



# An EXAFS study of the coordination chemistry of hydrogen hexachloroplatinate (IV)

## 2. Speciation of complexes adsorbed onto alumina

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### Abstract

The changes in coordination chemistry that occur as chloroaquohydroxo platinate complexes adsorb over alumina have been studied using extended X-ray absorption fine structure (EXAFS) analysis at the advanced photon source (APS) at Argonne National Laboratory. Our earlier study of Pt complexes in the liquid phase [Appl. Catal. A: Gen. 232 (2002) 219] is used as a starting point. Samples were prepared both in excess solution with 200 ppm chloroplatinic acid (CPA), and using pore volume impregnation with higher CPA concentrations to give loadings of 0.25 to 4.25 wt.% Pt. The changes in coordination chemistry of chloroaquohydroxo platinate complexes adsorbing over alumina need not invoke a “triple layer” theory, which incorporates surface grafting reactions, but are more readily explained by refinements to the “double layer” theory which is the kernel of the Revised Physical Adsorption model [Chem. Eng. Sci. 56 (2000) 2365]. The changes in speciation of adsorbing CPA complexes appear to be influenced first by the change in the bulk pH brought on by the oxide buffering effect, second by the additional pH change at the (single) layer of adsorption at the alumina surface, and third by the chloride concentration at this local level. At low surface loadings, pH shifts are minimized and the amount of chloride near the adsorption plane appears to be low. Platinum complexes adsorb with low Pt–Cl/Pt–O bond ratios, even when present in the bulk solution as hexachlorides. The adsorbed species appear to behave as in the liquid phase at the pH of the adsorption plane with no excess chloride. At high surface loadings such as with pore volume impregnation, the pH shifts toward the alumina PZC are very large but all chloride is kept in the pore volume. At high Pt loadings, high chloride concentration appears to dominate the Pt speciation and Pt–Cl coordination in the adsorbed complexes remains high, as occurs in the liquid phase in excess chloride. The adsorption of Pt from solutions in which zero-valent species are thought to initially exist can be explained by mechanisms in which either rapid OH–H<sub>2</sub>O exchange occurs at the higher pH of the adsorption plane, creating a dianionic adsorbing complex, or a surface protonation reaction, which creates a dianionic adsorbed complex in concert with surface charging. Both mechanisms are consistent with an electrostatic adsorption mechanism.

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### 1. Introduction

Platinum/aluminum catalysts are vitally important for many chemical processes, including, for example,

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naphtha reforming in the petroleum industry and exhaust gas abatement in the automotive industry. For naphtha reforming, the use of chloroplatinic acid as the precursor leads to the natural incorporation of chloride into the alumina, often at just the desired ratio of Pt to Cl [3]. The presence of chlorine is also essential in the regeneration of reforming catalysts, where through the intermediate formation of oxychlorides of platinum, a reacidification of the alumina and a redispersion of the platinum can be achieved [4–6].

Recent efforts have been directed to more thoroughly understand the genesis of these catalysts. In particular, more attention is being paid to the process of catalyst impregnation, whereby a liquid solution, typically aqueous, containing dissolved Pt chloride complexes is contacted with the high surface area oxide support. There are two basic mechanisms in the literature to account for Pt adsorption onto alumina. The first mechanism is purely physical; the early studies of noble metal adsorption onto alumina suggested that the interaction is essentially electrostatic ([7,8] and references within). Our own experimental [9–11] and theoretical [2] results suggest that the interaction is purely coulombic, occurring between the anionic complexes of Pt in solution and an alumina surface that is protonated and positively charged at low pH. The uptake of Pt versus pH over a wide range of aluminas (gamma, eta, theta, alpha, and low and high surface area) [11], and essentially all chloroplatinic acid (CPA)/alumina adsorption data found in the literature [2] can be simulated to a reasonable degree with the Revised Physical Adsorption (RPA) model [2,12]. This model employs a Langmuir isotherm and an a priori calculation of the adsorption equilibrium constant that is based solely on the coulombic energy of attraction, which varies as a function of pH. A typical simulation of the RPA model, in which Pt uptake is plotted versus pH, is shown in Fig. 1. At a pH of 8.5, the point of zero charge (PZC) of alumina, the surface is uncharged and no adsorption occurs. Below this pH Pt uptake increases as the surface becomes protonated and so positively charged. At the lowest pH values, however, high ionic strength diminishes the adsorption equilibrium constants and adsorption is severely retarded [9,11]. The maximum extent of adsorption, about 1.6 mmol/m<sup>2</sup>, or 1 Pt complex/nm<sup>2</sup>, corresponds to a close-packed mono-

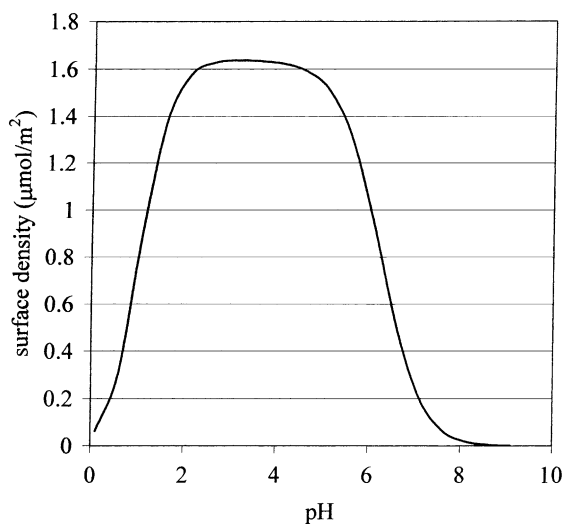


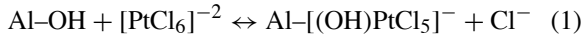
Fig. 1. A typical RPA simulation [2] of Pt uptake (from CPA) over alumina (g-alumina, PZC = 8.5, 500 m<sup>2</sup>/l, 200 ppm Pt).

layer of Pt complexes that retain one hydration sheath [10].

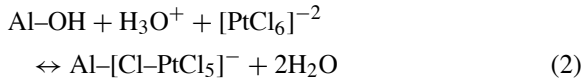
This model is simplistic, however, in that only one species, the doubly valent  $[\text{PtCl}_6]^{-2}$  complex is presumed. It is assumed that all other species that might form will have the same radius and charge as  $[\text{PtCl}_6]^{-2}$ . This assumption is called into question first of all by older sets of formation constants for the aqueous CPA [13]. Singly and zero-valent aquo and aquohydroxo species such as  $[\text{PtCl}_5(\text{H}_2\text{O})]^{-1}$ ,  $[\text{PtCl}_4(\text{OH})(\text{H}_2\text{O})]^{-1}$  and  $[\text{PtCl}_4(\text{H}_2\text{O})_2]^0$  can form at significant concentrations at certain pH values. Second are the results of the first paper in this series [1], a companion study of the coordination chemistry of Pt complexes dissolved in aqueous solutions. Those results reveal, in dilute solutions, the presence of highly exchanged, zero-valent chloroaquohydroxo species such as  $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$  at moderately low pH (2.4–2.6). The present work is aimed at a refinement of the RPA model in light of the existence of these species, and a comparison of this interpretation with other models in the literature.

