

The Promotion of CO Electro-oxidation by Ruthenium and Tin on Pt(111), Pt(110).

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The metal vapour deposition (MVD) of ruthenium and tin on Pt(111) and Pt(110) has been investigated using Low Energy Ion Scattering (LEIS), X-ray Photoelectron Spectroscopy (XPS), Low Energy Electron Diffraction (LEED) and Temperature Programmed Desorption (TPD) of carbon monoxide. The electro-oxidation of CO on the ruthenium and tin modified surfaces has also been investigated using cyclic voltammetry following clean transfer from UHV to an electrochemical cell.

Ruthenium lifts the Pt(110)-(1x2) reconstruction by a coverage of 0.5, with evidence of only a small amount of clustering following deposition at 300K. The alloy phases are not ordered, but more stable with respect to oxidative dissolution than the adsorbed phase. LEISS and XPS measurements indicate that ruthenium can be excluded from the top layer by flash annealing, but incorporated into the second and third layers. After annealing to over 1000K, bulk dissolution of ruthenium is observed. The incorporation of ruthenium in the top or second/third layer reduces the adsorption energy of the CO. It is shown, however, that only surfaces in which ruthenium is incorporated in the top surface layer provide a phase which promotes electro-oxidation. The effect of ruthenium is primarily to reduce the over-potential in the activation of water to produce the surface oxidising species in the electro-oxidation process, and that it is water activation that is rate limiting in the overall reaction. Oxidative cycling of surfaces with ruthenium in the second and third layers results in the segregation of ruthenium to the top layer, and re-establishment of the promotional effect of ruthenium.

The results for Pt(110)-(1x2)-Ru are contrasted with Pt(111)-Ru on which the ruthenium has a greater tendency to cluster during deposition. CO electro-oxidation on Pt(111) modified by ruthenium is characterised by two oxidation peaks (ca. 0.6V and 0.7V RHE) in the stripping voltammetry, both at an over-potential significantly lower than that found on Pt(111) under the same conditions. This overall promotion is also associated with the bi-functional mechanism, the reduction in over-potential being primarily associated with the promoted activation of water at the ruthenium atoms in the cluster (Figure 1). The first of the two promoted oxidation peaks (0.6V) is a result of fast Langmuir-Hinshelwood oxidation kinetics associated with platinum sites adjacent to the ruthenium cluster (zone I). The second oxidation peak (0.7V) is associated with oxidation of CO in the remaining sites that lie at least one platinum atom away from the ruthenium sites (zone II). We show that the mobility of CO between these sites is relatively low in the presence of the sulphate anion: The

diffusion of CO between sites is not responsible for the second peak in the stripping voltammetry. We suggest that the slower kinetics of the oxidation in the second peak is associated with the rate of spill-over and diffusion of the oxidant produced at the ruthenium sites to zone I sites.

Results are also presented for the electro-oxidation of CO on ordered alloy surface phases Pt(111)-($\sqrt{3}\times\sqrt{3}$)R30-Sn and Pt(111)-p(2x2)-Sn in order to use the well defined ensembles to support the proposition that the promotion of the electro-oxidation of CO on platinum based alloy surfaces takes place through a simple bi-functional mechanism.

Zone II

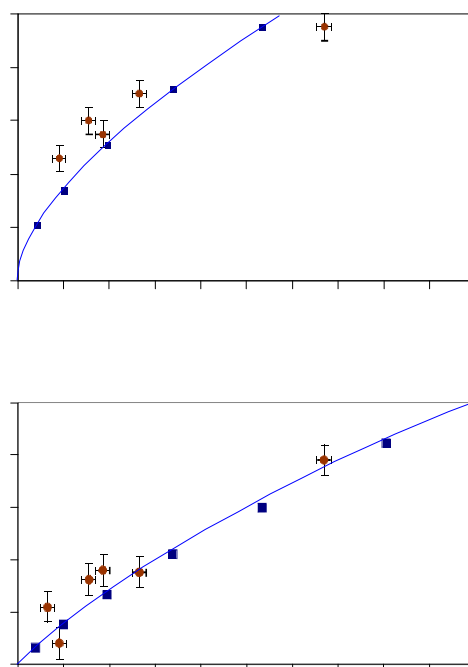
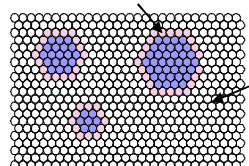


Figure 1

A) The square data points and curve correspond to a calculation of the ruthenium coverage measured by LEISS (a measure of the island footprint) as a function of the ruthenium coverage measured by XPS (total ruthenium coverage). A nucleation and growth model of hemispherical ruthenium clusters with a nucleation density of 1:90 has been assumed. The circles represent the measured LEISS and XPS data for the ruthenium modified Pt(111) surfaces.

B) Using the nucleation and growth model fit to the experimental data in (A), the percentage of platinum sites neighbouring the ruthenium islands (zone I, inset) has been calculated (square data points and curve). The experimental points (circles) correspond to the percentage of the charge associated with the first of the two CO oxidative stripping peaks on the ruthenium modified Pt(111) surfaces.