X-ray photoelectron spectroscopy study of thiols adsorbed on Pt(111) with and without the presence of a copper monolayer

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The displacement of an electrodeposited Cu monolayer on Pt(111) single crystal by 2-mercaptopyridine (2-MP) and 4-mercaptopyridine (4-MP) has been investigated by XPS. The results indicate that the Cu adatoms are partially displaced by the 4-MP and completely displaced by the 2-MP. An analysis of the S 2p spectra of 2-MP and 4-MP adsorbed on Pt(111) both with and without the presence of a Cu monolayer reveals a small binding energy shift between 2-MP and 4-MP emissions. This effect is probably due to the formation of a surface chelate for 2-MP via bonding through both nitrogen and sulphur atoms. An additional component is assigned to sulphur atoms in dimers, and its intensity correlates with that of the N–Pt component in the N 1s spectra, suggesting that N–Pt interaction decreases the dimer formation probability. In the case of the presence of the Cu adlayer on Pt(111) before mercaptopyridine adsorption, the N–Pt interaction decreases and thus favours dimerization. The presence of sulphates on the surface after the displacement reaction could originate in part from oxidation of the reduced mercaptopyridine. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Thiols chemisorbed on metallic surfaces form films that are suitable for application on electrochemical sensors.[1] Although this is their best-known application, these films can be used also as corrosion inhibitors[2] or for the construction of nanostructure-based devices,[3] among other uses. Aromatic thiols have been studied on Ag(111),[4] Pt(111)[5–7] and Au[8,9] by surface-enhanced Raman scattering (SERS),[10,11] electron energy-loss spectroscopy (EELS), low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS)[7] and electrochemical methods.[4,5] The behaviour generally accepted for both aliphatic and aromatic thiol compounds on these metals is the formation of an ordered layer on the metallic surface, in which the molecules are bound through the sulphur atom upon breakage of the S–H bond and formation of the Pt–S bond.

In this paper the adsorption process and mechanism of surface bonding of 2-mercaptopyridine (2-MP) and 4-mercaptopyridine (4-MP) on Pt(111) have been explored by XPS. Additionally, it has been established that the mercaptopyridines are able to displace copper and silver monolayers[9,12] deposited on gold[13] and platinum[7] electrodes. Therefore, in this work the interaction of these adsorbates with Pt(111) covered previously with a copper

monolayer is also studied and a possible mechanism for this reaction is suggested.

EXPERIMENTAL

The working electrode was a 10 mm diameter Pt single-crystal disc (oriented to ±0.5°) supplied by Goodfellow Cambridge Limited. The crystal was supported by two 0.5 mm Pt wires spot-welded to its sides in such a way as to allow only one face of the crystal to be in contact with the solution. The electrode pretreatment consisted of heating the crystal to ~1000 °C in a gas/oxygen flame for 3 min and then allowing it to cool for 60 s in the vapour of deaerated supporting electrolyte before quenching in the same solution. Surface cleanliness was determined by cyclic voltammetry in 0.5 M H_2SO_4, showing the characteristic 'butterfly' shape first described by Clavilier.[14] Evaluation of the electrochemical area (~1 cm²) of the platinum electrode was carried out by integrating the voltammetric peaks for hydrogen adsorption in 0.5 M H_2SO_4 and using a conversion factor of 210 μC cm⁻².[15] Copper monolayers were deposited at under potential onto Pt(111) electrodes by exposing them to 1×10^{-3} M $CuSO_4$ solution in 0.50 M H_2SO_4. The coulometric charge obtained for copper deposition on Pt(111) by integrating the voltammetric peaks (upd region) was 396 ± 6 μC cm⁻²,[16–19] corresponding to one copper monolayer.[16–19] Once the Cu monolayer on Pt(111) is formed, the electrode is put in contact with 2-MP or 4-MP (1 mM) solution at a constant potential of +0.20 V for 3 min.[20]

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The experimental set-up consisted of a three-compartment cell with provision for the addition and withdrawal of solutions under a positive pressure of prepurified nitrogen at all times. Rinsing of the electrode and/or solution exchange was carried out in a flow-through fashion inside the cell without exposing the electrode to the environment. This was particularly important in experiments where a pre-electrodeposited copper monolayer was subsequently exposed to 2-MP and 4-MP. All the solutions were prepared using water purified with a Millipore Milli-Q system. The 4-MP was purified by sublimation. All the other reagents were of high purity (Merck) and used as received.

