

Lead, Sulfur and Phosphorus Interactions with Platinum and Palladium Metal Foils

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This paper describes the chemical interactions at the active metal surface of platinum and palladium oxidation catalysts subjected to lead, phosphorus and sulfur contaminants. A method of probing the chemical environment of the supported metal surface in catalysts has been developed using Auger electron spectroscopy (AES).

The poisoning of Pt and Pd is seen as an accumulation dependent process. The noble metal surfaces first saturate with lead without accumulation of sulfur or phosphorus. The initial accumulation of lead on Pd is different than Pt. At low exposures lead is depleted from the Pd surface. It appears that lead is drawn from the surface into the bulk of the oxidized palladium because of the solubility of PbO in PdO. On platinum, however, no such driving force exists and lead depletion is not indicated. Subsequent accumulation on the lead poisoned Pt or Pd consists of oxidized sulfur, phosphorus and lead. Compound identifications on both Pt and Pd were accomplished using peak shift and structure analyses with respect to AES spectra obtained from PbSO₄ and Na₄P₂O₇.

INTRODUCTION

In an effort to understand gas-solid interactions in the field of catalysis, detailed knowledge about the surface of the active component of the catalyst is being continually sought. Recent advances in instrumentation and interpretation have yielded considerable information on the composition and reactivity of pure metal surfaces (1,2), but the important link to more complex multicomponent systems remains elusive. One example of this difficulty is the analysis of the composition at the active surface in a supported metal catalyst. Interpretation of data from most analytical techniques is difficult because of interference of the signals from the active metal and support. We decided to separate the metal catalyst from its support in order to develop a technique to probe the metal surface composition. Cleaned high purity foils are placed in contact with an active catalyst bed (in this case a noble metal oxidation catalyst) and subjected to automobile exhaust. After this exposure the

surface constituents of the contaminated foils are determined by Auger electron spectroscopy (AES).

A substantial body of information has been accumulated recently (3,4) on the storage of contaminants on noble metal catalysts and their influence on hydrocarbon oxidation reactions. We were interested in identifying the elements and compounds on platinum and palladium surfaces which previously had only been inferred from bulk analyses of poisoned catalysts.

The major species deposited during deactivation of automobile oxidation catalysts are probably represented (3-5) by four groups of compounds: lead (and lead oxide), sulfate (and oxysulfate), phosphate, and halides. The deactivation process may occur by a chemical mechanism which involves specific active metal-poison interactions and/or a physical method in which access to the active metal is blocked by these species. While it is difficult to establish the relative contribution of these

processes, it is possible to study the chemical interactions using metal foils, as outlined in this paper.

We will first give results of experiments designed to validate the metal probe technique, followed by AES compound identification of representative contaminants. The application of this technique to catalyst contaminant buildup will then be presented as a function of automobile exhaust exposure.

EXPERIMENTAL METHODS

Preparation of Metal Foils

"Marz" grade (99.999% pure) foils of the metals of interest were cut to a convenient size (2.5×1 cm), washed in methanol, suspended in a quartz tube, and cleaned in flowing oxygen and hydrogen. The typical schedule of 2 hr at 770 K in 1 atm of flowing oxygen, followed by 2 hr at 770 K in 1 atm of flowing hydrogen, proved to sufficiently clean platinum and palladium.

Contamination of Foils

The prepared foils were placed in an experimental converter in contact with active catalyst of the same metal at a nominal 0.1 wt% loading. The converter, containing 1000 cm³ of catalyst, was part of the stainless steel exhaust system of a 5735 cm³ V-8 engine. The engine was attached to an engine dynamometer. Engine operating conditions were air:fuel ratio = 15.8 (oxidizing atmosphere-excess air) and inlet manifold depression = 47.2 kPa. The catalyst was operated at 830 K and subjected to exhaust with contaminants of lead (as "Motor Mix"), phosphorus (as cresyl diphenyl phosphate), and sulfur (residual).

