

Structure of CPA in solution and upon adsorption onto γ -Al₂O₃ as a function of pH, chloride concentration and aging/light exposure

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Introduction

Alumina-supported platinum catalysts are used in a large number of important industrial processes and are frequently prepared by adsorption of platinum onto the support from an aqueous solution of chloroplatinic acid (H₂PtCl₆, or CPA). There are two major aspects to the adsorption that are of importance to industrial catalyst preparation. The first involves the total amount of metal that can be adsorbed and the preparation conditions that lead to the highest possible uptake. Our group developed the Revised Physical Adsorption (RPA) Model [1] that can be used to optimize platinum adsorption on alumina supports. The second issue concerns the distribution of platinum in a catalyst pellet. Normally, a homogeneous distribution is preferred over a so-called “eggshell profile,” where the Pt concentration is highest in the region close to the surface of the pellet and sharply decreases towards the center. It is known that in alumina spheres, eggshell Pt profiles result from adsorption of pure CPA, while homogeneous distributions can be achieved by addition of Cl⁻ to the solution. This is commonly explained with competitive chloride adsorption that drives the platinum deeper into the pellet [2]. Recent experiments, however, suggest that this is incorrect [3, 4]. An alternative hypothesis is that different Pt species exhibit different adsorption characteristics. It is known that the speciation of CPA in solution depends on several factors, such as the pH, chloride concentration, and aging light exposure [5–7]. However, only limited quantitative data is available in the literature, especially under the conditions used to prepare catalysts. In addition, no attention has been paid to the possibility of a species-dependent strength of platinum adsorption. The goal of this work is to investigate the CPA speciation in solution and its effect on the preparation of catalysts. Furthermore, this information may also substantially contribute to an improvement of the RPA model, which at this point considers only the charge of the metal complex, but does not further differentiate between the platinum species.

Methods and Materials

The solution samples were prepared from hydrogen hexachloro-platinate(IV) hydrate (Aldrich) dissolved in deionized water at room temperature (RT) under normal laboratory light conditions at a concentration of 200 ppm Pt. HCl, NaOH, and NaCl were used to adjust the pH and Cl level. The catalyst samples were prepared by adsorption of platinum from liquid solutions of CPA at its natural pH (2.5) onto γ -alumina (surface area 250 m²/g). Platinum loading was varied through different alumina loadings, while the initial solution concentration (200 ppm) was identical for all samples. The specimens were placed on a shaker under ambient conditions for one hour. The samples

were then filtered and the filter cake was air dried over night and further dried or calcined in a muffle furnace in air at temperatures varying from 110° C to 500° C.

X-ray absorption fine structure (XAFS) measurements were performed on the MR-CAT undulator beamline equipped with a double-crystal Si(111) monochromator. Spectra of the Pt solutions were taken in fluorescence mode using the Stern-Heald configuration with a 0.1 mm high-purity Zn foil filter. The resulting signal-to-background ratio was approximately 0.8 from a 1 cm thick solution. Solid catalyst samples were measured in transmission mode.

Results

The fits for the CPA solutions are given in Table 1. The Pt coordinate numbers (CN's) are larger than six due to the relatively low signal-to-noise ratio for the oxygen-containing samples beyond about $k = 10 \text{ \AA}^{-1}$ for these very dilute solutions. As seen from the fits (Table 1), at the natural pH of the freshly prepared CPA solution (pH = 2.6), 2–3 chlorine ligands have already been exchanged for oxygen ligands and PtCl₆⁻² is not present. The hydrolysis proceeds further and seems to stabilize at about 3–4 oxygen (or 2–3 chlorine) ligands as the solutions become more basic. An aged CPA solution, which had been standing in transparent polypropylene (PP) bottles in the lab for at least one day, already contains four oxygen and two chlorine. This ratio can be further shifted at high pH values to 5:1 under strongly basic pH. Interestingly, PtCl₆⁻² is observed only after the addition of Cl⁻ to the solution. At pH values below about 6, the addition of 0.1 M NaCl is sufficient to form the hexachloro-platinate ion, while solutions at higher pH values seem to require more chloride to complete the transformation. Figure 1 shows the Fourier transform of selected spectra, showing the transition from Cl ligands only to mixed O/Cl ligands.

