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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: Characterization of platinum chlorine proximity on supported reforming catalysts by XAS spectroscopy: high-resolution experiments supported by ab initio calculations	**Experiment number**: 16-01-789
Beamline: BM16	**Date of experiment**: from:22/11/2017 to:28/11/2017	**Date of report**: 02/02/2018 *Received at ESRF:*
Shifts: 18	**Local contact(s)**:Antonio AGUILAR; Isabelle KIEFFER	

Names and affiliations of applicants (* indicates experimentalists):

Dr. Christele LEGENS* - IFP Energies nouvelles
Dr. Celine CHIZALLET - IFP Energies nouvelles
Dr. Jean-Louis HAZEMANN - Inst. Néel
Dr. Yves JOLY - Inst. Néel
Dr. Pascal RAYBAUD - IFP Energies nouvelles
Dr. Anne-Sophie GAY* - IFP Energies nouvelles
Dr. Fabrice DIEHL – IFP Energies nouvelles
Ana Teresa FIALHO BATISTA* - IFP Energies nouvelles
Laurent LEMAITRE* - IFP Energies nouvelles

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. The objective of the experiment was to clarify the proximity of the metallic and acid sites, by searching for changes in the electronic state of Pt and its local structure when Cl is present on the surface, using High Energy Resolved Fluorescence Detection XANES and EXAFS.

Our samples consist of $Pt/\gamma\text{-}Al_2O_3\text{-}Cl$ catalysts with varying Pt and Cl loadings, prepared using two γ-alumina supports (A and B) with differing sizes and morphologies (A: 12.5x6x5 nm, round ;B: 14.5x9x4, rectangular), obtained from a different boehmite nature. During our first experiments (experimental report n° 30-02-1120) re-oxidation of *ex situ* reduced samples was found to occur during acquisition. Thus, in this present work, the catalysts were re-reduced *in situ* using an operando cell developed at the Institut Néel under pure H_2 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 L_3 edge was performed under He after cooling to RT and purge of H_2, with the exception of one sample for which data was also collected at RT under H_2. In total, 8 $Pt/\gamma\text{-}Al_2O_3\text{-}Cl$ catalysts were studied after *in situ* reduction. *Ex situ* analysis was performed for 4 more catalysts in oxide state and for 3 platinum references. Depending on the platinum content of the catalysts, data acquisition took 4-6h or 8-10h.

Data processing is still ongoing and the fitting of the EXAFS data will be essential to clarify the results.

The use of an operando reactor allowed for some extra observations. First, the XANES scans recorded during the re-reduction thermal treatment show, with increasing temperature: 1) an evolution of the white line (WL) towards lower energies, compatible with Pt reduction, 2) the post-edge feature at 11572 eV becomes clearer (**Figure 1**). Second, the influence of adsorbed H_2 on Pt was accessed for the one sample for which data was acquired both under H_2 and under He: $1\%Pt/\gamma\text{-}Al_2O_3$.B-1.3%Cl. In the absence of adsorbed H_2, 1) the WL is slightly shifted to lower energies and 2) the post-edge feature at 11572 eV disappears (**Figure 2**). This is in agreement with previous findings by our group on the influence of H_2 on $0.3\%Pt/\gamma\text{-}Al_2O_3$ catalysts (ref. 1), and it suggests that the presence of Cl has little observable impact on the general trend of the electronic state changes caused by H_2 adsorption already observed for non-Cl containing catalysts.

Now focusing on the impact of Pt and Cl contents on the metal's electronic state, the XANES spectra of oxide catalysts supported on γ-Al_2O_3.B are compared to those on γ-Al_2O_3.A, featured in our first experiment report (n° 30-02-1120). Visually, the XANES spectra of Pt/γ-Al_2O_3.B-Cl oxide samples show two main "states" that pair the samples with the same Cl content (**Figure 3, right**). The energy position of the WL is nearly the same. The two "states" are distinguishable mainly by a difference in WL intensity: samples with the highest chlorine content present lower WL intensity than samples with the least chlorine content. Lower WL intensity may be associated with an increased occupancy of the d band, which can indicate a transfer of electrons towards the metal, in agreement with previous calculations (ref. 2). On the other hand, the XANES spectra of Pt/γ-Al_2O_3.A oxide samples showed also two "states" that pair the samples with the same Pt content (**Figure 3, left**). For each pair, the sample with the highest chlorine content also exhibits a lower WL intensity than sample with the least chlorine. While difficult to interpret, the difference between the results for the two alumina supports hints at an influence of the support on the impact of the Cl on the metallic phase. Since the main difference between the two aluminas is their crystallite morphology, this support effect may be associated with different anchoring sites for Pt and/or Cl present on each alumina.

For the samples re-reduced *in situ* with data acquired under He, the XANES spectra are all similar. The EXAFS Fourier Transform shows three main signals in the ranges 1.5-2 Å, 2-2.5 Å and 2.5-3 Å. Interpretation of this data will be heavily dependent on its fitting.