A contrasting adsorption mechanism is “chemical” in nature, involving a more extensive interaction of the metal complex with the oxide surface in the form of surface ligand exchange or surface grafting. Exchange mechanisms have been proposed in which the

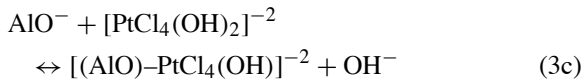
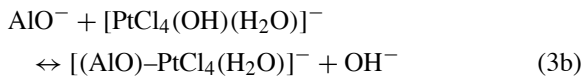
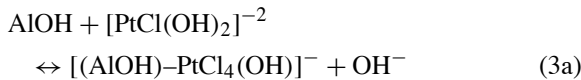
exchanged ligand is that of the  $\text{Cl}^-$  attached to the Pt complex [3,14],



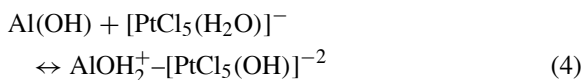
or in which the Pt complex replaces an OH group originally attached to the  $\text{Al}_2\text{O}_3$  surface:



The latter step involves the consumption of protons. Similar steps were presumed by Mang and coworkers to explain upward shifts in pH that occurred during adsorption [15]. They proposed a set of ligand exchange reactions involving the exchange of OH present in chlorohydroxo and chloroaquohydroxo complexes of Pt with a neutral or negatively charged surface:



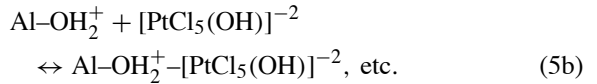
In more recent work, the group of Lambert supports these sorts of mechanistic steps at some conditions in addition to electrostatic adsorption, based on the decrease in the overall intensity of the  $^{195}\text{Pt}$  NMR signal during the aging of samples impregnated at moderately low pH [16–18]. They suggest another mechanism subtly different from electrostatic adsorption [18]; neutral alumina hydroxyl groups become charged by deprotonation of aquo ligands in chloroaquohydroxo complexes of Pt in the course of adsorption,



This is akin to electrostatic adsorption, in which case adsorption occurs over a previously charged hydroxyl group:



or



In the first paper of this series [1] the coordination chemistry of chloroplatinic acid in aqueous solutions was explored and a comprehensive pathway for it was proposed. The objective of this second work is to characterize, on the molecular scale, the changes in coordination that occur when Pt complexes are adsorbed onto alumina. This work will have both the fundamental consequence of lending further insight into the mechanism of adsorption, and the practical consequence of enabling precise control of the composition of adsorbed complexes.

## 2. Experimental

### 2.1. Preparation of solid samples

To explore the adsorption behavior of different complexes of  $[\text{PtCl}_x(\text{OH})_y(\text{H}_2\text{O})_z]^{4-x-y}$ , three series of equilibrium adsorption experiments and one kinetic study were conducted. LaRouche gamma alumina in powder form of surface areas 200 and 250  $\text{m}^2/\text{gm}$  was employed. Anhydrous chloroplatinic acid was purchased from Aldrich. Most of the adsorption experiments were carried out in an excess of liquid to enable the measurement of solution pH and to prevent large shifts in it from the “oxide buffering” effect [19]. The parameter of “surface loading” is convenient to indicate the amount of oxide surface in solution. For example, 0.1 gm of 250  $\text{m}^2/\text{gm}$  alumina in 50 ml of solution yields 500  $\text{m}^2/\text{l}$ , or about a 1000-fold excess of the pore filling volume. The 50 ml polypropylene bottles containing solution and oxide were normally shaken for 1 h, after which 3–4 ml was withdrawn and filtered for ICP analysis. Platinum uptake was determined as the difference in Pt concentrations in the precontacted and post-contacted solutions. The entirety of some solids was recovered by vacuum filtration and was air-dried overnight and calcined at various temperatures. One series of samples was prepared by incipient wetness (pore volume impregnation) with 0.8 ml solution/gm  $\text{Al}_2\text{O}_3$  using CPA at concentrations to yield 0.25–4.25 wt.% Pt.

## 2.2. EXAFS analysis

EXAFS measurements were performed at the advanced photon source (APS) at Argonne National Laboratory (Argonne, IL) on the undulator beamline of the Materials Research Collaborative Access Team (MRCAT). Details of the EXAFS data collection and analysis are given in the previous paper [1], the only difference here being that the data were collected in transmission as opposed to fluorescence mode. Most of the powdered solid samples were pressed into thin disks; some wet “just impregnated” samples were analyzed in plastic cuvettes. The fitting of the data was done with the software WinXAS 97, Version 1.0. Solid  $\text{H}_2\text{PtCl}_6$  and solid  $\text{Na}_2\text{Pt}(\text{OH})_6$  were used as standards for the Pt–Cl and Pt–O bond, respectively. The results were generally accurate to  $\pm 0.3$  in coordination number and were normalized to a total coordination number of 6. Unfortunately, EXAFS cannot distinguish between OH and  $\text{H}_2\text{O}$  ligands; for this reason we will occasionally report the Cl and O coordination in the chemically incorrect but succinct form such as “PtCl<sub>3</sub>O<sub>3</sub>” where the O can be in the form of either OH or  $\text{H}_2\text{O}$ .

## 3. Results

In the previous study it was observed that the speciation of 200 ppm CPA solutions required about 24 h

to equilibrate [1], evolving from a composition of about  $[\text{PtCl}_3(\text{H}_2\text{O})_3]^{+1}$  at pH 2.7 in the fresh solution to  $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$  at a pH of 2.4 in the aged solution. (The reconciliation of these species with the electrostatics-based RPA adsorption model will be made in the discussion.) The first set of data presented is then a comparison of the adsorption rates of fresh and aged solutions, each with 200 ppm CPA and over  $500 \text{ m}^2/\text{l}$  of oxide. This concentration of Pt is about 20% in excess of the monolayer capacity of the alumina, which is about  $1.6 \text{ mmol}/\text{m}^2$  [10]. Results are shown in Fig. 2.

The initial pHs of the fresh and aged solutions prior to contact with the alumina were about 2.7 and 2.4, respectively, and increased about 0.3–0.4 pH unit in the first 30 min of contact due to the oxide buffering effect [19]. The final pH converges to about 4 for both samples. While the aged solutions adsorb in their entirety after about 1 h to the maximum capacity, the fresh solutions attain an initial plateau of only 75% of this value. In the course of the next 24 h, the uptake increases slowly to the value of the aged solutions.

