able to get very well-controlled arrays of NPs (and thus, clear correlations with the catalytic activity), we decided to focus on the preparation procedure in order to get a better understanding of the critical parameters. We thus followed *in situ* the oxidation step leading to the thin alumina film. We recorded GIXRD spectra (and also GISAXS patterns) while heating the sample directly in the reactor chamber at roughly 920 K thanks to a diode laser in an oxygen pressure of  $3 \cdot 10^{-7}$  mbar. It turns out that the substrate surface is very sensitive to the quality of the base pressure either in the preparation chamber or in the reactor itself. A base pressure in the low  $10^{-8}$  mbar leads to the appearance of oxide signature, clearly evidenced by the diffraction spectra recorded at (1.17 0.75 0.01). We also followed diffraction peaks characteristic of the alloy chemical order. We finally conclude that the vacuum quality was not sufficient in order to get a good alumina film, in addition to the presence of the crystallites due to the ion bombardment step.