The reactive chemisorption of formic acid at A1(111) surfaces and the influence of surface

oxidation and coadsorption with water: a combined XPS and HREELS investigation

The reactive chemisorption of formic acid at Al(111) surfaces and the influence of surface oxidation and coadsorption with water: a combined XPS and HREELS investigation

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Abstract. In a combined photoelectron–vibrational spectroscopic study of the chemistry of formic acid interaction with Al(111) surfaces the influence of temperature, surface oxidation and coadsorption with water have been investigated. At the clean surface adsorption at low temperatures leads to deprotonation and on warming to room temperature the major species is formate. On the other hand direct interaction with Al(111) at room temperature leads to more extensive bond cleavage including the formation of chemisorbed oxygen, and carbidic carbon. At the preoxidized Al(111) surface deprotonation is facile at 80 K but there is no evidence for further reaction on warming to room temperature. When formic acid is coadsorbed with water at 295 K, HREEL and XP spectra confirm the formation of surface formate together with hydroxyl and chemisorbed oxygen species.

1. Introduction

The interaction of formic acid with transition metal surfaces has been investigated extensively [1–5] but less attention has been paid to non-transition metals [6–9], even though in related systems they have been shown to exhibit unique chemistry [10–12]. In the present work we extend our interest in reactive chemisorption at sp-metal surfaces to the adsorption of formic acid at Al(111). This system has been studied previously by Crowell *et al* using HREELS, [6], we extend their work to consider adsorption of formic acid at room temperature, adsorption at a preoxidized surface at low temperature and coadsorption of formic acid with water. We also take advantage of the combination of photoelectron and electron energy loss spectroscopies within a single spectrometer to obtain information on the chemisorbed products of the decomposition reaction since x-ray photoelectron spectra are capable of providing quantitative information on all the species present including those not observed by HREELS.

2. Experimental procedure

The spectrometer used for this study is a purpose-built single-chamber instrument combining facilities for photoelectron spectroscopy (XPS and UPS, VG Scientific, East

Grinstead), high resolution electron energy loss spectroscopy (HREELS, VSW Manchester) and low energy electron diffraction (LEED, VG Scientific, East Grinstead). The aluminium single crystal was obtained from Metals Research Ltd., Cambridge. After mechanical polishing (diamond paste, Hyprez, $0.25\,\mu$) it was subjected to several cycles of argon bombardment and annealing at 650 K until surface contamination was reduced below the detection level. The formic acid (BDH, Analytical Reagent grade) and water (distilled) were further purified by several 'freeze-pump-thaw' cycles and the oxygen (Masonlite, 99.99%) was dosed to the system via a liquid nitrogen trap. XPS binding energies are referenced to the clean Al(2p) peak at 72.6 eV [13]. Surface concentrations are calculated from XPS peak areas [13] using Scofield's calculated photoionisation cross-sections [14]. Composite spectra were smoothed and curve fitted with gaussian components using a least squares optimisation program, examples of curvefits to both the O(1s) and C(1s) regions are shown in figure 2(a).

3. Results

3.1. Evidence for chemisorption-induced surface roughening.

In figure 1 the intensity of an electron beam elastically scattered from the Al(111) surface is shown as a function of scattering angle. At the clean surface the beam typically had a resolution of ~ 65–$75\,\text{cm}^{-1}$ with a maximum intensity, sharply peaked in the specular direction, of about 10–15 000 counts/second, figure 1(a). In contrast, at a preoxidized surface ($O(a) = 14 \times 10^{14}\,\text{atoms cm}^{-2}$, $\theta \sim 1$) the elastic beam intensity was reduced by a factor of approximately 10 and found to be independent of the collection angle, figure 1(b). Similar effects were observed after exposure to water and formic acid at 298 K and also after the adsorption of more than a monolayer of formic acid at low temperatures. The chemisorption of oxygen leading to incorporation at aluminium surfaces has been studied by both XPS and LEED [13, 15, 16], and can result in 'strong disorder' of the surface. This would lead to the elastic beam being spread over a wide range of scattering angles and account for the behaviour seen in figure 1. This scattering must of course also apply to the inelastically scattered electrons and has important implications for the surface selection rule in HREELS since one can no longer expect to see dipole scattered and impact scattered electrons confined just to the specular and non-specular directions respectively.