In the study of equilibrium adsorption versus pH, a first set of samples was prepared to directly compare the adsorption of the chloroaquohydroxo complexes present in dilute solutions with  $[\text{PtCl}_6]^{-2}$ , which at the same dilution can be obtained with excess chloride [1]. These samples, designated “Series A”, were prepared with 200 ppm Pt solutions and are shown in Table 1. Surface loading was varied for three target Pt

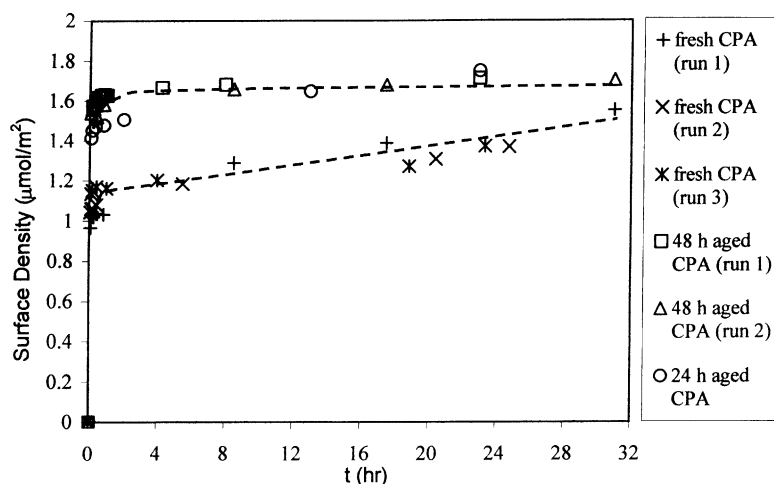


Fig. 2. Uptake of Pt versus time from 200 ppm fresh and aged CPA solution onto g-alumina at  $500 \text{ m}^2/\text{l}$ .

Table 1  
EXAFS Pt–Cl coordination number ( $\pm 0.3$ ) as a function of added NaCl and surface loading (series A)

Sample	Target wt.% Pt	Surface loading ( $\text{m}^2/\text{l}$ )	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) <sup>a</sup>	2.87	2.2	3.2

<sup>a</sup> Estimated from [1], not measured.

loadings of 1.0, 4.8 and 7.2 wt.%. The solutions were not initially pH adjusted but left at their natural pH of 2.50–2.63. The minor variation in pH is due to the aging of the common stock solution as the oxides were successively contacted with the solution. One sample in each pair was prepared without NaCl, the other with it. EXAFS was used to measure the composition of the Pt complexes of both the chloride free and chloride containing samples in the initial solutions before addition of alumina, and the solid samples. For the solid samples, the suspensions were filtered after the 1 h adsorption time and the still-wet filter cake was immediately analyzed by EXAFS. The EXAFS spectra were virtually unchanged after the samples were dried at room temperature and analyzed as pressed, dried wafers. Table 1 summarizes the important experimental parameters of these samples and the measured chlorine coordination numbers. The balance of the six-fold coordination is oxygen and is not listed in the table.

As seen previously [1], fully chlorinated hexachloro complexes (samples A2, A4, A6) are formed in the liquid phase in excess NaCl, while the CPA solutions without excess Cl (samples A1, A3 and A5) have on average only 2.7 chlorine ligands. Upon adsorption, however, both types of complexes converge to an identical chlorine content of about 2.0 Pt–Cl ligands. There is no definitive correlation between the complex composition in solution and the adsorbed Pt complex or the final Pt loading, although the samples with lower target Pt loading (A1 and A2), which equilibrate to the highest pH values, are perhaps slightly lower in chlorine than the other samples. The lower Pt loading obtained in the presence of excess NaCl (samples A2, A4, and A6) relative to the NaCl free samples is expected, due to the increased ionic strength of the NaCl

solutions [2,9–12]. The incomplete uptake of the NaCl free samples for the two higher loadings is due to the fact, as in Fig. 2, that the CPA solutions were not completely aged (which would have resulted in a pH of 2.4 and chloride coordinations closer to 2 [1]). Trends in the final pH of the oxide-contacted solutions are also expected. First, higher oxide loadings consume more protons and bring the solution pH closer to the PZC of alumina [19]. Second, the NaCl containing solutions arrive at a higher pH than the respective NaCl-free solutions. This is consistent with the surface charging model at high ionic strength [19,20].

A second set of experiments was conducted to explore the possible role of Pt coordination in the adsorption retardation phenomenon, seen in Fig. 1 and described in [8,10,11], manifested at pH values below 3. Thus a second set of experiments (labeled series B) was conducted in the pH range from the adsorption maximum at pH 3 down to about pH 1.5, where clearly retarded uptake can be expected (see Fig. 1). The pH was adjusted using hydrochloric acid, which promotes the formation of hexachlorides, and nitric acid which, as seen in Part 1 [1], results in complexes with more oxygen-containing ligands. To investigate the effect of ionic strength at constant pH, three more samples were prepared. At 200 ppm Pt and a pH of about 2.6, one sample was contacted with CPA only, one contained sodium nitrate as an ionic strength-increasing electrolyte, and one contained sodium chloride. The salt concentrations, 0.30 M, were set at the same ionic strength as an HCl solution at pH 1.5. The surface loading was 1,000  $\text{m}^2/\text{l}$ ; full uptake of 200 ppm Pt corresponds to a surface coverage of about 1 mmol/ $\text{m}^2$  (3.9 wt.% Pt), well below the steric limit of 1.6 mmol/ $\text{m}^2$ . Fresh solutions and 1 h contact times were used in all cases.

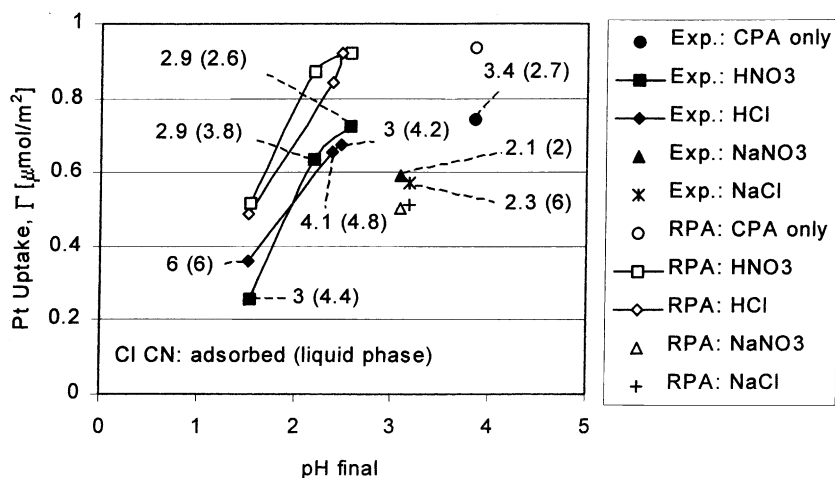


Fig. 3. Retardation of platinum adsorption at low pH and high ionic strength from solutions with different platinum species (series B, initial Pt concentration: 200 ppm, surface loading: 1000 m<sup>2</sup>/l). Numbers without parentheses signify the Cl coordination of the adsorbed complexes, and in parentheses the bulk solution over the adsorbed phase.