Table 1: EXAFS results of Pt coordination in solution.

pH	CN Pt-O/Pt-Cl		pH	NaCl (M)	CN Pt-O/Pt-Cl
	fresh	aged			
			1.5	0	0/6.3
2.6	3.5/4.5	6.1/2.6	1.5	0.1	0/6.2
4.5	5.6/3		2.7	0.1	0/6.2
7.7	5.4/3.1		5.9	0.1	0/6.3
12.6/12	6.6/4	6.9/0.7	12	0.01	4.6/3.1

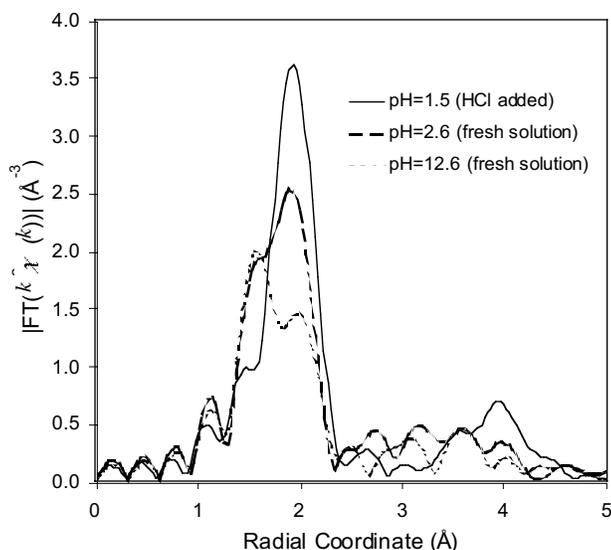


Figure 1: Fourier transform of selected Pt L_{3} -edge XAFS spectra for 200 ppm Pt in solution showing the transition from Pt-Cl bonds only (pH = 1.5) to a mixed Pt-O/Pt-Cl coordination environment (pH = 12.6). (k^2 weighting, k -range = 1.5–12.0, $dk = 0.5$)

Table 2 shows the results for Pt species adsorbed on high surface area alumina and after calcination. One weight percent Pt adsorbed from CPA (solution pH = 2.6) and dried at RT results in 3.6 oxygen and 2.4 chlorine ligands. A comparison with the liquid solution of CPA, which was used for the preparation of this sample and showed only 2.2 O and 3.8 Cl, indicates that the hydrolysis proceeded further during the adsorption or drying step. Drying at 110° C instead of RT has no effect on the hydrolysis, while at 300° C the beginning of the transformation to oxygen coordination is seen (which is complete at 500° C). The addition of 0.1 M NaCl to the solution prior to adsorption leads, as expected, to a shift in coordination towards chlorine. However, the fully chlorine-coordinated Pt complex, as seen in the corresponding solution, is not observed on the support. Again, hydrolysis seems to proceed during adsorption/drying. The set of samples with higher Pt loading of 7.2 wt % displays the same coordination shift with increasing calcination temperatures. However, these samples generally show more chlorine ligands than the 1 wt % samples do and even after calcination at 500° C, some Pt-Cl bonds are observed.

