EFFECT OF PRETREATMENT ON A PLATINIZED TIN OXIDE CATALYST
USED FOR LOW-TEMPERATURE CO OXIDATION

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ABSTRACT

A commercial platinized tin oxide catalyst used for low-temperature CO oxidation has been characterized using ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES) and electron spectroscopy for chemical analysis (ESCA) before and after reduction in 40 Torr of CO for 1 hour at various temperatures from 75 to 175°C. The reduction results in loss of surface oxygen, formation of metallic tin, conversion of platinum oxides to Pt-O-Sn and $Pt(OH)_2$ and a small amount of metallic Pt which alloys with the tin. These results should be useful in understanding how the pretreatment temperature affects the catalytic activity of platinized tin oxide toward CO oxidation.

INTRODUCTION

Low-temperature, CO-oxidation catalysts are important for long-life, closed-cycle operation of CO_2 lasers which are used in remote sensing applications such as weather monitoring from space vehicles. The electrical discharge in CO_2 lasers decomposes relatively small amounts of CO_2 into CO and O_2. While the power output of the laser decreases slowly with loss of CO_2 and buildup of CO, it decreases dramatically with buildup of very low O_2 concentrations. A solution to this problem is to recombine the discharge products back into CO_2 using a heterogeneous catalyst incorporated in some manner into the laser system. In order to meet volume and weight constraints, it is necessary for the catalyst to have a high activity at low temperatures (< 100°C).

Stark et al. (1) have found that platinized tin oxide with or without a Pd modifier is an effective low-temperature CO oxidation catalyst. Based on this finding, numerous studies of platinized tin oxide systems relating to CO oxidation have been carried out (2). A 2 wt. % platinized tin oxide catalyst is now commercially available from Engelhard Industries. Schryer et al. (3) have studied the catalytic behavior of this material toward CO oxidation and found that the activity of the catalyst depends upon the pretreatment conditions used as shown in figure 1. For the pretreatment and reaction conditions used (see figure 1), the unpretreated catalyst exhibits the lowest long-term activity. A 100°C pretreatment in CO greatly enhances the long-term activity, and a further enhancement occurs by carrying out the pretreatment at 125°C. Utilizing higher pretreatment temperatures up to 225°C yields no change in the catalytic activity compared to the 125°C pretreatment. In order to understand

how platinized tin oxide catalysts function in converting CO and O_2 to CO_2 at low temperatures, it is necessary to characterize the composition and chemical states of the species present at these surfaces. This has been accomplished in this study using several surface chacterization techniques including ion scattering spectroscopy (ISS), electron spectroscopy for chemical analysis (ESCA) and Auger electron spectroscopy (AES) to examine the surface of the Engelhard catalyst before and after pretreatment in CO as a function of pretreatment temperature. It is anticipated that these studies will lead to a better understanding of this catalytic process and eventually to the development of improved catalysts for this application.

EXPERIMENTAL

The Engelhard platinized tin oxide catalyst has an average particle size of 1 μm and a BET surface area of 6.9 m^2/g. For the characterization studies the powder was pressed into thin disks about 1 cm in diameter. These were inserted directly into the ultrahigh vacuum system for pretreatment and characterization. Pretreatment was carried out by moving the sample into a preparation chamber (base pressure of 10^{-7} Torr), adjusting the pressure to 40 Torr in CO and heating the sample at the prescribed temperature for 1 hour. Then the sample was allowed to cool while the preparation chamber was pumped down to 10^{-7} Torr before moving the sample into the characterization chamber (base pressure of 10^{-11} Torr) for analysis by ISS, ESCA and AES. The samples were heated at 75, 100, 125 and 175°C in the preparation chamber using a sample heater (4) which did not expose the reducing gas to hot spots which would have dissociated the CO. Two different as-prepared samples were analyzed without prereduction, and the results were found to be reproducible. A new sample was prepared and introduced into the analysis chamber for each reduction temperature used.

ISS, ESCA and AES data were taken using a double-pass cylindrical mirror analyzer (CMA) (Perkin-Elmer PHI Model 25-270) as the charged-particle energy analyzer. ISS spectra were collected in the nonretarding mode using a 147° scattering angle and pulse counting detection (5). A 1-keV, 100 nA $^4He^+$ primary ion beam was defocused over a 1-cm-diameter area, and spectra were collected as quickly as possible (typically 90 s) to minimize beam damage. AES was performed in the nonretarding mode using a 3-keV, 10-μA primary electron beam with a 0.2-mm spot diameter. ESCA was performed in the retarding mode using Mg Kα excitation and 50-eV pass energy for collection of survey spectra and 25 eV for obtaining elemental lineshape information.