Analysis by AES

The foils were placed in the prebaked chamber of the vacuum system and Auger electron spectra were taken with the aid of a double-pass analyzer (Physical Elec-

tronics, Model 12-250). Normal mode analysis, without electron retardation, was used to provide high sensitivity and sufficient resolution when the modulation was typically 2 Vp-p for energies less than 300 eV and 10 Vp-p otherwise. An angularly incident electron beam (3 μ A, 5 kV) was used to excite the Auger transitions. Standard lead sulfate spectra were obtained from lead-acid battery plates. The recorded spectra represent a steady state surface condition where the electron beam current or argon ion sputtering did not change the observed spectra. Phosphate samples were prepared by evaporation of dilute solutions of the appropriate salts on an acid etched surface of "Marz" grade silver. This procedure should be applicable to a wide range of inorganic compound sample preparations.

RESULTS AND DISCUSSION

Validation of the Foil Probe Technique

The utility of a method of remotely analyzing reactive surfaces without the need to perform *in situ* Auger analysis is easily recognized. An ideal series of operations would involve the preparation of a stable, clean metal surface which could be inserted in an active catalyst bed, removed and analyzed by AES, with the results being representative of the gas-solid interactions on the metal crystallite surface of the supported catalysts. Maintaining the chemical integrity of surfaces exposed to air is not possible for many samples due to adsorption of, and reaction with various ambient gases. However, recently the stability in transferring cleaned platinum surfaces in air has been noted by Pignet *et al.* (6).

Figure 1 shows the AES from platinum and palladium after a typical cleaning procedure when the foils were directly placed in a prebaked vacuum chamber. Both spectra indicate oxygen adsorption on the foils as would be expected for clean foils exposed to air. Calcium was detected at

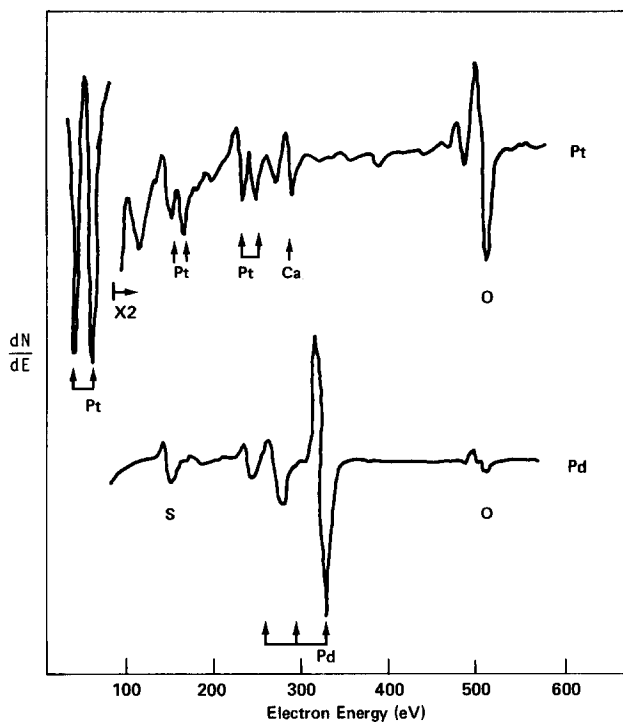


FIG. 1. Auger spectra from cleaned Pt and Pd foils (O_2 , 770 K, 2 hr; H_2 , 770 K, 2 hr).

platinum surfaces probably as the result of segregation from the bulk to the surface. The calcium surface concentration varies widely from sample to sample but all of our test foils had less than the sub-monolayer amount of calcium indicated in the Pt spectrum.

The small amount of sulfur detected at Pd surfaces is believed to result from post-cleaning pickup. In all of our studies the change in surface composition due to the exhaust exposure is larger than any residue of the cleaning procedure.

When the chamber is baked at 473 K to lower the residual pressure, we find that the samples actually become more contaminated (Fig. 2) with carbon. Surprisingly, we find that the "shelf-life" of cleaned foils is at least 1 wk. Foils cleaned and then stored for 1 wk in glass vials maintained the level of surface cleanliness as depicted in Fig. 1.

