Adsorption and Autocatalytic Decomposition of Acetic Acid on Pd(110)

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The adsorption and decomposition of acetic acid has been studied on Pd(110) using temperature-programmed desorption (TPD). On the clean surface, the acid dissociates to form a stable acetate, and hydrogen is desorbed at 300 K. Some of the acetate then decomposes at around 353 K to yield CO_2 and H_2 into the gas phase and leaves adsorbed carbon. The latter stabilises some of the acetates and results in the desorption temperatures being increased by as much as 100 K. Oxygen pre-dosing leads to changed characteristics including stabilisation of the acetate in a manner which produces an autocatalytic acetate decomposition, a 'surface explosion'. In this way, mixed surface layers can be obtained showing characteristics of the clean surface acetate, the carbon-contaminated acetate and the oxygen-induced explosion. A model based on atomic adsorbate-induced ordering of the acetate layer is used to describe the autocatalytic decomposition.

In a previous publication, the adsorption and decomposition of formic acid on a clean, as well as on an oxygen pre-dosed, Pd(110) surface have been described.[1] These thermal desorption studies showed that clean Pd is very reactive, leading to the decomposition of formic acid into CO, H_2O, H_2 and formate; the latter was retained on the surface up to 230 K before it was decarboxylated. Pre-adsorbed oxygen had a stabilising effect in that it suppressed the formation of CO and increased the temperature of formate decomposition into CO_2 and H_2 to 295 K. This is of technological importance as carboxylates may constitute intermediates in the catalysed synthesis of alcohols from CO and H_2. For instance, a recent review argues strongly in favour of acetate as the most stable intermediate in the production of ethanol over Rh, and it also highlights the importance of oxygen or oxide as the promoter which is thought to 'lock' the acetate onto the surface and hence stabilise it for further hydrogenation.[2]

Recent work in this group has shown that acetate can be formed on Rh(110) either by adsorption of acetic acid or by co-adsorption of oxygen and ethanol.[3] In both cases, although only in the presence of an atomic co-adsorbate, the acetate was found to decompose into CO_2 and H_2 in an autocatalytic way, that is, this reaction once started was self-accelerating, and the evolution of these fragments appeared as very narrow peaks in the desorption spectrum. It is as part of the long-term aim of studying the stability of reaction intermediates on group 8–10 metals in this Centre that these experiments were repeated on a Pd(110) surface. The results reported here show some similarities with those from the Rh(110) surface, but are even more like those from Rh(111).

Experimental

The experiments were performed in a VG single-chamber UHV instrument, which allowed low-energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), ion-scattering spectroscopy (ISS) and TPD analysis to be carried out. The background pressure after bake-out was 2×10^{-10} mbar which increased to 1×10^{-9} mbar during the adsorption experiments. The crystal was initially cleaned by cycles of argon ion bombardment and annealing. Prior to the experiments any contamination was removed by an oxidation–reduction treatment. The cleanliness of the Pd sample was assessed by monitoring the thermal desorption pattern of CO, which was known to be very sensitive to small amounts of surface carbon.[4]

The adsorption studies were carried out at 325 K. Acetic acid was dosed *via* a leak valve through a narrow tube of 1/8 in† outer diameter which had been pointed at the sample. This gave a dose enhanced by a factor of five compared with background dosing the acid. As oxygen was always dosed from the background, all doses are quoted in relation to background dosing. In between successive exposures, the crystal was heated in oxygen to remove any deposited carbon. The sample was heated by radiation from a tungsten filament which had been mounted close behind the crystal. In this way, temperatures of 850 °C could be reached quickly. However, the heating rate in this constant current mode was not linear over the whole temperature range. In the temperature range of interest it was 1 K s^{-1}. The quadrupole for recording the TPD spectra was a VG Sensorlab which was controlled by an Opus PC5.

XP spectra were generated using Al-Kα X-radiation of 180 W (VSW twin anode X-ray gun). The pass energy of photoelectrons into the VSW hemispherical analyser was 44 eV, and the angle of electron detection was 30° with respect to the sample surface.

LEED patterns were obtained by bombarding the sample with an electron beam of 50–100 eV using the Omicron rear-view optics.

Results

Acetic Acid Adsorption on the Clean Surface

The desorption spectrum from the sample following its exposure to a saturation dose of 2.0 L‡ acetic acid is illustrated in Fig. 1. The adsorbed species, which is proposed to be acetate, decomposed by decarboxylation into CO_2 and H_2 at 350 and 375 K. This evolution of CO_2 was accompanied by the deposition of methyl groups on the surface which were unstable and decomposed further to adsorbed carbon and H atoms, the latter being evolved as H_2 simultaneously with CO_2 in the ratio $H_2 : CO_2$ of 1.5 : 1. These desorptions always consisted of a set of two peaks. Heating up to 500 K did not reveal any further desorptions to higher temperatures.

