

Evidence of Alloy Formation during Reduction of Platinized Tin Oxide Surfaces

STEVEN D. GARDNER,* GAR B. HOFLUND,* MARK R. DAVIDSON,*
AND DAVID R. SCHRYER†

*Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611,
and †NASA Langley Research Center, Hampton, Virginia 23665-5225

Received April 26, 1988; revised August 23, 1988

Ion scattering spectroscopy, Auger electron spectroscopy, and electron spectroscopy for chemical analysis have been used to examine a platinized tin oxide catalyst surface before, during, and after reduction by annealing under vacuum at 250 to 450°C. These techniques were then used to examine the reduced surface after a room-temperature, low-pressure oxygen exposure. The spectral results and the behavior of the reduced surface toward oxygen exposure both indicate that a Pt/Sn alloy is produced during reduction. © 1989 Academic Press, Inc.

INTRODUCTION

Platinized tin oxide surfaces have proven to be efficient, low-temperature, CO-oxidation catalysts which makes them useful in CO₂ laser applications (1, 2). However, relatively little is understood about the oxidation of CO over Pt supported on reducible oxides, and attempts to understand the mechanism are in the initial stages (3). In order to understand the mechanism, it is necessary to determine the surface composition, chemical states of the surface species, and types of interactions between the surface species. It also appears that surface hydrogen has a large influence on the catalytic behavior of these surfaces (4).

Alumina-supported Pt/Sn bimetallic catalysts are important in hydrocarbon reforming processes (5-7). The addition of Sn generally leads to prolonged catalyst lifetime through an improved resistance toward coke formation. Furthermore, the reaction selectivity is enhanced toward aromatization which results in an increase in the reformate octane number.

It is important to understand the nature of the Pt/Sn interaction in both the CO oxidation catalysts and the reforming catalysts. This point has been controversial for

many years with regard to Pt/Sn reforming catalysts. Many studies suggest that a Pt/Sn alloy is formed during reduction (8, 9) while others suggest that tin is present as an oxide (10-15). Recent studies by Davis and co-workers (16, 17) are particularly convincing in demonstrating that an alloy forms during reduction using electron spectroscopy for chemical analysis (ESCA) and *in situ* X-ray diffraction. The diffraction patterns indicate that the composition of the alloy is PtSn, but other alloys such as Pt₃Sn may form at different metal loadings.

The purpose of this present study is to investigate the Pt/Sn interaction on a platinized tin oxide surface similar to those used in CO oxidation. Auger electron spectroscopy (AES), ion-scattering spectroscopy (ISS), and ESCA have been used to examine the heavily Pt-loaded tin oxide surface before, during, and after reduction of the surface by vacuum annealing and after exposure of the reduced surface to oxygen at room temperature.

EXPERIMENTAL

A tin oxide film was prepared on a titanium foil using a spray hydrolysis method described previously (18). The film was about 5000 Å thick, and it contained signifi-

cant amounts of hydrogen (19–23). Pt was deposited by impregnating the tin oxide film in a saturated chloroplatinic acid solution. Then the film was rinsed with distilled water and calcined in air at 500°C for 1 h.

The sample was inserted into a vacuum system (base pressure of 10^{-10} Torr) which contained a double-pass cylindrical mirror analyzer (Perkin–Elmer PHI Model 25-270) used for AES, ISS, and ESCA. AES was performed in the nonretarding mode using a 3-keV, 10- μ A primary beam with a 0.2-mm spot diameter. ISS spectra were collected in the nonretarding mode using a 147° scattering angle and pulse counting detection (24). A 1-keV, 100-nA $^4\text{He}^+$ primary beam was defocused over a 1-cm-diameter area to minimize sputter damage. ESCA spectra were collected in the retarding mode using a 25-eV pass energy and $\text{MgK}\alpha$ excitation. The sample was heated radiantly using a tungsten filament, and its temperature was measured using an optical pyrometer.

RESULTS AND DISCUSSION

An AES spectrum and an ISS spectrum taken from the as-prepared surface are shown in Fig. 1. The AES spectrum exhibits peaks due to Pt, Sn, O, Cl, and C.

