An Evaluation of Platinum Sulfite Acid (PSA) as Precursor for Supported Pt Catalysts*

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Introduction

Platinum sulfite acid (PSA) is a traditional source of Pt for the synthesis of Pt/carbon black fuel cell electrocatalysts [1]. It is easy to use, relatively inexpensive, and is a potentially attractive precursor for many other types of supported catalysts. It's ultimate usefulness for many applications, however, will depend on the extent to which Pt can be dispersed to make small metallic particles and eliminate sulfur.

Methods of preparation using PSA have been investigated on high surface area oxide supports, including alumina, silica, magnesia, niobia, titania, and carbon black. At each step in the preparation (impregnation, calcination, and reduction), extended x-ray absorption fine structure (EXAFS) has been used to characterize the Pt species present. While high calcination temperatures followed by reduction in hydrogen partially eliminated S, such pretreatments results in the formation of large Pt particles. With all supports and pretreatment conditions, it was not possible to prepare small metallic particles and completely eliminate S from the catalyst.

Methods and Materials

Platinum sulfite acid was obtained from Heraeus and was diluted such that impregnation by pore filling (dry impregnation) onto the various oxide and carbon supports yielded about 1.5 wt% Pt. Catalysts were calcined at 300 and 500°C. Impregnated and calcined catalysts were reduced in flowing H_2 at 250 or 500°C. EXAFS measurements were performed in controlled atmosphere cells at the MRCAT undulator beam-line. Phase-shift and backscattering amplitudes were obtained from reference compounds. The details of the experimental and fitting procedures have previously been published [2,3].

Results and Discussion

EXAFS results are shown in Figure 1 for a progression of deposition and pretreatments of PSA impregnated onto alumina. The dried state (solid line), which was virtually identical to the solution species, could be fit with two Pt-S bonds and two Pt-O bonds [4]. After 300°C calcination, there were six Pt-O bonds (dotted line, Pt^{+4} oxide), while a 300°C reduction of the dried sample yielded only Pt-S bonds (dashed line, Pt^{+2} sulfide).

The removal of sulfur from the Pt phase was attempted by higher temperature reduction (at 500°C), and by a 300°C calcination followed by a 300°C reduction. The retention of sulfur after these pretreatments was strongly dependent on the support; representative results are shown in Figure 2. For alumina, Figure 2a, neither higher temperature reduction nor the calcination-reduction sequence removes much sulfur, and only a small fraction of Pt is reduced to metallic particles.

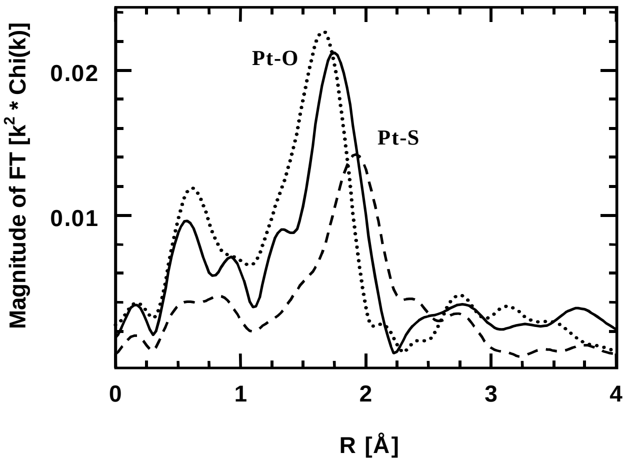

Figure 1. *Magnitude of Fourier transform of PSA on alumina (k^2: $\Delta k = 3.0 – 13.0$ Å^{-1}), solid line: dried only at RT; dotted line: calcined at 300°C; dashed line: reduced at 300°C.*

Over silica, Figure 2b, a larger fraction of Pt is reduced to metallic particles. Nevertheless, even under the best pretreatment conditions (500°C reduction) there are on average 0.6 S per Pt. As discussed below, it is estimated that approximately 20% of the Pt is non-metallic in this sample and the particles are approximately 60 Å. In such moderately sized Pt particles approximately 15% metallic atoms are at the surface of the particles. This suggests that nearly every surface atom in the metallic particles is oxidized to Pt^{+2} and is coordinated, i.e., poisoned, by S.

