



Experiment title: Impact of tin on platinum-chlorine proximity on supported reforming catalysts evaluated by XAS spectroscopy: high-resolution experiments supported by ab initio calculations

Experiment number:
16-01-798

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Report:

Highly dispersed supported Pt particles have various industrial applications as catalysts, such as in the case of catalytic reforming. In this process a bi-functional catalyst is needed, where the acidity of the alumina support is enhanced by chlorine. Also, bi-metallic catalysts are routinely used industrially. A study of the influence of chlorine on platinum's electronic state and its close environment, as a medium to evaluate the proximity between the sites was undertaken on the FAME and UHD-FAME beamlines for monometallic Pt/Al₂O₃-Cl catalysts with varying Pt and Cl loadings in both oxide and reduced state, using a dedicated *operando* reactor for *in situ* re-reduction (experimental reports n° 30-02-1120 and n°16-01-789). An equivalent study was now completed for Pt-Sn/ γ -Al₂O₃-Cl catalysts in order to find the impact of tin on the environment of platinum as a way of probing if it has an influence on the proximity between metallic and acid active sites using High Energy Resolved Fluorescence Detection XANES and EXAFS.

Our bimetallic samples consist of 0.3% wtPt and 0.3% wtSn deposited on a commercial γ -alumina support with either 1.4%wt or 0.1%wt Cl. As in our previous experiment (report n°16-01-789), the catalysts were re-reduced *in situ* using an *operando* cell developed at the Institut Néel. [1] under pure H₂ at 500°C (XANES scans were used to follow the thermal treatment). The thermal treatment took around 3h. XANES and EXAFS data acquisition on the Pt L₃ edge was performed under He after cooling to RT and purge of H₂. The extent of this purge (taking up to 4h) proved to have a marked impact on the XANES spectra, so several "try outs" were needed to control this stage of the treatment in order to have acquired data that can be compared between samples. Two PtSn/ γ -Al₂O₃-Cl and three Pt/ γ -Al₂O₃-Cl were studied after *in situ* reduction. *Ex situ* analysis was performed for 2 more catalysts in oxide state and for 2 platinum references. Depending on the platinum content of the catalysts, data acquisition took 4-6h or 8-10h.

The impact of the purge under He of remaining H₂ in the cell is here shown for a monometallic sample 1%wtPt/ γ -Al₂O₃-1.4%wtCl. As it can be seen in **Figure 1**, there are two main effects of the purge on the XANES profile: 1) gradual disappearance of the post-edge feature at 11570eV that is present when H₂ is adsorbed on the Pt NPs [2]; 2) an abrupt (XANES scans 10 minutes apart) increase in white line intensity and change of post-edge features towards an "oxide like" profile (the cell was thoroughly checked for leaks

multiple times). We thus tried to launch the full XANES and EXAFS acquisition when the post-edge feature at 11570eV was minimal and before the abrupt change in white line.

Data processing is still ongoing and the fitting of the EXAFS data will be essential to clarify the results. For the bimetallic catalysts in oxide state, **Figure 2** shows a clear impact of the Cl loading on the white line. The sample with the lowest Cl loading presents higher edge energy and intensity, both indicative that platinum is in a more oxide state. This agrees with previous results for monometallic catalysts (report n°16-01-789), but the differences between spectra are much clearer for the bimetallic samples. It may be suggested that, for oxide bi-metallic catalysts, the Cl loading has an impact on the support-NP interaction.

Concerning the re-reduced PtSn samples, **Figure 3** shows that the XANES spectra are identical for both Cl loadings. Thus, after reduction, there is no longer an observable impact of Cl on the XANES spectra, as already observed for the monometallic samples. When compared to its monometallic counterpart, the bimetallic sample presents an edge energy shift of +1.1eV and a clear difference in post-edge features (this is much clearer than in previous reports thanks to HERFD-XANES acquisition). These features being attributed to multiple scattering of the emitted photoelectron, one can suppose the environment surrounding the Pt atoms has changed, possibly through the partial formation of Pt-Sn alloys. Those could also explain the change in Pt electronic structure evidenced by the shift in edge energy.

