Adsorption and decomposition of formic acid on Ni{110}

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Abstract

The adsorption of formic acid on Ni{110} has been extensively studied over a wide temperature range using RAIRS. At 300 K, the decomposition of the acid produces adsorbed CO and formate, the ratio of which is dependent on the exposure. The IR spectra show initially the presence of CO alone. Subsequently, however, coadsorbed CO and formate do exist on the surface. With prolonged exposure the coadsorbed CO is completely removed, leaving only formate on the surface. These observations are correlated with two competitive mechanisms for the decomposition of the surface formate: C–H and C–O bond cleavage to produce CO_2 and adsorbed CO, respectively. For low exposures there is a high probability for C–O bond cleavage, and with increasing exposure this changes to favour C–H bond cleavage. The change in selectivity with exposure is attributed to accumulation of very small quantities of carbon from the initial decomposition sequence, which stabilise the formate and destabilise the adsorbed CO. With preadsorbed carbon and oxygen IR spectra reveal significant stabilisation of the surface formate, with the change in the decomposition pathway. Adsorption at 120 K shows the presence of both CO and formate regardless of exposure. At this temperature coadsorbed CO only accounts for a small fraction of the overlayer and is produced from the dissociation of the acid at defect sites.

1. Introduction

The surface formate species has attracted considerable interest, as it has often been implicated as a reaction intermediate in catalytic reactions, for example in methanol synthesis. On unreactive metals such as Ag [1] and Au [2,3] molecular adsorption and desorption of formic acid is seen, despite the rela-

tively high acidity of the acid. On the {110} planes of these metals preadsorbed oxygen readily abstracts the acidic hydrogen to give a stable formate [1,3]. At the other extreme palladium [4] completely dissociates the acid into CO, CO_2 and H_2 with no identifiable surface formate species ever present. With adsorption onto most other metals such as Cu [5–9], Ni [10–18], Pt [19,20], Ru [21–23], Mo [24], Fe [25] and W [26], the molecule initially readily dehydrogenates to produce a stable formate, which then subsequently decomposes autocatalytically to produce H_2, CO_2, either exclusively as seen on Cu and Pt, or in some cases there is additional evolution of CO, as on Ni and Ru, suggesting that there is cleavage of the formate C–O bond.

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The low Miller index planes of nickel single crystals show similar surface chemistry towards the adsorption and decomposition of formic acid [10–18]. In general a distribution of temperature dependent desorption products are seen, with water being liberated at low temperatures (230 K) and evolution of CO_2 and H_2 (390 K) and CO (440 K) at higher temperatures. The CO_2 and H_2 are produced in a reaction-limited step, whereas the CO evolution is desorption limited. These results were once commonly rationalised using a bimolecular dehydration reaction, leading to an adsorbed intermediate of $HCOO \cdot HCO$ stoichiometry. This intermediate was readily assigned to formic anhydride, which was thought to subsequently decompose in a single auto-catalytic step to yield CO_2 and H_2, and adsorbed CO. However, for Ni{110} vibrational spectroscopy has established that the only readily identifiable intermediate is a surface formate species [17,18]. This contrasts with Ni{111} where the vibrational data obtained using RAIRS has been correlated with formic anhydride [16], although the observed vibrational structure is clearly outside the range for which one would expect the dominant anhydride modes to occur.

For Ni{110} the two independent HREELS studies identify the surface formate. However, in one study a significant amount of coadsorbed CO is observed [17], which may be expected in the absence of the formic anhydride and in accord with the dehydration reaction, as the latter indicates cleavage of a C–O bond. Some of these small differences indicate that the reactive adsorption of formic acid on nickel surfaces may be even more complex than previously envisaged. The difficulty in establishing a common reaction mechanism seems to be particular to the nickel surfaces, although ruthenium surfaces show comparable behaviour [21–23]. On other transition metal surfaces, although there is variation in the reaction mechanism, it is however well understood. For example, the relatively unreactive copper surfaces show much simpler behaviour, producing only H_2 and CO_2 as the desorption products. Here, the decomposition proceeds via a dehydrogenation reaction, where the formic acid adsorbs to produce a formate and an H adatom, with the formate subsequently decomposing by C–H bond cleavage to produce CO_2 and H_2. In another example, Fe{100}, the

formate has equal probability of decomposing via C–H or C–O bond cleavage to give CO_2, H_2 and CO, although on this surface there is no production of water, and the surface is left oxidised [25]. On these latter types of surfaces the decomposition pathway has been correlated with the metal–oxygen bond strengths, i.e. increasing strength of M–O in the formate increases the decomposition probability via C–O bond cleavage to produce CO. Calculations for the formate decomposition on nickel surfaces show that this later mechanism is a probable decomposition pathway. A recent detailed TDS and RAIRS study for formate decomposition on Ru{001} finds equal probability for the C–H and C–O bond cleavage to produce CO_2 and CO respectively [23].

In this paper RAIRS has been used to monitor the adsorption sequence of formic acid on clean (1×1), (4×5) carbidic and (2×1) *oxide* surfaces. It was of particular interest to resolve (i) the previous dispute regarding the presence of coadsorbed CO and its significance to the reaction mechanism, as the theoretical studies indicate; and (ii) whether the high resolution IR data can be reconciled with formic anhydride, as in the case for Ni{111}. The observed vibrational data is correlated with the vast amount of thermal desorption data that already exists for this system.

2. Experimental

All RAIRS experiments were carried out in a UHV chamber described elsewhere [27], equipped with LEED, AES and TPD for crystal preparation and characterisation. All spectra were collected at 4 cm^{-1} resolution, with the co-addition of 100–400 scans (52–208 s), using an MCT detector. The Ni{110} crystal was cleaned by repeated cycles of argon ion bombardment and annealing to 900 K until both LEED and AES indicated a clean, ordered surface.

The formic acid used in this study (Aristar grade, BDH chemicals) was dried using boric acid anhydride and vacuum distilled, and was further purified using many freeze thaw cycles which removed any residual adsorbed gases in the liquid. The deuterated formic acid (DCOOD from Janssen Chemica) was purified using freeze thaw cycles only. The purity of

both was confirmed by mass spectrometry upon admission into the chamber. All exposures are by background dosing via a leak valve, are uncorrected for any ion gauge effects, and are given as measured in the main chamber and *not* the infrared cell.

The carbidic surface experiments were performed on a (4 × 5) carbon overlayer which was generated by cracking ethylene at 550 K; a 20 L exposure produced a sharp (4 × 5) LEED pattern. The *oxide* surface was prepared using a 1 L exposure of oxygen at 400 K which produced a sharp (2 × 1) LEED pattern. In both cases the crystal was exposed to the gases in the main chamber.