3.2. HCOOH adsorption at a clean Al(111) surface at 80 K

The XP and HREEL spectra in figures 2(b) and 3(b) respectively were recorded at 298 K after the adsorption of formic acid at 80 K. The conditions of the experiment differ slightly from those reported by Crowell *et al* [6] since XP spectra at 80 K (not shown) indicate that the coverage of formic acid is equivalent to several monolayers, whereas Crowell *et al* were probably working at submonolayer coverages.

The HREEL spectrum in figure 3(b) shows strong bands at $1380\,\text{cm}^{-1}$, and $2980\,\text{cm}^{-1}$ which, in agreement with Crowell *et al* [6], are assigned to the $\nu_{\text{sym}}(\text{C–O})$ and $\nu(\text{C–H})$ modes respectively of a surface formate. Weaker features at $1640\,\text{cm}^{-1}$ and $1040\,\text{cm}^{-1}$ can also be attributed to surface formate but the vibrational modes to which they are assigned, $\nu_{\text{asym}}(\text{C–O})$ and $\pi(\text{C–H})$ [2], would only be dipole active for a formate species with low symmetry. The broad feature at 700–$800\,\text{cm}^{-1}$ has been
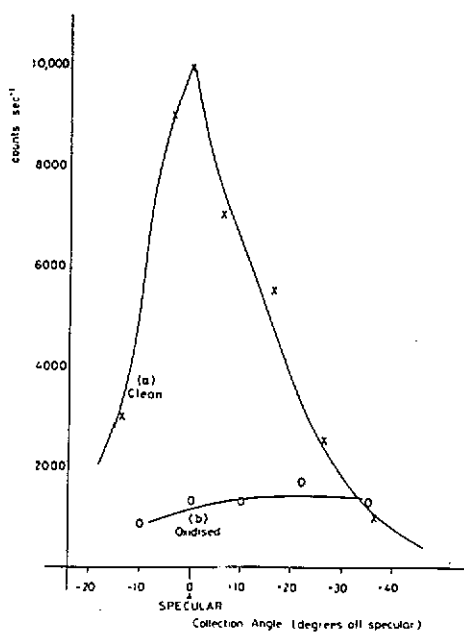
Figure 1. The intensity of the elastically scattered electron beam from aluminum surfaces as a function of collection angle. (*a*) clean Al(111); (*b*) oxidized Al(111) surface (14×10^{14} atoms O(a) cm^{-2}, $\theta \sim 1$).

observed in separate studies of the Al(111)–O system and attributed (see also Erskine and Strong [17]) to chemisorbed oxygen. Crowell *et al* have interpreted similar data to imply decomposition of the formic acid to its 'elemental state'. The extent of decomposition cannot be judged from the HREEL spectra alone; x-ray photoelectron spectroscopy, however, provides quantitative concentration data for the surface species present.

From the XP spectra figure 2(*b*), we calculate a total surface oxygen concentration of 18×10^{14} atoms cm^{-2} and a total surface carbon concentration of 7.9×10^{14} atoms cm^{-2}. Peaks at 531.8 eV in the O(1s) region and 284.0 eV in the C(1s) region have been observed previously at aluminium surfaces [10] and are attributed to chemisorbed oxygen and graphitic carbon respectively, indicating that complete decomposition of at least some of the formic acid occurred. However, the area of the peaks corresponds to only 45% of the total XP peak area and the majority of the adsorbed species (9.9×10^{14} oxygen atoms cm^{-2} and 4.3×10^{14} carbon atoms cm^{-2}) is associated with XP peaks at 533.6 eV and 290.5 eV. These peaks have an oxygen to carbon stoichiometry of approximately 2.3:1 and binding energies close to those typical of chemisorbed formate at other metal surfaces [8, 1]. The presence of molecular formic acid at 298 K can be ruled out on the basis of its characteristic C(1s) and O(1s) binding energies of 291.0 eV and 535.0 eV respectively and the absence of the ν (O–H) band in the HREEL spectra. The O(1s) and C(1s) peaks at 533.6 eV and 290.5 eV can therefore be assigned unambiguously to surface formate.