The results of this set of runs are shown in Fig. 3, as Pt uptake versus pH. Simulations from the RPA model are also included. The filled markers are experimental results, while the open markers indicate adsorption as simulated by the RPA model. The experimental uptake values are lower than the theoretical values, most likely because the solutions were fresh, as noted above. The results do show the expected trends, which are the decreasing adsorption with lower pH, highest uptake from pure CPA solution, and lowered uptake from solutions containing additional electrolyte (i.e. higher ionic strength). The RPA model, fresh solutions notwithstanding, captures all these trends (open markers) to a reasonable degree and proved to be a useful tool in designing the experiments.

The Pt–Cl coordination numbers for the complexes initially in the liquid phase and adsorbed onto the solid alumina are displayed in the plot. Those in parentheses are for the liquid phase complexes. Lowering the pH with the different acids results in very similar uptake behavior, even though the chlorine coordination numbers were consistently higher for the HCl samples than for the HNO<sub>3</sub> samples, both in the liquid and adsorbed onto the support. As in series A, the Pt–Cl coordination decreases upon adsorption for almost all samples, with the exception of the HCl-acidified sample at the lowest pH, and the sample containing NaNO<sub>3</sub> which already had high O coordination. Also, the samples with added

electrolyte show identical (and retarded) adsorption even while their solution chlorine coordination number varied greatly (2 for NaNO<sub>3</sub> and 6 for NaCl). The adsorbed complex Pt–Cl coordination numbers for these two samples is almost identical, as seen for the similar runs conducted in series A. The similarity of results for the two sets of complexes seems to justify the use of a single, representative species in the RPA model.

In both of the previous series of experiments, the oxide was contacted with an excess of solution. In the filtered solid, only those species that had a strong affinity for the surface would appear. In contrast, a third set of samples (series C) was prepared by incipient wetness (pore filling) to enable a comparison of results when all platinum and chloride species are forced onto the oxide surface. Six samples were prepared using a  $\gamma$ -alumina with a surface area of 200 m<sup>2</sup>/g and an approximate pore volume of 0.8 ml/g. This results in a very high surface loading of about 250,000 m<sup>2</sup>/l. Platinum loadings of 0.25, 0.5, 1, 1.5, 2, 3 and 5 wt.% Pt were targeted and the initial platinum concentration was accordingly set from 3,500 ppm for the 0.25 wt.% sample to 52,500 ppm for the 5 wt.% sample. At these high concentrations, the CPA complexes can be assumed fully chlorinated [1]. After wetting of the alumina powder with the solutions, the samples were air-dried overnight. EXAFS was run on the dried samples. Fig. 4 shows the chlorine coordination

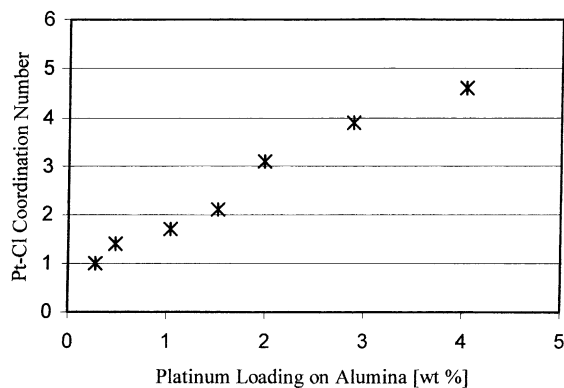


Fig. 4. EXAFS Pt–Cl coordination numbers of adsorbed CPA complexes (series C) dried at room temperature for 24 h, prepared by pore volume impregnation as a function of the platinum loading.

number as a function of the platinum loading. In this series there appears to be a strong correlation between the platinum loading and the chlorine content of the complexes. In the discussion below it will be proposed that this correlation is indirect.

The effect of calcination on the composition of the Pt complexes is shown in Table 2, with a series of samples, A\*, analogous to series A (Table 1) but with surface loadings higher by about 10%. Calcination was performed in a muffle furnace in air for 3 h after the samples had been air-dried over night. It appears that drying at room temperature and calcination at temperatures up to 300 °C have no effect on the coordination sphere of the adsorbed complexes. Only with a calcination at 500 °C can a marked decrease in the chlorine content of the samples be seen, however, one chloride ligand remains in the complex even at this temperature. This is in agreement with two previous EXAFS studies. Lambert and co-workers [17], also found that the composition of platinum complexes does not change upon calcination in air at temperatures up to 270–350 °C. An older EXAFS study of

Lagarde et al. reported that the majority of Pt–Cl bonds in adsorbed  $\text{PtCl}_6$  were converted to Pt–O after a 530 °C calcination [21].

## 4. Discussion

### 4.1. Ligand exchange/grafting mechanism

The contrasting mechanisms of Pt adsorption can now be examined in light of the data above and that reported in the literature. First of all, the ligand exchange reactions of Eq. (3) have been used to explain the upward shifts in pH observed during Pt adsorption [15], and have been cited more recently [18]. However, it has been shown both theoretically [19] and experimentally [11,19] that these shifts occur even in the absence of Pt, and can be attributed simply to the transfer of protons from the bulk aqueous solution to the surface (the oxide buffering effect). The RPA model was used to simulate not only the adsorption data in [15] but also the pH shifts [2,19]. In the RPA model, surface charging and proton transfer are taken to be completely independent of Pt adsorption.

Ligand exchange mechanisms have also been hypothesized to explain changes in the chlorine/oxygen ligand ratio upon adsorption, as seen by Lambert and co-workers [16–18] and in several earlier studies with characterization techniques such as NMR, TPR, UV-Vis, Raman or EXAFS [6,15,22–24]. In the former work, a decrease in the integrated intensity of  $\text{PtCl}_6$  and  $\text{PtCl}_5$   $^{195}\text{Pt}$  NMR signals was taken as evidence of extensive grafting/surface ligand exchange. Lambert and co-workers also propose adsorption over uncharged OH groups Eq. (4) to explain conversion of the  $^{195}\text{Pt}$  NMR signal from the  $[\text{PtCl}_5(\text{H}_2\text{O})]^{-1}$  chloroaquo species to the  $[\text{PtCl}_5(\text{OH})]^{-2}$  chlorohydroxo species after contact with alumina [16].

