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A Time-of-Flight SIMS Study of the Chemical Nature of Highly Dispersed Pt on Alumina

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Time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been employed to examine the chemistry of highly dispersed Pt on alumina. In particular, we have characterized various negatively charged Pt cluster ions emitted from Pt powder and fresh and discharged 0.6% Pt/Al_2O_3 after bombardment with 25-keV Ga^+ ions. For Pt powder, PtO^- and PtO_2^- dominate the spectrum of negative ions, which indicates the presence of surface Pt oxides. The most important observation, however, is that $PtCl^-$, $PtClO^-$, and $PtCl_2^-$ cluster ions dominate the negative ion spectrum of 0.6% Pt/Al_2O_3. These chlorinated Pt ions provide direct spectroscopic evidence that some Cl atoms are still bound to Pt after high-temperature oxidation and reduction. © 1994 Academic Press, Inc.

INTRODUCTION

Chlorinated Pt/Al_2O_3 is the most commonly used petroleum reforming catalyst. The role of chlorine is generally believed to be to enhance the acidity of the alumina substrate (1). It has also been suggested that an oxychlorinated Pt species formed during catalyst pretreatment may strongly interact with the progressively dehydrogenated alumina support, leading to higher metallic dispersions after hydrogen reduction (2). In fact, chlorine or chlorine-containing compounds are widely used in redispersion of Pt in spent reforming catalysts during catalyst regeneration (3–5). A question remains, however, as to whether some Cl atoms are still bound to Pt following hydrogen reduction (6–8). Most recent XPS studies on 4–10% Pt/Al_2O_3 suggest that Pt is present in a metallic form (8). Unfortunately, the overlap of Al(2*p*) and Pt(4*f*) peaks in XPS (9) for the Pt/Al_2O_3 system prevents making an accurate measurement of the amount of Pt that is present in an oxidized state and as Pt^0. For practical reforming catalysts with the Pt loadings less than 1 wt%, it is exceedingly difficult to detect the existence and chemical state of Pt with XPS.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) offers a potentially powerful new approach to characterizing these materials. In TOF-SIMS, a short pulse of energetic ions (e.g., Ar, Ga, Cs, etc.) bombards the target. The secondary ions (either positively or negatively charged) desorbed from the surface are extracted into a field-free flight tube where they are separated based on their flight time. Since all ions associated with each primary pulse are detected, the transmission efficiency for TOF-SIMS is 10^3–10^4 higher than that of conventional SIMS instruments employing scanning detectors such as magnets or quadrupoles. Although TOF-SIMS is a potentially powerful tool for obtaining molecular structure information of inorganic, organic, and biological compounds (10–12), few studies have utilized TOF-SIMS in the investigation of oxide-supported catalytic systems.

Studies of molecular clusters desorbed from inorganic solids are potentially interesting if we can be sure that these clusters in some way represent the chemistry of the surface. It is possible, for example, that observed clusters can be formed by recombination during the desorption event (10). Yu has proposed, however, that since the electron affinity of negatively charged ions is usually low that unless the cluster components are in their ground vibrational states, electron detachment is very favorable. To produce ground state molecules it is most likely that they are synthesized from nearest neighbors on the surface (13). For many inorganic systems, then, the composition of positive ions may arise from recombination while negative ions are more likely to be formed by direct lattice fragmentation.

In this work, we utilize TOF-SIMS to characterize a variety of negatively charged clusters produced from Pt powder, fresh 0.6% Pt/Al_2O_3 and 0.6% Pt/Al_2O_3 discharged from a heptane reforming reaction. The cluster ions of $PtCl^-$, $PtClO^-$, and $PtCl_2^-$ observed in fresh and heptane reaction discharged 0.6% Pt/Al_2O_3 present the first spectroscopic evidence that some Cl atoms are still bound to Pt after catalyst pretreatment. The presence of

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these Pt chlorides indicate that the influence of Cl during reforming reactions might not be limited to the modification of alumina acidity alone. These results suggest that a study of the correlation between the concentration of these chlorides with the reforming reaction activity, selectivity, and catalyst stability should provide useful insight into the role of these chlorides in catalytic reforming reactions.