RESULTS AND DISCUSSION

An ESCA survey spectrum taken from the as-received, Engelhard platinized tin oxide catalyst is shown in figure 2. The peaks present of significant size are due only to O and Sn, and no peaks due to C or other typical contaminants appear. In fact, this spectrum is essentially identical to an ESCA spectrum obtained from a very clean tin oxide surface. It is most interesting that the predominant Pt 4f peaks are so small that they cannot be readily discerned in this spectrum. A corresponding Auger spectrum taken from the same surface is shown in figure 3. Again, the predominant features are due to Sn and O, and this spectrum is similar to one obtained from a clean tin oxide surface. However, a feature due to Pt appears at about 64 eV. It can be described as an edge rather than a typically shaped Auger peak. Similar Pt

features have been observed in a study of the electrochemisorption of Pt on tin oxide (6). This feature is more prominent than the Pt ESCA peaks in figure 1. In agreement with the ESCA data, no contaminant peaks are apparent in this Auger spectrum. As the catalyst is reduced at various temperatures, very small changes are observed in the ESCA and Auger spectra corresponding to figures 1 and 2 but taken from the reduced surfaces. Therefore, these survey spectra are not shown.

ISS is a particularly useful technique for examining catalytic surfaces because it is very highly surface sensitive (outermost one or two atomic layers). ISS spectra taken before (a) and after (b-e) reduction are shown in figure 4. The spectrum shown in (a) consists of peaks due to O, Sn, and Pt, and the high inelastic background is characteristic of ISS spectra taken from nonmetallic surfaces. In such a case inelastically scattered ions are not efficiently neutralized since the electron mobility at a nonmetallic surface is low so these ions contribute to the background signal. A previous study by Asbury and Hoflund (7) showed that O penetrates beneath the surface during a room-temperature, oxygen exposure of polycrystalline Sn. This suggests that the fairly large O peak in (a) is due to O associated with the Pt and/or perhaps with hydroxyl groups attached to Sn (8) which may lie above the surface.

The ISS spectra shown in figure 1 (b) to (e) were obtained from samples reduced in 40 Torr of CO for 1 hour at 75, 100, 125 and 175°C respectively. All four spectra have two characteristics in common. Firstly, the pretreatments have resulted in negligible inelastic backgrounds which is indicative of the formation of surfaces with a metallic nature. Secondly, the O peak is no longer discernable after the reductions which is also consistent with the observation that the surfaces appear to be metallic. The reductive pretreatment results in an increase in the Sn-to-Pt ratio, and the extent of this increase is greater at higher reduction temperatures. An increase in the ISS Sn/Pt ratio during reduction has been found to be indicative of alloy formation as described in a study of platinized tin oxide model catalysts by Gardner et al. (9). All of the ISS spectra shown in figure 4 were taken using the same instrument settings, but the maximum peak heights vary considerably. Although the variation is not understood, it could be due to changes in ion neutralization probability, surface morphological changes or changes in the concentration of surface hydrogen which have been shown to alter the ISS signal strength (10,11).

Sn 3d ESCA spectra and Sn(MNN) AES spectra taken before and after reduction are shown in figures 5 and 6 respectively. Before pretreatment (air-exposed sample) the Sn $3d_{5/2}$ lineshape and peak position (486.4 eV) indicate that the Sn is present in the +2 or +4 oxidation states most likely as SnO, $Sn(OH)_2$, SnO_2 or $Sn(OH)_4$ and that metallic Sn is absent. As discussed by Hoflund et al. (12), it is not possible to distinguish between these species based on the ESCA Sn 3d peaks, but more specific information can be gained about these species using electron energy loss spectroscopy (ELS) (13,14), valence-band ESCA (8, 14), electron stimulated desorption (ESD) (8, 15) or secondary ion mass spectrometry (SIMS) (16-18). The metallic ESCA Sn $3d_{5/2}$ peak appears at an energy of 484.6eV (19). When a small amount of metallic Sn and a relatively large amount of tin oxides or hydroxides are present, a slight broadening appears on the low binding energy sides of the oxidic ESCA Sn 3d features. This is the case for the 175°C-reduced sample as shown in

figure 5.   Samples reduced at lower temperatures also yield this metallic shoulder, and the amount of metallic Sn produced generally increases as the annealing temperature increases with the most being produced at 175°C.   However, the amounts of metallic Sn produced at 75 and 100°C appear to be similar.   Similar observations can be made by considering the AES Sn(MNN) peaks shown in figure 6.   The high kinetic energy oxidic peak lies at 430 eV while the high kinetic energy metallic peak lies at 423 eV.   The peaks shown in figure 6a are characteristic of oxidic Sn.   When metallic Sn is present, the height of the splitting between the two primary peaks decreases.   This is observed in spectra (b) to (e) taken from the reduced samples.   In agreement with the ESCA Sn 3d spectra, the extent of metallic Sn formation is greater at elevated reduction temperatures with the maximum amount of metallic Sn being produced at 175°C.   Further reduction either for prolonged periods or at higher temperatures than used in this study would undoubtedly result in the production of increased amounts of metallic Sn.