Table 2

EXAFS Pt–Cl coordination numbers of solid samples (series A\*) after air drying and calcination at 25, 100, 300 and 500 °C

Temperature (°C)	Sample A*1	Sample A*2	Sample A*3	Sample A*4	Sample A*5	Sample A*6
25	1.8	1.5	2.9	2.5	2.6	2.7
100	1.9		3	2.5	2.6	2.7
300	1.8				2.5	2.7
500	1	1.1	1	1.2	1.1	1

The powerful array of spectroscopies employed by the Lambert and co-workers in [16,17] is perhaps the most comprehensive characterization of the Pt-alumina system performed to date, and the gist of their firmly documented results that the oxygen-content of Pt complexes increases when CPA solutions are contacted with alumina is entirely supported by our own results. We would argue, however, that “contact” with alumina does not necessarily imply “adsorption” over alumina. While all Pt in those systems were presumed adsorbed, a closer accounting of the proton consumption by the oxide surface suggests a very different picture. (The oxide buffering effect was mentioned in this work, but it was not sufficiently accounted for.) In many cases a relatively high surface loading was employed; impregnation using twice the pore volume (0.6 ml/gm) of solution, for a 195 m<sup>2</sup>/gm alumina [16] gives a surface loading of 163,000 m<sup>2</sup>/l. Noh and Schwarz [25] were the first to demonstrate significant shifts in solution pH; in their landmark paper on “mass titration,” a solution of initial pH 7 was brought down to 3.5 by adding only 10 wt.% of a 100 m<sup>2</sup>/gm silica to the liquid (1000 m<sup>2</sup>/l). In our own earlier simulation of alumina surface charging and proton consumption, solutions at pH 3 were brought all the way up to the alumina PZC with 180,000 m<sup>2</sup>/l of surface [19]. These large shifts over alumina at high surface loading have been verified in many sets of experiments [11,19].

The pH shifts in the 163,000 m<sup>2</sup>/l preparations of Lambert and co-workers will likewise be very large, even when starting with a strongly acidic pH of 1.15 [17]. A simple calculation is illustrative. For one gram of alumina, 1.2 ml of pH 1.15 solution is used. In this solution there are  $8.4 \times 10^{-5}$  moles of H<sup>+</sup> ( $1 \text{ gm} \times 1.2 \times 10^{-3} \text{ l/gm} \times 10^{-1.15} \text{ mole H}^+/\text{l}$ ). The number of OH groups on the alumina surface, assuming a conservative value of 5 OH groups/nm<sup>2</sup> [19], is  $1.4 \times 10^{-3}$  moles of OH groups ( $1 \text{ gm} \times 195 \text{ m}^2/\text{gm} \times 5 \text{ OH}/\text{nm}^2 \times 10^{18} \text{ nm}^2/\text{m}^2 \times 1 \text{ mole OH}/6.02 \times 10^{23} \text{ OH}$ ). Thus, there are roughly 20 times more OH groups on the alumina surface than protons in the liquid phase. Put another way, only about 5% of the surface can be charged.

The pH shift predicted by the proton balance of the RPA model for the conditions of the Lambert preparations is shown in Fig. 5, along with the predicted Pt

uptake. The two initial pH values employed, 1.15 and 2.8 [17], are indicated. The proton balance (Fig. 5a) predicts that the final pH of the more acidic initial pH is approximately 7.4, while that of the initial pH 2.8 solution is virtually at the PZC of alumina, or about 8.5. The Lambert group estimated a final pH of 4.6 for the former sample, based on a correlation of the Pt NMR signals of the various complexes with pH [17].

According to the RPA model, in the latter sample, no Pt should be adsorbed (Fig. 5b) while in the former, over a surface that is charged to only 5% of its capacity, perhaps half of the available Pt is adsorbed. The majority of the Pt complexes in these preparations appears to be dissolved and not adsorbed. In fact, the NMR spectra of the liquid phase species at high pH, observed in the first Lambert and co-workers work [16], are not inconsistent with the spectra of the “adsorbed,” aged species reported in the later work [17]. The loss of intensity of the PtCl<sub>6</sub> and the PtCl<sub>5</sub>O species taken as evidence of grafting in adsorbed samples [16–18] might instead be just a conversion to liquid phase PtCl<sub>4</sub>O<sub>2</sub> species that were observed by Pt NMR in the liquid phase at high pH [16]. It is not reported in the later work [17] why PtCl<sub>4</sub> and below were not detected, or even if they were sought. The highly exchanged PtCl<sub>3</sub>O<sub>3</sub> species seen by EXAFS after drying of the pH<sub>initial</sub> 2.8 sample [17] is more likely the result of an unadsorbed complex undergoing ligand exchange in the liquid phase at pH near 8, the PZC of alumina, than the grafting of an adsorbed species. A direct comparison of the EXAFS spectra of wet and dried samples in the present work, series A above, showed no difference brought about by drying; the change in coordination had already occurred prior to adsorption.

Before these results are interpreted in light of the RPA model, a number of further circumstantial arguments can be made against the surface grafting/ligand exchange adsorption model. First, in Fig. 2 it is seen that the aged solutions, which contain a higher degree of oxygen [1], adsorb slightly faster and to a greater extent than do the fresh solutions with more chlorine. This is the opposite of what would be expected with a ligand exchange mechanism. Second, the high-Cl and low-Cl series of complexes (series B) shown in Fig. 3 exhibit the same degree of uptake. In particular, the [PtCl<sub>6</sub>]<sup>−2</sup> complex, formed at the lowest pH in HCl,