EXPERIMENTAL

The instrument used in this experiment is a Kratos TOF-SIMS reflectron based mass spectrometer equipped with a FEICO liquid metal gallium ion gun. The ion gun was typically operated at 10 kHz repetition rate with pulse width of 30 ns and a current of 600 pA. The total ion dose was between 10^8 and 10^9 Ga^+ ions. The probing area of the sample surfaces was 300 × 300 μm, corresponding to about 4×10^{12} surface atoms. Charge compensation for the insulating samples was achieved by flooding the samples with 30-eV electrons between primary ion pulses. The analyzer has a nominal mass resolution of 1 part in 10,000 amu with transmission efficiency of 50%. Total acquisition time was between 2 and 20 min.

Pt powder was obtained from Aldrich without further treatment. A 20 : 1 (mole ratio) NaCl/Pt physical mixture was made by mixing Pt powder with ground NaCl powder. A 0.6% Pt/Al_2O_3 sample was prepared by impregnating γ-Al_2O_3 with chloroplatinic acid (H_2PtCl_6) followed by drying at room temperature, calcining in air at 800 K, and then reducing in flowing hydrogen at 700 K for 1 h. The average particle size of the Pt is 10 ~ 12 Å. Discharged 0.6% Pt/Al_2O_3, which had been subjected to a 24-h heptane reforming reaction at 800 K, was also analyzed. Both the fresh and discharged catalysts were exposed to air after being cooled to room temperature.

RESULTS AND DISCUSSION

To gain a better understanding of supported catalysts, we first examine the TOF-SIMS spectra of Pt powder. As shown in Fig. 1a, there are a series of intense negative ion clusters associated with Pt. The most prominent peaks between 180 and 300 amu can be assigned to Pt^-, PtO^-, PtO_2^-, and $Pt(OH)_3^-$. Due to the association with hydrogen, the distribution of Pt isotopes does not correspond to the expected natural abundance. By sputtering the sample to remove hydrogen, we could obtain the correct isotope distribution of Pt^- (not shown). In comparison, the SIMS spectrum of the positive ions shown in Fig. 1b shows mainly Pt^+, $Pt(OH)^+$, $PtAl^+$, $PtK^+(PtCa^+)$, $Pt[(H_2O)_2(OH)]^+$, and PtK_2^+. The intensity of positively charged Pt clusters is an order of magnitude lower than that found for the negative ions.