The ESCA O 1s peaks are shown in figure 7.   These were taken before (a) and after reduction at (b) 175°C.   The peak shown in (a) exhibits a distinct asymmetry on the high binding energy side due to the presence of hydroxyl groups which are responsible for a shoulder at about 531.8 eV (8, 20).   It is also possible that the very small shoulder at about 533.0 eV is due to adsorbed water.   This assignment is consistent with results obtained in the study of hydrated polycrystalline tin oxide films by Tarlov and Evans (20). Pretreatment at 75°C slightly reduces the amounts of adsorbed water and hydroxyl groups present while pretreatment at 100°C or above eliminates the adsorbed water and further reduces the concentration of hydroxyl groups.   The 175°C pretreatment results in the lowest surface hydroxyl group concentration.   It is interesting to note that these hydroxyl species are strongly bonded to the surface and require annealing at 600°C in vacuum for nearly complete removal (8, 14, 21).

The O content of the near-surface region is decreased by the pretreatment process.   The AES and ESCA O/Sn atomic ratios obtained at the various pretreatment temperatures are listed in table I.   A decrease in the O/Sn ratio is caused by loss of adsorbed water, a decrease in hydroxyl group concentration, reduction of tin oxides and hydroxides to metallic Sn and reduction of SnO_2 to SnO.   However, the relative importance of these factors cannot be completely assessed from the types of data taken in this study.   The amount of Pt present on these surfaces is so small that changes in the Pt oxidation state, which are discussed below, would not affect the O/Sn atomic ratios presented in table I.   The AES and ESCA results in table I are different both with respect to magnitude and trend.   The AES data indicate that the near-surface region loses about 20% of its O regardless of the reduction temperature.   The ESCA O/Sn atomic ratios are considerably larger than the AES values and decrease monotonically as the pretreatment increases.   Either the ESCA values differ from the AES values due to inaccuracies in the tabulated cross sections or the variation is due to the fact that AES and ESCA probe different volumes of the near-surface region.   If the difference were due only to inaccurate cross sections, then the ESCA O/Sn ratios obtained from the reduced samples would not show such a large variation with reduction temperature.   Thus, the variation is due to the fact the ESCA probes more deeply than AES, which is consistent with mean-free-path arguments also.   The kinetic energies of the ESCA O 1s electrons are 723 eV and the Sn 3d electrons are about 770 eV, while the kinetic energies of the AES O electrons are about 510 eV and the Sn electrons are about 430 eV. The corresponding average mean free paths (λ) are about

6A for ESCA and 4A for AES (24). Since most of the ESCA and AES electrons originate within a depth of about 3λ, ESCA probes about 18 A beneath the surface while AES probes about 12 A . Then, the data of table I indicate that the near-surface region probed by AES contains less O than the region probed by ESCA for the untreated sample and samples reduced from 75 to 175°C. Reduction at any of the temperatures used causes the AES O/Sn ratio to drop from 1.32 to about 1.06 whereas to ESCA O/Sn ratio decreases monotonically as the reduction temperature increases. The essentially constant AES value probably results from a competing process, i.e., O leaving the surface as CO_2 during the reduction and O migrating to the near-surface region from further beneath the surface. This is consistent with the trend of the ESCA data implying that subsurface reduction takes place to a greater extent at higher temperatures. A similar phenomenon has been observed previously for the reduction of a $TiO_2(001)$ surface (25).

The ESCA Pt 4f peaks obtained from the unpretreated samples are shown in figure 8a, and the peak assignments used in this study are listed in table II. Most of these assignments were taken from a standard reference (19), but the 72.3 eV feature has been assigned as Pt-O-Sn in previous studies of platinized tin oxide surfaces (12, 23). The spectrum shown in figure 8a indicates that very little metallic Pt is present and that the Pt species consist mostly of Pt-O-Sn, $Pt(OH)_2$ and Pt oxides. In fact, a spectrum very similar to this one has been taken from a codeposited platinum/tin oxide film after calcining in air at 725 K for 1.5 hours (12).

