

Standard Project

Experimental Report template

In situ XAS study of photocatalytic production of H₂ with bifunctional catalysts		Proposal number: 20 120 191
Beamline: FAME	Date(s) of experiment: from: Sept 12, 2012 to: Sept 12 2012	Date of report: 10/01/2013
Shifts: 18	Local contact(s): Denis Testemale	<i>Date of submission:</i>

Objective & expected results (less than 10 lines): The objective of the proposal was to study investigate the state of platinum during in situ photocatalytic production of hydrogen from gas phase methanol reduction or water splitting.

Results and the conclusions of the study (main part): In-situ XAS characterization of nanoparticles of platinum photodeposited on TiO₂ (as a reference), g-C₃N₄ (doped by Ag, Sn, Al, Au) and mpg-C₃N₄. To achieve these experiments, a new *in-situ* XAS cell was designed, with the possibility to work in transmission or fluorescence mode, optical fibers allowing an UV irradiation (Fig.4). The purpose of these experiments is to obtain electronic (XANES) and structural (EXAFS) data occurring during the hydrogen production.

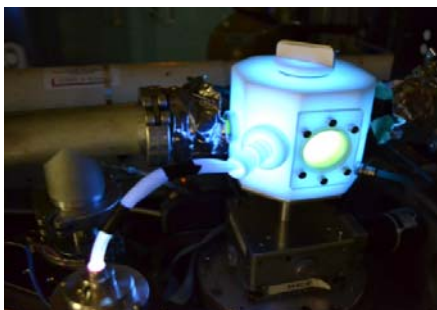


Fig. 4 : Picture of the *in situ* XAS cell under UV irradiation

The position of the edge of platinum-L₃ (11 564 eV) provides information of the oxidation state of the platinum. The value of each catalyst is compared to the reference value obtained for the platinum foil (11 564 eV - + 0 eV). On TiO₂ (as reference), platinum particles are completely reduced (+ 0.5 eV). On g-C₃N₄, the platinum is mostly reduced Pt^{+e} (+ 1 eV). Moreover, the adding of co-catalysts doesn't modify significantly the oxidation state of platinum. For the mpg-C₃N₄, an appreciable difference is observed because of the important shift of the edge (+ 1.9 eV). Platinum particles are mostly oxidized.

The treatment of the absorption spectra (EXAFS) especially the oscillations leads to the characterization of the neighborhood of one platinum atom. Thanks to the software VIPER, the experimental spectra are fitting, by modifying different parameters: coordination number (CN), Debye-Waller factor, distance of the neighbor (R), reduction factor (S_0^2) and the phase shift. Phase shift and backscattering amplitudes were given by the reference compounds: Na₂Pt(OH)₆ for the bond Pt-O (2.06 Å), H₂PtCl₆ for Pt-Cl (2.3Å) and platinum foil for Pt-Pt (2.77Å).

The determination of those parameters has been done for the first shell of the platinum. For TiO₂ and g-C₃N₄ (doped or not), the fit of the experimental curve is obtained only using the bond Pt-Pt, in agreement with the observations on the XANES. The modification of the conditions (under helium or methanol flow, with or without UV irradiation) does not change the values of the fitting parameters. The dispersion and the particle size can be determinate thanks to the coordination number (about 2/3 nm). This value is in agreement with the particle size determinate with the TEM picture.

These informations highlight the fact that the difference observed during the photocatalytic tests for all the samples could be partly due to the electronic transfer from the semi-conductor to the platinum particle (same particle size, slight difference in oxidation state). Photocatalytic reduction is observed on TiO₂.

Justification and comments about the use of beam time (5 lines max.):

1 shift has been used for the setting of the new in situ cell and optimization of data acquisition. Then, the several samples were acquired in fluorescence mode under dark and illuminated conditions. Acquisition in fluorescence mode takes 3x 45 min.

Publication(s):

- not yet published

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