3.3. HCOOH adsorption at a clean Al(111) surface at 298 K

An exposure (5 L) to formic acid saturates the Al(111) surface at 298 K, giving a total surface carbon concentration of 7.0×10^{14} atoms cm^{-2}. The HREEL spectrum of this

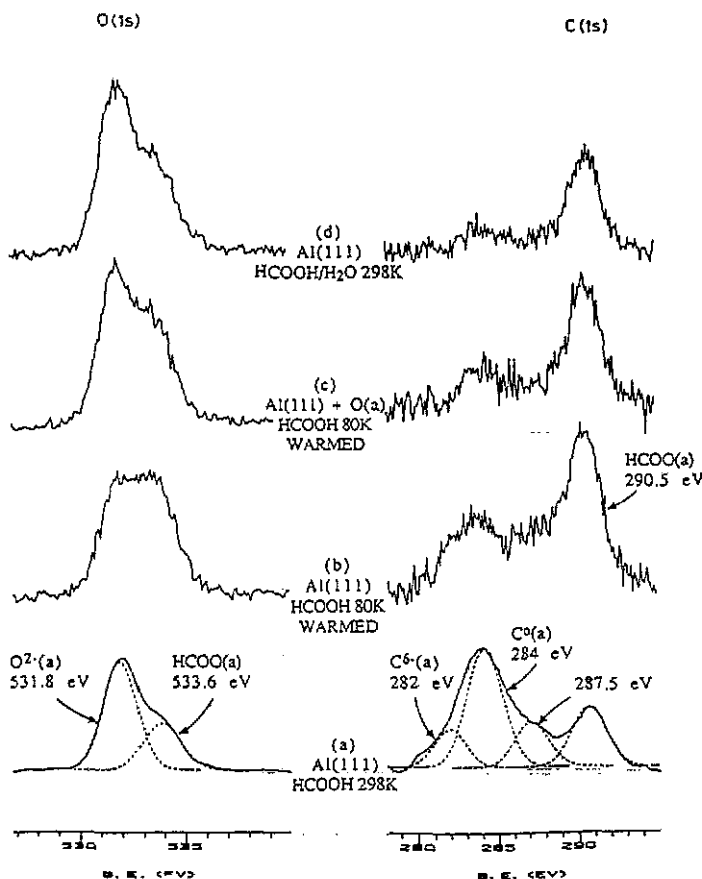O(1s)   C(1s)

Figure 2. X-ray photoelectron spectra of the adsorption of formic acid at an Al(111) surface; (a) 5 L HCOOH at 298 K, spectra have been smoothed and curve-fitted (see text); (b) HCOOH adsorbed at 80 K (multilayers) warmed to 298 K; (c) multilayers of HCOOH adsorbed at a preoxidized Al(111) surface (14×10^{14} atoms O(a) cm^{-2}) at 80 K and then warmed to 298 K; (d) HCOOH/H$_2$O mixture (ca. 1:10), exposed (10 L) to Al(111) surface at 298 K.

surface, (figure 3(a)) is very similar to that observed following low temperature adsorption (figure 3(b)) with strong bands at 700–800 cm^{-1}, 1380 cm^{-1}, and 2980 cm^{-1}, and a weaker feature at 1640 cm^{-1}. As discussed above, these bands can be assigned to surface formate and to the chemisorbed products of formic acid decompositon, O(a), C(a) etc. Despite the similarity in the HREEL spectra in figure 3(a) and 3(b), the XP spectra of the surface reveal a very different surface chemistry following adsorption at the different temperatures (figure 2(a) and 2(b)).