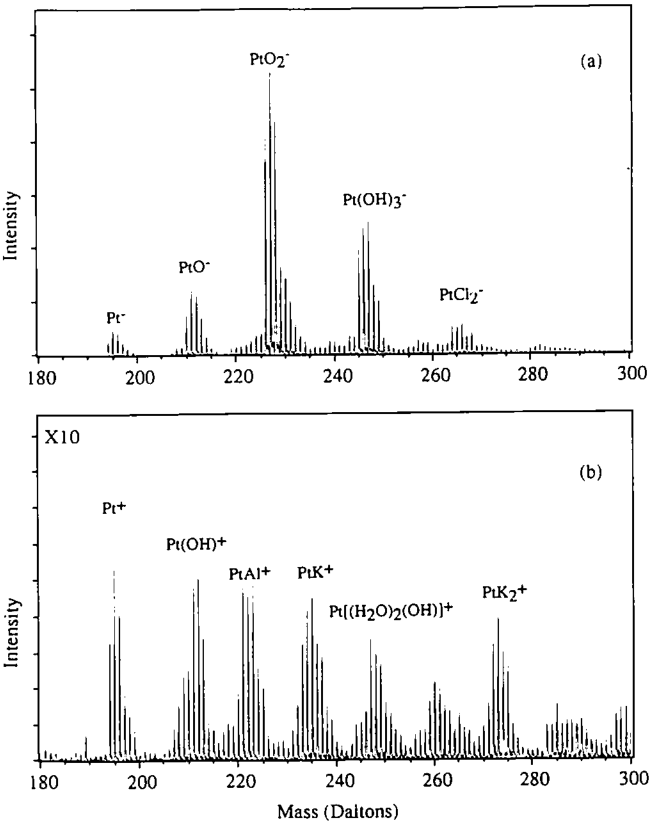

FIG. 1. TOF-SIMS of Pt powder in the mass range 180–300 amu: (a) negative ions and (b) positive ions. Note that the spectrum in (b) is magnified ten-fold.

The negatively charged Pt cluster ions that are associated with oxygen indicate the presence of surface oxides and hydroxides. In fact, we observed the similar distribution of negative ions in the SIMS spectra of PtO_2 (not shown). On the other hand, $PtAl^+$, PtK^+, and PtK_2^+ cluster ions reflect metal contamination in the Pt powder sample. As we have discussed before, these positively charged bimetallic Pt clusters probably form through the recombination of sputtered Pt and K^+ (or Al^+) above the surface. Since the positive ion yield of Al and K are at least 10^3 higher than that of Pt (14), strong intensity of Al and K associated Pt cluster ions does not necessarily mean that the surface is covered with K or Al. The surface concentration of these metal contaminates are likely less than 1% of a monolayer.

The TOF-SIMS spectrum of fresh 0.6% Pt/Al_2O_3 is shown in Fig. 2a. Clusters between 180 and 300 amu arise from Pt^-, PtO^-, $PtCl^-$, $PtClO^-$, and $PtCl_2^-$ ions. In the lower mass range, intense peaks of O^- and Cl^- were observed. The intensity ratio of O^-/Cl^- is 10 times higher than that found from Pt powder. Other major peaks observed in the lower mass range are O_2^-, AlO^-, and

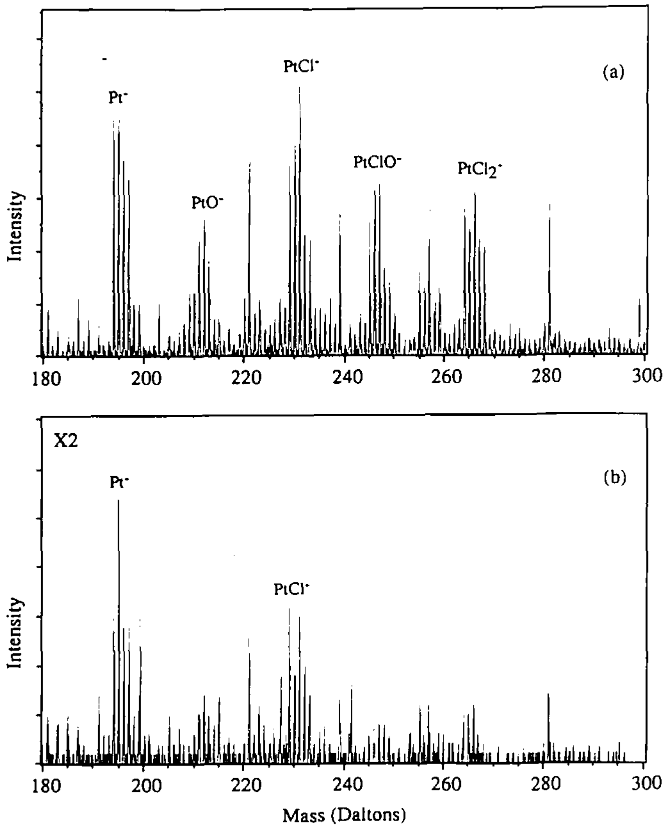

FIG. 2. (a) TOF-SIMS of fresh 0.6 wt% Pt/Al_2O_3 in the mass range of 180–300 amu (negative ions) and (b) TOF-SIMS of discharged 0.6 wt% Pt/Al_2O_3 following 24 h of heptane reforming reactions (negative ions). The spectrum in (b) is magnified two-fold.