There are a number of precautions that must be observed in preparation of clean

foils. The foil cleaning should be done with pure gases and clean quartz tubes. We have found, like Pignet *et al.* (6), traces of iron on the platinum surface after the cleaning procedure. These might be due to segregation of the iron from the bulk to the surface of the platinum where it is stabilized as an oxide. Alternatively, these may arise from a vapor transport mechanism. In one case where a foil was positioned near a stainless steel sheathed thermocouple, the "cleaned" platinum surface was totally covered with iron oxide; no other elements were detected. Thus, the foil should be checked by AES each time it is prepared.

In order to demonstrate that the transportation of the foils to our test reactor, the placement in the active catalyst, and the recovery of the foils did not interfere with our results, we examined foils that were at different positions in the catalyst bed. After 30 min exposure to the exhaust from an engine operating on fuel con-

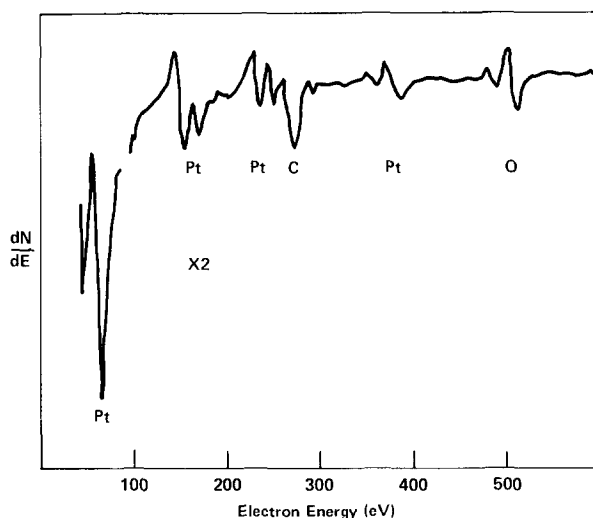


FIG. 2. Spectrum from cleaned Pt foil (as Fig. 1) subjected to vacuum chamber bake-out.

taining 110, 147, and 8 $\mu\text{g}/\text{cm}^3$ Pb, S, and P, respectively, the foils adsorbed Pb, S, and P exclusive of other contaminants. Indeed, the high energy (>1900 eV) more bulk sensitive regions of the spectra in Fig. 3 indicate about 30 times more lead on the leading foil (a) than on the last (b). Most catalyst beds develop a contaminant concentration gradient (3,7); we have shown that this is the case for lead accumulation

on foils at different bed positions. Thus, the foil probes appear to act as if they are part of the supported catalyst. Further evidence for validity of this method of probing platinum surface chemistry comes from a comparison of Auger spectra taken from a copper foil and a platinum foil that were exposed to exhaust from fuel containing 110, 147, and 0.55 $\mu\text{g}/\text{cm}^3$ Pb, S, and P, respectively. This simultaneous ex-