The large Pt feature at 64 eV indicates that the surface is heavily loaded with Pt which is consistent with the ISS spectrum shown in Fig. 1b. Several features appear in the ISS spectrum. The Sn peak is a shoulder on the Pt peak, and the peak at $0.6 E/E_0$ is due to contamination (probably Na). The secondary ions apparently desorb with a threshold at $0.12 E/E_0$. This suggests that charging is occurring on this surface which shifts the elemental features to higher E/E_0 than predicted by the binary collision model (25). A very small oxygen peak is at $0.49 E/E_0$, and the peak at 0.28 may be due to C. A crude estimate of the elemental cross sections (26) and surface composition suggests that the outermost layer of atoms contains about 60 at.% Pt.

Next the sample was annealed under vacuum in 50°C increments from 250 to 450°C for 30 min at each temperature. The ISS spectra taken after annealing at 300 and 450°C are shown in Figs. 2a and 2b respectively. Several changes have occurred after annealing the as-prepared sample at 300°C. The tin shoulder has become a more prominent peak, and its size has increased relative to the Pt peak. Charging is no longer apparent on this surface so the peak posi-

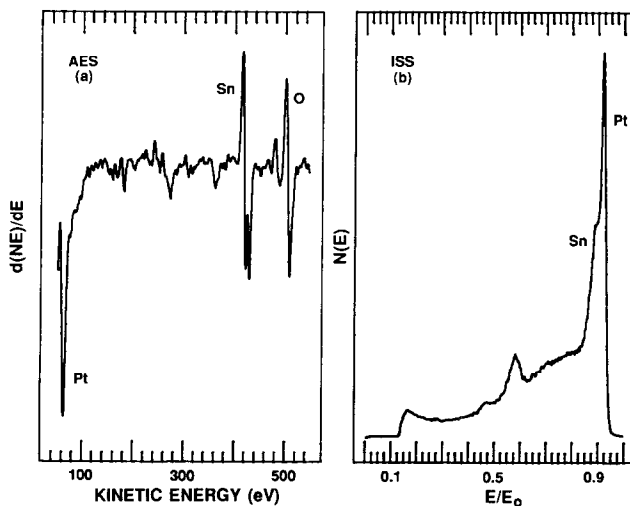


FIG. 1. (a) AES and (b) ISS spectrum taken from the as-prepared sample after insertion into the vacuum system and pumpdown.

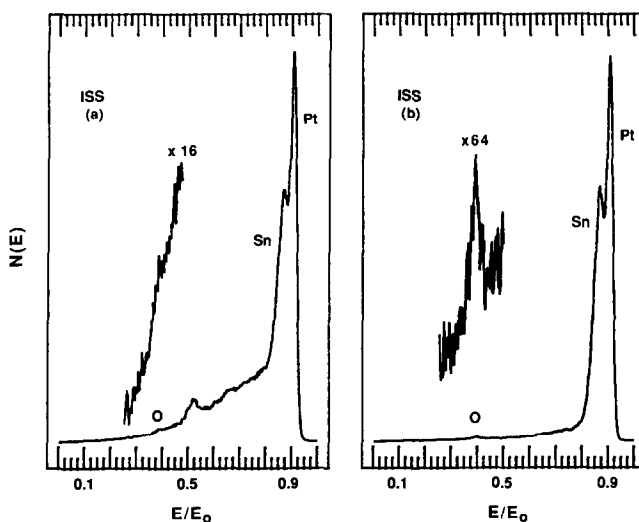


FIG. 2. ISS spectra taken after annealing the sample in vacuum at (a) 300°C and (b) 450°C.

tions are approximately those predicted by the elastic binary scattering equation. Both the contamination peak at $0.52 E/E_0$ and the O peak at $0.39 E/E_0$ are reduced in intensity, and the C peak is no longer apparent. Furthermore, the background intensity is significantly decreased from that observed in Fig. 1b. A possible explanation is discussed below.

The trends observed in annealing to 300°C are continued by annealing to higher temperatures. Figure 2b shows that the surface formed after annealing at 450°C is very different from the as-prepared surface. In comparing Figs. 2a and 2b, the Sn peak is increased with respect to the Pt peak and is even more well defined. The contaminant peak is no longer present, and the oxygen peak apparently is further decreased in intensity. Also, the inelastically scattered ions composing the background are greatly decreased in intensity. Several similarities are observed between the ISS spectrum shown in Fig. 2b and the spectra taken from Pt₃Sn surfaces in previous studies (see Ref. 27, Fig. 5b). Both surfaces produce comparable inelastic backgrounds and display similar Pt, Sn, and O features with regard to peak shapes and relative peak heights. The small inelastic background is characteristic

of spectra taken from metallic surfaces where the electron mobility is sufficiently high to rapidly neutralize inelastically scattered ions. The fact that the ISS spectrum taken from a reduced platinized tin oxide surface closely resembles an ISS spectrum taken from a Pt/Sn alloy surface rather than an ISS spectrum taken from a nonreduced platinized tin oxide surface supports the assertion that a Pt/Sn alloy forms during reduction of the platinized tin oxide surface.