In the experiments where the overlayer is annealed the procedure used was to slowly warm the crystal to the required temperature and then maintain it constant during data acquisition. The data acquisition was always repeated several times to ensure that the recorded results corresponded to steady state conditions for a given temperature.

3. Results

3.1. Adsorption of CO on (4 × 5) carbidic Ni{110}

In the course of this study the adsorption and decomposition of formic acid on Ni{110} produced a significant amount of coadsorbed CO on the surface, together with decomposition products C(a) and, possibly, O(a). Adsorption of CO onto a clean Ni{110} surface proceeds with the CO adsorbed in two different coordination sites, two-fold bridge and atop bonded, the latter being the majority species [28]. The vibrational frequencies for these shift from 1860 and 2000 cm^{-1} to 1940 and 2060 cm^{-1}, respectively, for the coverage range $0 \leqslant \theta_{co} \leqslant 0.7$ ML. Above this coverage a sharp single band at 1998 cm^{-1} is seen, corresponding to the tilted (2 × 1)p2mg CO overlayer. The ratio of the atop and bridge CO species is dramatically modified with the presence of coadsorbed hydrogen. Hydrogen has been shown to stabilise the two-fold bridged species for relatively low coverages of CO.

RAIRS spectra for the adsorption of CO on a (4 × 5) carbidic surface at 180 K are shown in Fig. 1. As for the clean (1 × 1) surface, CO adsorbs in terminal atop sites, but the major difference is that
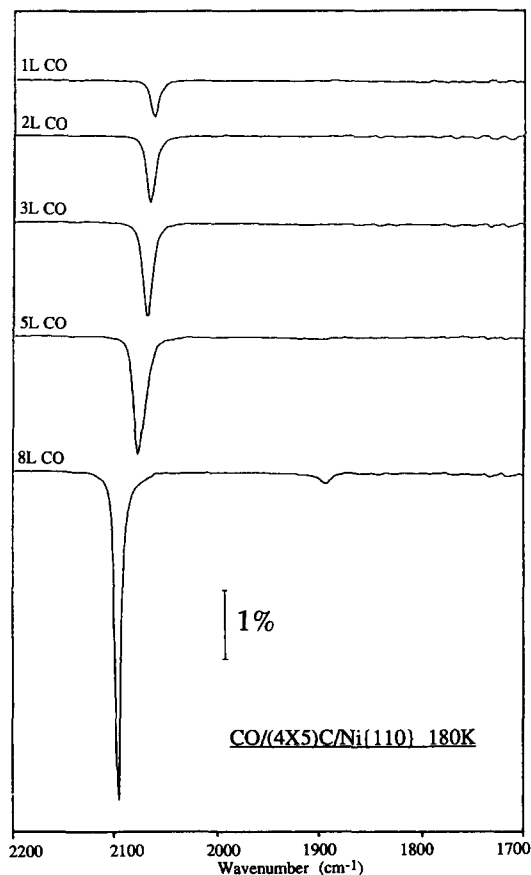

Fig. 1. Successive RAIR spectra obtained during exposure of Ni{110}-(4×5)-C to CO at 180 K at the exposures indicated in langmuir (1 L ≡ 10^{-6} Torr·s).

the CO stretching frequency is initially at 2063 cm^{-1} at low coverages (cf. 2000 cm^{-1}) which steadily shifts to 2105 cm^{-1} (cf. 2060 cm^{-1}) at saturation, where a very intense and narrow ($\Delta\omega = 4$ cm^{-1}) band is seen. At saturation a band also appears at 1893 cm^{-1}, corresponding to two-fold bridged CO, although this band attenuates completely when a further large exposure of CO is added, with the band at 2105 cm^{-1} being left unchanged in frequency and intensity. It is now fairly well established that on carbidic nickel surfaces the heat of adsorption of CO is reduced with respect to the clean surface. The heat of adsorption has been reported to drop from 120 kJ mol^{-1} to < 85 kJ mol^{-1} on the clean and carbidic surfaces respectively [29]. This trend is seen in the infrared data: on warming the saturated CO over-

layer from 180 to 300 K CO desorbs during data acquisition, thus reflecting the lower desorption temperature for CO. Adsorption of CO at 300 K onto this surface is achieved only through dynamic equilibrium with CO in the gas phase. In summary, the vibrational frequency of the internal stretching mode of CO serves as an indirect indicator for the presence of coadsorbed species, especially hydrogen and carbon.

3.2. Adsorption of formic acid at 120 K

Fig. 2 shows the development of the vibrational structure with increasing exposure of formic acid on a clean surface at 120 K. The immediate conversion of the formic acid to the surface formate is seen, marked by the appearance of the characteristic vibrational frequencies generally associated with the formate species. The vibrational modes and the corresponding frequencies are gathered together in Table 1 and illustrated in Fig. 3. Initially there is a complete absence of any vibrational structure that can be associated with molecular HCOOH adsorption; in particular RAIRS would show intense bands at 1720, 1240 and 960 cm^{-1} for $\nu(C=O)$, $\nu(C-O)$ and $\delta(OH)$ respectively. For initial low exposures the formate is identified by the relatively strong $\nu_s(OCO)$ which in this case consists of two components at 1364 and 1344 cm^{-1}, indicating two different surface formate species. In addition there is a band at 1874 cm^{-1} associated with CO stabilised in two-fold bridge sites, presumably by the presence of coadsorbed hydrogen, indicating that even at low temperatures some of the formic acid dissociates to give coadsorbed H and CO. No other species can be detected from the dissociation or reaction of formic acid. However, with increasing exposure the bands increase in intensity and at 8 L exposure the weaker
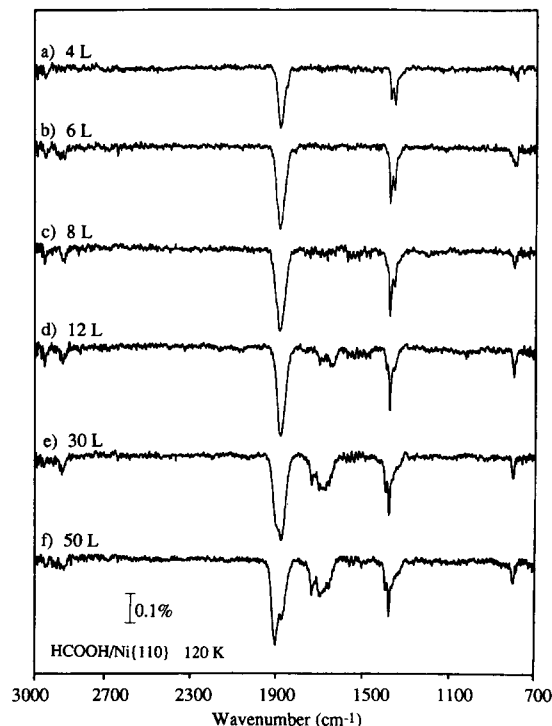

Fig. 2. Successive RAIR spectra obtained during exposure of clean Ni{110} to HCOOH at 120 K.