AlO_2^-. This is consistent with the negative ion spectrum obtained from aluminum oxide (15, 16). For positive ions, the intensity of Al^+ is 100 times higher than surface impurities such as Si^+, Na^+ and K^+, indicating the surface is predominantly alumina. Following the heptane reforming reaction, the intensity of Pt^- cluster ions was reduced by 70% (Fig. 2b) for the discharged 0.6% Pt/Al_2O_3. The most intense species are Pt^- and $PtCl^-$ ions.

It is clear from this data that high quality TOF-SIMS spectra can be obtained from 0.6% Pt on supported catalysts in the static mode. Since γ-Al_2O_3 has a surface area of 200 m^2/g, and assuming an ideal Pt dispersion of 1, the Pt coverage on the surface is less than 0.5% monolayer. Since the Pt loading for most of the practical catalysts is between 0.1 and 1%, our results show that it is feasible to detect Pt and other metals in small quantities under static SIMS condition. Taking into account that Pt has a relatively low ion yield, the sensitivity for detecting other elements should be considerably higher.

The substantial decrease in the intensity of negatively charged Pt clusters in discharged 0.6% Pt/Al_2O_3 is consistent with a large portion of the Pt surface being covered with carbonaceous (coke) deposits following prolonged heptane reactions. Our TOF-SIMS spectra of the discharged catalyst also show that we are capable of detecting much less than 0.5% monolayer Pt. Hence, in future studies, it may be valuable to compare the Pt cluster intensity between fresh and discharged catalysts and to correlate these results with reactivity decay.

Negatively charged Pt related cluster ions observed in TOF-SIMS of fresh and discharged 0.6% Pt/Al_2O_3 also reveal information about the chemical environment of highly dispersed Pt. As shown in Fig. 2a, PtO^- clusters are clearly seen. The presence of these species is consistent with the notion that small Pt particles are covered with chemisorbed oxygen upon exposure to the air under ambient conditions. Most interestingly, however, is the strong intensity of chlorinated Pt ions. Does the observation of these chlorinated Pt clusters suggest the presence of Pt chlorides? Is it possible that these cluster ions result from the recombination of ejected Pt with ejected chlorine contaminates? To confirm the origin of the $PtCl_x^-$ clusters in our studies, we performed TOF-SIMS on a 20 : 1 (mole ratio) NaCl/Pt physical mixture. If $PtCl_x^-$ ions result from the recombination of Pt and Cl contaminates above the surface, increasing the Cl concentration in the vicinity of Pt atoms should significantly increase the intensities of $PtCl_x^-$ ions. As shown in Fig. 3, the physical mixture yields Pt clusters which are virtually identical to those found from Pt powder. Moreover, negatively charged chlorinated Pt clusters dominate the SIMS spectrum of 0.6% Pt/Al_2O_3 even though the surface oxygen concentration is overwhelmingly larger than that of chlorine. These experimental results strongly suggest that some chlorine atoms are bound directly to Pt. These platinum chlorides are likely due to incomplete decomposition of impregnated chloroplatinic acid and/or reaction of Pt with Cl^- in the oxide during catalysts pretreatment. The strong bond between Pt–Cl–Al^{3+} may prevent complete removal of Cl from Pt during the oxidation and reduction process.

This direct spectroscopic evidence that some Cl atoms are still bound to Pt indicate that the role of Cl in Pt/alumina during reforming reactions is not limited to modification of the acidity of the alumina substrate alone. How these platinum chlorides influence the hydrocarbon reforming reactivity and selectivity, and catalysts stability remains an open question. Since the ion yield for the same species can vary significantly depending on the surface chemical environment in SIMS, we cannot quantitatively determine the percentage of Pt bound to Cl. However, for a series of similar types of catalysts, the correlation between $PtCl_x^-$ cluster intensity and catalytic reactivity and selectivity, catalyst stability should yield quantitative information about the role of these platinum chlorides.