The XPS spectra of 2-MP and 4-MP adsorbed on Pt(111) were recorded using a commercial VG-CLAM hemispherical electron energy analyser and a twin-cathode x-ray source, set to Al Kα excitation (1486.7 eV). The base pressure in the ultrahigh vacuum (UHV) chamber during measurements was better than 10^{-9} mbar. During transport from the electrochemical cell to the UHV chamber, the samples were briefly ($\sim$5–10 s) exposed to air. Nevertheless, a direct interaction between sample and air was avoided by allowing a small drop of solution to remain on the sample surface during transport. This remaining solution was subsequently pumped inside the UHV chamber.

RESULTS

When 2-MP or 4-MP (in water) is adsorbed into Pt(111) at a +0.20 V constant potential for 3 min, the corresponding XPS spectra in both cases show similar features with the expected platinum, carbon and oxygen peaks as well as the sulpher and nitrogen emissions. The spectra of the S 2p core level are shown in Fig. 1(a,c). The solid line through the data points is the result of a least-squares fitting procedure consisting of Lorentz functions convoluted with a Gaussian to account for the experimental resolution ($\delta(E) \sim 0.6$ eV) and a Shirley function to simulate the intensity of inelastically scattered photoelectrons (not shown). The Lorentz lines represent the S 2p spin–orbit–split doublet, with a splitting of 1.18 eV and an intensity ratio of $\sim$2 : 1. A small difference in the binding energy (BE) position (see vertical lines) is observed between the 2-MP and the 4-MP samples: 163.1 eV for 2-MP and 162.7 eV for 4-MP. These peaks are assigned to S–Pt bonds[21] and the different BE position observed between 2-MP and 4-MP must be related to the different electronic environment around the sulphur atom in both molecules. In 2-MP the nitrogen atom is close to the sulphur atom, allowing the formation of chelates structures of type S–Pt–N, whereas in 4-MP the nitrogen atom is located in the 'para' position and the sulphur atom only interacts with Pt.

The XPS spectra show an additional S 2p subspectrum at $\sim$164.2 eV appearing in the case of the 4-MP/Pt (III) sample, although it is absent for the 2-MP/Pt (III) sample. The presence of this subspectrum could be related to the possibility of 4-MP to form dimers, bound by the sulphur atom whose electronic environment is different to that of the sulphur atoms in 4-MP alone. This result is in agreement with that obtained for aldrithiol onto polycrystalline platinum.[20] The similarity between these spectra
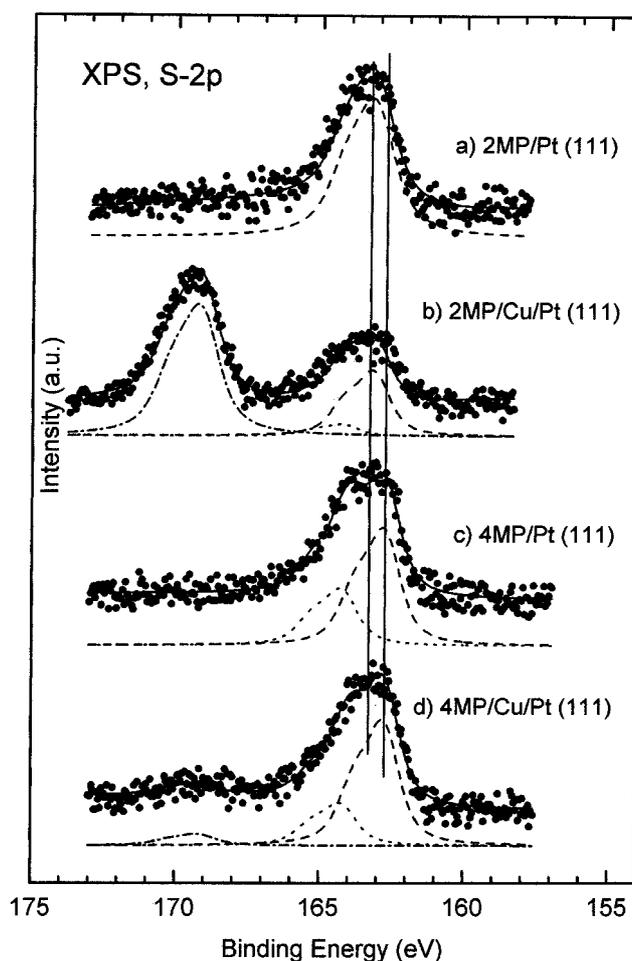

