CHEMISTRY LETTERS, pp. 1263-1264, 1978. Published by the Chemical Society of Japan

THE CHARACTERIZATION OF A PLATINUM-TIN OXIDE CATALYST BY X-RAY PHOTOELECTRON SPECTROSCOPY

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A Pt-SnO_2 catalyst in various compositions of Pt and SnO_2 was prepared and its properties were studied by XPS. Some of platinum of Pt-SnO_2 were observed to be stabilized by SnO_2 in Pt^{+2} and Pt^{+4} forms, and Pt^0 form still remained in Pt-SnO_2. However, platinum, prepared in the same manner with the method of preparation of Pt-SnO_2, stayed at the state identical to platinum metal. Tin existed in an SnO_2 form, indifferent to the presence of platinum.

A platinum-tin (Pt-Sn) electrode is known to show a higher catalytic activity in an electrochemical oxidation of methanol than a pure platinum electrode.[1,2] XPS spectra of Pt-Sn electrode were reported for the photoejected electrons of tin and platinum, i.e., the surface tin[1,2] exists only in a form of SnO_2 and platinum[1] in forms of Pt^0, Pt^{+2}, and Pt^{+4}. These suggest that platinum-tin oxide (Pt-SnO_2) electrode will exhibit a high catalytic activity in methanol electrochemical oxidation and it will be interesting to characterize the properties of Pt-SnO_2.

Pt-SnO_2 catalysts were prepared from an ethanol solution of $SnCl_4$ and $H_2PtCl_6 \cdot 6H_2O$, in which $SbCl_3$ was always present with $SnCl_4$. The solution was sprayed several times onto a sheet of Pyrex glass which had been heated at 550 ∿ 600°C in air and Pt-SnO_2 was formed on the glass. The composition of solutions was varied in 0, 3.7, 16, and 100 atom% Pt. The catalysts from the solutions are denoted as SnO_2, 3.7 atom% Pt-SnO_2, 16 atom% Pt-SnO_2, and 100 atom% Pt. The resistance of Pt-SnO_2 thus prepared was less than 300 ohm (ca. 1 cm apart). Electrochemical oxidation of methanol on the Pt-SnO_2 electrode was measured by potentiostat. The Pt-SnO_2 catalyst, being washed with ethanol, was inserted into XPS spectrometer of Vacuum Generators. The XPS was taken at $4 \times 10^{-9} \sim 8 \times 10^{-10}$ Torr at ambient temperature. We carried out methanol electrochemical oxidation on the Pt-SnO_2 electrodes in 1 N sulfuric acid solution at room temperature and the rates as steady current densities at 0.6 V vs. R.H.E. were observed to be higher than those on Pt metal, i.e., ca. 50 times per platinum atom on 3.7 atom% Pt-SnO_2 and 20 times on 16 atom% Pt-SnO_2.

Figure 1 shows Pt 4f electron XPS spectra at different composition of platinum and tin oxide. Spectrum consists of the asymmetric spectra of the doublet with components at 71.2 and 74.5 eV, which are in good agreement[3] with those of platinum metal, Pt^0. This means that H_2PtCl_6 becomes metallic on glass at 550 ∿ 600°C in air. This is expected from the fact that platinum of H_2PtCl_6 decomposes to metal when being heated above 200°C.[4] The asymmetry is discussed to be due to the presence of species I in Fig. 1.[6]

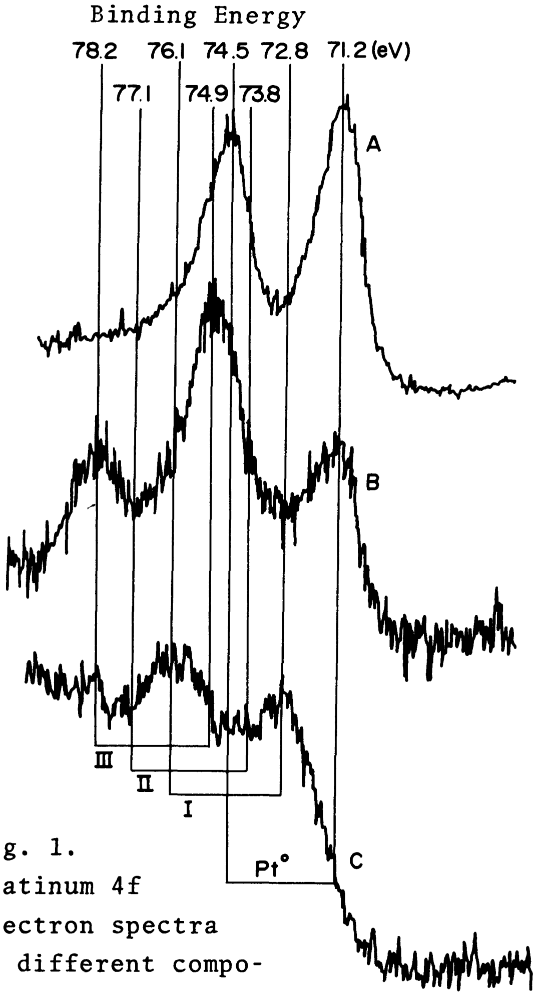

Fig. 1. Platinum 4f electron spectra at different composition of platinum and tin oxide. Spectrum A: 100% Pt, B: 16 atom% Pt-SnO_2, and C: 3.7 atom% Pt-SnO_2. The binding energy is with respect to C 1s = 284.8 eV.

Spectra B and C show that the presence of SnO_2 gives a change of the state of platinum. The spectra were deconvoluted into four species, Pt^0, and species I ∿ III, as shown in Fig. 1. The contribution of species II of the doublet with components at 73.8 and 77.1 eV,[3)] assigned to PtO by Kim et al.,[5)] was found small from the decovolution of spectra B and C. Species III of the doublet with components at 74.9 and 78.2 eV, giving a shift of 3.7 eV from those of Pt^0, is assigned to PtO_2 according to Kim et al.[5)]

Species I of the doublet with components at 72.8 and 76.1 eV was assigned to a satellite of Pt^0, PtO_{ads}, and $Pt(OH)_2$ in Refs. (6), (5), and (3), respectively. Species I and Pt^0 did not give a proportionality in the change of their intensities by Ar^+ ion bombardment. This is identical to the results by Allen et al.[3)] Thus species I is independent of Pt^0, not being the latter satellite. According to Allen et al.[3)] we assign species I to $Pt(OH)_2$.

Spectra B and C was thus found to consist of the spectra due to Pt^0, $Pt(OH)_2$, PtO, and PtO_2. Sn 3d spectrum was observed to be due to SnO_2 which was not changed by the introduction of platinum. These results are in conformity with the results on Pt-Sn catalyst.[1),2)]

Andrew et al.[1)] did not distinguish the reason of a high catalytic activity of Pt-Sn electrode between the modification of platinum by SnO_2 and the cyclic operation of Sn^{+2}/Sn^{+4} redox system. However, our present results will convey that the primary change of Pt-SnO_2 from platinum and SnO_2 themselves is that the platinum is stabilized into Pt^{+2} or Pt^{+4} form by SnO_2. The so-called anodic activation treatment, setting the platinum electrode at the potential where the oxygen layer forms, enhances the rate of electrode reaction. These facts suggest that the platinum in an ionic state exhibits a high catalytic ability for the methanol electrochemical oxidation.

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(Received August 10, 1978)