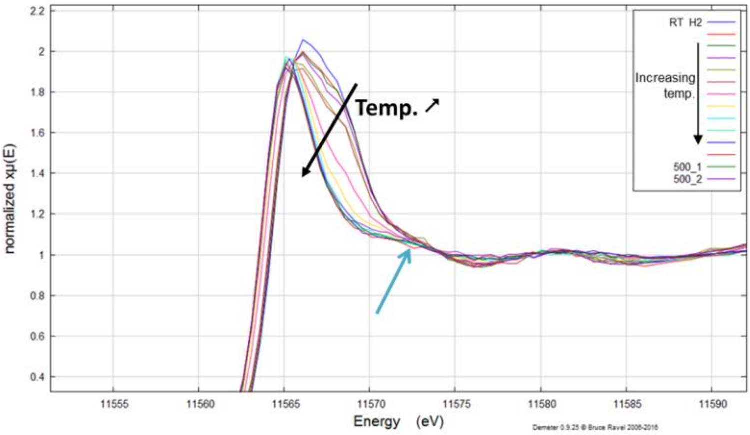

Figure 1- HERDF XANES Pt L_3 spectra of 0.3%Pt/ γ-Al_2O_3.A-1.4%Cl during *in situ* re-reduction thermal treatment under H_2 (5°C/min; 10 min per scan), blue arrow shows post-edge frature at 11572eV

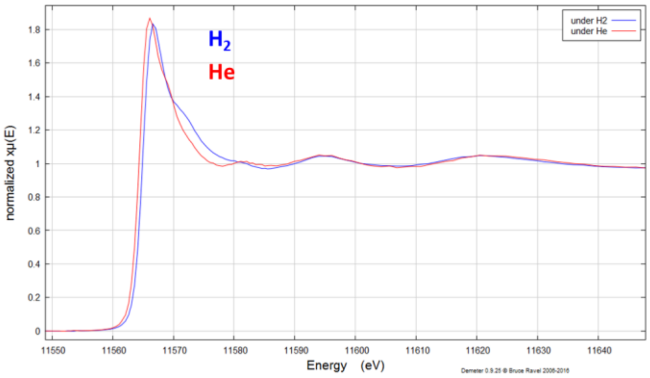

Figure 2- HERDF XANES Pt L_3 spectra of 1%Pt/ γ-Al_2O_3.B-1.3%Cl acquired under H_2 and under He at room temperature after in-situ re-reduction

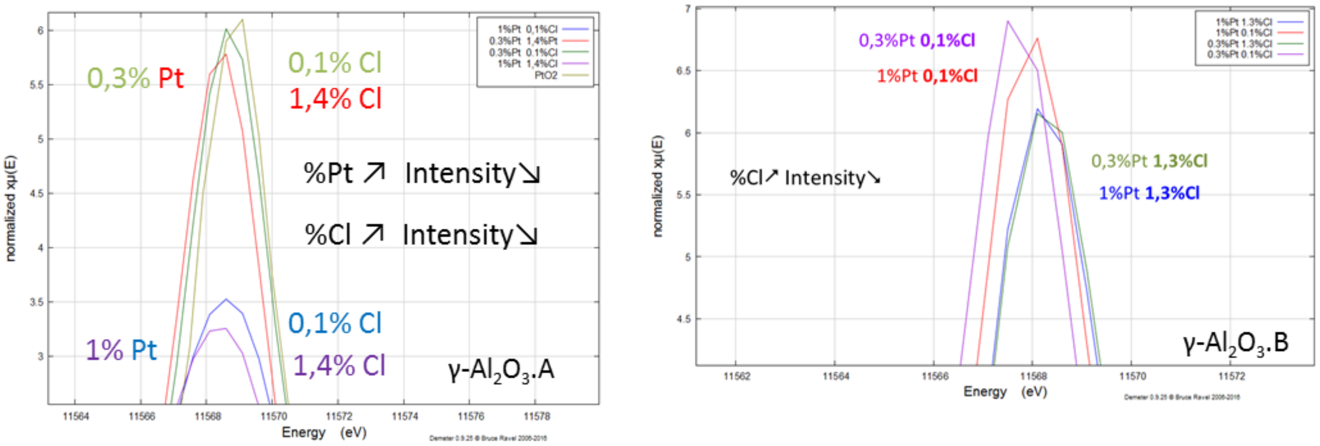

Figure 3- Zoom on white line intensity differences in HERDF XANES Pt L_3 spectra of four oxide catalysts supported on alumina A (left) and alumina B (right)

References:

1- A. Gorczyca, *et al*, Angew. Chem. Int. Ed. **2014**, 53, 12426-12429
2- C. Mager-Maury, *et al*, ACS Catalysis **2012**, 2, 1346-1357