Figure 1. X-ray photoelectron spectra showing the S 2p core levels of: (a) 2-MP adsorbed on Pt(111); (b) one monolayer of Cu on Pt(111) displaced by 2-MP; (c) 4-MP absorbed on Pt(111); (d) one monolayer of Cu on Pt(111) displaced by 4-MP. The solid line through the data points, as well as the subspectra, are the results of a least-squares fitting procedure (see text).

suggests that the dotted component can be associated with the formation of dimers. The absence of this component in the S 2p spectrum of 2-MP/Pt(111) is probably due to the presence of the chelate structure that hinders dimer formation. As we mentioned above, in the 2-MP adsorption the presence of an S–Pt–N chelate is favoured and this structure will hinder dimer formation.

When a Cu monolayer deposited on Pt(111) is put in contact with mercaptopyridines in water or sulphuric acid solution, the copper monolayer is completely displaced at constant potential [+0.20 V vs. HNE (Hydrogen Normal Electrode)] by 2-MP, whereas 4-MP does it only partially. In preliminary works on polycrystalline Pt, this Cu displacement phenomenon was observed by XPS[20] and by cyclic voltammetry.[9] This effect occurs in part because in 4-MP there is no possibility to form a chelate structure, thus diminishing the bond strength with the surface electrode and also not reaching the full coverage at such potential. For Pt(111) this phenomenon has been observed by cyclic voltammetry[7] and by XPS measurements of the Cu 2p core level.

The XPS spectra at the S 2p core level do not show differences between the MP/Pt(111) spectra and those of the corresponding MP/Cu/Pt(111) system except for the presence of the dash-dotted subspectrum at $\sim$169.2 eV

(Fig. 1). Recent studies of XPS have detected the presence of various oxidized forms of sulphur[22] (i.e. sulphonates, sulphates and polysulphides as part of the monolayer structure). The presence of such species has been correlated with both the extent of exposure to the laboratory ambient and the length of the alkyl chain. By comparison, in this case the subspectrum at 169.2 eV observed in the MP/Cu/Pt(111) samples can be assigned to sulphates.[23] They could originate from partial oxidation of the mercaptopyridine molecules, either in aqueous solution or by oxygen diffusion through the water drop during transport to the UHV chamber, as was observed previously for polycrystalline platinum.[20] However, this subspectrum appears only in the case of the MP/Cu/Pt(111) samples. It is known from studies performed on deposition of the Cu monolayer on Pt(111) that the sulphate ions form a $\left(\begin{smallmatrix} 2 & 1 \\ 1 & 2 \end{smallmatrix}\right)$ structure on the (1 × 1) copper layer partially discharged.[16-19] The mechanism of copper monolayer displacement by the mercaptopyridines is not well known (see Discussion). However, the presence of sulphate ions on the electrode surface after copper displacement, which is observed only for this kind of sample, could have its origin in the SO_4^{2-} adsorption on $Cu^{\delta+}$. Additionally, in these samples the subspectrum corresponding to the formation of dimers (~164.2 eV) is also present in 2-MP/Cu/Pt(111), contrary to the 2-MP/Pt(111) case. This effect is probably due to the role played by the Cu monolayer.