The AES spectrum shown in Fig. 3a and the Sn 3d ESCA spectrum shown in Fig. 3b were also taken from the sample after annealing at 450°C. Comparing Figs. 1a and 3a shows that the Pt-to-Sn peak height ratio essentially remains constant at a value of 1.12 during the annealing. However, the Sn-to-O peak height ratio increases from 1.10 to 1.37 during annealing by either migration of oxygen below the near-surface region or desorption of oxygen from the surface. These facts suggest an increased interaction between Sn and Pt in the near-surface region. The Sn 3d ESCA spectrum shown in Fig. 3b has a dominant peak at a binding energy of 486.4 eV. This feature is due to Sn present as an oxide, but it is difficult to determine the precise nature of this oxide from the Sn 3d features as discussed

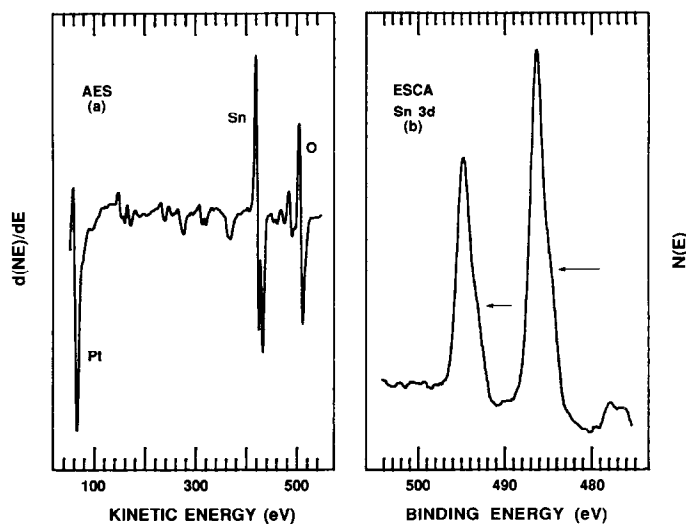


FIG. 3. (a) AES spectrum and (b) ESCA spectrum taken after annealing the sample under vacuum at 450°C.

previously (5). The arrows in Fig. 3b indicate shoulders which are apparent at an approximate binding energy of 484.5 eV. This binding energy suggests that Sn is also present in metallic or alloyed form. Only the oxidic feature at 486.4 eV is present before annealing the sample so tin oxide is reduced to metallic or alloyed Sn during the vacuum annealing, which is a reductive process. A study by Paffett and Windham (28) provides evidence that the form of the tin is alloyed rather than metallic. They deposited metallic tin on a Pt(111) surface and showed that an alloy forms during annealing at or above 450 K. The 450°C annealing temperature used in this present study then should result in alloy formation. Thus, the ISS, AES, and ESCA results are all consistent with the assertion that a Pt/Sn alloy is formed during the reduction of platinized tin oxide.

Similar annealing treatments have been carried out on tin oxide films which did not contain Pt (18, 21, 23, 29). In these studies vacuum annealing to 450°C or above did not result in reduction of the tin oxide to metallic tin. Water of hydration or hydroxyl groups are removed from the surface by vacuum annealing and a portion of the SnO₂

is reduced to SnO, but metallic tin does not form. In fact, a tin oxide surface which has been reduced by argon-ion sputtering is actually enriched in oxygen by vacuum annealing through migration of bulk oxygen to the surface (29). These observations demonstrate the important role which Pt plays in reducing the tin to metallic form which then alloys with the Pt.