ESCA Pt 4f spectra taken after pretreating at 75 and 100°C are shown in figures 8b and c respectively. These two spectra are quite similar in that very little metallic Pt is present and the predominant species consist of Pt-O-Sn and $Pt(OH)_2$. The metallic Pt apparently is in the form of small crystallites. A shoulder due to PtO_2 may also be present in both spectra, but this shoulder is smaller after the 100°C reduction. The relative amounts of Pt-O-Sn and $Pt(OH)_2$ are similar in both spectra. Pretreating at a temperature 25°C higher produces a significant change in the Pt species present as shown in figure 8d. The predominant Pt species after the 125°C reduction are $Pt(OH)_2$ and Pt-O-Sn in approximately equal amounts. Also, a small amount of metallic Pt is present after this treatment, and features due to Pt oxides do not appear.

Reduction at 175°C produces a further and more pronounced shift in Pt chemical state toward $Pt(OH)_2$ as shown in figure 8e. The Pt-O-Sn feature is now a shoulder on the $Pt(OH)_2$ peak, and the amount of metallic Pt present is decreased compared to the lower temperature reductions. The spectrum shown in figure 8a, taken from the untreated sample, exhibits a prominent feature at 79.8 eV. Since the splitting between the Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks is about 3.35 eV, this feature does not correspond to the Pt $4f_{5/2}$ peak of any of the species listed in table II. The 75°C pretreatment reduces the size of this feature, and it does not appear after the 100 or 125° pretreatment. Therefore, it behaves like an oxidic feature and reappears in figure 8e.

It is interesting to compare the spectral information contained in figure 8 with the kinetic information contained in figure 1. The unpretreated catalyst exhibits a low activity compared to any reduced catalyst. This correlates with the facts that the Pt is predominantly oxidic on the unpretreated catalyst and that significant changes in the Pt chemical state occur during

the reductive treatments used in these studies. As the pretreatment temperature increases, more of the Pt is converted into $Pt(OH)_2$. This fact suggests that the $Pt(OH)_2$ plays an important role in the conversion of CO and O_2 into CO_2 at low temperatures as has also been found to be the case for a silica-supported platinized tin oxide catalyst (26) for which the catalytic activity increases by addition of water to the reaction mixture after pretreating the catalyst at 225°C (27). The previous characterization study (26) demonstrates that pretreatment of this catalyst at 225°C removes most of the Pt hydroxyl species thereby lowering its catalytic activity. This does not occur with the Engelhard catalyst which yields identical catalytic behavior for pretreatments from 125 to 225°C. The ESCA data are consistent with this fact in that much of the Pt is present as $Pt(OH)_2$ after the 125° reduction, and it becomes the predominant Pt chemical state after the 175°C reduction. In this discussion a relationship is being drawn between the long-term catalytic behavior (past the first 500 minutes of operation) and the chemical state of the Pt after the pretreatment but before the reaction is run (time = 0 on figure 1). The initial catalytic behavior is quite complex (3) and changes may occur in the Pt chemical state during this period. Consequently, characterization studies are in progress in which the state of the catalytic surface is being examined as the reaction is run for various periods of time. These studies should lead to an understanding of the chemical changes responsible for the unusual initial catalytic behavior and the long-term decay in catalytic activity.

A small amount of metallic Pt forms during both the 125 and 175°C pretreatment, and metallic Sn is also present as stated above. Paffett and Windham (28) have deposited layers of Sn on Pt (111) and found that alloy formation during annealing at or above 150°C is strongly suggested by their data. Also Fryberger* has found that Pd deposited on $SnO_2(110)$ alloys with the Sn even at room temperature. It is anticipated that alloy formation occurs in the Engelhard catalyst under the pretreatment conditions used in this study. Since the amount of Pt present on this surface is small, most of the metallic Sn probably is not alloyed while all of the Pt probably is alloyed.

SUMMARY

A platinized tin oxide catalyst commercially available from Engelhard Industries for low-temperature CO oxidation has been examined using surface analytical techniques including ISS, AES and ESCA before and after pretreatment by annealing in 40 Torr of CO for 1 hour at 75, 100, 125 and 175°C, and the results have been correlated with catalytic activity data. The unpretreated sample consists primarily of oxidic Sn (SnO_2, SnO and $Sn(OH)_x$) with a very small amount of Pt present as Pt-O-Sn, $Pt(OH)_2$, PtO and PtO_2 species. Reduction results in loss of both O and OH from the Sn and produces metallic Sn. The extent of these processes increases as the pretreatment temperature increases. The chemical state of the Pt changes with pretreatment temperature. At or below 100°C, the predominant forms are Pt-O-Sn and $Pt(OH)_2$. As the reduction temperature increases, more $Pt(OH)_2$ forms. This fact suggests that $Pt(OH)_2$ plays an important role in the low-temperature catalytic oxidation of CO. The results demonstrate that the application of surface analytical techniques in studies of real catalysts can provide information which is useful in understanding catalytic behavior.