The interpretation of the S 2p data is consistent with the results obtained at the N 1s core level (Fig. 2). The N 1s
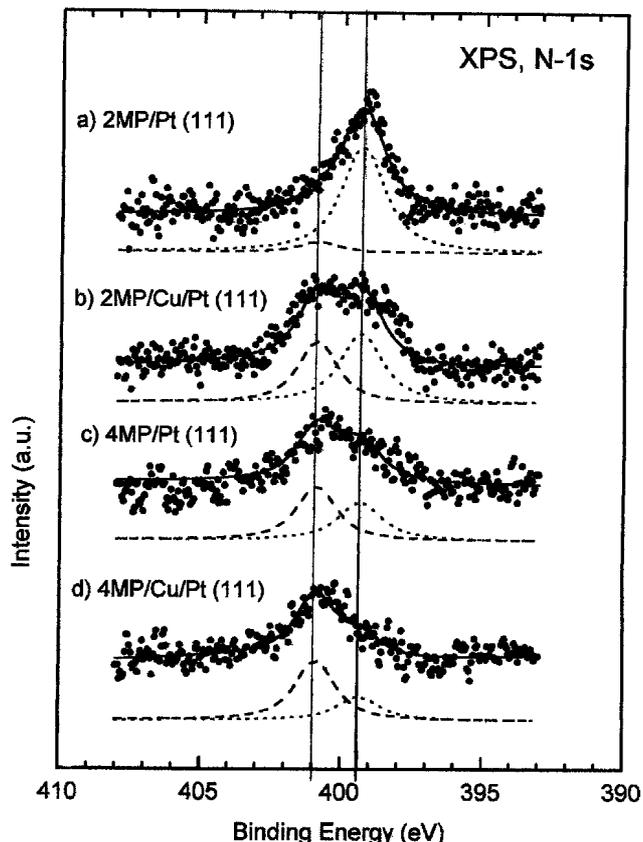
signal has two components located at ~400.8 eV (dashed lines) and 399.3 eV (dotted lines). A similar double structure has been observed in previous works on adsorbed pyridine molecules and other systems.[24,25] According to these works, the component at higher binding energy can be assigned to nitrogen in the pyridine ring, with weak or null N–Pt interaction,[24] and the structure at lower binding energy to N–Pt bonding.[25] The possibility of 2-MP to form chelate structures (S–Pt–N) can explain the higher intensity of the peak at 399.3 eV in spectra 2(a) and 2(b) as compared to spectra 2(c) and 2(d). The presence of this component for 4-MP, where the nitrogen atom is in the 'para' position, indicates some interaction between nitrogen and Pt, probably through deviations of the adsorption geometry with respect to normal geometry.

The formation of a chelate structure should hinder dimerization. A correlation between the dimer component in the S 2p spectra (164.2 eV) and the N–Pt component in the N 1s spectra (399.3 eV) is observed. In fact, the N 1s spectra corresponding to 2-MP/Pt show the highest intensity of the N–Pt component [Fig. 2(a)] and the lowest of the dimer component [Fig. 1(a)]. The presence of the Cu adlayer seems to promote dimer formation and to hinder N–Pt interaction, as is observed in Figs 1(b,d) (dotted lines) and 2(b,d) (dashed lines). Copper adatoms could favour the formation of strong S–Pt bonding in a similar way to the Cu-promoted sulphidation of Pt,[26] diminishing the interaction of nitrogen with Pt.

DISCUSSION

Either 2-MP or 4-MP (in water) is adsorbed onto Pt(111) at constant potential according to the reaction
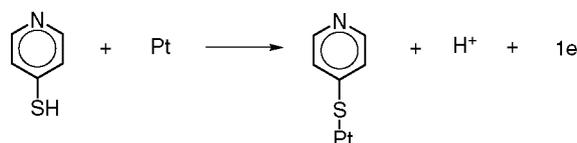
The oxidative adsorption process for thiols has been proved by open-circuit potential (OCP) measurements as well as current–time transients,[27] confirming a net electron transfer from sulphur to the metal as part of the monolayer formation process. However, the sulphur behaves as an electron acceptor when it is bonded to gold[27] or platinum,[28] due to the large difference between the electronegativities of sulphur and gold or platinium.[29] For thiols adsorbed on gold the OCP changes to less negative values, after the initial stages of adsorption, due to a gradual retro-donation of the negative charge that is accumulated on the electrode towards the sulphur adatom. For sulphur adsorbed on Pt(111) it has been determined that the sulphur adatoms have a negative charge as a consequence of a Pt 5d → S 3p electron transfer.[28] As the negative charge on the sulphur becomes larger, the S 2p binding energy becomes smaller.[30] The S 2p BE for 4-MP is smaller (162.7 eV) than for 2-MP (163.1 eV). This result agrees with a larger negative charge on the sulphur, adatom for 4-MP than for 2-MP. In the last case, the presence of the nitrogen atom in the 'ortho' position