Whereas after low temperature adsorption the major surface species was formate, the XP spectra recorded following adsorption at 298 K are dominated by peaks at lower binding energies indicating extensive decomposition of the molecule. The XP spectra have been smoothed and curvefitted in order to quantify the contribution made to the spectrum by the different surface species. In the O(1s) region the spectrum is composed of two components with binding energies of 531.8 eV and 533.5 eV, the calculated surface coverages of the two species are 9.1×10^{14} atoms cm^{-2} and 4.6×10^{14} atoms cm^{-2} respectively. These peaks are assigned as described above to chemisorbed oxy-

gen and chemisorbed formate. In the corresponding C(1s) spectrum there are four peaks with binding energies of 282 eV, 290.6 eV, 284 eV and ~ 287.5 eV. The four species are present at surface concentrations of 1.1×10^{14}, 3.0×10^{14}, 1.2×10^{14} and 9.1×10^{14} atoms cm^{-2} respectively. The features at 284 eV and 290.6 eV are assigned to graphitic carbon and chemisorbed formate as discussed in section (ii), and the C(1s) peak at the lowest binding energy, 282 eV, is attributed to a surface carbide [10].

The band at 287.5 eV however has not been observed previously at aluminium surfaces. Its binding energy indicates a carbon atom with a slightly higher electron density than the formate (290.6 eV) but slightly lower than a CH$_x$ species. The most likely assignment of this peak is to a metastable intermediate in the decomposition of the formate. There are two possibilities, CHO(a) and CH(a), which involve the scission of either one or both of the C–O bonds respectively. In view of the relatively high binding energy we judge the former to be most probable. There is no clue to the identity of the species from the HREELS, either because the molecule has no strong vibrational bands or because the bands overlap with those due to formate and chemisorbed oxygen.

3.4. HCOOH adsorption at a preoxidized Al(111) surface at 80 K

The Al(111) surface was preoxidized at 295 K to give a surface oxygen coverage of 15×10^{14} atoms cm^{-2}. After cooling to 80 K the sample was dosed (5 L) with formic acid. XP spectra at this temperature indicated that several monolayers of formic acid had been adsorbed. The XP and HREEL spectra in figure 2(c) and 3(c) respectively were recorded after warming the adlayer to 298 K.

Only a single peak is observed in the C(1s) region of the XP spectrum, with a binding energy of 290.6 eV; this corresponds to a species with a surface coverage of 3.8×10^{14} atoms cm^{-2}. In the corresponding O(1s) spectrum, a shoulder has developed at 533.6 eV; after curve fitting it is shown that this corresponds to a species with a surface coverage of 8.0×10^{14} atoms cm^{-2}. These O(1s) and C(1s) peaks are assigned as above, to surface formate. There is no evidence for any decomposition of the chemisorbed formate, the small contribution from graphitic carbon observed in the C(1s) region at 284 eV developed during preoxidation of the Al(111) surface.

The HREEL spectra for this experiment (figure 3(c)) contrast sharply with the other spectra of figure 3. Although the elastic peak intensity is approximately the same for the four experiments reported here, some of the vibrational bands observed with the preoxidized surface are much more intense whilst others are missing. The ν_{sym}(C–O), and ν(C–H) modes of formate at 1380 cm^{-1} and 2980 cm^{-1}, are again the strongest in the spectrum with a new feature at 340 cm^{-1} assigned to the ν(Al–O) stretch of the formate. The latter was observed by Crowell *et al* for chemisorbed formate at the clean aluminium surface at low temperatures [6] but was lost upon warming to room temperature. Bonds at 1040 cm^{-1} and 1640 cm^{-1} are assigned as above to the ν_{sym}(C–O) and π(C–H) modes of surface formate.