*T. Fryberger, personal communication

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TABLE I
O/Sn Atomic Ratios Versus Pretreatment Temperature

Pretreatment	AES[†]	ESCA[††]
untreated	1.32	1.56
75°C	1.08	1.45
100°C	1.05	1.39
125°C	1.04	1.33
175°C	1.05	1.21

[†]Calculated using methods described in reference 22.

[††]Calculated using methods described in reference 19.

TABLE II
ESCA Pt 4f Peak Assignments

Species	Binding Energy (eV)
Pt°(bulk) [1]	70.9
Pt°(crystallite) [2]	71.3
Pt-O-Sn [2]	72.3
Pt(OH)$_2$ [1]	72.8
PtO [1]	74.2
PtO$_2$ [1]	74.9

1. Assignments taken from reference 19.

2. Assignments taken from references 12 and 23.
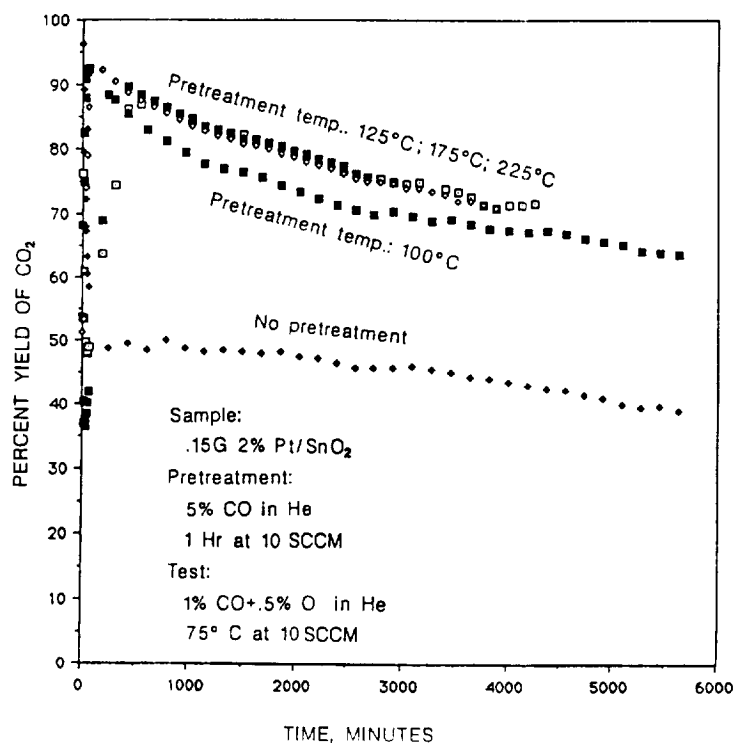
Figure 1.   Catalytic activity of the Engelhard platinized tin oxide catalyst for CO oxidation shown as a function of time and pretreatment temperature.   The pretreatment and reaction test conditions are given in the figure.
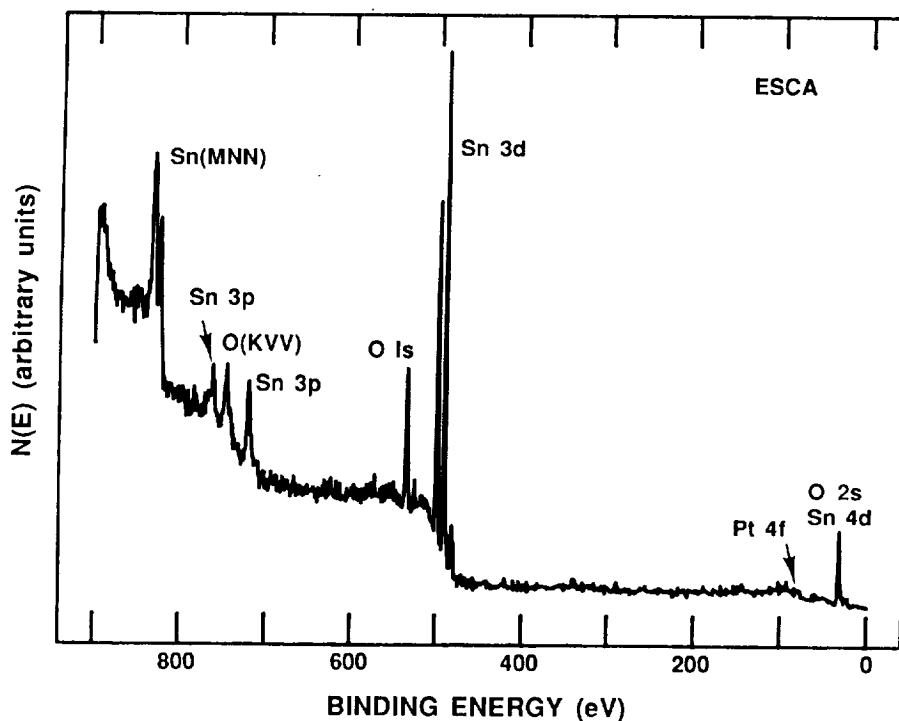
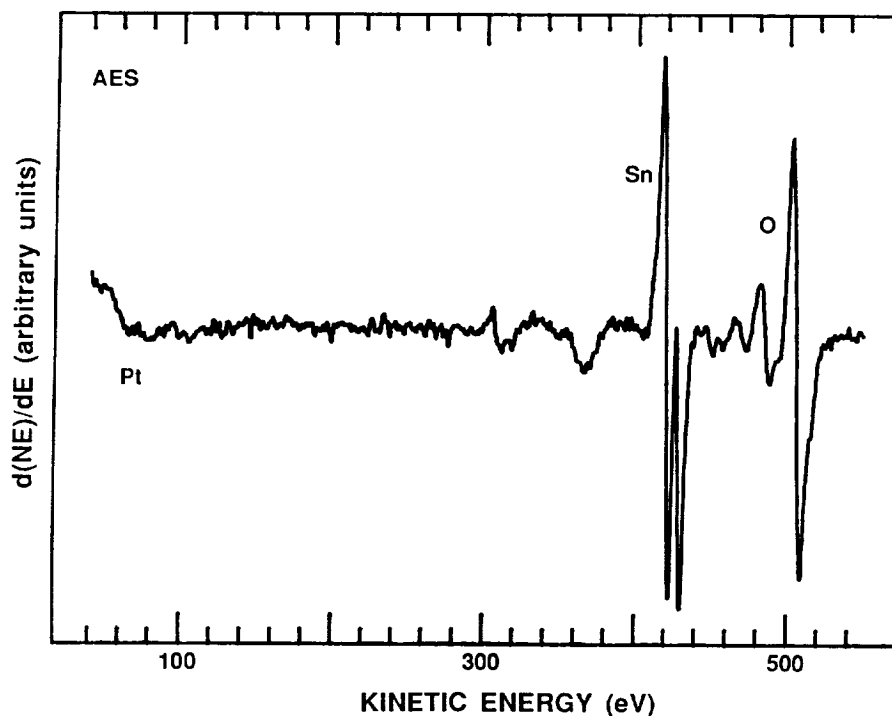Figure 2.   ESCA survey spectrum taken from the as-received Engelhard platinized tin oxide catalyst.

