

EXAFS Study of Noble Metal Coordination Complexes in Aqueous Solution and Adsorbed onto Alumina

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Introduction

The high sensitivity of Argonne's APS has permitted the study of dilute solutions (200 parts per million [ppm] and above) of noble metal catalyst precursors such as H_2PtCl_6 , NaAuCl_4 , Na_2PtCl_4 , $(\text{NH}_3)_4\text{PtCl}_2$, Na_2PdCl_4 , and $(\text{NH}_3)_4\text{PdCl}_2$. The changes in coordination chemistry of these materials upon adsorption have been investigated. Results appear to be consistent with the Revised Physical Adsorption (RPA) model [1, 2], that is, with a totally electrostatic adsorption mechanism as opposed to one invoking "chemical" interactions or surface ligand exchange.

Methods and Materials

Solid chloroplatinic acid (CPA) was dissolved to make aqueous solutions of various concentrations. These were acidified with HCl or HNO_3 and basified with NaOH . Some solutions were contacted with 200 m^2/gm gamma-alumina (LaRouche). Extended x-ray absorption fine structure (EXAFS) measurements were performed at the APS Materials Research Collaborative Access Team (MR-CAT) undulator beamline equipped with a double-crystal $\text{Si}(111)$ monochromator with a resolution of more than 4 eV at 11.5 keV (Pt L_3 edge). Spectra of the metal solutions contained in plastic cuvettes were taken in fluorescence mode, and spectra of solids as pressed powders were taken in transmission mode. Phase-shift and backscattering amplitudes were obtained from various solid reference compounds. Details of the experimental and fitting procedures can be found in Reference 3.

Results and Discussion

Liquid-phase speciation of the Pt(II) coordination complexes was found to be mostly consistent with published formation constants [4]. In dilute CPA solutions, however, the degree of hydrolysis was much greater than reported. For instance, the species immediately formed by dissolving 200 ppm of CPA in water, which results in a pH of 2.70, is $[\text{PtCl}_3(\text{H}_2\text{O})_3]^{+1}$, which, upon 24 h of aging, becomes $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$ at pH 2.40 [3]. Fourier transforms of EXAFS spectra of 200-ppm Pt solutions at various pH values are shown in Fig. 1. The spectrum of CPA in HCl at a pH of 1.5 is characteristic of $[\text{PtCl}_6]^{-2}$, while at a pH of 12 in NaOH , the average Pt coordination is 1.8 Pt-Cl and 4.2 Pt-O

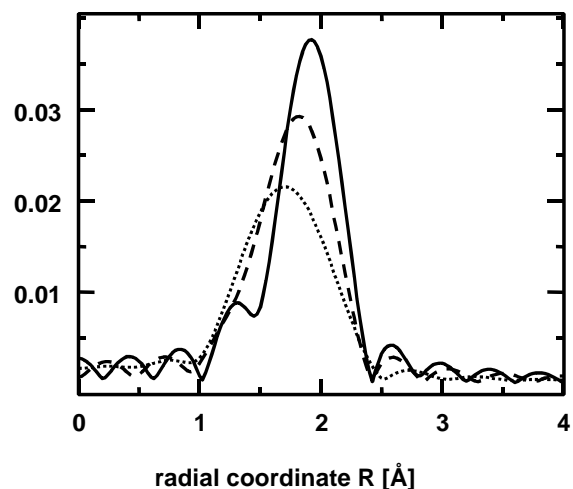


FIG. 1. Magnitude of the Fourier transform for Pt coordination sphere. Solid line indicates CPA at pH = 1.5 HCl (k^2 : $\text{Dk} = 3.0\text{-}10.7$, $\text{Dr} = 1.0\text{-}2.7$; fit: 6.0 Pt-Cl). Dashed line indicates CPA at pH = 2.7 (k^2 : $\text{Dk} = 3.0\text{-}10.0$, $\text{Dr} = 1.0\text{-}2.4$, fit: 2.8 Pt-Cl and 3.2 Pt-O). Dotted line indicates CPA at pH = 12.5 (k^2 : $\text{Dk} = 3.0\text{-}8.6$, $\text{Dr} = 1.0\text{-}2.4$, fit: 1.8 Pt-Cl and 4.2 Pt-O).

bonds. The spectrum for fresh CPA at its natural pH (about 2.7) indicates the chlorine coordination between the two.

Surprising results were obtained when the adsorption of the chloroaquohydroxo complexes was compared to hexachloroplatinate $[\text{PtCl}_6]^{-2}$, which, at the same dilution, can be obtained with excess chloride [3]. Data on these samples are shown in Table 1. The surface loading (amount of oxide) was varied for three target Pt loadings of 1.0, 4.8, and 7.2 wt%. One sample of each pair was prepared without NaCl , and the other one was prepared with it. Table 1 summarizes the important experimental parameters of these samples and the measured chlorine coordination numbers (the balance of the sixfold coordination is oxygen and is not listed on the table).

Upon adsorption, both types of complexes lose chloride (much more is lost by the hexachloroplatinate complexes), and, in fact, they converge to an identical, low chlorine content of about 2.0 ligands. The loss of Cl

Table 1. Chlorine coordination number as a function of added NaCl and surface loading.

Sample	Target wt% Pt	Surface loading (m ² /L)	NaCl (mol/L)	Initial pH	CN Cl liquid	Final pH	CN Cl solid	Actual wt% Pt
A 1	1	5000	---	2.63	2.7	4.34	1.6	1.0
A 2	1	5000	0.1	2.60	6	5.59	1.5	0.7
A 3	4.8	1000	---	2.59	2.7	2.84	2.1	3.7
A 4	4.8	1000	0.1	2.54	6	3.43	1.9	1.9
A 5	7.2	650	---	2.50	2.7	2.81	2.1	4.1
A 6	7.2	650	0.01	2.55	(6) ^a	2.87	2.2	3.2

^aEstimated from Reference 3, not measured.

and gain of O during adsorption have been taken as an indication of adsorption via surface ligand exchange [5]. However, if the chloride coordinations of the adsorbed complexes are plotted vs. the pH at the adsorbed layer (determined from electric double-layer theory), they are seen to overlap with the coordination of the liquid-phase species. The adsorbing complexes appear to respond to the local environment of the surface, where the Cl⁻ concentration is lower and the pH is higher than the bulk, as they adsorb via an electrostatic mechanism. A much more detailed set of experiments and their interpretation is reported in Reference 6.

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