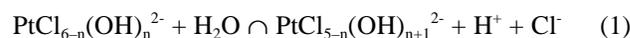
Discussion

Previous information on CPA speciation in aqueous solution is limited and only partially quantitative. The most comprehensive set of equilibrium constants for the hydrolysis is given by Anderson [5] and Sillen [6]. Their data, however, does not consider the addition of bases, but is limited to acidic solutions. Mang [2] cites data extending into the basic region. Both studies predict only the fast ligand exchange of two chloride ions and also disregard the

Table 2: EXAFS results of Pt coordination adsorbed on alumina.

wt % Pt	Alumina loading (g/l)	NaCl (M)	Calc.Temp (°C)	CN Pt-O	CN Pt-Cl	Final pH
1.0	19.8	0	25	3.6	2.4	5.3
1.0	19.8	0	110	3.4	2.6	5.3
1.0	19.8	0	300	4.1	1.9	5.3
1.0	19.8	0	500	6	0	5.3
1.0	19.8	0.1	25	1.9	4.1	6.8
1.0	19.8	0.1	500	1.6	4.4	6.8
7.2	2.6	0	25	2	4	3.1
7.2	2.6	0	110	1.8	4.2	3.1
7.2	2.6	0	300	2.3	3.7	3.1
7.2	2.6	0	500	4.7	1.3	3.1

effect of light exposure over longer times. In sufficiently dilute solutions, all chloride ions can be exchanged for hydroxide leading to formation of an insoluble hexahydroxy-platinate(IV) [7]. The last steps of this sequence are reported to be slow, but can be substantially accelerated by light exposure [7, 8]. Precipitation is indeed seen from dilute (30 ppm) CPA solutions that were exposed to daylight over a period of several weeks. Generally, the hydrolysis occurs as follows in Equation 1 [7]:



where $n = 0, 1, 3, 4$ or 5 depending on concentrations and equilibration times. According to [2, 5, and 8], chlorine can also be replaced by water to form chloroaquohydroxo platinates of lower or no charge.

Our solution data is in general agreement with the stepwise substitution of chloride by oxygen-containing ligands as suggested by [7]. High pH and aging shift the coordination toward the oxygen, while low pH and high chloride concentration shift it toward the chlorine. The speciation models by Mang and Anderson both fail to predict the formation of species with a Cl:O ratio lower than 4:2 as observed in our samples.

The catalyst results demonstrate that the solution chemistry directly manifests itself in the structure of the platinum adsorbed on the support. The influence of chloride concentration and pH is the same as with the solutions. The final pH values of the alumina suspensions are higher than that of the initial CPA solutions. This is due to the strong pH buffering effect that high surface area oxide supports typically exhibit [9]. According to this pH change, the Cl:O ligand ratio of the complex ions in solution drops as they adsorb onto the support and is consistent with the solution data at the same pH. The degree of the pH and the ligand-ratio shift depends on the alumina loading in the suspension. These results show that different preparation conditions result in different Pt species on the alumina

support, which now enables us to further investigate the adsorption properties of these species, including the metal distribution phenomenon in catalyst pellets.

Acknowledgments

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science (DOE-BES-SC), under Contract No. W-31-109-Eng-38. The MR-CAT beamlines are supported by the member institutions and DOE-BES-SC under Contracts DE-FG02-94ER45525 and DE-FG02-96ER45589.

References

- [1] K. Agashe, *et al.*, *J. of Coll. Int. Sc.* **185**, 139 (1997).
- [2] T. Mang, *et al.*, *App. Catal. A: Gen.* **106**, 239–258 (1993); and references within.
- [3] J.R. Regalbutto, manuscript in preparation.
- [4] S. Shadid, MS thesis, Univ. of Illinois, Chicago, (1998).
- [5] J.R. Anderson, *Structure of Metallic Catalysts*, (Academic Press, London, 1975).
- [6] L.G. Sillen and A.E. Martell, *The Stability Constants of Metal-Ion Complexes, Supplement 1, Special Publication, The Chemical Society*, (Burlington House, London, 1971).
- [7] *Gmelins Handbuch der anorganischen Chemie*, (Platin, Teil C Lieferung 1, 8. Auflage, Verlag Chemie, Weinheim, 1939).
- [8] C. Davidson, *et al.*, R. F., *Trans. Farad. Soc.* **61**, 2462 (1965).
- [9] J. Park and J.R. Regalbutto, *J. Coll. Int. Sc.* **175**, 239 (1995).