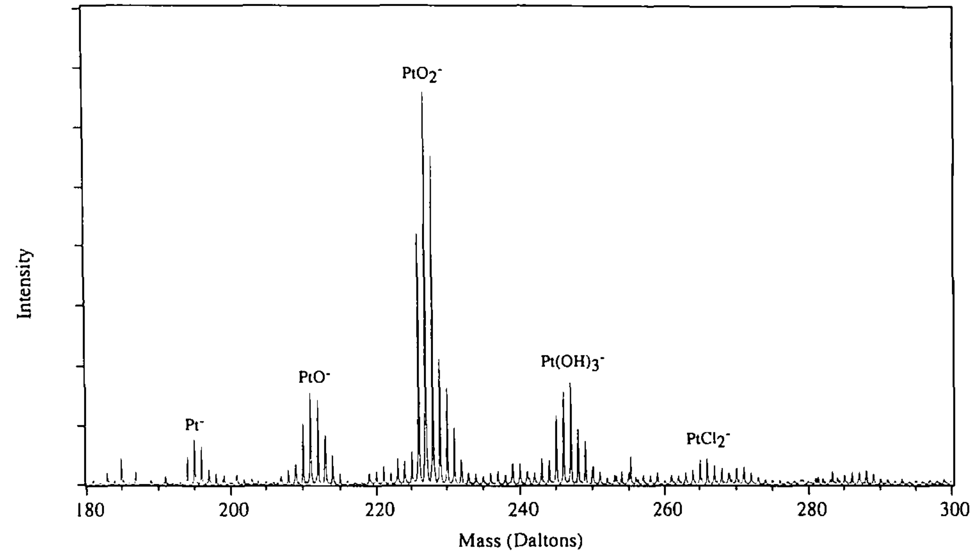

FIG. 3. TOF-SIMS of 20 : 1 (mole ratio) NaCl/Pt physical mixture (negative ions).

CONCLUSIONS AND PROSPECTS

Our results show that TOF-SIMS is capable of detecting less than 0.5% monolayer Pt on supported catalysts. The significant intensity decrease of Pt clusters following the use of the catalyst in heptane reforming reactions is consistent with Pt being covered by coke deposits. Most importantly, it is possible to unravel the chemical environment of Pt through detection of negatively charged Pt related clusters. In this case, we find that some Cl atoms are still bound to Pt even after high-temperature oxidation and reduction.

The sensitivity of these techniques also appears to be sufficient to examine the behavior of multimetallic systems. As shown in Fig. 4, clusters with up to 12 Pt atoms are observed to be desorbed from Pt powder. If it is possible to detect multimetallic clusters for higher metal loading catalysts, we should also be able to elucidate the metal–metal interactions that occur in multimetallic catalysts. One such example is the Pt–Sn/Al_2O_3 reforming catalyst. If Sn forms an alloy with Pt, negatively charged Pt_xSn_y clusters should be detectable in SIMS. If Pt and Sn form separate islands, we expect isolated Pt and Sn clusters in the SIMS spectra of negative and positive ions.