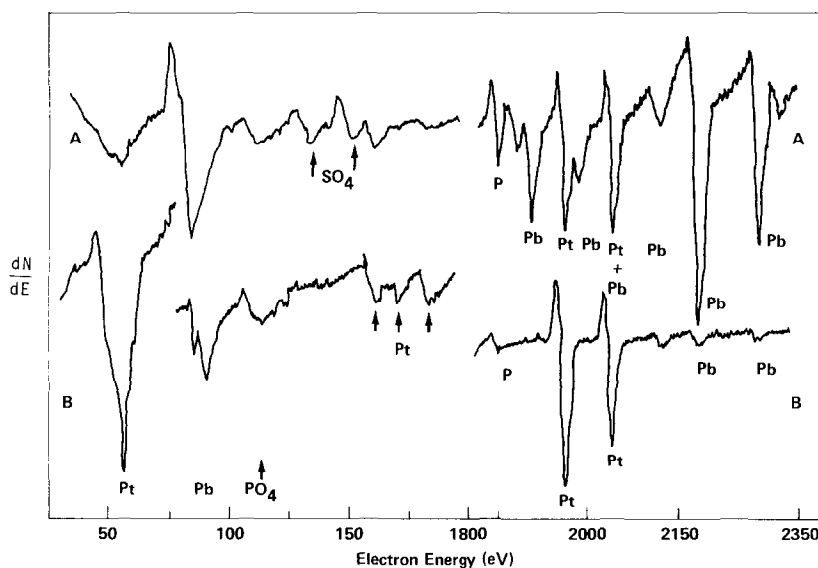


FIG. 3. Contaminant gradient shown by Pt foil probes. (A) upstream (B) downstream within catalyst bed. Fuel ($\mu\text{g}/\text{cm}^3$): Pb = 110, S = 147, P = 8.

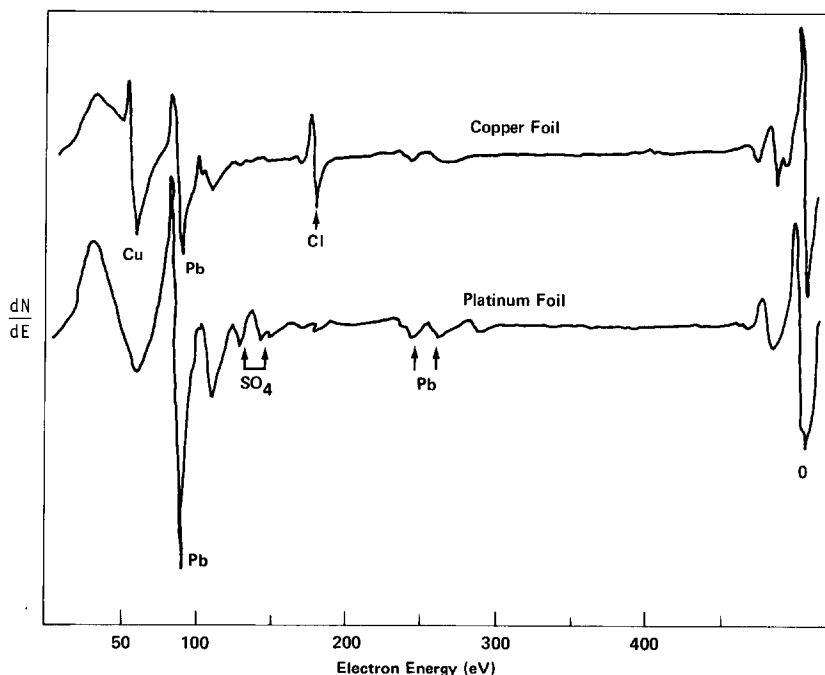


FIG. 4. Comparison of Pt and Cu foil probes simultaneously exposed to exhaust. Fuel ($\mu\text{g}/\text{cm}^3$): Pb = 110, S = 147, P = 0.55.

posure was carried out in the absence of alumina or active catalyst to modify the exhaust composition. The two spectra (Fig. 4) are quite different. The copper foil accumulated lead, chlorine, and oxygen, while the platinum accumulated lead, sulfur, and oxygen. Note that the presence of the 60 eV Cu peak indicates that copper is still in the outer region of the sample. The accumulation on copper is typical of that found on other inactive surfaces in the exhaust stream. However, the accumulation on platinum indicates the chemical changes that can occur on this noble metal in the exhaust.

The technique may be useful in other studies where adsorbed species on the active metal surface rather than the support need to be known. Strongly bound species that do not react with ambient gases during transfer will be more meaningfully detected than volatile reactive substances.

Compound Identification by AES

In our studies, sulfur and phosphorus were found to give distinctive "Auger sig-

nature" when oxidized and reduced. The derivative spectra of lead sulfate and sodium phosphate are shown in Fig. 5. The "normal" reduced sulfide and phosphide Auger structures are indicated by the broken lines. Our energy measurements are in agreement with the sulfate signature previously detected by Farrell (8). The phosphate gives a similar signature with respect to phosphide as sulfate to sulfide. These standard spectra were used to identify the chemical state of sulfur and phosphorus in the adsorbed layers on platinum and palladium. Detailed analyses of the peak positions and structures are not warranted for this work. We report these spectra as AES fingerprints of the compounds under electron-beam excitation.