Additional attempts were made to remove sulfur from silica-supported catalysts by reduction/calcination/re-reduction cycles. Representative results are shown in Figure 3. Direct reduction of dried PSA on silica at 300°C (solid line) gives 2 S bonds per Pt, with the formation of little metallic Pt, Pt-Pt CN = 3.5. Calcination at 400°C removes all the Pt-S bonds and an oxide phase is formed with 4.1 Pt-O bonds. A portion of the metallic Pt remains reduced despite oxidation at this high temperature, (dashed line). Upon re-reduction at 300°C, there are slightly fewer Pt-S bonds with slightly more metallic Pt (dotted line). Since silica does not form surface sulfates, it is likely that the sulfur is present as SO_x species, bonded through the O atom to the Pt. Thus, even at 400°C, Pt-O-S-O_x species are strongly bound and cannot easily be removed by oxidation treatment.

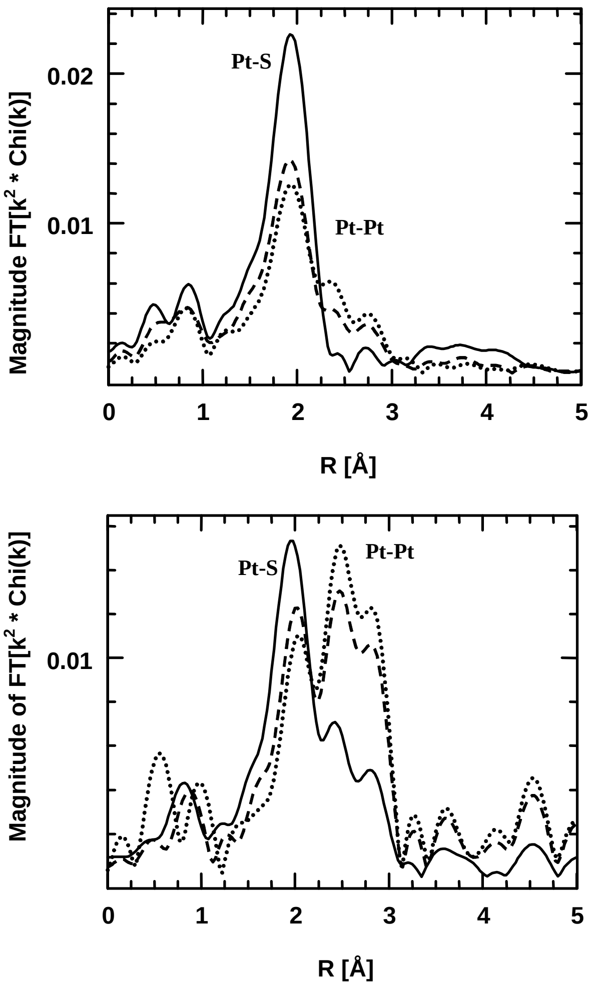

Figure 2. *Magnitude of Fourier transform of PSA (k^2: $\Delta k = 3.0 – 13.0$ Å^{-1}), solid line: reduced at 300°C; dashed line: calcined at 300°C then reduced at 300°C; dotted line: reduced at 500°C; on* a) *alumina, b) silica.*

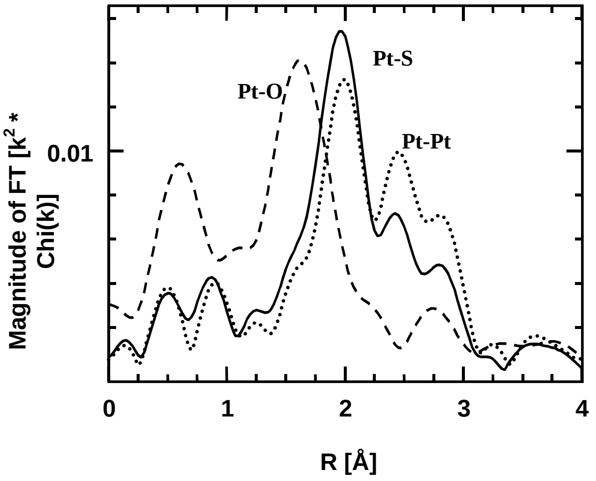

Figure 3. *Magnitude of Fourier transform of PSA on Silica (k^2: $\Delta k = 3.0 – 13.0$ Å^{-1}), solid line: reduced at 300°C; dashed line: reduced followed by 400°C calcination; dotted line: reduced, oxidized, followed by reduction at 300°C.*

Figure 4 shows the EXAFS results for Pt catalysts prepared on carbon black and magnesia compared to those on alumina and silica. After a 500°C reduction in H_2, no catalyst is free of sulfur, and the amount of sulfur depends greatly on the catalyst support. Carbon and alumina appear to retain the greatest amount of sulfur and little metallic Pt is formed, while magnesia and silica appear to retain less S, there is still sufficient S to strongly poison any catalytic activity.

