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TEMPERATURE DEPENDENCE OF THE CHEMICAL PROPERTIES OF PT-RH SURFACES

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SUMMARY

Field emission (FEM) has been used to study the behaviour of Pt-Rh surfaces towards adsorption of nitrogen and CO. Adsorption of CO on a Pt-Rh (50\%:50\%) FEM tip, previously annealed at about 1600 K, shows a Pt-like behaviour of the Pt-Rh tip.

On a Pt-Rh(12\%:88\%) tip, the work function change, caused by nitrogen adsorption, was found to vary with annealing temperature from -0.3 eV following previous annealing at 650K to -0.6 eV after annealing at 1450K.

Both the FEM pattern and the work function change point towards a platinum surface enrichment of the Pt-Rh alloy, in particular, following previous annealing at a temperature of 1000K and higher. The most drastic changes in surface composition take place around 1000K on the rough surfaces of the tip.

INTRODUCTION

Platinum and rhodium are used as catalysts for a large number of reactions. Both metals form the principal constituents of the catalytic converters, used to suppress the air pollution by automobiles. In order to understand the superior properties of the 'three way' catalysts in the reactions involving nitric oxide, it is of interest to compare the chemical properties of Pt-Rh alloy surfaces with those of pure Pt and pure Rh surfaces.

Although much work has already been done on supported Pt-Rh catalysts (1), on single crystal (2,3) and also on polycrystalline Rh and Pt surfaces (4,5), literature data concerning well defined Pt-Rh alloy surfaces are very scarce.

ToF Atom Probe measurements by Ahmad and Tsong (6) on a set of Pt-Rh alloys, annealed at 1000 to 1200K showed a Rh enriched top layer, depletion of Rh in the second layer and an oscillatory composition depth profile. ISS experiments by Williams and Nelson (7) and AES experiments by van Delft and Nieuwenhuys...
(8) showed a Pt enrichment of the top layer using annealing temperatures of about 1300K. In our laboratory FEM has been used in the past to study the adsorption properties of pure Pt and Rh surfaces (9,10,11). In the present work some FEM results, obtained on two Pt-Rh alloys, one with 50 atom%Pt and the other 12 atom%Pt in the bulk, are described. The results suggest that the surface composition and, hence, the chemical properties of atomically rough surfaces vary drastically with the annealing temperature. In order to obtain some information about the surface composition of our Pt-Rh FEM tips, nitrogen and CO were used to titrate the surface. These molecules are very suited to that purpose since the work function changes, produced by nitrogen and CO differ significantly (9).

EXPERIMENTAL

The experiments were carried out in a conventional U.H.V. apparatus equipped with a glass field emission microscope. Base pressure was better than 2*10^{-10} mbar. The purity of the used gases was better than 99.997%. Emitters were prepared by electrolytically etching 0.10 mm diameter Pt-Rh wire, spotwelded to a support consisting of 0.25 mm diameter, in a saturated KNO solution at room temperature. The purity of Pt-Rh wire was better than 99.99%. The emitters were cleaned by several cycles of heating up to 1200K alternately in oxygen and hydrogen under a pressure of 1*10^{-8} mbar, followed by flashing up to 1500K. The temperature was measured by monitoring the electrical resistance of the central part of the filament to which thin Pt-Xh leads had been spotwelded. The filament was calibrated in the high temperature range using an optical pyrometer.

Work function changes were derived from the slopes of ln(I/V^2) vs 1/V plots using the Fowler Nordheim equation I=AV^2 exp(-B\phi^{3/2}/V) where I is the field emission current, V the applied voltage, \phi the work function of the emitter and A the field independent preexponential term. A value of 5.0 eV was used for the average work function of the emitter. In all experiments the alloy surface was exposed to 13 nbarsec of gas at 80K unless stated otherwise. The filament with the attached tip are equilibrated for 90 min. at 830K, 60 min. at 970K, 15 min. at 1100K, 5 min. at 1200K, 90 sec. at 1270K and 20 sec. at 1550K.

