

Synchrotron X-Ray study of platinum- nanoparticle catalysts

Better knowledge of metal nanoclusters supported on an oxide is of paramount fundamental and technological importance especially in the field of energy. In particular, dispersed platinum particles on alumina (aluminium oxide Al_2O_3) are widely used as heterogeneous catalysts, from the laboratory scale to the industrial plant. A specific case is catalytic "reforming" where petroleum refinery naphthas (liquid hydrocarbon mixtures) are converted into high-octane products. The catalyst's reactivity and selectivity are intimately related to the local geometry and the electronic density of the active sites. They strongly depend on the coverage with hydrogen, often present in the reactive medium, and on the alumina support. It is now possible to characterize such systems at the atomic level, and *in situ*, that is at a temperature and hydrogen pressure close to the catalytic process conditions. X-Ray Absorption Near Edge Spectroscopy (XANES) is one of the few techniques allowing such a study in disordered materials.

The XANES experiments were performed at the European Synchrotron Radiation Facility, Grenoble, on a system containing 0.3 weight % Pt supported on 10 nanometer width alumina platelets. The platelets have mainly (110) and (100) faces for 70% and 20% of the exposed surface, respectively. The platinum is in the form of a cluster of atoms of size smaller than 1 nm. We choose Pt_{13} particles to model the clusters in an appropriate way. A comparison between data from the XANES experiments and modelling enables us to obtain the atomic positions within the clusters and the hydrogen coverage, as well as providing information about the sites and faces of the supporting material on which the nanoparticles are adsorbed. Note also that, in the experiment, hydroxyl (OH) groups remain present on the alumina (110) face and some dispersion in the nanoparticle size was observed by Scanning Tunnel Microscopy.

The number of parameters involved, and the lack of reference X-Ray spectra to compare with, makes simulations mandatory to gain quantified insights from the experimental data. Recording the spectra using the High Energy-Resolution Fluorescence-Detection mode is also necessary. The spectra were obtained in the energy region of the Pt-L₃ X-Ray absorption edge where the X-Ray photoelectric process generates a transition from a core 2p level of the Pt atom up to the Pt metal 5d valence band states. Experiments were realized at two temperatures, 25°C and 500°C, and two values of hydrogen pressure, 10⁻⁵ and 1 bar. The higher temperature is typical of operating conditions in catalytic reforming.

The quantitative assignment is then done in two steps: First, a set of structural models is provided by the Density Functional Theory - Molecular Dynamics (DFT-MD) approach. This is done for the 2 alumina faces, including effects of the reconstruction of the alumina surface induced by the Pt cluster itself and the different possible hydrogen coverages. Secondly, using these models, we perform *ab initio* simulations of the XANES spectra, based on the full multiple scattering theory, and compare them to the data.

We found that the sensitivity of the calculated spectra to the geometrical models is high. In Fig. 1, we show only the final result, with the best agreement we got, for two operating conditions. In this way, we obtain the corresponding solutions for the hydrogen coverage and the cluster structure at the two main faces. For example, at 25°C and 1 bar, models containing 18 and 20 hydrogen atoms give the best fit to the spectra. We also found

from the calculations that, whatever the H-coverage, the clusters on the (100) face remain bi-planar whereas they have a 3D morphology on the (110) face, although strongly distorted compared with the original cluster calculated without hydrogen. On the (110) face, the hydroxyl groups reduce the negative charge of the metallic clusters and therefore the number of electrons available for hydrogen adsorption. Consequently at low pressure, we find more hydrogen atoms on clusters on the other face. In contrast, in the experiment performed at 25°C and 1 bar, the cluster morphology on the (110) face is changed into a distorted cuboctahedron, with fewer direct Pt-alumina bonds, leaving more adsorption sites available for hydrogen atoms.

Thus, high resolution XANES analysis, *in situ* under hydrogen reaction conditions, coupled to DFT-MD calculations, have allowed us to discriminate the different morphologies of supported nanoparticles and to quantify hydrogen coverage. This detailed understanding of highly dispersed platinum particles should help to achieve better control of catalysts under reductive environment. This work also brings new methodologies for the interpretation of XANES analysis, used in the characterization of many systems.

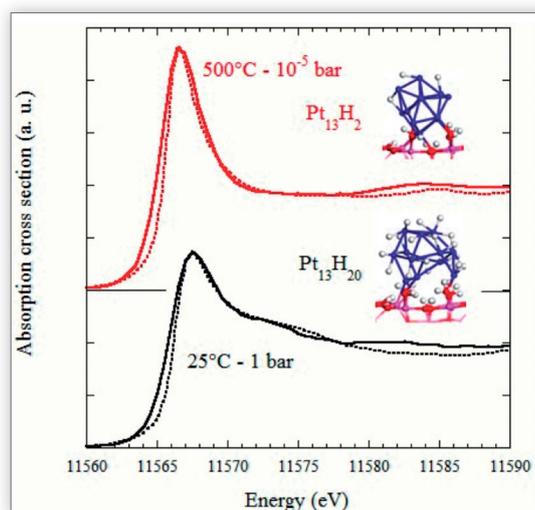


Fig. 1: Sensitivity of the XANES spectra, at the Pt-L₃ X-Ray absorption edge, to the morphology and hydrogen coverage of platinum clusters on alumina. Simulated spectra (solid line) are compared with the data (dashed line) recorded under two different temperatures and hydrogen gas pressures. The models shown are the best models for the clusters on the Al_2O_3 110 face under these operating conditions. Colour code: blue = Pt, grey = H, purple = Al, red = Oxygen.

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FURTHER READING

"Monitoring Morphology and Hydrogen Coverage of Nanometric Pt/ γ - Al_2O_3 Particles by In Situ HERFD-XANES and Quantum Simulations"
A. Gorczyca, V. Moizan, C. Chizallet, O. Proux, W. Del Net, E. Lahera, J.-L. Hazemann, P. Raybaud and Y. Joly
Angew. Chem. Int. Edition 53, 12426 (2014).