

# An *in situ*, Real-time XAFS Characterization of Noble Metal Catalyst Impregnation

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## Introduction

The high sensitivity of the Advanced Photon Source (APS) at Argonne National Laboratory has permitted the molecular characterization of dilute solutions (200 ppm and above) of noble metal catalyst precursors, such as  $\text{H}_2\text{PtCl}_6$  (chloroplatinic acid or CPA),  $\text{NaAuCl}_4$ ,  $\text{Na}_2\text{PtCl}_4$  and  $(\text{NH}_3)_4\text{PtCl}_2$ , and  $\text{Na}_2\text{PdCl}_4$  and  $(\text{NH}_3)_4\text{PdCl}_2$ . The changes in coordination chemistry of these materials upon adsorption have been investigated. The results appear to be consistent with the Revised Physical Adsorption Model (RPA) [1,2], that is, with a totally electrostatic adsorption mechanism as opposed to one invoking “chemical” interactions or surface ligand exchange [3].

## Results and Discussion

In order to discriminate between the physical and chemical mechanisms of adsorption, we’ve characterized dissolved and adsorbed complexes both at equilibrium and just after contact with the support. A representative data set is shown in Fig. 1, an EXAFS analysis of dissolved and adsorbed complexes arising from tetrachloroaurate,  $[\text{AuCl}_4]^-$ . Here the Au-Cl coordination number is plotted versus pH (the coordination is always 4, and the balance of ligands are O-containing and are not shown). The Au(III) solutions show little dependence on Au or excess Cl<sup>-</sup>

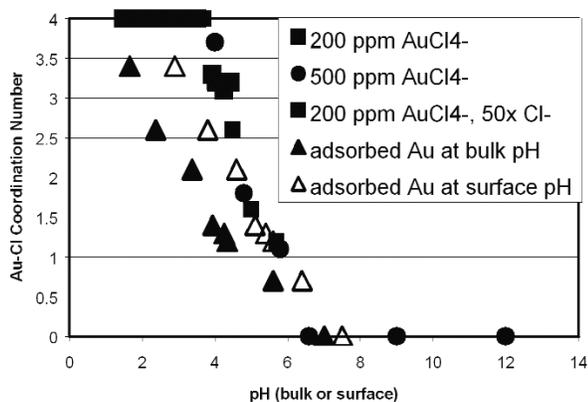


FIG. 1. Au-Cl coordination numbers of dissolved and adsorbed complexes stemming from  $[\text{AuCl}_4]^-$ .

concentration. The Au-Cl coordination numbers for the adsorbed samples, if plotted versus the equilibrium bulk pH at which the sample was prepared, fall below the species in solution. Thus, Au on the alumina support contains less Cl and more O than that in solution. If the Au-Cl coordination number is plotted versus the pH at the adsorbed layer [4], however, the chloride coordination numbers of the adsorbed complexes overlap with the coordination of the liquid phase species. This is to say that the adsorbing complexes speciate as if in the liquid solution—but at the local conditions of the adsorption plane. In other words, the pH at the oxide surface of alumina is significantly higher than in the bulk solution.

A chemical, ligand exchange mechanism has been proposed for CPA adsorption on carbon. X-ray photoelectron spectroscopy studies reveal the reduction of  $\text{PtCl}_4^{2-}$  to  $\text{Pt}^{+2}$  after drying at  $100^\circ\text{C}$  [5]. We used real-time, *in situ* XANES to try to determine if Pt reduction occurs upon adsorption or happens afterwards. A representative set of XANES spectra is shown in Fig. 2. The CPA was adsorbed onto carbon black at an initial pH below 3.0. The decrease in the white line intensity (from back to front) indicates an

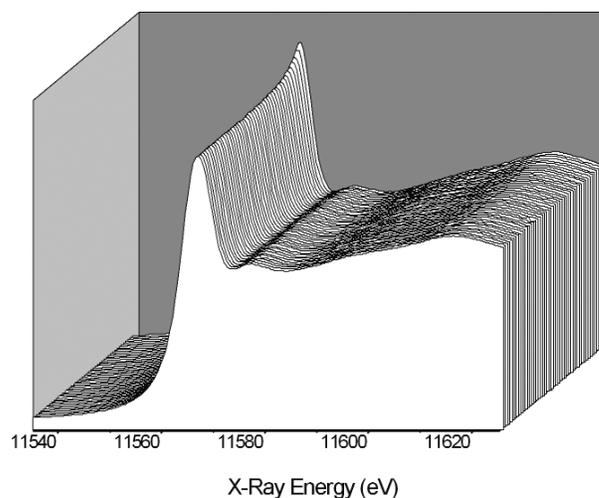


FIG. 2. XANES spectra illustrating the reduction of  $\text{Pt}^{+4}$  to  $\text{Pt}^{+2}$  during contact with an activated carbon surface, over a 50-minute period (back to front).