Table 1
Tabulated vibrational frequencies for sodium formate and the corresponding values for the surface species

Assignment	Symmetry	Na(HCOO) [a]	HCOO/ Ni{110}	DCOO/ Ni{110}
$\nu(CH)$	A$_1$	2824	2840	2180
$\nu_a(OCO)$	B$_1$	1584	1600	1600
$\nu_s(OCO)$	A$_1$	1352	1352	1330
$\delta(CH)$	B$_1$	1384	1384	1000
$\pi(CH)$	B$_2$	1072	1000	
$\delta(OCO)$	A$_1$	776	770	750

The values for (a) are taken from Ref. [30].
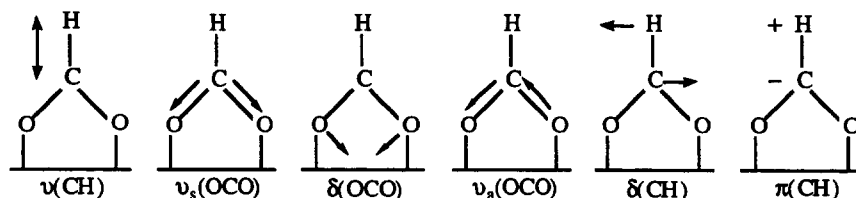

Fig. 3. A schematic illustration of the six normal modes of vibration of adsorbed formate. For a C$_{2v}$ symmetry only the $\nu(CH)$, $\nu_s(OCO)$ and $\delta(OCO)$ modes have a dynamic dipole perpendicular to the surface and are IR active.

δ(OCO) and ν(CH) bands are more clearly resolved at 794 and 2840 cm^{-1} respectively. The ν_s(OCO) band remains unchanged at 1345 and 1365 cm^{-1}, although the low frequency component maximises in intensity at an early stage and remains constant thereafter. At higher exposures (spectrum d) an additional broad structure consisting of two bands centred at 1670 and 1628 cm^{-1} appear together with a shoulder on the high frequency side of the ν_s(OCO) bands. At saturation the high frequency shoulder clearly develops into a band at 1383 cm^{-1} together with an additional band at 1720 cm^{-1}. The CO band remains relatively constant in frequency and intensity, although at saturation it is split into components at 1892 and 1865 cm^{-1}. At this temperature it was not possible to form condensed multilayers of the acid.

3.3. Warming the formate to 300 K

Fig. 4 shows the effect of warming the saturated layer formed at 120 K. It can be seen that at 160 K the structure centred around 1600 cm^{-1} starts to diminish, and the 1720 cm^{-1} component has completely disappeared. At 200 K only a small band remains at 1671 cm^{-1} and the band at 1383 cm^{-1} is present only as a shoulder. The increase in intensity of the CO band at 1892 cm^{-1} may be attributed to increased ordering in the overlayer and decomposition of adsorbed formic acid. At this temperature the low frequency component of the ν_s(OCO) is once again resolved into an individual component. On warming further there is an increase in the size of the ν_s(OCO) at 1365 cm^{-1}. At and above 240 K for coadsorbed CO there is switching of sites from two-fold bridge (1916 cm^{-1}) to terminal atop (2035 cm^{-1}), presumably as the coadsorbed hydrogen stabilising the former is removed from the surface, as either H$_2$ or H$_2$O. At 285 K, a shoulder develops on the high frequency side of the main CO band, now at 2042 cm^{-1}. On further warming this band increases in intensity and shifts back down in frequency to 2034 cm^{-1}. This trend suggests that the formate anion and CO exist in separate islands, which, in the case of CO leads to a relatively high density structure. As the formate decomposes producing more coadsorbed CO on the surface, the CO islands occupy more space and become less dense, and struc-
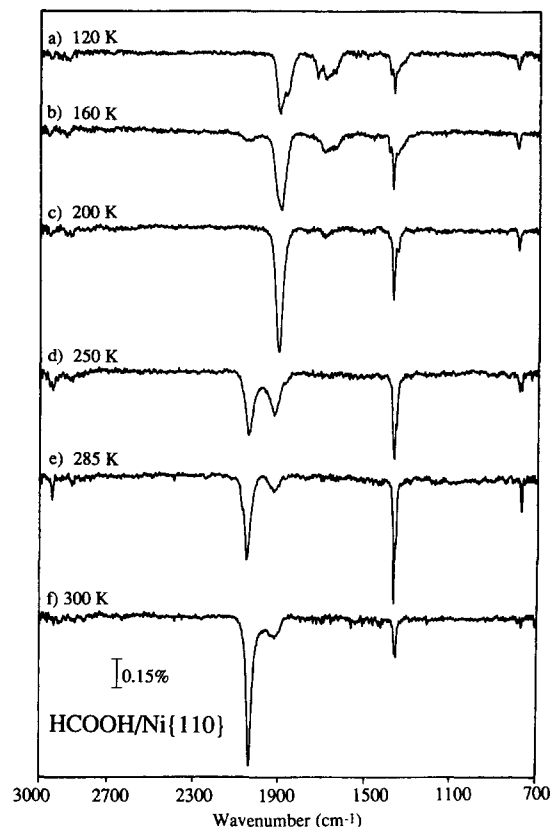

Fig. 4. (a) A RAIR spectrum from a saturated layer of HCOOH on Ni{110} at 120 K; (b)–(f), successive spectra observed while the surface is warmed to 300 K demonstrating the decomposition of the formate species formed at 120 K.

ture relaxes to that of the clean surface, hence reducing dipole–dipole interactions. This indicates that the interaction between CO and formate is repulsive. At 240 K the low frequency component of the ν_s(OCO) at 1338 cm^{-1} increases considerably in intensity and the δ(OCO) also consists of two components at 790 and 773 cm^{-1}. All three vibrational modes of the formate increase in intensity considerably at 285 K. The band at 2942 cm^{-1} is a combination band, δ(CH) + ν_a(OCO), gaining intensity by Fermi resonance with the ν(CH) [6]. At 300 K the formate has almost completely decomposed to leave CO on the surface; after a few minutes, the bands at 1355 and 1338 cm^{-1} in spectrum f are completely attenuated. Hence formate is unstable on a clean surface at 300 K. The increase in the CO bands indicate that the formate partially decomposes via C–O bond cleavage.