What is particularly interesting about spectrum 3c is lack of any strong features in the region between 400 cm^{-1} and 1000 cm^{-1} since the formate bending mode δ(OCO) is known to occur in this region [2]. Its absence is surprising in view of the strong formate bands at 1380 cm^{-1} and 2980 cm^{-1}. The bending mode was observed at 760 cm^{-1} by Crowell *et al* at the clean surface at 120 K but became obscured by the oxide bands at 273 K [6]. Very similar HREEL spectra to figure 3(c) have been reported by Sen and Rao for formic acid adsorption at a preoxidized zinc crystal [7] and by
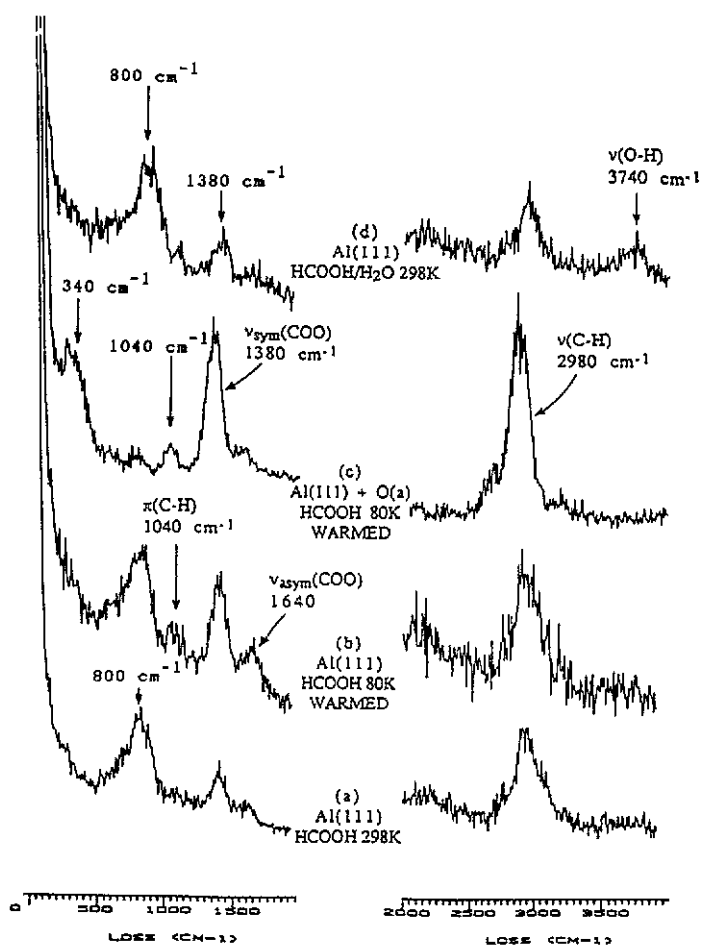
Figure 3. Electron Energy Loss Spectra: legends as for figure 2.

Petrie and Vohs at the (0001) Zn surface of ZnO [9], though in the latter case the absence of the $\delta(OCO)$ band may be due to the method by which the data were collected.

3.5. Coadsorption of H_2O and HCOOH at Al(111)

Coadsorption of water and formic acid was studied at 298 K, and figures 2(*d*) and 3(*d*), show XP and HREEL spectra after exposure (10 L) to a 10:1 water/formic acid mixture. The O(1s) region of the XP spectrum exhibits two peaks with binding energies of 531.8 eV and $\sim$ 533.3 eV. The former, due to chemisorbed oxygen, corresponds to a surface concentration of 12×10^{14} oxygen atoms cm^{-2}, the latter corresponds to approximately 7.0×10^{14} oxygen atoms cm^{-2} and may contain contributions from both surface formate and hydroxide species. these two species have very similar O(1s) binding energies. The presence of the formate is evident from a peak in the C(1s) region at 290.5 eV, and the presence of the hydroxide is confirmed by the characteristic $\nu(O–H)$ stretch in the HREEL spectrum at 3740 cm^{-1}. From the C(1s) spectrum we calculate the surface concentration of the formate to be 3.0×10^{14} moleculate cm^{-2}. This corresponds to 6×10^{14} oxygen atoms cm^{-2} which suggests a hydroxide concentration of

approximately $1.0 \times 10^{14} \, \text{cm}^{-2}$.

It is clear from the XP spectra that the coadsorbed water has completely blocked the decomposition path for the chemisorbed formate (cf. figure 2(a)). The HREEL spectrum, figure 3(d), however differs from that recorded with the preoxidized surface where decomposition of the formate was also blocked and resembles more closely spectrum 3a where the XPS shows extensive decomposition.