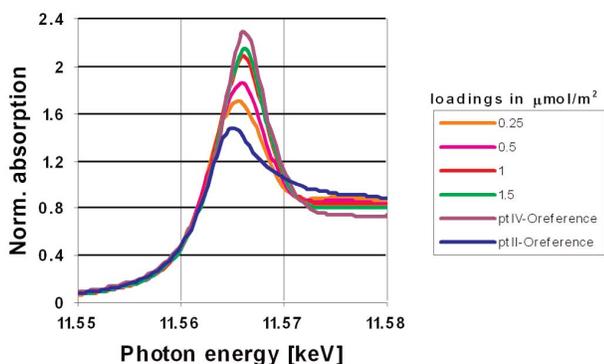


FIG. 3. XANES Pt white line survey of CPA adsorbed onto Vulcan XC-72 (carbon black) at pH 3.0 as a function of surface loading.

almost complete reduction of  $\text{Pt}^{+4}$  to  $\text{Pt}^{+2}$  over a time span of fifty minutes. Chloride appears to be the predominant ligand at all times.

A comprehensive survey of the slow reduction of CPA has been conducted in which the carbon type, pH and Pt adsorption densities were varied. A typical set of results is shown in Fig. 3. Standard spectra for both Pt(IV) and Pt(II) are seen as the uppermost and lowermost spectra respectively. Over Vulcan XC-72, at pH near 3, the degree of reduction of Pt is inversely proportional to the surface loading. From this observation, we speculate that the mechanism for reduction involves an adsorbed complex and open carbon area; at full Pt coverage, the absence of exposed carbon precludes reaction.

A comparison of the reduction kinetics obtained from XANES data (shown in Fig. 4) at the same pH and surface loading reveals that the high-surface-area/small-pore-size activated carbons reduce more slowly than do the lower surface area/larger pore size carbon black and graphite. We interpret this difference to stem from mass transfer limitations.

The rate of CPA adsorption onto carbon was much more rapid than that for reduction. For example, about 95% of the saturation equilibrium adsorption is complete in less than 5 minutes. Since the time scales

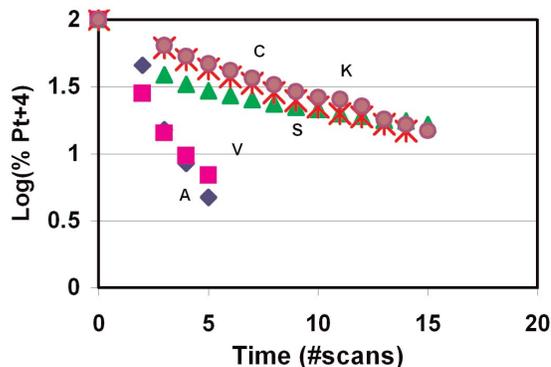


FIG. 4. Decreasing amounts of Pt(IV) versus time for three activated carbons (S, C, and K), one graphitic carbon (A) and a carbon black (V) at an initial pH of 3.0 and a loading of  $0.5 \mu\text{mol}/\text{m}^2$ .

for adsorption and reduction are very different, we conclude that adsorption and reduction are independent phenomenon and can be modeled as such.

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### References

- [1] W.A. Spieker and J.R. Regalbuto, *Chemical Engineering Science* **56**, 3491 (2001).
- [2] W.A. Spieker, J. Liu, X. Hao, J.T. Miller, A.J. Kropf, and J.R. Regalbuto, *Applied Catalysis A: General*, in press.
- [3] B. Shelimov, J.-F. Lambert, M. Che, and B. Didillon, *Journal of Molecular Catalysis A: Chemical*, **158**, 91-99 (2000).
- [4] J. Liu, J.G. Kim, J.T. Miller, A.J. Kropf, and J.R. Regalbuto, manuscript submitted.
- [5] M.A. Fraga et al., *Journal of Catalysis* **209**, 355 (2002).