3.4. Adsorption of formic acid at 320 K

The instability of formic acid on clean Ni{110} at 320 K was also demonstrated by direct adsorption at this temperature. When the crystal is exposed to relatively small doses of the acid the infrared spectra show only the presence of adsorbed CO, with bands characteristic of CO on the clean surface (ν_{CO} = 2027 and 1900 cm^{-1}). There is a complete absence of the bands characteristic of a formate or any other species derived from formic acid, except CO. However, as the exposure to HCOOH is continued, it was noted that a small band at 1348 cm^{-1} appeared and then decayed with time. This can be associated with the ν_s(OCO) of formate temporarily stabilised prior to decomposition. In order to deduce the decomposition sequence to complete saturation of the surface either by CO or any other species, a series of spectra was acquired during exposure to a constant pressure of 4×10^{-8} mbar HCOOH. The results are shown in Fig. 5. The initial indication of formate on the surface is from the appearance of the small band at 1348 cm^{-1} alongside the CO bands at 2030 and 1902 cm^{-1}. Its relatively low concentration at this stage makes the much weaker C–H stretch and OCO deformation virtually undetectable. At around 35 L exposure we observe probably the most interesting spectra of this particular sequence. An increase in the coverage of the surface formate is seen, demonstrated by the growth of three absorption bands at 2944, 1362 and 777 cm^{-1}, corresponding to ν_{comb}, ν_s(OCO) and δ(OCO), respectively. In addition, in the CO stretching frequency region there are also three bands at 1918, 2052 and 2070 cm^{-1} associated with three different CO species. The surface formate coverage continues to steadily increase with longer exposure. Concurrently, a gradual attenuation of the CO-related bands are observed, indicating the removal of CO from the surface. After the complete removal of CO only those bands associated with formate are observed, as shown in spectrum d. Evacuation of the background formic acid pressure at this point did not change the infrared spectra at all, and it was noted that the formate layer formed in this way was stable to 400 K. The subsequent decomposition proceeds with the gradual decay of the formate peaks with no new vibrational bands being observed.

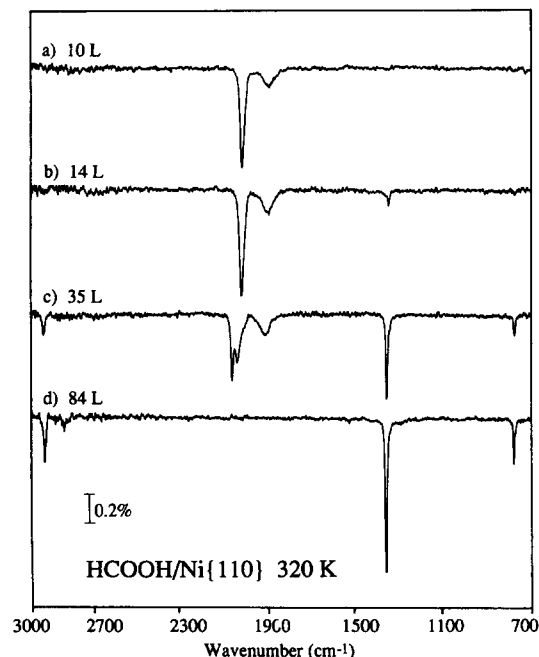Adsorption at 300 K was identical, although the

Fig. 5. Successive RAIR spectra obtained during the exposure of an initially clean Ni{110} surface to HCOOH with the surface maintained at 320 K. Initially, only the decomposition produce CO is seen; at intermediate exposures, both formate and CO are present, and at high exposures the only species present is the formate. A comparison between spectrum (c) and spectrum (d) provides a resolution of the controversy between Madix et al. [17] and Jones et al. [18].

CO could not be completely removed. The appearance of the CO band at 2070 cm^{-1} can be related to the presence of carbon on the surface, which may arise from the decomposition of the formic acid, formate or some other short-lived intermediate derived from these two species, such as a formyl species (HCO). The interaction of formate with CO has been suggested to be attractive since the two species have opposite net dipoles [17], and this interaction may lead to a frequency shift of the CO. The absence of the 2070 cm^{-1} band at low temperatures, where some interaction would be expected within the saturated overlayer, makes this an unlikely explanation. Benziger and Schoofs find that the CO–formate interactions on Ni{111} are strongly repulsive from the decomposition kinetics of the adsorbates [32], consistent with island formation discussed above.

3.5. Adsorption onto Ni{110}-(4 × 5) carbidic surface

The increased stability of the surface formate by prolonged exposure at 320 K, together with the appearance of a CO band above 2070 cm^{-1}, may indicate a role for surface carbon in its stabilisation. Hence we studied the adsorption of the acid onto a (4 × 5) carbidic overlayer on the surface. Results from the adsorption of DCOOD at 300 K are shown in Fig. 6. Adsorption of the acid immediately produces the formate together with a very small band at 2063 cm^{-1} associated with CO on the carbidic surface. The bands shift with increasing coverage from 746, 1328 and 2179 cm^{-1} to 746, 1331 and 2183 cm^{-1} for δ(OCO), ν_s(OCO) and ν(CD) respec-
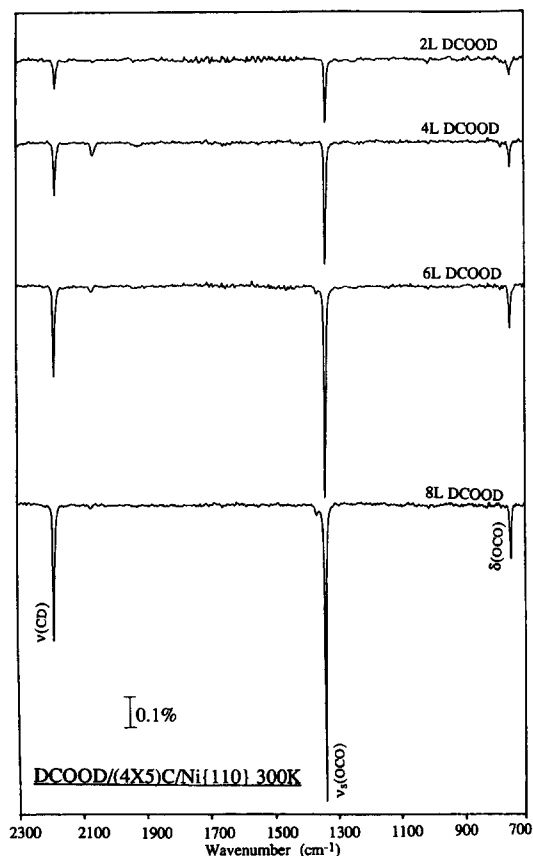

