



	Experiment title: Characterization of platinum chlorine proximity on supported reforming catalysts by XAS spectroscopy: high-resolution experiments supported by ab initio calculations	Experiment number: 30-02-1120
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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 used, 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 in the catalyst, using High Energy Resolved Fluorescence Detection XANES.

In this experiment sixteen Pt/ γ -Al₂O₃-Cl catalysts (in both reduced and oxide state) were analyzed (at variable Pt and Cl content), as well as four references. Each catalyst required a 8-10h, 6-8h or 4-6h accumulation time depending on the Pt content. Due to some observed effects, namely sample color change after beam exposure and edge peak shape evolution during analysis, three catalysts were re-analyzed.

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

The first observations for the four catalysts in oxide state and for the reduced catalysts with 1% wt Pt will be here presented, at variable Cl content. Starting with the catalysts in oxide state, we found that they have very similar XANES spectra, sharing the same edge peak energy and four post edge features (**Figure 1**). The intensity of the edge peak is, however, different. It is more intense for the samples with the lower Pt content (0,3% wt). hence, for the samples at 0,3% wt Pt the intensity of the edge peak is in the same range as the one for the reference compound PtO₂, which spectra was obtained in one of the previous experiments of A. Gorczyca. We consider in light of this result that the samples at 0,3% wt Pt are in a more oxidized state than the samples at 1% wt Pt. This could be explained by a smaller particle size on the 0,3% wt Pt sample in comparison with the 1% wt Pt catalyst(as our Temperature Programed Reduction results seem to indicate). Smaller Pt particles exhibit a stronger interaction with the support (as reported for reduced catalysts in ref. 1) that has a stabilizing effect on the particle (ref. 2), making it more liable to be in a more oxidized state than larger particles after the same thermal treatment. Also, for each Pt content, there is a slight increase in the edge peak intensity when the chlorine content decreases from 1,4% wt Cl to 0,1% wt Cl. The proposed explanation is that for an increased Cl content there is a larger interaction between Cl and Pt particles, therefore diminishing the metal-oxygen interaction and also contributing to a lower oxidation state due to the electron donning effect of chlorine (ref. 3).

Looking now at the EXAFS results of the reduced catalysts with 1% wt Pt content, we can identify three main peaks between 1.8 Å and 3 Å for samples at 1.2%; 1% and 0.5% wt Cl, while the sample at 0.1% Cl differs from the others with a main peak in the 1.5-1.8 Å interval (**Figure 2**). Comparison with references PtO₂, Pt foil and Pt precursor used during impregnation H₂PtCl₆ suggests: i) main peak of 0.1% Cl sample could be Pt-O distance by comparison with PtO₂, meaning that the catalyst reoxidized (conclusion supported by XANES spectra, not shown here); ii) peak in the 1.8-2.1 Å interval for 1.2%; 1% and 0.5% wt Cl could be a Pt-Cl distance by comparison with H₂PtCl₆, however this distance is not observed for reduced catalysts in the literature (ref. 4); iii) peaks in 2.1-3 Å interval for 1.2%; 1% and 0.5% wt Cl are not exactly in line with the Pt foil peak indicating Pt-Pt distance and are for the moment a question mark, but it could be suggested that this Pt-Pt distance is shortened for highly dispersed small particles on supported catalysts (ref. 2,5). These results are not of immediate interpretation and, as for the catalysts at 0.6% and 0.3% wt Pt, fitting the data (possibly considering DFT structural data such as reported in ref.4,5) will have an important role in clarifying them. We also found that for each catalyst group with the same Pt content, there is one sample, always at different Cl content, that seems to be reoxidized. This could be avoided by performing *in situ* re-reduction of the samples and performing the analysis under H₂ flow.

