ESRF	**Experiment title:** Characterisation of supported metal catalysts by XANES spectroscopy: high-resolution experiments supported by ab initio calculations	**Experiment number**: 30-02-1034
Beamline:	**Date of experiment**: from: 18th July 2012 to: 24th July 2012	**Date of report**: 01/09/2012
Shifts:	**Local contact(s)**: Jean-Louis Hazeman	*Received at ESRF:*

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Report:

The physics and chemistry of oxide supported metal nanoclusters are of paramount fundamental and technological importance especially in the field of energy. Platinum nanoparticles supported on γ-alumina are widely used as highly dispersed heterogeneous catalysts, in particular in the presence of H_2. Their reactivity and selectivity are intimately related to the local geometry and the electronic density of the active site.

For a better understanding of the chemical interplay between the metallic nanoparticles, the support and the atmosphere, preliminary in-situ XANES analysis at the Pt L_3 edge were conducted under different operating conditions coupled with simulation tools, at ESRF, on the FAME beamline. An in situ cell was therefore installed on the beamline to study X-ray absorption spectroscopy of Pt nanoparticles (about 0.8 nm) supported on γ-Al_2O_3 under hydrogen (at 10^{-6} mbar and 1 bar) and at room temperature and 500 ° C. Due to the very low platinum concentration (~ 0.3 wt%), and in order to have more precise information on the geometric and electronic structure of the particles on the XANES spectrum, High Energy Resolution Fluorescence Detection (HERFD) [1] was used in addition to the conventional

fluorescence detection to increase the spectra resolution. The crystal analyzer, set up with four Si(555) crystals, was tuned on the $L_{\beta 2}$ (L_3-$N_{4,5}$) fluorescence line at 11232 eV. Fig. 1 displays the experimental set up.

Finally, the experimental data were compared to simulated XANES spectra by FDMNES program [2]. Models of particles obtained by quantum molecular dynamical calculations were used for the simulations [3]. Then these comparisons allow the discrimination between different morphologies (Fig. 2) and hydrogen coverage. The clusters present a more biplanar geometry than cuboctahedral. Although at this time, the calculations were performed only on one surface of the support, this work give deep insights into the influence of hydrogen on morphology and electronics properties of supported metallic nanoclusters.

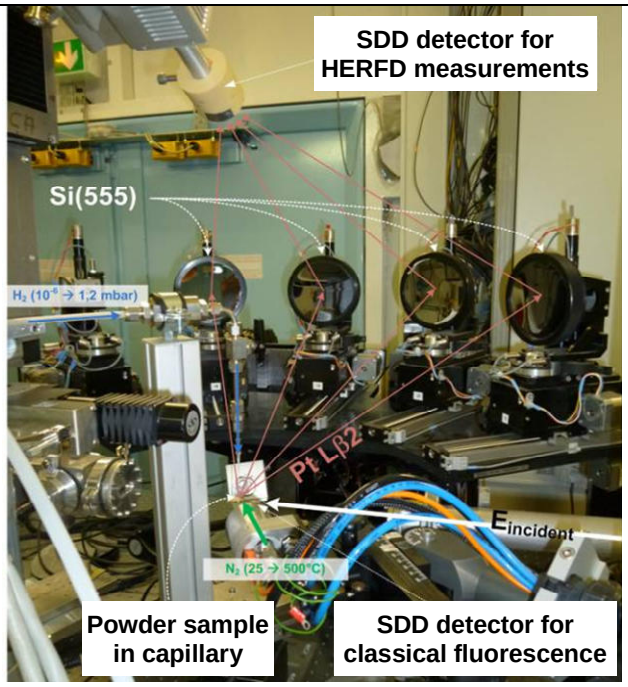

Fig. 1 : Experimental set up. The powder sample, kept under controlled atmosphere in the glass capillary, is heated from outside with a nitrogen heat gun.

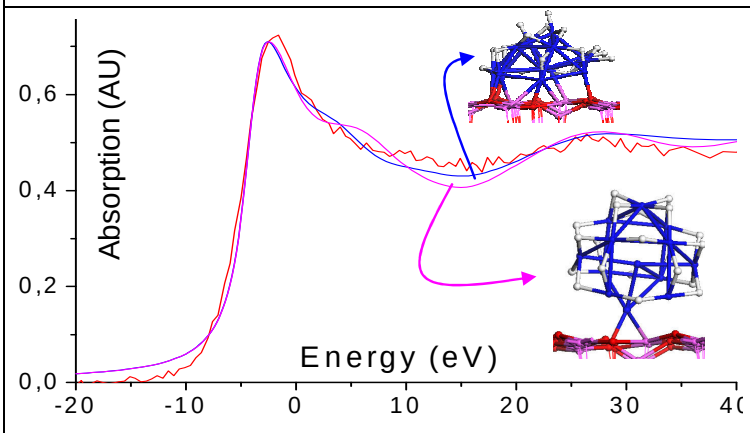

Fig. 2 : Pt L_3 HERFD XANES spectrum of Pt catalysts supported on γ-Al_2O_3 under hydrogen pressure (1 bar) at room temperature (red) compared with FDMNES calculated spectra for a $Pt_{13}H_{18}/\gamma Al_2O_3$ cluster (blue) and $Pt_{13}H_{20}/\gamma Al_2O_3$ (pink) from [3]

REFERENCES

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2. Joly *et al.*, *J. Phys.: Condens. Matter*, 21, 345501 (2009)
3. Mager-Maury et al., *ChemCatChem*, 3, 200 (2011)