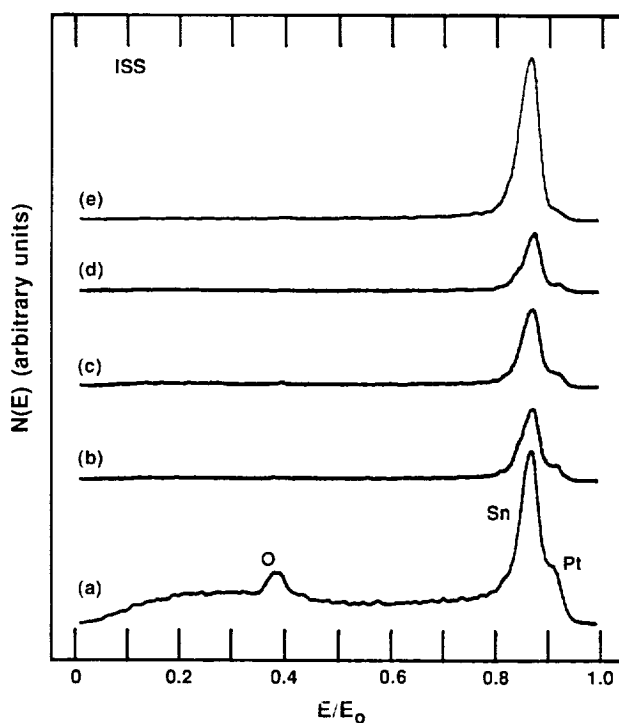Figure 3.   Auger spectrum taken from the same as-received sample as the ESCA spectrum shown in figure 2.