Fig. 6. Successive RAIR spectra obtained during the exposure of Ni{110}-(4×5)-C to DCOOD at 300 K. The spectra are dominated by the formate species, although some dissociation to CO is detected (band at 2063 cm^{-1}) at low exposures.
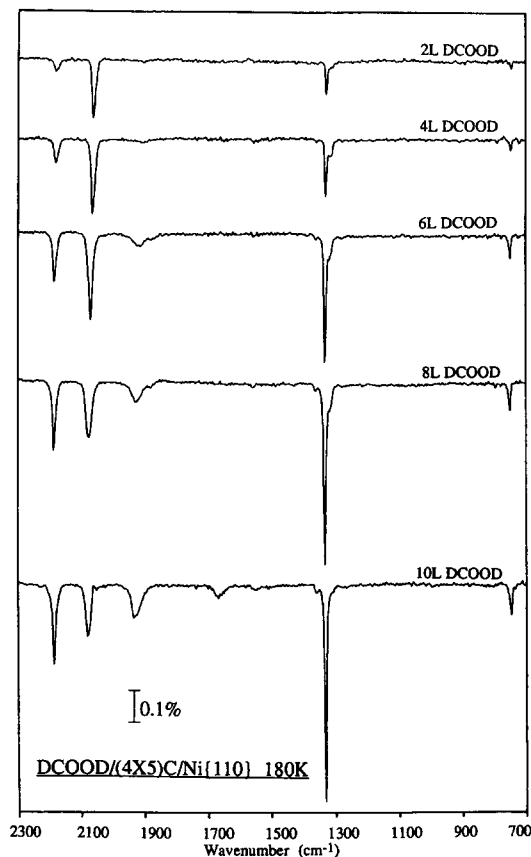

Fig. 7. Successive RAIR spectra obtained during the exposure of Ni{110}-(4×5)-C to DCOOD at 180 K. At this temperature the CO decomposition product is retained on the surface even at high DCOOD exposures.

tively. Saturation is achieved with only 8 L exposure. The small band at 1355 cm^{-1} seen near saturation is associated with ν_s(OCO) from a hydrogenated formate (HCOO) species. The appearance and disappearance of the CO indicates that even the heavily carburised nickel surface is active towards the dissociation of the acid. This activity of the carbidic surface is perhaps better illustrated in Fig. 7, where formic acid adsorption is at 180 K, the temperature now being well below the desorption temperature of CO on the carbidic surface. Concentrating initially on the CO-related vibrational structure, at the earliest stages of adsorption a band is observed at 2070 cm^{-1}, representing CO on atop sites. There is no effect at this stage from hydrogen produced from the deprotonation of the acid. As the coverage increases
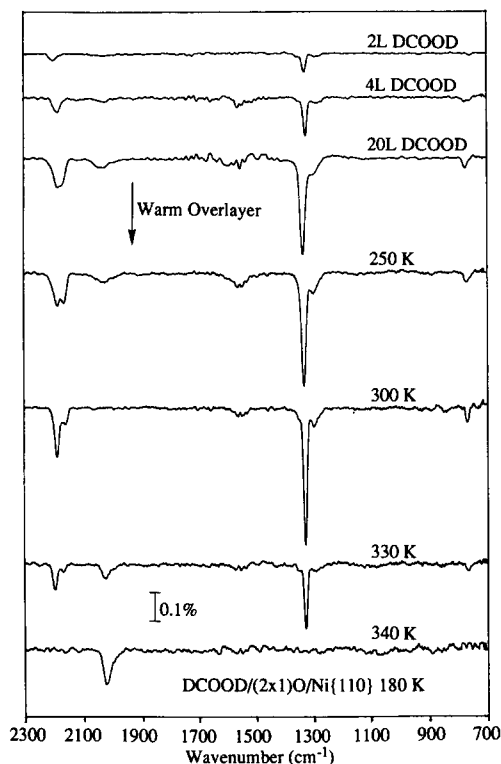
Fig. 8. Successive RAIR spectra obtained during the exposure of Ni{110}-(2×1)-O to DCOOD at 180 K; spectra are also shown during a subsequent warming sequence to 340 K.

adsorbed hydrogen causes a partial switch of CO to bridge positions, with a band appearing at 1920 cm^{-1}. This sequence is clearly different to that observed for the clean surface, and may be due to limited diffusion of hydrogen on the carbidic surface. As the stabilisation of CO on bridge sites is due to local interactions with hydrogen, a reduction in the mobility of the hydrogen could account for this. On warming, CO molecules occupying ontop sites are always removed before those adsorbed on bridge sites. At 180 K, the formate symmetric OCO stretch has two components, the main band at 1330 cm^{-1} and a low frequency shoulder at 1306 cm^{-1}, which shifts up in frequency as the coverage increases and eventually collapses to give a single band at 1330 cm^{-1}. Again the small band on the high frequency side at 1356 cm^{-1} is due to a small amount of hydrogenated formate (HCOO) present with the deuterated formate. Additionally, at saturation in this sequence we see a broad band at 1660 cm^{-1}, which

remains small in intensity regardless of additional exposure, thus representing a saturated surface. It should be noted that adsorption to saturation at 180 K on the clean surface does not produce this band.

3.6. Adsorption onto Ni{110}-(2 × 1)-O

The interaction of formic acid with oxygen is more complex than that for a carbidic surface, not only because the surface oxygen coverage is reduced by a titration reaction with formic acid, but also because the chemical and structural properties of Ni{110} vary with oxygen coverage. The (2 × 1)-O surface is easily prepared and identified with the appearance of a sharp LEED pattern after 1 L exposure. This is an added-row reconstructed surface phase, which grows on top of (1 × 1) terraces with nickel atom diffusion from steps to form chains oriented along the [001] direction [33]. The oxygen atoms occupy bridge positions in the topmost layer.