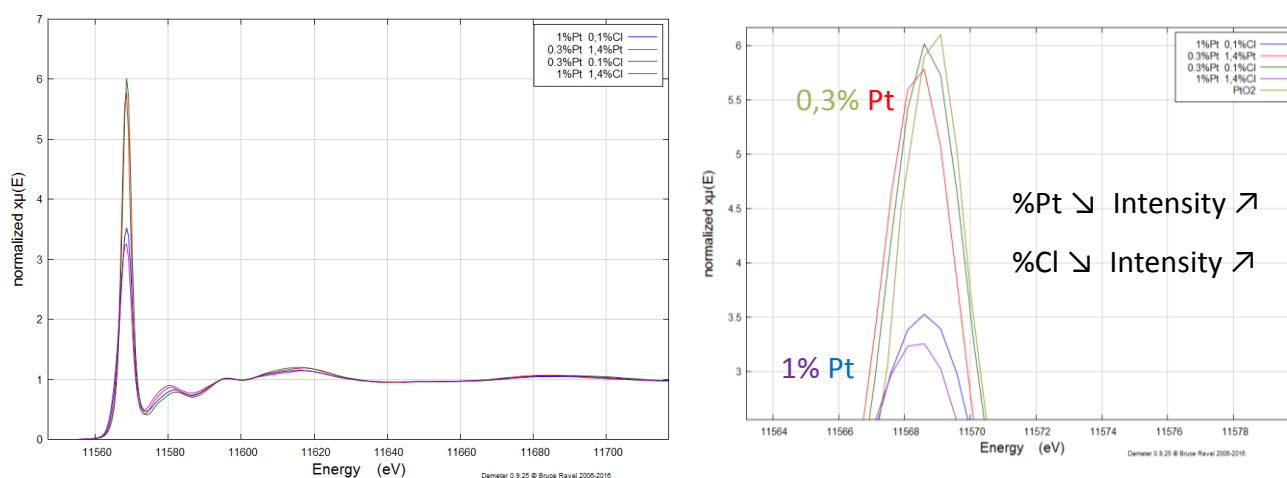


Figure 1- on the left: HERDF XANES Pt L₃ spectra of catalysts in oxide state at two Pt contents and two Cl contents; on the right: Detail of the edge peak of catalysts in oxide state and of PtO₂ reference.

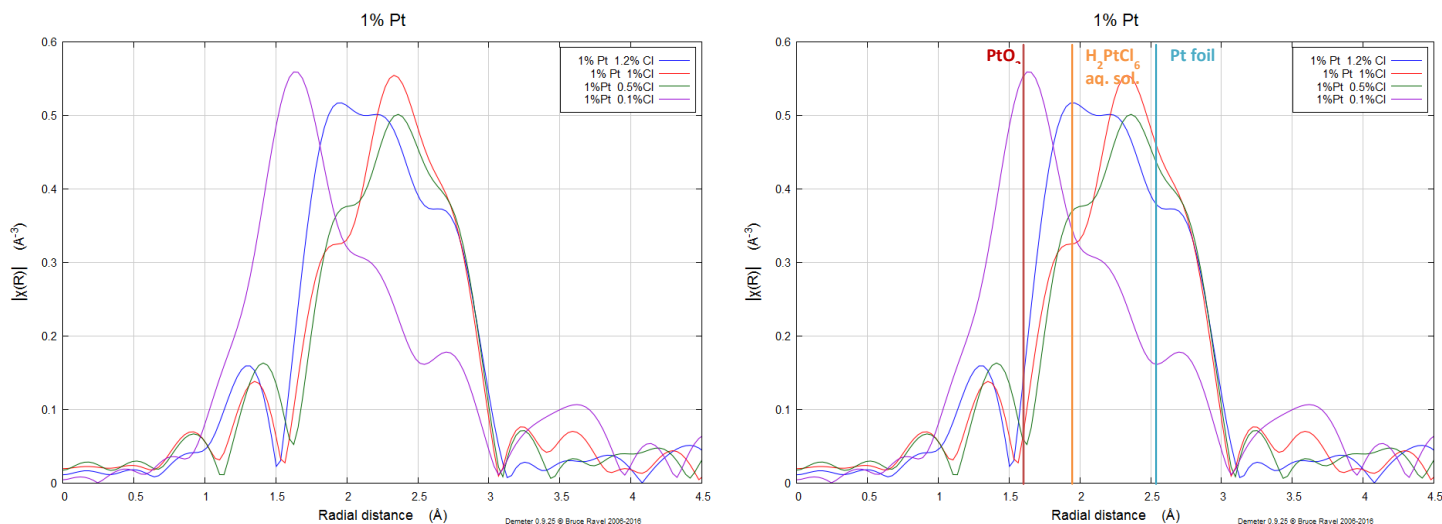


Figure 2- on the left: EXAFS spectra of reduced catalysts with 1% wt Pt content and varying Cl content; on the right: EXAFS spectra of reduced catalysts with 1% wt Pt content in comparison with maximum position of main peak of references PtO₂, Pt foil and Pt precursor H₂PtCl₆ in aqueous solution. (all k₃; without phase correction)

References:

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