Figure 4.   ISS spectra taken from (a) an unpretreated sample and samples reduced at (b) 75, (c) 100, (d) 125 and (e) 175°C in 40 Torr of CO for 1 hour.
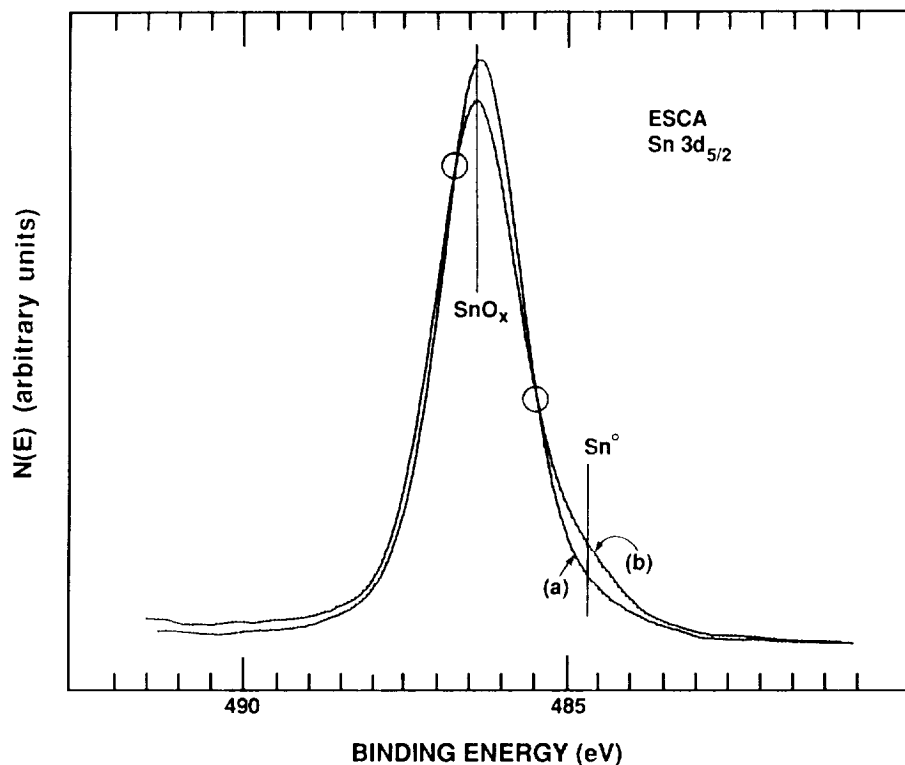
Figure 5.   ESCA Sn 3d peaks obtained from (a) an unpretreated sample and (b) a sample reduced at 175°C in 40 Torr of CO for 1 hour.   The circled regions indicate crossing points.
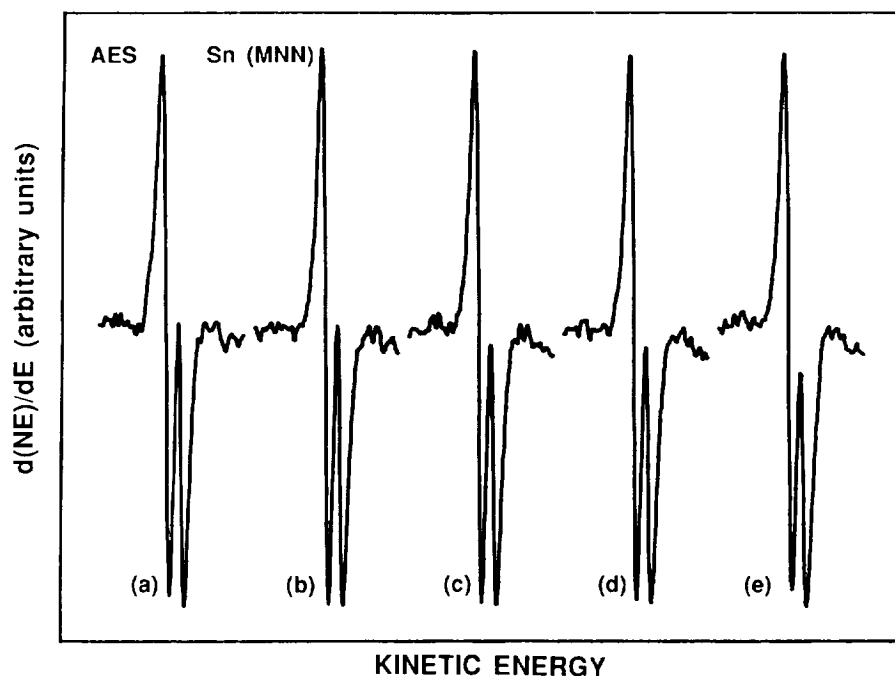