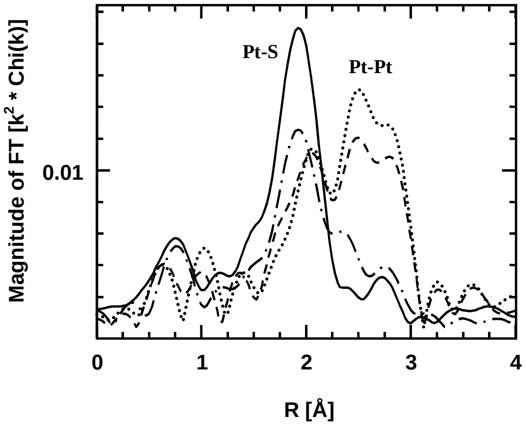

Figure 4. *Magnitude of Fourier transform of PSA on different supports reduced at 500°C (k^2: $\Delta k = 3.0 – 13.0$ Å^{-1}), solid line: sarbon black; dot-dashed line: alumina; dashed line: magnesia; dotted line: silica.*

Discussion

In order to evaluate the catalytic potential of these materials it is necessary to determine the particles size, and thus the fraction of surface atoms, and the surface coverage of Pt by S. Although Pt finds wide application for a number of important catalytic reactions, for many of these nearly all activity is lost when less than one-third of the surface atoms are bonded to S.

While estimates of the Pt particle size and fraction of surface atoms are readily determined by the hydrogen chemisorption capacity for S-free Pt particles, hydrogen chemisorption is strongly supressed for S-poisoned catalysts. Using a previously obtained correlation between the Pt-Pt coordination numbers with Pt dispersion measured by H_2 chemisorption [5], the particle size can be estimated if one can determine the fraction of metallic Pt in these PSA catalsyts.

Estimates of the non-metallic fraction of Pt was made using the Pt-S CN. For several reduced catalyts (alumina, Vulcan and Black Pearl carbon blacks), there were only Pt-S bonds in the EXAFS spectra. In addition, the XANES spectra were similar to Pt^{+2}. The average CN for these small Pt-S particles on these three catalysts was 3.4. For all other catalysts reduced at 300°C, the fraction of Pt^{+2} was taken as the Pt-S CN/3.4. The remaining Pt is then metallic. The fitted Pt-Pt CN was then divided by the fraction of Pt^0 to get the corrected Pt-Pt CN. From that, the fraction of surface Pt atoms in the metallic particle could be estimated (this fraction is not properly termed “dispersion” since they have S on them) using the correlation of H_2 chemisorption and Pt-Pt CN. Assuming spherical geometry, the size can also be estimated as 1/dispersion x 10 Å. For the catalysts reduced at 500°C, the same approach was taken. However, 2.9 Pt-S, which is the value for BP carbon reduced at 500°C, was used as 100% Pt^{+2}.

Analysis shows that there is a significant fraction (25-50%) of Pt^{+2}, i.e., a high fraction of Pt is bonded to S, in most catalysts.

For example, while silica yields small to moderately sized particles, 25-75 Å, respectively, they also contain a high fraction of sulfur. For most catalysts the fraction of surface Pt atoms is similar to the fraction of Pt^{+2}, i.e, most surface atoms are bonded to S. Thus, there is not a lot of exposed, reduced and unpoisoned Pt. The best support appears to be Nb_2O_5, over which the particles are small-medium in size, but have a much smaller fraction of Pt-S, about 10-15%. These appear to have the greatest potential for development of Pt catalysts utilizing PSA as the source of Pt.

Conclusion

While all catalysts show retention of some S, reasonably small particle sizes with relatively little Pt-S can in some instances be produced using PSA. While the preparation of catalysts using PSA would not, in general, appear to be attractive for catalysts used for hydrogenation reactions, several catalysts might be suitable for oxidation applications such as automobile exhaust catalysts where poisoning by sulfur is less detrimental.

References

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Acknowledgements

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Office of Science (DOE-BES-SC), under Contract No. W-31-109-Eng-38. Work performed at MRCAT is supported, in part, by funding from the Department of Energy under grant number DE-FG02-04ER46106. JRR gratefully acknowledges the support of the National Science Foundation (NSF CTS-0243210).

*Accepted for presentation at the Spring 2005 ACS meeting, Division of Fuel Chemistry.