

**Experiment title:****Effect of the structure of gold-palladium nanoparticles supported on a nanostructured alumina template on their catalytic properties for the butadiene hydrogenation reaction****Experiment number:**

SI 2288

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The aim of this proposal was to analyze the effect of different Pd compositions on the efficiency of bimetallic gold-palladium nanoparticles (AuPd NPs) during the hydrogenation of 1,3-butadiene. These experiments have been carried out on GMT using the specific equipment developed by the Institut Néel team. By combining GIXRD, GISAXS and mass spectrometry measurements, it allows to correlate the structure and the morphology of model catalysts to their catalytic activity in the course of the reaction. This equipment has been upgraded very recently in order to be more sensitive to the low catalytic activity arising from small amounts of catalyst. Indeed the size of the reactor in which the X-ray and mass spectrometry measurements are performed has been decreased by a factor of 10 (see figure 1). This synchrotron run was the first one using this new configuration; thus enabling us to check whether the equipment matches the requirements. During this experiment, we were able to combine GISAXS, GIXRD and mass spectrometry in order to follow the changes undergone by the catalysts in the course of the hydrogenation reaction. GISAXS patterns, GIXRD scans and mass spectra have been recorded for Pd amounts as low as 0.1 ML; thus confirming the suitability of this experimental set-up for performing such *in operando* measurements with a good sensitivity.

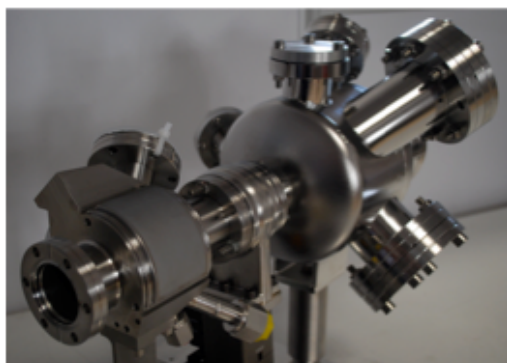


Figure 1: New reactor for the *in operando* measurements using X-rays. It is normally coupled to a preparation chamber (not shown here). The X-rays are detected through the large semi-cylindrical beryllium window of the main left-hand side chamber (in which the sample is vertically positioned). The mass spectrometer (not shown) is implanted on the right-hand side chamber; both chambers being connected by a gate valve. The gases are collected in the main chamber and analyzed via a leak valve.

The NPs were grown *in situ* (in the preparation chamber) on a ultrathin nanostructured alumina film obtained by the direct oxidation of a Ni₃Al(111) single crystal. This Al₂O₃ film acts as a template promoting the self-organized growth of either mono- (Pd) or bimetallic (AuPd) nanoparticles. By adjusting the respective amount of Pd and Au, the size and the composition of the bimetallic nanoparticles can be independently controlled.

We deposited different thicknesses of pure Pd and pure Au, ranging from 0.1 to 1 ML. We also focused on one specific bimetallic system: 50% Pd-50% Au (0.3 ML in total). In a first step of the experiment and for each system, we checked that the obtained arrays of nanoparticles were effectively very well-ordered. It was evidenced by the GISAXS patterns recorded in UHV, just before exposure to the gases (figure 2, #1).

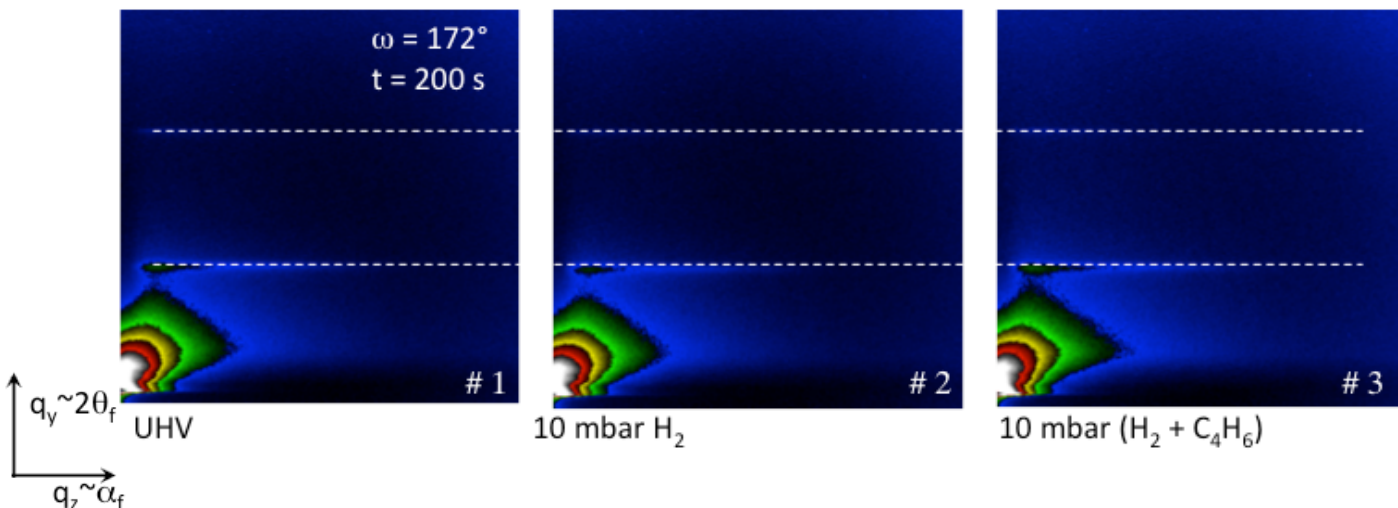


Figure 2: GISAXS patterns obtained for a 0.3 ML deposit of Pd on a Al₂O₃/Ni₃Al(111) substrate in different environments: #1 in UHV, #2 in 10 mbar of hydrogen and #3 in a mixture of hydrogen and butadiene (ratio 10:1). The white lines indicate the position of the first and second order correlation peaks characteristic of the long-range order of the NPs' array. ω and t are the azimuthal angle and the exposure time, respectively.

More surprisingly, the long-range order is preserved under gases, as shown by the GISAXS patterns #2 (recorded in the presence of hydrogen) and #3 (in the butadiene + hydrogen mixture) of figure 2. This result is of primary importance since the thorough understanding of the catalytic performances implies to be able to quantify the importance of each parameter, i.e. size, shape, crystallographic structure and composition in the case of bimetallic NPs. Thus a disorganization of the NPs array under gases would have precluded any detailed analysis of their catalytic properties.

Additionally, some slight changes have been observed by X-ray diffraction when hydrogen is introduced. It seems that hydrogen favors one kind of epitaxy relation with respect to the alumina substrate; the detailed analysis being now under progress.

Finally, we were able to record mass spectra for catalyst equivalent amounts as small as 0.1 ML in the course of the butadiene hydrogenation. It was also possible to detect differences in the catalytic activity rate of each sample.

Although our results are still mainly qualitative, they indicate that a more detailed analysis, as well as complementary experiments, should make it possible to establish a link between the size, the composition and the catalytic activity of the mono- or bimetallic nanoparticles.