Next, the oxidative behavior of this surface was examined by exposing the sample to 1×10^{-7} Torr of O₂ for 1 h at room temperature. ISS and ESCA spectra taken from this surface are shown in Figs. 4a and 4b, respectively. The expanded O feature in the ISS spectrum indicates that the amount of oxygen in the outermost surface layer of atoms increases by about 30% during the oxygen exposure. By comparison of Figs. 2b and 4a, it can be seen that the oxygen exposure has increased the height of the Sn peak with respect to the height of the Pt peak. This behavior is characteristic of Pt/Sn alloys as described in previous studies (27, 30). The differences between the ISS spectra shown in Figs. 2b and 4a are quite similar to those obtained by exposing a Pt₃Sn alloy surface to low-pressure oxygen at room temperature (see Ref. 30, Figs. 5a

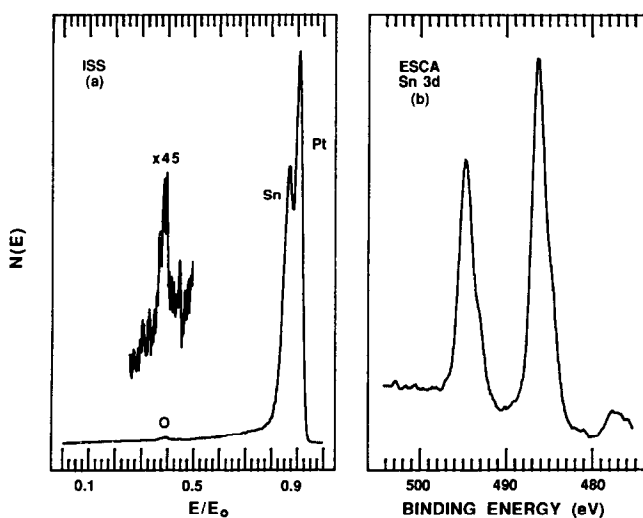


FIG. 4. (a) ISS and (b) ESCA spectra taken after exposing the 450°C-reduced surface to 10^{-7} Torr of O_2 for 1 h at room temperature.

and 5b). Also, there is a very slight reduction in the size of the shoulders on the ESCA Sn 3d peaks. The extent of this reduction is so small that it is necessary to hold an expanded version of Fig. 3b over Fig. 4b in order to observe the decrease in the size of the shoulder. The nonreactive behavior of this surface toward oxygen as detected by ESCA is also characteristic of Pt/Sn alloy surfaces (30, 31). Using ESCA, Cheung (31) found that Sn alloyed with Pt exhibits greater resistance toward oxidation than metallic Sn. It appears that the Pt/Sn alloy bond causes the Sn to be less susceptible to oxidation. Therefore, this finding also supports the assertion that the shoulders observed in the ESCA Sn 3d spectra are due to alloyed Sn rather than elemental Sn, but quantification of the rates of oxygen adsorption on a Pt/Sn alloy and polycrystalline Sn has not yet been carried out.

It is interesting to compare the oxidative and reductive properties of platinumized titania with those of platinumized tin oxide presented in this study since both titania and tin oxide are reducible, conductive oxides. A recent study by Hoflund *et al.* (32) of platinumized titania shows that the outermost

layer always exhibits a large ISS O peak. Reduction of this surface results in encapsulation of the Pt by TiO , and oxygen exposure forms TiO_2 which migrates back off the Pt. This behavior is quite different than that for the platinumized tin oxide surface for which the oxygen lies under the Sn and Pt. It is interesting to note that oxygen exposure of a polycrystalline tin surface results in incorporation of oxygen beneath an outermost layer of tin atoms (33). One possible explanation for the dramatically different behavior of platinumized tin oxide and platinumized titania is that tin oxide is more readily reduced to metal than titania in the presence of Pt. Reduction of a platinumized tin oxide surface by annealing under vacuum then results in the formation of a Pt/Sn alloy rather than encapsulation of the Pt by reduced oxidic support species as observed on platinumized titania.

CONCLUSIONS

The Pt/Sn interaction at a platinumized tin oxide catalyst surface has been examined using ISS, AES, and ESCA after reduction of the surface by vacuum annealing and exposure of the reduced surface to O_2 . After reduction ESCA shows that metallic or al-

loyed tin is formed, AES shows an increase in the Sn-to-O peak height, and the ISS spectrum becomes similar to that taken from a Pt/Sn alloy surface. Furthermore, exposure to oxygen at room temperature induces changes similar to those found for a Pt₃Sn alloy surface. These facts all support the assertion that a Pt/Sn alloy is formed during reduction.

ACKNOWLEDGMENT

Financial support for this research was received from NASA under Grant NAG-1-794.

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