ESRF	**Experiment title: Characterization of supported metal catalysts by XANES spectroscopy : high-resolution experiments supported by ab initio calculations.**	**Experiment number**: CH 3815
Beamline: BM 30B	**Date of experiment**: from: 17th April 2013 to: 23rd April 2013	**Date of report**: 21/05/2013
Shifts: 18	**Local contact(s)**: Olivier Proux	*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, 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^{-2} 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 to increase the spectra resolution. The crystal analyzer, set up with one Ge (660) crystal, was tuned to the $L\alpha_1$ (L_3-M_5) fluorescence line at 9442 eV. Fig. 1 displays the experimental set up. A global bandwidth of energy was achieved at 1.3 eV. This resolution allowed to observe a much more featured spectrum than the total fluorescence one, as shown on Fig. 2.

The set up has been improved from the previous experiment in order to have more precision on the pressure and temperature. By this way, it is now possible to confirm that this experiment is reproducible and reversible.

Finally the experimental data are actually compared to simulated XANES spectra by the FDMNES program [2]. Models of particles obtained by quantum molecular dynamical calculations are thus used as input geometry for the simulations [3]. Then these comparisons allow the discrimination between different morphologies and hydrogen coverage. For example we have already obtained

for a specific condition of temperature and hydrogen pressure, the agreement shown in fig. 3. This allows a very safe determination of the cluster morphology in this case. This work gives already deep insight into the influence of hydrogen on morphology and electronics properties of supported metallic nanoclusters.

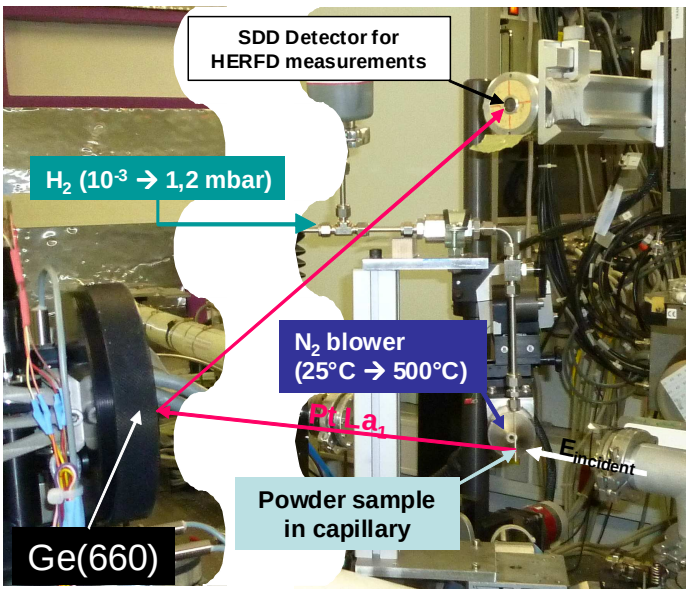

Fig. 1 : Experimental set up. The powder sample, kept under controlled atmosphere in the glass capillary, is heated from outside with a nitrogen heat gun.

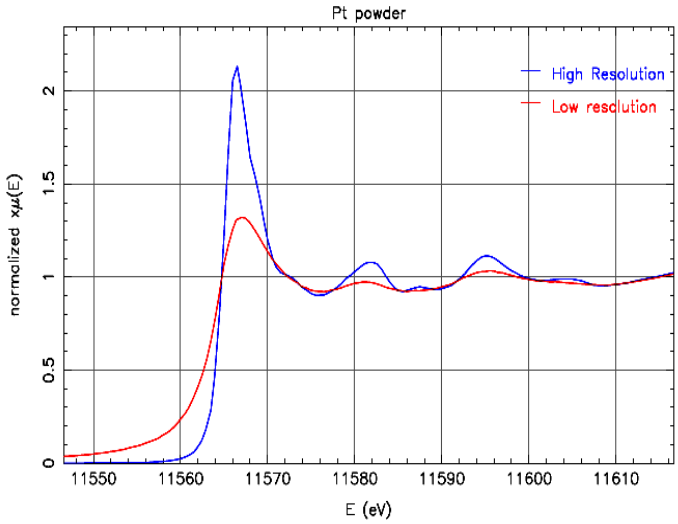

Fig. 2 : Pt L_3 HERFD XANES spectrum (blue) compared to classical fluorescence XANES spectrum (red) of 20 wt% Pt powder in BN.

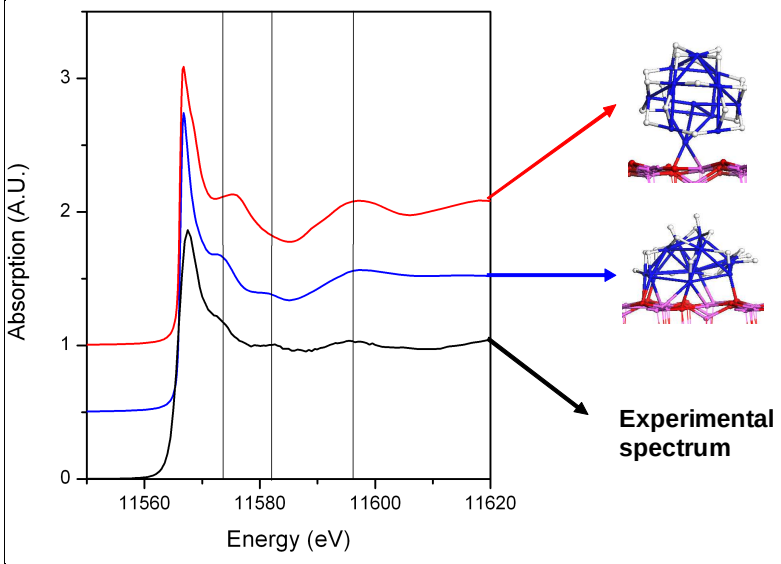

Fig. 3 : Pt L_3 HERFD XANES spectrum of Pt catalysts supported on γ-Al_2O_3 under hydrogen pressure (1 bar) at room temperature (black) compared with FDMNES calculated spectra for a $Pt_{13}H_{18}/\gamma Al_2O_3$ cluster (blue) and $Pt_{13}H_{20}/\gamma Al_2O_3$ (red) from [3]

REFERENCES

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