The EXAFS Fourier Transform of the reduced bimetallic samples also suggest a distinct environment surrounding Pt. Interpretation of this data will be heavily dependent on its fitting.

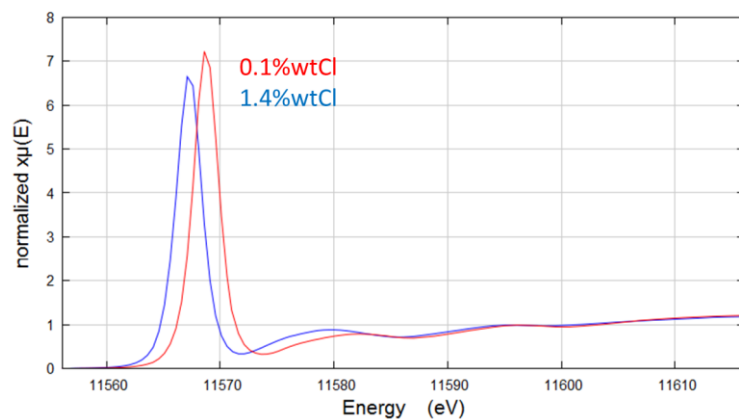
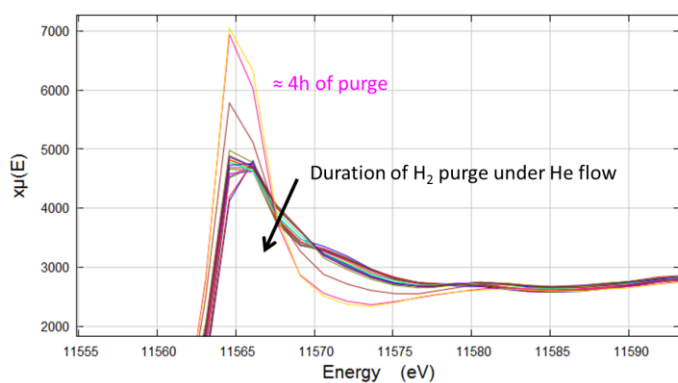


Figure 1 – HERDF-XANES Pt L₃ spectra of 1%Pt/γ-Al₂O₃-A-1.4%Cl during purge under He following *in situ* re-reduction. **Figure 2** - HERDF-XANES Pt L₃ spectra of oxide 0.3%Pt 0.3%Sn/γ-Al₂O₃ -1.4%Cl (blue) and -0.1%Cl (red).

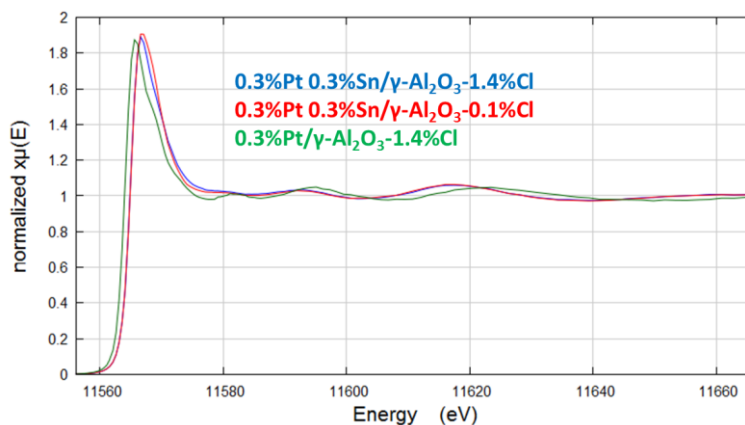


Figure 3 - HERDF-XANES Pt L₃ spectra of 0.3%Pt 0.3%Sn/γ-Al₂O₃ -1.4%Cl (blue) and -0.1%Cl (red) and of 0.3%Pt/γ-Al₂O₃-1.4%Cl (green) acquired under He at room temperature after *in situ* re-reduction.

[1] A. Aguilar-Tapia, *et al.* The Review of scientific instruments **2018**, 89, 035109

[2] A. Gorczyca, *et al.* Angew. Chem. Int. Ed. **2014**, 53, 12426-12429