Figure 6.   AES Sn (MNN) peaks obtained from (a) an unpretreated sample and samples reduced at (b) 75, (c) 100, (d) 125 and (e) 175°C in 40 Torr of CO for 1 hour.
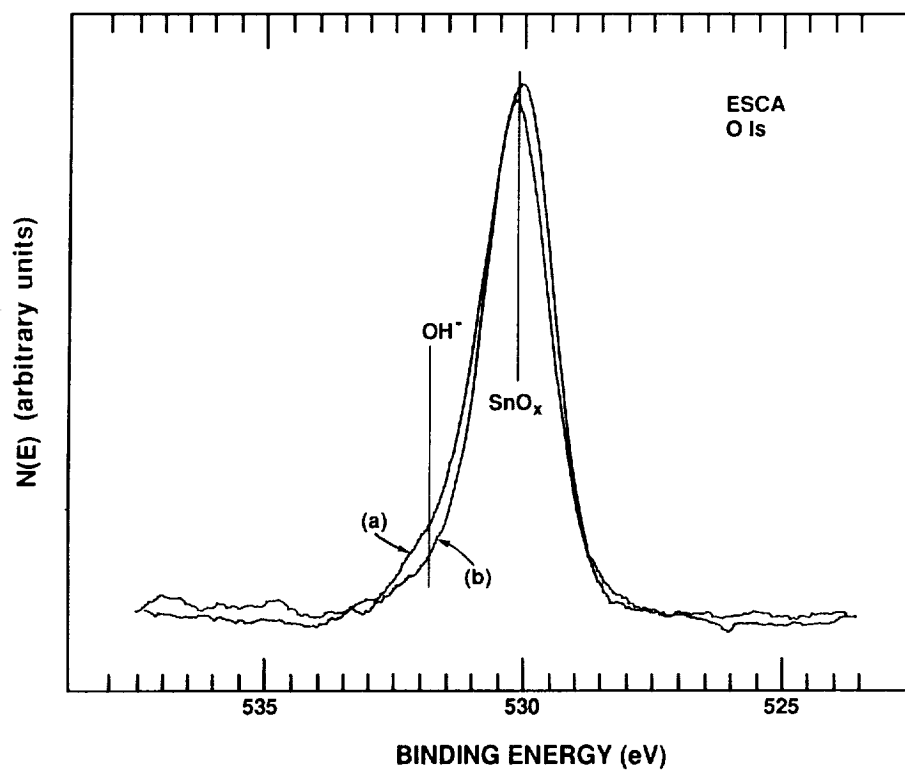
Figure 7.   ESCA O 1s peaks obtained from (a) an unpretreated sample and (b) a
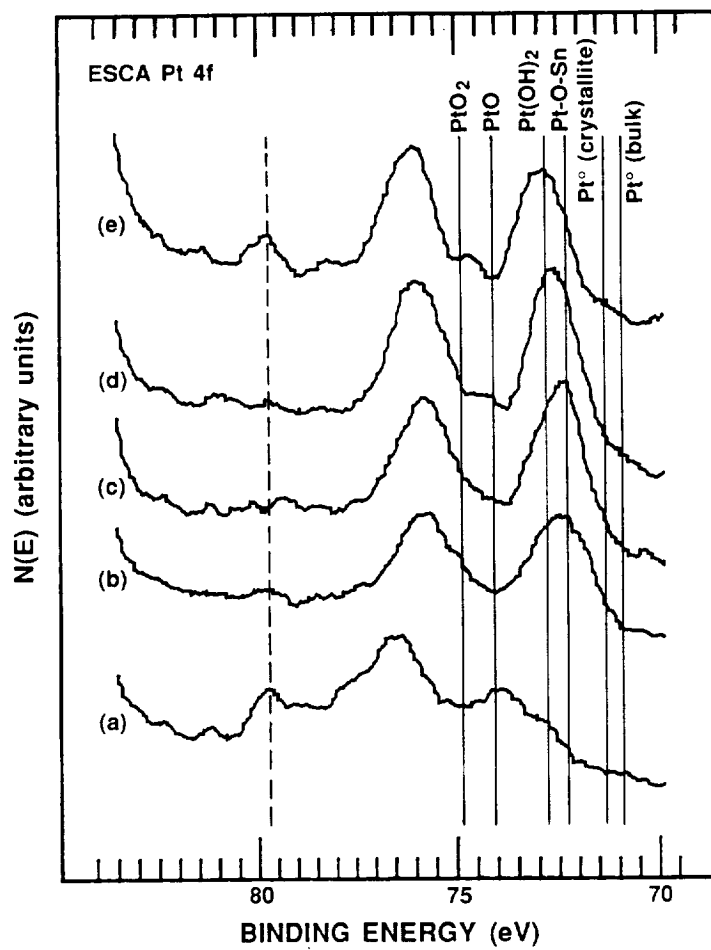sample reduced at 175°C in 40 Torr of CO for 1 hour.

Figure 8. ESCA Pt 4f peaks obtained from (a) an unpretreated sample and samples reduced at (b) 75, (c) 100, (d) 125 and (e) 175°C in 40 Torr of CO for 1 hour.