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Surface Composition of Platinum Heated in Oxygen

During a study of NH_3 oxidation on Pt we examined by Auger electron spectroscopy (AES) the surfaces of platinum foils which had been heated in O_2, air, and NH_3–O_2 mixtures at a pressure of 1 atm. These experiments showed that (a) oxygen efficiently removes carbon, sulfur, and all other contaminants and (b) such surfaces are not seriously contaminated by carbon or sulfur upon exposure to ambient gases for long periods of time. We believe that these results have important implications with regard to the surfaces of supported and unsupported platinum catalysts.

High purity platinum wires (Sigmund-Cohn 99.99% purity) were rolled into foils ~0.02 cm thick. The foils were then chemically etched in aqua regia or molten nitrates. A 4 cm length of foil was welded to tungsten heating leads in a Pyrex flow system and heated in flowing O_2 (commercial purity) for various times and substrate temperatures. After this treatment, the foils were removed from the system and transferred to an ultrahigh vacuum AES–ion bombardment sputtering system, having been exposed to the laboratory atmosphere for at least several hours in the transfer process.

An electron energy of 2000 V was used in a cylindrical mirror AES analyzer. Argon bombardment was assumed to remove surface material at the rate estimated for platinum (*1*). No contamination of the surface which had been cleaned by sputtering was produced by cycling between 1×10^{-9} Torr for AES to 10^{-5} Torr of Ar for sputtering. The possibility of the AES electron beam inducing changes in the surface (such as oxygen desorption) was eliminated by showing that the AES spectrum of a previously unbombarded surface obtained at low current (1 μA) was the same as that at 50 μA. Electron beam induced desorption of oxygen could be observed only for bombardment times greater than 10 min at 50 μA.

Figure 1a shows the AES spectrum of a surface which had not been heated in O_2. As expected it showed considerable C, some S and O, and very small Pt peaks. This agrees well with many experiments (*2*) which have shown by LEED and AES that etched or polished single crystals of Pt invariably have a thick surface layer of graphite which can only be removed by extensive heating, ion bombardment sputtering, or heating in oxygen at low pressures (10^{-7} to 10^{-5} Torr). We observed similar spectra from untreated wires as well as for specimens treated in aqua regia, molten nitrate salts, or electropolished. Occasionally additional metal contaminants were noted. Spectra of clean Pt from these specimens could only be obtained by sputtering off 100 to 1000 monolayers.

Figure 1b shows the spectrum of the original surface of a foil which had been heated at 400°C in O_2 at 1 atm pressure for 4 hr and Fig. 1c shows the same foil after removal of nominally 1 monolayer. The only pretreatment of any specimens was by etching; no vacuum heating was employed.

Qualitatively similar behavior was observed on all samples heated more than 1 hr at temperatures greater than 300°C. In all cases the carbon peak on the initial surfaces was much less than the Pt or O peaks, and negligible carbon was detected after a few monolayers of material had been removed. Approximately 30 different samples were analyzed using several reactors and platinum of different purities; all results were consistent with those described except for cases where improper handling before or after heating introduced impurities.

From AES data from O_2 on W we find (*3*) that an oxygen density of 1×10^{15} atoms/cm^2 produces a ratio of peak heights