Contaminant Accumulation on Pt and Pd

The chemical nature of the collected contaminants on the platinum and palladium catalysts was studied as a function of lead accumulation on the metal probes. A typical spectrum obtained for low lead

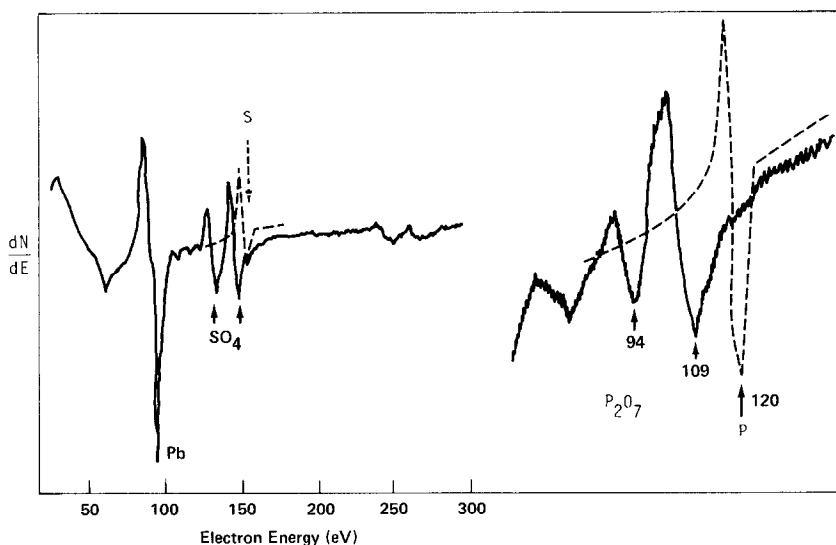


FIG. 5. Compound identification by AES. PbSO_4 and $\text{Na}_4\text{P}_2\text{O}_7$; (--) normal sulfur and phosphorus. The oxidized phosphorus trace is expanded to show details of the structure.

levels is shown in Fig. 3b. The spectrum is from a foil that was placed at the bottom of a bed of active $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst subjected to the exhaust from leaded ($0.11 \text{ mg}/\text{cm}^3$) fuel with residual sulfur ($147 \text{ } \mu\text{g}/\text{cm}^3$) and phosphorus ($8 \text{ } \mu\text{g}/\text{cm}^3$). The Auger spectrum shows predominately platinum and lead, coexisting on the surface, with the

former being more abundant. This suggests that at *low* exposures lead alone is associated with the platinum, rather than being present as a sulfate, phosphate (to any appreciable extent), or halide.

The accumulation of low levels of lead from an active catalyst, with residual lead from a previous experiment, could also be

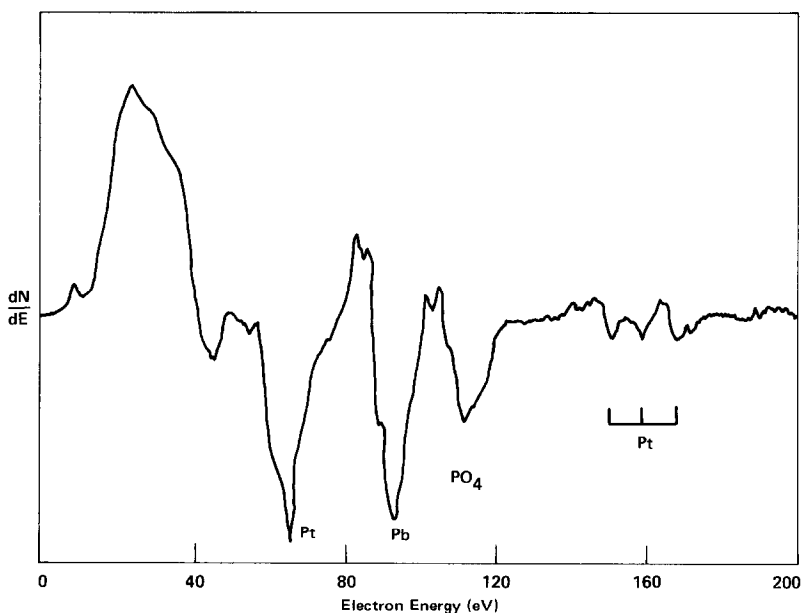


FIG. 6. Low lead accumulation on Pt foil. Fuel ($\mu\text{g}/\text{cm}^3$): Pb = 3, S = 147, P = 0.55.