4. Discussion

The photoelectron spectra in this study reveal the extent of the decomposition of formic acid at clean and modified aluminium surfaces and the nature of the chemisorbed products of the reaction. Extensive decomposition of the formate was only observed after room temperature adsorption at the clean surface. The decomposition pathway was blocked by both preadsorbed oxygen and coadsorbed water and in the case where high coverages of formic acid were adorbed at low temperatures, decomposition was also restricted. Crowell *et al* suggested that 'dramatic decomposition' occurred after warming a low coverage of chemisorbed formate from 120 K to 273 K. Our results do not contradict these conclusions (we examined only high formic acid coverages at low temperature) but the similarity of the spectra in figures 3(b) and 3(a) shows that HREELS does not discriminate easily between very different surface conditions.

The inhibition of decomposition by adsorbed oxygen, water and the formate molecules themselves suggests that the decomposition reaction is controlled by the availability of free aluminium sites; low temperature adsorption leads to very high surface concentrations of chemisorbed formate resulting in few surface aluminium sites being available for the decomposition step that occurs at higher temperature.

Where decomposition of the formate does occur the chemisorbed products are mainly oxygen, graphitic carbon and carbidic carbon but with some evidence from the C(1s) spectra for a surface species characterized by a peak at 287.5 eV (figures 2(a) and 2(b)). This we suggest reflects a metastable surface intermediate HCO(a) present in the decomposition of the chemisorbed formate to surface oxide and carbon. No evidence for this species is however available in the corresponding HREEL spectrum.

There is generally less information to be gained from the HREEL spectra but some interesting points are raised. In particular after the adsorption of high coverages of formic acid, bands assigned to the $\nu_{\text{asym}}(\text{COO})$ and $\pi(\text{C-H})$ modes of chemisorbed formate are observed even though they are 'forbidden' by the surface selection rule for formate with C_{2V} symmetry. Crowell, Chen and Yates interpret similar data [6] as evidence of a lower symmetry for the formate but the issue becomes less clear when the effects of surface roughening are taken into account.

We suggest that in the present studies the 'forbidden' bands may arise from a significant contribution to the 'specular' spectrum from impact excited electrons, the latter being due to the absence of a well defined specular direction. A similar conclusion was reached by Wolkow and Moskovits for benzene adsorbed at silver film surfaces [18].

Surface roughening however cannot account for the HREELS spectrum of the chemisorbed formate species at the preoxidized surface, figure 3(c), where the $\nu_{\text{sym}}(\text{C-O})$ and $\nu(\text{C-H})$ bands are very strong but the $\delta(\text{OCO})$ bending mode absent. As mentioned earlier there is close similarity between this spectrum and that

reported by Sen and Rao, for formate present at an oxidized zinc crystal [8], and by Petrie and Vohs for formate at ZnO [10]. In each case the $\delta(OCO)$ band is missing and the dipole 'forbidden' $\nu_{asym}(C-O)$ and $\pi(C-H)$ bands are observed. These commom features may indicate a particular orientation of the formate at oxidized surfaces, Petrie and Vohs suggesting that the molecule adopts a monodentate structure with the C–H bond approximately parellel to the surface [10], figure 4. Such an orientation would result in C_s symmetry for the chemisorbed formate (providing the plane of the molecule is prependicular to the surface) and both the $\nu_{asym}(C-O)$ and $\pi(C-H)$ modes would be allowed, whereas the $\delta(OCO)$ band would be forbidden. For this orientation the C–H stretching mode would also be forbidden but the strong band at $2980\,\mathrm{cm}^{-1}$ can be explained by impact scattering which is known to make a strong contribution to the excitation of vibrational modes involving hydrogen atoms. If this explanation of the spectra in figure 3(c) is correct however it implies a strong surface selection rule at the oxidized surface.
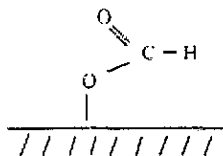

Figure 4. The structure of formate at oxidized sp-metal surfaces (after [9]).

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