RESULTS

Experiments of CO adsorption at 80K on a Pt-Rh (50:50%) FE tip, annealed at 1600K, showed a \Delta \phi of +0.35eV after saturation with CO. This should be
compared to a value of 0.35eV (12) for CO on pure platinum and 1.4eV for CO on pure rhodium (13). The changes in FEM pattern observed during exposure to CO, were similar to those published for Pt (12) and quite different to those found for Rh. Adsorption of CO on Rh (13) causes a relative increase of emission on the surfaces around (221) and (211). Adsorption of CO on platinum causes a more isotropic decrease in emission from the different surfaces of the tip. Pt-Rh showed a small relative decrease in emission on the stepped surfaces between the (111) and the (100) surface (Fig.1).

The relative work function change for a clean Pt-Rh (12%:88%) tip was measured as a function of the annealing temperature. Between 1000K and 1200K, a change in work function of -0.3eV was measured (Fig.2). All work function values shown are relative to the work function of the clean tip, annealed at 1450K. Similar measurements with Rh tips showed that the work function of a Rh tip was independent of the annealing temperature within experimental accuracy (0.05 eV).

The work function change as a result of nitrogen adsorption at 80K on a Pt-Rh (12%:88%) tip varies with the annealing temperature as is shown in Fig.3. Nitrogen adsorption causes an increase in emission on Pt. On Rh, however, the emission decreases upon nitrogen adsorption. For Pt-Rh a decrease in emission is observed upon exposure of the tip to nitrogen.

The changes in the field emission pattern upon adsorption of nitrogen were not very drastic and similar to those reported for Pt tips (11). A relative decrease in intensity was observed on the stepped surfaces between the (111) and the (100) surface (Fig.1). Adsorption induced segregation effects are not likely because of the rather weak binding between nitrogen molecules and the Pt or Rh surface atoms.

Fig.1 (a) CO adsorption on Pt/Rh (50%:50%) at 80K (b) CO adsorption on Rh at 80K (c) N_2 adsorption on Pt/Rh (12%:88%) at 80K (d) N_2 adsorption on Rh at 80K
DISCUSSION

Both the change in FEM pattern and the work function change brought about by CO adsorption point to a Pt like behaviour of a Pt-Rh (50%:50%) tip following annealing at 1600K. The observed work function change is even equal to that observed on pure platinum within our experimental accuracy. Since the heat of adsorption of CO on Pt and Rh is the same within 10% (14), it is unlikely that adsorption induced surface segregation occurs. We therefore conclude that the surface of Pt-Rh (50%:50%), previously annealed at 1600K consists largely of Pt atoms. Roughening of the surface or a change of distribution of the different surfaces on the tip might contribute to the observed change in $\Delta\phi$ values of nitrogen adsorption on the Pt-Rh surface with higher annealing temperatures. Because a field emitter exhibits a quite well defined and thermodynamically equilibrated surface, more defined perhaps than the single crystals, very often used in surface science studies, it is not likely that these possibilities would have such a profound influence on the $\Delta\phi$ values as shown for the adsorption of nitrogen. Moreover we found that the work function of a Rh emitter did not change with the annealing temperature and it is known that for several gases the change in work function upon adsorption is the same for thermally cleaned and field evaporated emitters.

The apparent work function of the clean Pt-Rh (12%:88%) tip increases with about 0.3 eV upon increasing the annealing temperature from 600K to 1540K. In this context, it should be noted that the work function of a clean Pt tip is about 0.5 eV higher than that of a rhodium emitter. The $\Delta\phi$ for a completely nitrogen covered Pt tip is -0.65eV and for a nitrogen covered Rh tip +0.02eV. The observed values suggest strongly a Pt enrichment of the surface. Comparison of the field emission patterns shows that the alloy behaves Pt-like in the adsorption of nitrogen. A more quantitative analysis of the gathered $\Delta\phi$ values is hampered by the fact that there is not yet a straight theory which relates the work function of an alloy to the surface composition of this alloy.

Comparison of Fig.2 and Fig.3 shows a difference of about 100K in the temperature at which the largest effect was found (around 1000K). Since the two series of experiments were carried out on two different Pt-Rh (12%:88%) tips, this effect can be due to an error in the temperature calibration of the filaments.

Conclusions

In conclusion, the observed variation of the work function of a Pt-Rh (12%:88%) emitter, combined with the work function changes, produced by nitrogen
adsorption, suggest an enrichment of platinum in the top surface layer, following annealing temperatures above 1000K. Platinum segregation increases with increasing annealing temperature. The largest change in surface composition occurs upon annealing around 1000K.

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