seen. We placed a Pt foil in such a catalyst and exposed it for 7.5 hr to the exhaust from sterile fuel containing residual lead ($3 \mu\text{g}/\text{cm}^3$), sulfur ($147 \mu\text{g}/\text{cm}^3$), and phosphorus ($0.55 \mu\text{g}/\text{cm}^3$). Previous experiments had shown that this low exposure did not deposit detectable amounts of lead species in the bulk of a fresh catalyst, and furthermore, more lead did not accumulate on this catalyst. This treated foil (Fig. 6) showed *low* accumulation of lead along with some phosphate (presumably carried over from previous tests) on the platinum surface. The lead-platinum signals coexists, indicative of the migration of lead from the support to the active metal.

As a contrast, increasing the contaminant exposure of Pt leads to the formation of oxidized sulfur and phosphorus deposits and the disappearance of the platinum low energy signal. An example of the AES spectra from a heavily contaminated Pt foil is shown in Fig. 3a. The foil was

placed at the top of the same active catalyst bed as the foil of Fig. 3b. The sulfate and phosphate (due to phosphorus from previous tests) fingerprints are clearly seen. The obscured platinum Auger signals at energies less than 300 eV indicate that multiple layers of deposits have accumulated on the platinum foil. An example of extensive sulfate formation is shown in Fig. 7 (broken line). This is an Auger spectrum from a foil in contact with a catalyst subjected to heavily leaded fuel ($725 \mu\text{g}/\text{cm}^3$ with 147 and $0.55 \mu\text{g}/\text{cm}^2$ sulfur and phosphorus, respectively). Substantial buildup of lead sulfate has occurred as shown by the fact that it took 510 sec of argon ion sputtering of the platinum foil [Fig. 7 (solid line)], which corresponds to 50 monolayers of deposit, to remove most of the accumulated compounds.

Comparisons were also made between platinum and palladium. At high rates of

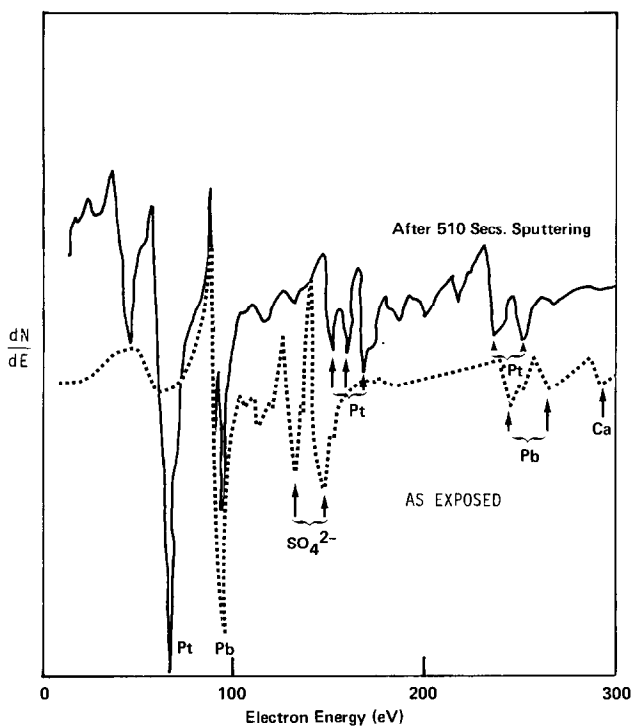


FIG. 7. High lead accumulation on Pt foil. Fuel ($\mu\text{g}/\text{cm}^3$): Pb = 725, S = 147, P = 0.55. (---) surface as exposed to exhaust; (—) after 510s argon ion bombardment.