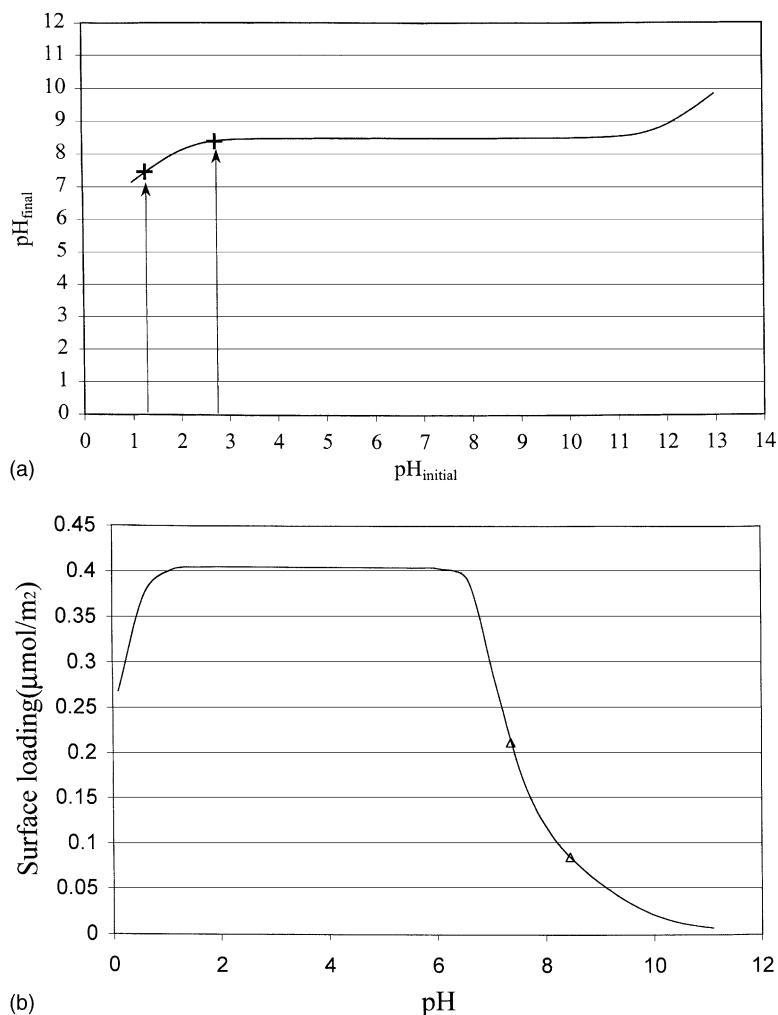


Fig. 5. pH shift and Pt uptake simulations of the Lambert preparations ( $\text{pH}_{\text{initial}}$  1.15 and 2.8,  $163,000 \text{ m}^2/\text{l}$ ,  $\text{PZC} = 8.5$ , 13,200 ppm Pt).

is adsorbed at the same level as the  $\text{PtCl}_4\text{O}_2$  complex formed in  $\text{HNO}_3$ . A grafting mechanism would predict different extents of uptake for these two species. Third, while grafting of a  $\text{PtCl}_5\text{O}$  or  $\text{PtCl}_4\text{O}_2$  species may be reasonable to assume, the grafting of  $\text{PtCl}_3\text{O}_3$  or  $\text{PtCl}_2\text{O}_4$  to the surface via three or even four hydroxyl groups seems unrealistic for steric reasons. The existence of adsorbed  $\text{PtCl}_2\text{O}_4$  and  $\text{PtClO}_5$  species seen in series A, B, and C (Table 1, Figs. 3 and 4), can definitely not be explained by the grafting mechanism, which would require each CPA complex to form four or five bonds with the surface.

#### 4.2. Electrostatic adsorption mechanism

The present results and literature data might be more easily interpreted by a refined physical adsorption model, paying due attention to the liquid phase speciation, the oxide buffering effect, and the electric double layer properties. Our hypothesis is that the adsorbing complexes speciate as if in the liquid phase, at the conditions of the local environment, i.e. in proximity to the oxide surface. It follows that the shift in coordination away from chlorine and toward oxygen is not due to a chemical interaction with the surface,

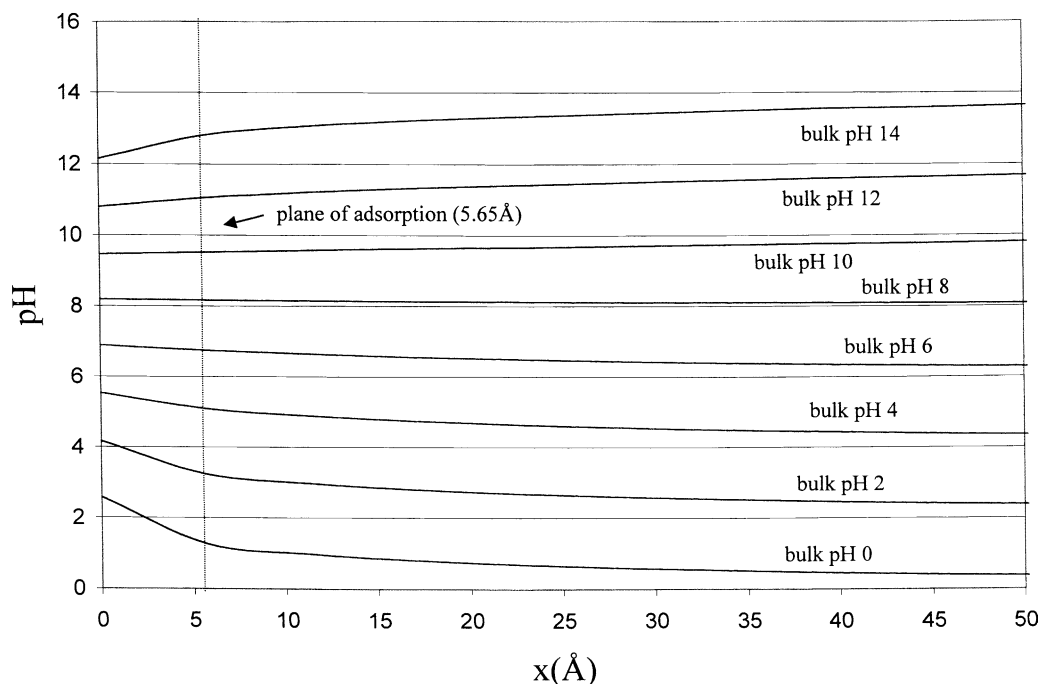


Fig. 6. Variation of pH from the bulk liquid to the surface, for various bulk pH values (PZC = 8.5).

but is in response to the higher pH near the adsorption plane. The equality of electrochemical potential in the bulk liquid and at the surface dictates a Boltzman distribution of pH in the electric double layer, that is,

$$[H]_{\text{surface}} = [H]_{\text{bulk}} \exp\left(\frac{-\psi_0}{kT}\right)$$

where  $\psi_0$  is the surface potential corresponding to the surface charge produced by the protonated hydroxyls. While not quantifying it, Lambert and co-workers also recognized this effect [16,17]. Fig. 6 shows the variation in pH from different values in the bulk, as the surface is approached. The plane of adsorption is approximately at the radius of  $[\text{PtCl}_6]^{-2}$ , 2.95 Å, plus the thickness of the hydration layer ( $2 \times 1.35$  Å, the radius of water), or 5.65 Å. At pH values substantially below the PZC, the pH at the adsorbed plane can be several pH units above the bulk value.

A telling plot is then made by superimposing the speciation of the adsorbed complexes, at the pH of the adsorption plane, onto the results for speciation in the bulk liquid phase at the bulk pH. The latter data are obtained from the previous paper [1]. This over-

lay is shown in Fig. 7 for the series A samples. Both series of samples fall closely together between curves of the fresh and aged liquid phase samples. Once again, half these samples began as fully chlorided complexes (filled squares), the others as half-chlorine, half-oxygen (unfilled squares). Our hypothesis is that at the adsorption plane, little chloride is present (the dianionic Pt complexes adsorb much more strongly) and the pH is higher than the bulk, so the complexes speciate accordingly. Since this series was prepared with an excess of liquid, the chloride could be far from the surface and much would be removed when the solid was filtered from the solution. In a previous work we reported that chloride did not appear to adsorb strongly or competitively in the presence of Pt [9]; that conclusion is consistent with the current hypothesis.