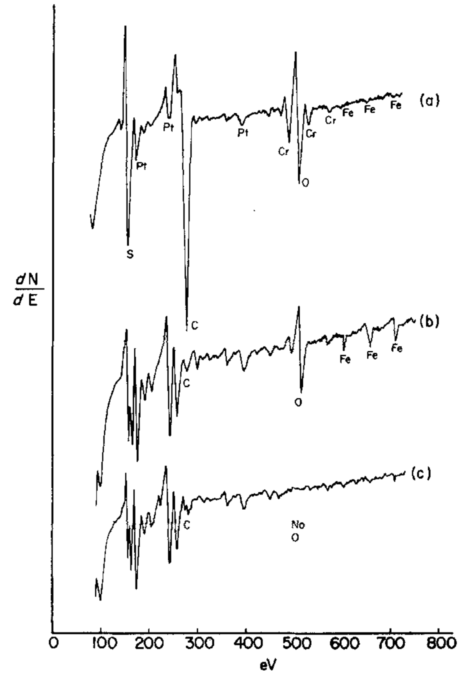

FIG. 1. Auger electron spectra of platinum foils; (a) surface which had not been heated in oxygen, (b) original surface of foil which had been heated in oxygen at 400°C for 4 hr, and (c) surface as in (b) after sputtering away approximately one monolayer. Sputtering removal rates were estimated from ion currents and times assuming tabulated rates for platinum. Energies of various Auger peaks are indicated. It is seen that surfaces (b) and (c) have small contaminant concentrations even though they had been exposed to ambient gases after oxygen treatment.

O_{510}/W_{170} of 0.37. Auger spectra of CO on W give $C_{270}/O_{510} = 2.45$ in a cylindrical mirror analyzer. Assuming that this calibration is reasonably accurate for Pt (expected because W and Pt should have similar cross sections and backscattering coefficients by virtue of their similar atomic numbers), we estimate this oxygen treated surface (Fig. 1b) to contain 2×10^{15} oxygen atoms and 3×10^{14} carbon atoms. On the samples which showed negligible metal contamination after heating the apparent carbon concentrations varied between 0.1 and 1 monolayer and the oxygen between 1 and 3 monolayers. The spectra in Fig. 1 show some iron and chromium which were apparently introduced in the rolling process. The amounts were always a fraction of a monolayer and did not influence the C and O concentrations.

The only instances in which oxygen was detected at depths more than a few monolayers below the original surfaces were those where all carbon had not been removed or where metal contaminants were present, presumably as oxides. In no cases was sufficient oxygen detected to infer the existence of a PtO_2 phase of more than a few monolayers in thickness. Bulk PtO_2 has been formed only by heating platinum in O_2 at much higher pressures for long times (*4*). Oxygen has been observed to adsorb readily on platinum (*5*), presumably to a coverage of a monolayer or less, with a heat of adsorption of ~60 kcal $mole^{-1}$.

These experiments are obviously not capable of giving quantitative information about monolayers of adsorbates on platinum surfaces because the surface is exposed to atmospheric gases for extended times. However, it is not expected that such exposures at room temperature should alter the composition beyond a few atom layers below the surface. In the presence of atmospheric contamination one can still demonstrate the *absence* of species on and near the surface. First there are no detectable (probably less than 0.1 monolayer) metals, sulfur, halogens, silicon or alkalis. This shows that experiments in a Pyrex tube with commercial purity oxygen did not produce contamination by these species. Second the carbon concentration was small and was confined exclusively to the external surface. This shows that heating in oxygen efficiently removes the carbon which is always present on and in the highest purity samples. The small amount of carbon observed on the treated surface probably comes from atmospheric CO_2 and hydrocarbons. Its concentration corresponds to less than a monolayer of a carbon containing species.

The third and, to us, the most surprising conclusion from these experiments is that an oxygen treated platinum surface is effectively passivated toward decomposition of carbon and sulfur containing species in the atmosphere.

These results imply that platinum is effectively cleaned of all contaminants by heating in oxygen at a pressure of 1 atm even in systems where ultrahigh vacuum cleanliness is not maintained. Evidently high O_2 pressures shift the equilibrium with S and C sufficiently to remove them completely as volatile oxides. Such cleaned surfaces apparently remain passivated toward contamination from atmospheric gases.

Thus we conclude that the cleaning steps usually employed in preparing commercial supported platinum catalysts (heating in air at 400°C for several hours) may well produce a surface which is essentially clean except for a few monolayers of oxide. Laboratory experiments employing platinum catalysts at 1 atm may also be expected to remain clean if kept in an oxidizing atmosphere. This has been confirmed by AES in the NH_3 oxidation reaction.

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