lead contamination, with sulfur in the exhaust system, lead sulfate was deposited on both platinum and palladium. Striking differences, however, were recorded from an experiment carried out using platinum and palladium foils in active catalyst beds subjected to exhaust containing low lead and high phosphorus levels ($3 \mu\text{g}/\text{cm}^3$ and $50 \mu\text{g}/\text{cm}^3$, respectively, in the fuel). On platinum, lead phosphate seems to be the major species (Fig. 8a), with the lead arising from previous experiments run in the system. The spectrum from a palladium foil exposed simultaneously with the platinum foil of Fig. 8a is shown in Fig. 8b. Oxidized phosphorus is on the palladium surface but lead is conspicuously absent. We feel the lead was deposited on the palladium but diffused into the bulk. The solubility of PbO in PdO (that is also being formed in the presence of the oxygen) could allow this process (9).

Lead halides are generally regarded as one of the major species formed by the combustion of fuel containing lead additives (basically tetraethyl lead and ethylene dihalides). However, halides were not found on noble metal foil placed in active catalyst beds. When chlorine was found on platinum foil it was localized in very small areas and in small quantities deposited on top of larger amounts of lead sulfate. In contrast, copper foils (Fig. 4) and stainless steel in the absence of an active bed collected substantial amounts of halide. This is in agreement with the view that lead halides are the principal carriers of lead to the catalyst (10).

We envisage the mechanism of deactivation of platinum catalysts to involve the initial decomposition of lead halides on the clean platinum forming a strong lead-platinum interaction with the halides desorbing from the surface. As a result, ha-

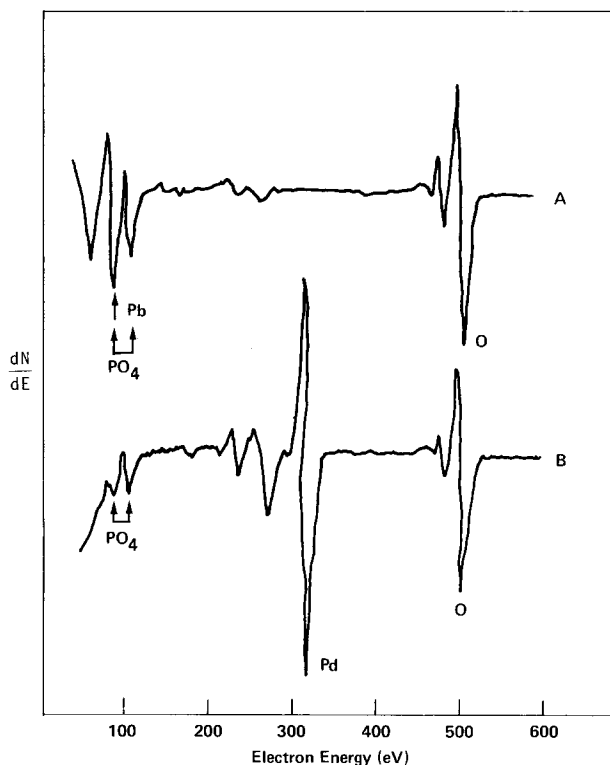


FIG. 8. Lead and phosphorus accumulation on Pt (A) and Pd (B). Fuel ($\mu\text{g}/\text{cm}^3$): Pb = 3, S = 147, P = 50.

lides are unlikely to contribute to the irreversible deactivation of the catalyst. This lead accumulation process can continue until the platinum becomes saturated with lead. Sulfur from the gasoline (as sulfur dioxide in the exhaust) can be oxidized on unsaturated platinum to sulfur trioxide, which reacts with lead oxide to form lead sulfate overlayers on lead saturated platinum.

From these studies we cannot estimate the activities of these poisoned surfaces. We are undertaking detailed studies to establish the oxidation activities of platinum and palladium surfaces as they become lead saturated.

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