If the B and C series are overlaid onto this sort of plot (Fig. 8), allowance must finally be made for high local chloride concentration. Unlike series A and B, the series C samples were prepared by pore filling such that all chloride remains in the pore volume, and ultimately on the surface of the dried samples. The low

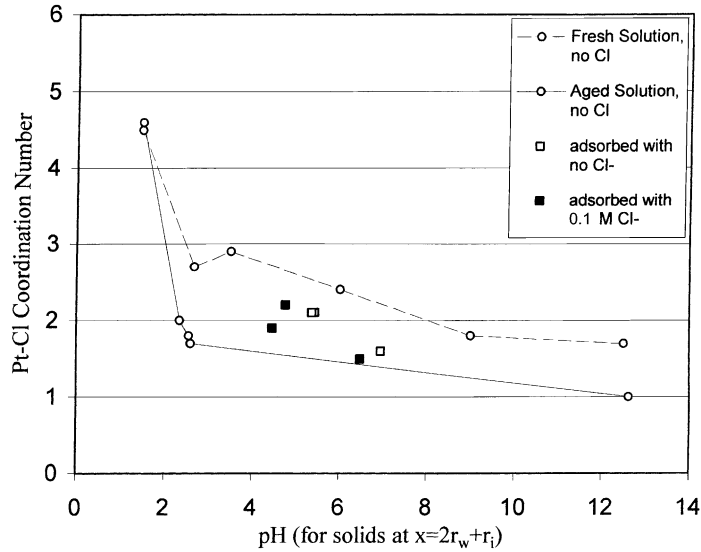


Fig. 7. Comparison of the chlorine coordination numbers of adsorbed (series A) and fresh and aged liquid phase (200 ppm) CPA complexes.

pH series B samples acidified in HCl also contained relatively high amounts of chloride. To help interpret the effect of high local Cl<sup>-</sup> concentration, the liquid phase speciation curves for 200 ppm CPA in 0.05 and

0.1 M excess chloride [1] are added to this figure. The chloride concentration remaining in the liquid phase pore volume of the pore-filled series (C) can be estimated as the total amount of Cl<sup>-</sup> added to the liquid

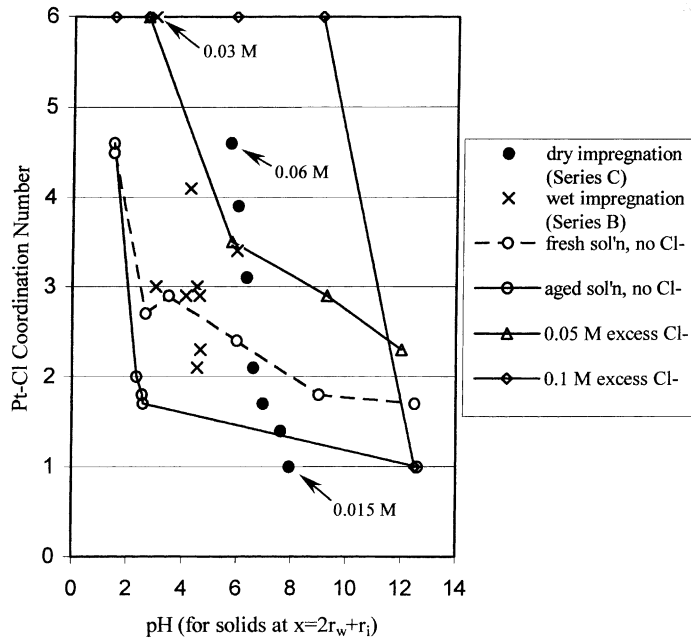


Fig. 8. Chlorine coordination number of adsorbed CPA complexes (series B and C) prepared in dry and wet impregnation as a function of the adsorbate layer pH, and liquid phase speciation of various CPA solutions.

(from the known CPA concentrations in the impregnating solution) less the amount of  $\text{Cl}^-$  still affixed to adsorbed Pt (which can be calculated from the Pt–Cl coordination numbers in Fig. 8). The chloride concentration in the pore volume of the highest Pt loading, which is the uppermost filled circle in Fig. 8, is thus estimated to be 0.06 M, while that for the lowest loading (lowest filled circle) is 0.015 M. The pore volume  $\text{Cl}^-$  concentration of the series B sample acidified to pH 1.5 with HCl would be likewise high, at  $10^{-1.5}$  or 0.030 M. We conclude that when forced into the pore volume, chloride can effect speciation at the adsorption plane.

A final issue is the rectification of the charge of the adsorbing complexes with the RPA model assumption of divalence. There are many situations in which CPA is sufficiently concentrated [2,16,21] or is dilute but in sufficient excess chloride (Fig. 3, HCl acidified sample at lowest pH) such that the adsorbing species is and remains  $[\text{PtCl}_6]^{-2}$ . In these cases the RPA model is applied straightforwardly. But how can the adsorption of predominantly zero-valent species such as  $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$ , estimated previously to exist at an equilibrium pH of 2.40 for 200 ppm CPA [1], be explained?

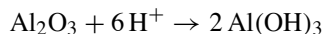
The data in Fig. 3 indicate that species with different numbers of chloride and oxygen ligands adsorb in similar fashion at the same pH. It is not implausible to suggest that all the adsorbed species are dianionic. The purely electrostatic interpretation would be that once again, as a neutral chloroaquohydroxo complex is contacted with oxide and draws near the surface, it speciates to the divalent hydroxo complexes in response to the pH at the adsorption plane. In Part 1 [1] it was noted that the complexes at 200 ppm undergo significant OH exchange for water beginning at a pH of about 2.6; in the pH range 2.8–3.4, the composition of Pt complexes appears to be a mixture of  $[\text{PtCl}_1(\text{OH})_3(\text{H}_2\text{O})_2]^0$ ,  $[\text{PtCl}_1(\text{OH})_4(\text{H}_2\text{O})]^{-1}$  and  $[\text{PtCl}_2(\text{OH})_4]^{-2}$ . It is generally held that Pt aquo complexes convert to hydroxo complexes as the pH increases [13,14,16].

When the aged 200 ppm CPA solutions at pH 2.4 (Fig. 2), containing mainly the neutral  $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$  complex, are contacted with alumina, the solution undergoes a shift of about 0.3 pH units upward in about the first 30 min, due to the oxide buffering effect. At a bulk pH of about

2.7, the corresponding pH of the adsorption plane, from Fig. 6, is about 4.0. Held at this high pH, it might speciate quickly and completely to the divalent  $[\text{PtCl}_2(\text{OH})_4]^{-2}$  species.