Figure 2. X-ray photoelectron spectra showing the N 1s core levels of: (a) 2-MP adsorbed on Pt(111); (b) one monolayer of Cu on Pt(111) displaced by 2-MP; (c) 4-MP absorbed on Pt(111); (d) one monolayer of Cu on Pt(111) displaced by 4-MP.

with the possibility of bonding with the platinum surface favour the withdrawal of the π-electron cloud from the ring towards the nitrogen atom. This effect diminishes the negative charge on the sulphur atom. Therefore, although 2-MP is adsorbed more strongly on Pt(111) (due to the chelate formation) than 4-MP, the S–Pt bond is stronger in 4-MP than in 2-MP. The same results have been obtained previously on polycrystalline platinum, indicating that in this case the surface morphology has no influence. In fact, in the S 2p spectrum only one peak has been obtained for thiol–Pt interaction. Studies of aliphatic thiols adsorbed on gold[31] show two peaks in the S 2p spectrum located at 163.6 and 163.3 eV, depending on whether the sulphur atom adsorption is on step sites or on terraces sites. In the case of sulphur adsorbed on Pt(111),[28] the S 2p spectrum shows two peaks located at 162.31 and 161.37 eV for hollow and bridge sites, respectively. Following this result, it could be possible that 2-MP could be adsorbed on sites of higher interaction energy (two platinum atoms) than 4-MP (one platinum atom).

The mechanism proposed to explain the displacement of the Cu monolayer by both mercaptopyridine solutions is not clear yet. The results obtained from the S 2p spectra indicate that after such displacement the molecules remaining on the surface are the mercaptopyridines, with dimers promoted by the presence of copper and sulphate ions. However, the displacement of the Cu monolayer from the surface (although the Cu has a residual charge) implies their oxidation and consequently mercaptopyridine reduction, as is shown in the following reaction:
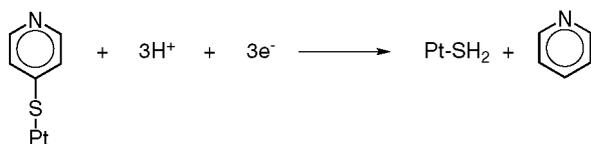
On the other hand, the surface free energy of Cu (1.93 J m^{-2}) is lower than that of Pt (2.69 J m^{-2})[32] and therefore the mercaptopyridines could be adsorbed on the Cu monolayer. Nevertheless, the reduced mercaptopyridine will remain bonded to Pt because the heat of formation of S–Cu is lower than that of the S–Pt bond.[33] Finally, it is possible that the presence of sulphate ions on the surface could originate in part from the oxidation of Pt–SH$_2$, either in aqueous solution or by oxygen diffusion through the water drop during transport to the UHV chamber.[22]

CONCLUSIONS

We have performed an XPS study of the effects of the adsorption of 2-MP and 4-MP on Pt(111) with and without the presence of a Cu monolayer deposited in the upd regime. The results indicate that 4-MP displaces only partially the Cu adatoms whereas 2-MP displaces then totally. To study the displacement mechanism, XPS S 2p and N 1s spectra for 2-MP and 4-MP adsorbed on Pt(111) with and without Cu monolayer were measured. The S 2p emission exhibits a main structure that shows a small binding energy shift between 2-MP and 4-MP signals. This difference in energy position could be associated with the different electronic environment of both molecules. In the case of 2-MP adsorption, the formation of a surface chelate of type S–Pt–N is favoured due to the proximity of the nitrogen atom with respect to the sulphur atom. However, for the 4-MP case, the nitrogen atom located in the 'para' position does not interact with the sulphur atom. In that case, therefore, the chelate structure does not tend to be formed. The presence of a small additional structure in the S 2p spectrum appearing in the case of 4-MP adsorption (and absent for 2-MP) is associated with the possibility of dimer formation. These dimers are bounded by the sulphur atom. This effect of bonding through sulphur atoms in the case of dimer formation is expected to hinder the chelate formation in which the bonding is via nitrogen and sulphur atoms. The results observed for the N 1s spectra are in agreement with this assertion. The signal corresponding to N–Pt bonding exhibits the highest intensity for 2-MP, which is expected to favour chelate formation. However, the lowest intensity of that peak is shown by 4-MP, which promotes dimer formation. The S 2p spectra exhibit the presence of sulphates on the surface in the case of the reduced mercaptopyridines, originating probably from partial oxidation.

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