Fig. 8 shows the adsorption of DCOOD on (2 × 1)-O at 180 K and the effect of annealing the saturated overlayer. The ν_s(OCO) band at 1321 cm^{-1} shifts with increasing coverage to 1331 cm^{-1} at saturation, while the small broad low frequency shoulder at 1290 cm^{-1} stays constant in frequency. The δ(OCO) band at 762 cm^{-1} and ν(CD) band at 2181 cm^{-1} also stay at constant frequency, although at saturation ν(CD) appears to be composed of two bands. There is a very small broad feature at 1541 cm^{-1} which can only be associated with ν_a(OCO). The structure at 2030 cm^{-1} is due to a very small amount of CO. As the surface is warmed to 250 K the ν(CD) band clearly splits into two bands centred at 2182 and 2163 cm^{-1}, and the ν_a(OCO) band becomes more clearly visible. At 300 K the high frequency component of ν(CD), now at 2185 cm^{-1}, grows in intensity as the low frequency component is attenuated. Increased ordering at this temperature is reflected in the narrower lineshape for all the formate bands; the ν_s(OCO) shifts down to 1325 cm^{-1} whilst ν(CD) has shifted up to 2185 cm^{-1}. On warming to 330 K all the bands associated with the formate are significantly attenuated in intensity, and are completely removed at 340 K. Unlike the clean surface only a small amount of CO is seen on the surface, from the decomposition of the formate. This is in agreement with previous desorption studies [14]

where oxygen was observed to change the decomposition mechanism. Although in this study the interaction of CO with the (2×1) oxygen surface was not studied, this surface has been shown to adsorb CO [14]. Surface oxygen is reduced by formic acid, and two adsorption/desorption cycles effectively removed most oxygen from the surface. This was marked with the reappearance of coadsorbed CO with the formate.

4. General discussion

4.1. Bonding and structure

A comprehensive symmetry analysis of the vibrational modes of the formate adsorbed on Ni{110} at 300 K has shown that the molecule is bound symmetrically with C_{2v} symmetry [18]. Both oxygen atoms are equivalently positioned directly on top of the nickel atoms, with the C_2 axis of the molecule perpendicular to the surface and the molecular plane aligned parallel to the close-packed [1$\bar{1}$0] rows. (From the present work it is now clear that this study by Jones et al. [18] refers to the formate species formed on a Ni{110} surface covered by the initial decomposition products of HCOOH.) Photoelectron diffraction data for formate on Cu{110} have shown a similar bonding geometry [34]. This geometrical orientation allows only three normal modes of vibration to be infrared active, ν(CH), ν_s(OCO) and δ(OCO). This is the case for majority of the data presented. Observation of any of the other three modes indicates the lowering of symmetry, which is achieved by tilting the molecule.

At 120 K the appearance of absorption bands near saturation between 1383 and 1720 cm^{-1} indicates that there is either a change in the orientation of adsorbed formate, resulting in a lowering of the symmetry at higher coverages, or there is molecular adsorption. The band at 1720 cm^{-1} is clearly due to molecular acid, although the bands at 1620, 1680 and 1383 cm^{-1} can be assigned to either the acid or the formate species. Molecular adsorption of the acid on Cu{110} at low temperature produces similar IR spectra, with the appearance of bands at 1620 and 1680 cm^{-1} before the 1720 cm^{-1} band [6]. The production of formate on Cu{110} is activated and

occurs only above 270 K; these bands could only be due to the molecular acid. A formate-covered Cu{110} surface cooled to low temperatures was shown to adsorb molecular acid, giving rise to similar bands [6]. Dubois et al. [8] have shown that formic acid interacts with the formate to give a canted species, which gives a band at 1640 cm^{-1} on Cu{100}. Therefore it is likely that a similar adsorption sequence may occur on Ni{110}, and these bands are due to the influence of formic acid in the first layer. The high intensity of the δ(CH) at 1383 cm^{-1} is unusual as generally in the gas, liquid and condensed phases this is very small in intensity compared to ν(C=O) for the acid. However mode mixing can transfer intensity between bands of similar frequency, which in this case may be with the ν_s(OCO) band of the formate. This was confirmed with the deuterated isotope, which showed a much weaker band at 1003 cm^{-1} for δ(CD).

The structure between 1600 and 1700 cm^{-1} was not observed after adsorption of DCOOD on the clean surface at 180 K. However, with both preadsorbed oxygen and carbon, small broad bands were seen at 1540 and 1660 cm^{-1} respectively. At this temperature there is clearly no influence of the acid, and therefore this is attributed to ν_a(OCO), which, is generally found to be the most intense component of the vibrational structure in bulk formate salts [30] and inorganic compounds [35]. In this case it is difficult to establish the proportion of the overlayer that gives rise to this band, as clearly there is no change in the frequency or intensity of the dominant ν_s(OCO). Additionally, the correct symmetry for the tilted species cannot be established as none of the other modes are observed due to their inherent weakness. Therefore the only conclusion that can be made is that at least part of the overlayer is reduced in symmetry.

Finally, two bands were consistently observed in the ν_s(OCO) stretching region at low temperatures. Similar structure has been observed with similar frequency separation and intensity ratio on Cu{110} [36] and Ni{111} [16]. For Ni{111} the bands have been assigned to ν(C=O) and ν(C–O) of formic anhydride. However, the ν(C=O) band of the anhydride would be expected between 1700–1800 cm^{-1}, which is clearly well above the values observed here. Furthermore, the behaviour of the low frequency

band for adsorption onto the carbidic surface at 180 K, where it is completely attenuated at saturation, is clearly consistent with the idea that this is due to a second formate species. Adsorption at defect sites, such as step edges, has also been considered as a possible explanation for the second species. A recent review has highlighted the important contribution of adsorption at defect sites to the observed vibrational structure [37]. Adsorption at step edges can show large frequency shifts for adsorbed molecules, and often accounts for multiple bands at low coverages. However, in this case an unreasonably large density of defect sites would be implied, especially as dipole coupling can redistribute intensity from the low to high frequency component of the $\nu_s(OCO)$. This would explain the complete attenuation of the low frequency mode at saturation on the carbidic surface at 180 K, but is inconsistent with the increase in intensity of this mode on warming the clean surface structure to 285 K. Therefore the existence of two different formate species may simply arise from adsorption at two different sites on the surface.