The assumed rapidity of this transformation is questionable, however. The rate at constant pH is quite difficult to measure since the transformation itself involves a lowering of pH. In the presence of an oxide surface, which would keep the pH constant (at particular values depending upon the surface loading of the oxide), the process of adsorption competes with and so obscures the study of the liquid phase speciation. Our first work, in which pH was allowed to vary, showed that this transformation is very slow in the bulk liquid phase at low initial pHs [1], requiring more than 24 h to equilibrate, but is faster at higher initial pH. We believe it occurs via a slow  $\text{OH}-\text{H}_2\text{O}$  substitution mechanism [1] as opposed to the deprotonation of the aquo ligands, which is normally thought to be fast. In contrast, the rate of adsorption of the aged 200 ppm solutions (Fig. 2) containing predominantly  $[\text{PtCl}_2(\text{OH})_2(\text{H}_2\text{O})_2]^0$  is rapid. Our hypothesis should account for this and should also explain the initially incomplete and slowly increasing deposition of the fresh solution complexes (Fig. 2), which initially contain a significant fraction of  $[\text{PtCl}_3(\text{H}_2\text{O})_3]^{+1}$  [1].

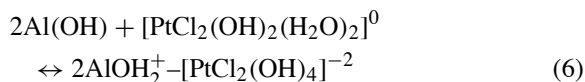
Several explanations might be offered. First, if the zero-to-divalence conversion is presumed to accompany adsorption, the rapid rate of  $\text{OH}-\text{H}_2\text{O}$  exchange can be attributed to the higher pH (near 4.0) of the adsorption plane, in the case of the aged solution. However, the fresh solution (Fig. 2) begins at pH 2.7 and increases to about 3.0 in the first 30 min after contact with the alumina. The portion of complexes that are  $[\text{PtCl}_3(\text{H}_2\text{O})_3]^{+1}$ , while being repelled from the surface, would still experience this bulk liquid pH of 3.0. This pH is apparently not sufficient to cause rapid  $\text{OH}-\text{H}_2\text{O}$  exchange, or  $[\text{PtCl}_3(\text{H}_2\text{O})_3]^{+1}$  would quickly become  $[\text{PtCl}_3(\text{OH})_3]^{-2}$  and would adsorb completely. We are left with the not easily substantiated assumption that the process of  $\text{OH}-\text{H}_2\text{O}$  ligand exchange to produce dianionic adsorption complexes increases rapidly from a pH of 3 to 4. The ultimate bulk pH of both fresh and aged solutions (Fig. 2) is about 4.0, due to the long-term dissolution of aluminum at the expense of protons, according to:



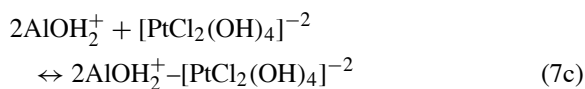
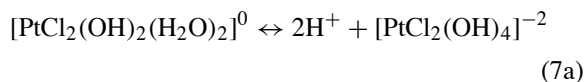
As this process occurs in the fresh solutions, pH would be increased sufficiently for all complexes to become dianionic.

Some of our earlier experimental evidence, however, suggests the presence of zero-valent species beyond pH 4.0. While the amount of Pt adsorbed onto alumina equilibrates in about 1 h in the low pH range (pH 1.4–4) [11], long-term deposition much in excess of the RPA model predictions is seen in the mid pH range (pH 5–9). In that work we postulated that the long-term deposition was due to the precipitation of zero-valent species.

If zero-valent species are indeed present in the mid-pH range, an alternative adsorption mechanism can be proposed that, instead of rapid OH–H<sub>2</sub>O ligand exchange, involves a surface protonation reaction as in Eq. (4). Written for the zero-valent dichloro-dihydroxo-diaquo species, this would be:



From a thermodynamic point of view, this mechanism is indiscernible from the coulombic mechanism of dianion adsorption,



since these three parts sum to Eq. (6) above.

According to this mechanism, the aged, zero-valent CPA complexes of Fig. 2, exposed to an initially uncharged alumina surface, would rapidly adsorb to completion as the surface attained its equilibrium charge in concert with the adsorption process. On the other hand, positively charged complexes in the fresh solutions would be repelled as the surface charging began, and the surface charge would be attained in greater part by protons from the bulk and not from adsorbing complexes. Over a fully charged/equilibrated surface, deposition of zero-valent species at long contact times might occur via precipitation. Thus, while both the fresh and aged samples might show the same

overall uptake of Pt at long times, the former adsorption scenario would likely result in well dispersed Pt adsorbates, and the latter in poorly dispersed precipitates. This long-term deposition process is being studied further in an attempt to refine this mechanism.

## 5. Conclusions

The changes in coordination chemistry of chloro-aquohydroxo platinate complexes adsorbing over alumina need not invoke a “triple layer” theory that incorporates surface grafting reactions, but are more readily explained by refinements to the “double layer” theory that is the kernel of the Revised Physical Adsorption model. The changes in speciation of adsorbing CPA complexes appear to be influenced first, by the change in the bulk pH brought on by the oxide buffering effect; second, by the additional pH change at the (single) layer of adsorption at the alumina surface; and third, by the chloride concentration at this local level. At low surface loadings, pH shifts are minimized and the amount of chloride near the adsorption plane appears to be low. Platinum complexes adsorb with low Pt–Cl/Pt–O bond ratios, even when present in the bulk solution as hexachlorides. The adsorbed species appear to behave as in the liquid phase at the pH of the adsorption plane with no excess chloride. At high surface loadings such as with pore volume impregnation, the pH shifts toward the alumina PZC are very large but all chloride is kept in the pore volume. At high Pt loadings, high chloride concentration appears to dominate the Pt speciation and Pt–Cl coordination in the adsorbed complexes remains high, as occurs in the liquid phase in excess chloride.

The adsorption of Pt from solutions in which zero-valent species are thought to initially exist can be explained by mechanisms in which either rapid OH–H<sub>2</sub>O exchange occurs at the higher pH of the adsorption plane, creating a dianionic adsorbing complex, or a surface protonation reaction, which creates a dianionic adsorbed complex in concert with surface charging. Both mechanisms are consistent with an electrostatic adsorption mechanism.

This understanding provides a practical formula to prepare catalysts with either low or high chloride contents. If highly chlorided Pt is preferred, pore volume impregnation should be employed using excess

chloride if metal concentration is low. If low chloride levels are desired, impregnation should be performed with a large excess of solution, or using pore filling impregnation with low Pt loadings. In either case, for strong adsorption, the initial pH of CPA solutions must be adjusted to account for the oxide buffering effect; the final pH in the oxide-solution slurries should be in the range 3–4, that is, far enough away from the alumina PZC for a strong surface charge.

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