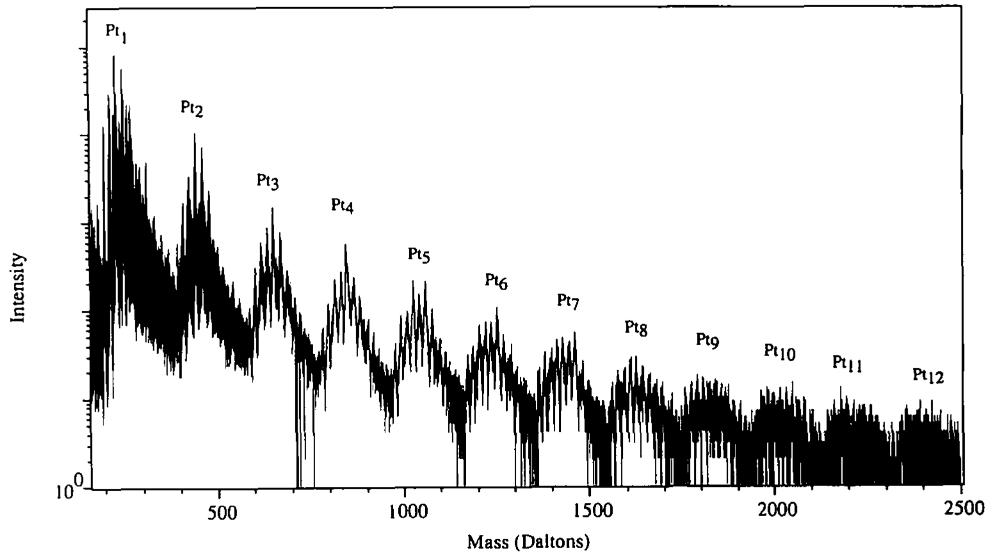

FIG. 4. TOF-SIMS of Pt powder in the mass range of 180–2500 amu (negative ions). Note that the intensity is given in a log scale.

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REFERENCES

1. Srivastava, R. D., "Heterogeneous Catalytic Science." CRC Press, Boca Raton, FL, 1988.
2. Malet, P., Munuera, G., and Caballero, A., *J. Catal.* **115,** 567 (1989).
3. Kearby, K. K., Cranford, J. P., Thorn, E., and Hinlicky, J. A., U.S. Patent 3, 134, 732.
4. Parmaliana, A., Fruster, F., Mezzapica, A., and Giordano, N., *J. Catal.* **111,** 235 (1988).
5. Parmaliana, A., Fruster, F., Mezzapica, A., and Giordano, N., *in* "Catalysts Deactivation" (B. Delmon and G. F. Froment, Eds.). Elsevier, Amsterdam, 1987.
6. McHenry, K. W., Bertolacini, R. J., Brennan, H. M., Wilson, J. L., and Seelig, H. S., *in* "Proceedings, Second International Congress on Catalysis, Paris, 1960," Vol. II, paper 117. Technip, Paris, 1961.
7. Johnson, M. F. L. and Keith, C. D., *J. Phys. Chem.* **67,** 200 (1963).
8. Sethuraman, A. R. and Davis, B. H., *Catal. Lett.* **18,** 401 (1993).
9. "Handbook of X-ray Photoelectron Spectroscopy" (C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moudler, and G. E. Muilenberg, Eds.). Perkin–Elmer Corporation, 1979.
10. Winograd, N. and Garrison, B. J., *in* "Ion Spectroscopies for Surface Analysis" (A. W. Czanderna and D. M. Hercules, Eds.). Plenum, New York, 1992.
11. "Secondary Ion Mass Spectrometry—Principles and Applications" (J. C. Vickerman, A. Brown, and N. M. Reed, Eds.). Oxford Science Press, Oxford, 1989.
12. Benninghoven, A., Rudenauer, F. G., and Werner, M. W., "Secondary Ion Mass Spectrometry—Basic Concepts, Instrumental Aspects, Applications, and Trends." Wiley, New York, 1987.
13. Yu, M. L., *Appl. Surf. Sci.* **11/12,** 196 (1982).
14. Storms, H. A., Brown, K. F., and Stein, J. D., *Anal. Chem.* **49,** 2023 (1977).
15. Benninghoven, A., *Surf. Sci.* **35,** 427 (1973).
16. Benninghoven, A., *Surf. Sci.* **53,** 596 (1975).