4.2. Decomposition products

The adsorption of formic acid at 120 K clearly leads to the production of adsorbed CO together with the surface formate. The appearance of CO at this temperature suggests that either the formate or the parent acid decomposes via C–O bond cleavage. Decomposition of the formate is generally activated and is therefore unlikely at this temperature. Production of CO from the acid would suggest that the parent acid has two pathways for decomposition. The primary mechanism would be O–H bond cleavage to produce the formate and a H adatom. A second mechanism would involve C–O bond cleavage to produce OH and a formyl species, the latter being short lived and immediately decomposing to give CO and H. The intensities of the IR absorption bands for the formate and CO are comparable at saturation, but, since the two species do not have the same absorption coefficient this can be misleading. The intensity of the CO absorption bands on the clean and carbidic surfaces at low temperatures when ratioed against saturation coverage of pure CO represents only a small fraction of the overlayer, estimated to be less than 0.05 ML. This indicates that

decomposition of the acid to produce CO may be a side reaction at step edges. A similar coverage of CO was estimated from the adsorption of formic acid on Ru{001} at low temperatures [23], which shows very similar IR spectra in all respects to those presented in this study. Benziger and Schoofs [32] have identified an alternative pathway for the production of coadsorbed CO, which involves decomposition of dimers of the acid on the surface to produce a formate and CO. With this mechanism equal amounts of formate and CO would be expected. The conditions used in the present study minimised the extent of dimerisation in the gasline, although, dimerisation in the gas phase upon admission into the chamber could not be avoided. This mechanism may account for a small fraction of the adsorbed CO, but it is not the dominant mechanism for the production of the CO at 120 K. This is supported by the absence of significant amounts of CO on the oxygen-precovered surface at low temperatures.

Formate produced at 120 K on the clean surface is stable to just below room temperature. Subsequently, IR data shows that there is equal probability for its decomposition via C–O or C–H bond cleavage to produce CO and CO_2 respectively. The ratio of $CO_2 : CO$ is often referred to as the selectivity. For the clean surface at 300 K thermal desorption data show that this ratio is coverage dependent [11]. For low exposures it was found to be 0.3, thus favouring C–O bond cleavage, and it increases to 1 with increasing exposure. The evolution of CO was shown to be desorption limited, which is consistent with this infrared study. The stability of the formate at 300 K and above is clearly dependent on the state of the surface. Exposure of the acid to a freshly prepared clean surface produces formate, which readily decomposes. Of the decomposition products at this temperature the only surface species that remains is adsorbed CO, as shown in Fig. 5. However, with increasing exposure the formate is stabilised on the surface, indicating that the surface has been modified in some way during exposure. Of the two mechanisms outlined, decomposition of the formate by C–H bond cleavage to produce H_2 and CO_2 would not be expected to modify the surface as these species desorb immediately they are produced. Decomposition by C–O bond cleavage suggests that the surface could be steadily oxidised, as the products of

this reaction are adsorbed O and HCO. The latter formyl species is expected to decompose immediately into adsorbed CO and H; it does, however, have a second pathway to decompose into its atomic constituents which would result in atomic C and O adsorbed on the surface. Progress of the reaction could therefore lead to the build up of either of these species, both of which have been previously implicated in stabilising the formate and changing the selectivity of the decomposition products [13,14]. Indeed the spectra in Fig. 5 in the first instance would indicate that this does occur at the surface, especially with the removal of the adsorbed CO from the surface coinciding with the appearance of a CO band at 2070 cm^{-1} which has been shown to have the same frequency as that for adsorption of CO onto a carbidic surface. Wachs and Madix [38], using molecular beam reaction spectroscopy, have shown that formic acid reacting with Ni{110} deposits carbon and oxygen between 400–600 K, which build up with increasing exposure. The adsorbed carbon and oxygen was found to react and desorb at 667 K as CO. For example, at 407 K the estimated coverages for carbon and oxygen are 0.19 and 0.27 ML respectively, after 1×10^{-7} Torr HCOOH for 30 min ($\sim$ 180 L). In the present work the temperature was lower and it is expected that much lower coverages of the atomic species would result. Additionally it is expected that oxygen would be partially reduced and removed from the surface by the reaction with hydrogen which is also a decomposition product.

The stabilisation of the formate with preadsorbed oxygen and carbon is clearly seen with RAIRS. The IR spectra recorded for the interaction of formic acid with carbon and oxygen precovered surfaces are those for extreme situations where the precoverages used are at the saturation level. However, these do illustrate the effect of atomic coadsorbed species on the adsorption and decomposition of formic acid. The carbidic surface has the greatest influence on the stabilisation of the formate, and changes the selectivity to an overall dehydrogenation reaction. McCarty et al. [10] have compared the CO_2 : CO ratio for the clean and (4×5) carbidic Ni{110} surfaces. They find that this ratio increases by an order of magnitude for the carbidic surface. The CO_2 desorption peak was found to shift from 390 to 440 K for the clean and carbidic surfaces respectively, thus reflect-

ing the higher stability of the formate. The oxygen surface stabilises the formate to a lesser extent, but the (2×1)-O overlayer does change the selectivity in a similar manner to the carbidic surface to produce predominantly CO_2 and H_2 as the decomposition products. Recent work on the adsorption of formic acid on the (2×1)-O overlayer on Cu{110} using molecular beam spectroscopy [36] has shown that only 1/4 of the original 1/2 ML of oxygen is removed as H_2O from the surface at 300 K. A second adsorption cycle removed the remainder of the oxygen. This is consistent with the IR work presented here, since two adsorption/desorption cycles resulted in the IR spectra resembling those of the clean surface. However, for the Cu{110} surface, removal of the oxygen resulted in extreme complexities in the surface structure as a number of major reconstructions have been observed with LEED and STM which are dependent on the initial oxygen precoverage [36]. Similar reconstructions are envisaged on the Ni{110} surface as the removal of oxygen releases metal atoms that were involved in the oxygen-induced (2×1) reconstruction. The reconstruction may influence the reaction and decomposition of the acid on the Ni surface although this effect appears to be minimal for the copper surface in which only a lower temperature decomposition state for the formate is produced, similar to that reported by Johnson and Madix [14] for the Ni{110} surface. It is likely therefore that the appearance of two peaks in the C–D stretching region may be due to either the presence of oxygen or adsorption on a reconstructed surface.

It is well known that the distribution of decomposition products from the reaction of formic acid with polycrystalline and single crystal Ni surfaces shows complex behaviour. Inglis and Taylor [39] were the first to show that the CO_2 : CO ratio increases from freshly deposited nickel films as they were progressively used. This was attributed to (unknown) contamination. Subsequently it has been shown that several adsorption–desorption cycles can oxidise Ni{100} [15] and Ni{111} [32] surfaces. Therefore the change in CO_2 : CO selectivity in these two cases has been regarded as solely due to the presence of oxygen. However in the present study the influence of carbon is also considered and regarded to be a major contributor to the stabilisation and decomposi-

tion of the formate for large exposures on a freshly prepared surface. The IR results presented here are consistent with the wide body of thermal desorption data that already exists for this system.

Finally, there is disagreement between the two previous HREELS studies [17,18] for this system regarding the presence of coadsorbed CO which can now be reconciled. Fig. 5 illustrates the dependence of the RAIR spectra on the exposure to the acid at 320 K. At saturation only the formate vibrational spectrum is seen, although in the adsorption sequence prior to this both formate and CO are observed. Therefore the differences are simply due to the different exposures used as only the 'saturation' spectra were shown in the two previous studies. We have shown that at 300 K CO is not completely removed from the surface, although the initial sequence is similar to that seen at 320 K. At 280 K no decomposition of the formate was observed at any coverage, and coadsorbed CO and formate were seen at all exposures. This indicates that there is a complex temperature and exposure dependence for the ratio of the surface species involved. Hence a large exposure to saturation at different temperatures would lead to different ratios of the products.

5. Conclusions

Vibrational spectra for the adsorption and reaction of formic acid with clean Ni{110} at 320 K show three distinct phases. For low exposures only adsorbed CO is observed, and subsequently both CO and formate coexist on the surface. At saturation CO is completely removed from the surface, leaving just the surface formate species. The production of adsorbed CO is correlated with decomposition of the surface formate via C–O bond cleavage. The removal of CO coincides with the appearance of a band for ν_{CO} at 2070 cm^{-1}, which is not seen on the clean surface. This has been shown to have the same frequency as that for CO adsorbed on a carbidic surface. Preadsorbed carbon and oxygen have been shown to significantly stabilise the surface formate and change the decomposition selectivity to increase the $CO_2 : CO$ ratio, favouring decomposition via C–H bond cleavage. Collectively these results indicate that the initial decomposition of the formate on the

clean surface produces surface carbon and oxygen which subsequently modifies the decomposition pathway. Carbon is recognised to have the greatest influence on the adsorption sequence. Adsorption at 120 K is independent of exposure producing both formate and CO, although the latter is only a small fraction of the overlayer.

The vibrational spectra are consistent with the formate adsorbed symmetrically with C_{2v} symmetry. The observation of two bands in the $\nu_s(OCO)$ region at low temperatures indicate that there are two different surface formate species on the surface. At low temperatures on both the carbidic and oxide surfaces a small band is observed in the $\nu_s(OCO)$ region, indicating that some of the overlayer is reduced in symmetry.

Acknowledgements

References

[1] B.A. Sexton and R.J. Madix, Surf. Sci. 105 (1981) 177.
[2] M. Chtaib, P.A. Thiry, J.J. Pireaux, J.P. Delrue and R. Caudano, Surf. Sci. 162 (1985) 245.
[3] D.A. Outka and R.J. Madix, Surf. Sci. 179 (1987) 361.
[4] W. Erley and D. Sanders, J. Vac. Sci. Technol. A 8 (1990) 3357.
[5] B.A. Sexton, Surf. Sci. 88 (1978) 319.
[6] B.E. Hayden, K. Prince, D.P. Woodruff and A.M. Bradshaw, Surf. Sci. 133 (1983) 589.
[7] M. Ito and W. Suetaka, J. Catal. 54 (1978) 13.
[8] L.H. Dubois, T.H. Ellis, B.R. Zegarski and S.D. Kevan, Surf. Sci. 172 (1986) 385.
[9] F.C. Henn, J.A. Rodriguez and C.T. Campbell, Surf. Sci. 236 (1992) 282.
[10] J.G. McCarty, J.L. Falconer and R.J. Madix, J. Catal. 30 (1973) 235.
[11] J.L. Falconer and R.J. Madix, Surf. Sci. 46 (1974) 473.
[12] R.J. Madix and J.L. Falconer, Surf. Sci. 51 (1975) 546.
[13] J. McCarty and R. Madix, J. Catal. 38 (1975) 402.
[14] S.W. Johnson and R.J. Madix, Surf. Sci. 66 (1977) 189.
[15] J.B. Benziger and R. Madix, Surf. Sci. 79 (1979) 394.
[16] W. Erley and D. Sanders, J. Vac. Sci. Technol. A 7 (1989) 2238.
[17] R.J. Madix, J.L. Gland, G.E. Mitchell and B.A. Sexton, Surf. Sci. 125 (1983) 481.

[18] T.S. Jones, M.R. Ashton and N.V. Richardson, J. Chem. Phys. 90 (1989) 7564.

[19] M.R. Columbia, A.M. Crabtree and P.A. Thiel, J. Am. Chem. Soc. 114 (1992) 1231.

[20] N.R. Avery, Appl. Surf. Sci. 14 (1982) 149.

[21] N.R. Avery, B.H. Toby, A.B. Anton and W.H. Weinberg, Surf. Sci. 122 (1982) L574.

[22] Y.-K. Sun and W.H. Weinberg, J. Chem. Phys. 94 (1991) 4587.

[23] M.D. Weisel, J.G. Chen, F.M. Hoffmann, Y.-K. Sun and W.H. Weinberg, J. Chem. Phys. 97 (1992) 9396.

[24] S.L. Miles, S.L. Bernasek and J.L. Gland, Surf. Sci. 127 (1983) 271.

[25] J.B. Benziger and R.J. Madix, J. Catal. 65 (1980) 49.

[26] J.B. Benziger, E.I. Ko and R.J. Madix, J. Catal. 58 (1979) 149.

[27] R. Raval, M.A. Harrison, D.A. King and G. Caine, J. Vac. Sci. Technol. A 9 1991) 345.

[28] S. Haq, J.G. Love and D.A. King, Surf. Sci. 275 (1992) 170.

[29] J.C. Bertolini and B. Tardy, Surf. Sci. 102 (1981) 131.

[30] K. Ito and H.J. Bernstein, Can. J. Chem. 34 (1956) 170.

[31] C.M. Mate, C.T. Kao and G.A. Somorjai, Surf. Sci. 206 (1988) 145.

[32] J.B. Benziger and G.R. Scoofs, J. Phys. Chem. 88 (1984) 4439.

[33] L. Eierdel, F. Besenbacher, E. Laesgaard and I. Stensgaard, Ultramicroscopy 42–44 (1992) 505.

[34] D.P. Woodruff, C.F. McConville, A.L.D. Kilcoyne, Th. Lindner, J. Somers, M. Surman, G. Paolucci and A.M. Bradshaw, Surf. Sci. 201 (1988) 228.

[35] J.R. Shapley, G.M. St. George and M.R. Churchill and F.J. Hollander, Inorg. Chem. 21 (1982) 3295.

[36] S. Haq, F.M. Leibsle and M. Bowker, to be published.

[37] P. Hollins, Surf. Sci. Rep. 16 (1993) 51.

[38] I.E. Wachs and R.J. Madix, Surf. Sci. 65 (1977) 287.

[39] H.S. Inglis and D. Taylor, J. Chem. Soc. A (1969) 2985.