The presence of acetate on the surface could be confirmed with XPS as shown in Fig. 2. Acetate contains two carbon atoms in chemically different environments which are well

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† 1 in = 2.54×10^{-2} m.
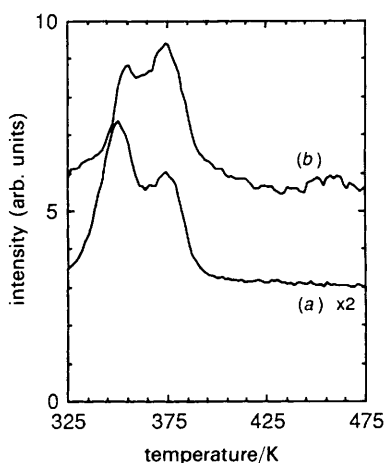‡ 1 L (Langmuir) = 10^{-6} Torr s. 1 Torr = (101 325/760) Pa.

Fig. 1 Thermal desorption spectrum of 2.0 L acetic acid dosed at 325 K onto Pd(110): (a) CO_2, (b) H_2
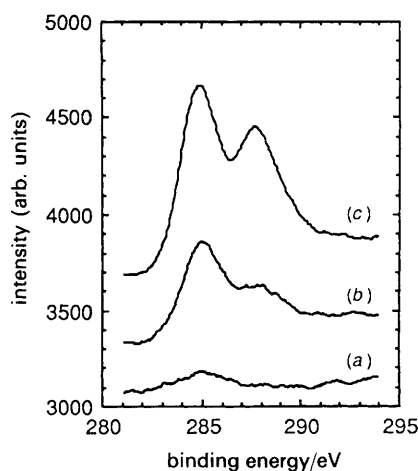

Fig. 2 XP spectra showing the C 1s region of the clean Pd (a), after adsorption of 2.0 L acetic acid (b) and after adsorption of 5.0 L O_2 followed by 2.0 L acetic acid (c)

separated in binding energy E_b. These two peaks, were located at 287.9 and 285.0 eV,† the former being representative of a carboxylate carbon and the latter of a methyl carbon. The peak positions and the corresponding separation were in good agreement with acetate adsorbed on Cu(110).[5] Note that the two peaks were not of equal intensity. This was also observed by Bowker and Madix[5] who found the lower E_b peak to be of larger peak height, while the higher E_b peak tended to be of greater peak width. As the acetate is thought to bond to the surface through the two oxygen atoms the methyl group would thus be located above the carboxyl group. This would attenuate the carboxylate carbon in relation to the methyl carbon and account for the differing peak heights. In this case, there was also some residual carbon on the Pd surface which overlapped with the lower E_b carbon peak and hence increased it in intensity (see Fig. 2). From the reduction in the Pd 3d peak area after the adsorption of acetic acid, the coverage of acetate was estimated to be 0.15 ML though this is a very approximate determination.[6]‡ Although the O 1s region of the spectrum was also recorded it was not very suitable for this analysis because of the

overlap of the O 1s with the Pd $3p_{3/2}$ peak. The presence of acetate did not seem to affect the peak maximum at 533.0 eV or the peak width of 3.5 eV. However, the peak area was also essentially unaffected, which is contrary to the behaviour of the Pd 3d peaks, and hence indicated that some oxygen was present. Although the 1s photoelectron peak of oxygen could not be resolved when superimposed on this Pd signal, the X-ray induced Auger signal O KLL could be seen as a broad feature of low intensity at 974.9 eV.

An LEED pattern other than the (1×1) pattern of the crystal itself was not seen for acetate adsorbed under these conditions.

Acetic Acid Adsorption on the Carbon-covered Surface

As pointed out above, the adsorption and subsequent decomposition of acetic acid led to the build-up of a layer of carbon on the Pd surface. Further evidence of the presence of carbon was obtained by exposing this surface to oxygen. Following the adsorption of oxygen at 325 K the TPD spectrum showed a CO_2 desorption which started at 345 K and peaked between 390 and 395 K. Successive exposures of oxygen led to a diminished CO_2 evolution until this disappeared, and instead, a peak typical of oxygen desorption from Pd(110) appeared.

Although it initially seemed plausible that the presence of increasing amounts of carbon on the surface would block any further acetic acid adsorption, this was not the case for small amounts as deposited here. Fig. 3 shows how successive doses of acetic acid and their subsequent decompositions led to the shift of the CO_2 desorption peaks to higher temperatures. A similar shift of the H_2 desorption peaks was also observed, but this has, for the sake of clarity, not been shown in the figure. The higher temperature peak was of low intensity at first, but with continued exposures it grew at the expense of the one at lower temperature. This shift in intensity was accompanied by a gradual increase in desorption temperature. The effect of stabilising the acetate was seen even more clearly when the carbon deposition was carried out at a high temperature. After the exposure of the sample to 12.0 L acetic acid at 473 K and the subsequent adsorption of 2.0 L of acetic acid at 325 K, the spectrum showed a single set of CO_2 and H_2 desorption peaks, which were as intense as the peaks obtained at low exposures, but which were shifted by

† 1 eV $\approx$ 1.602 18 $\times$ 10^{-19} J.

‡ Note that the monolayer thickness, a, of Pd was calculated to be 0.245 nm, and the escape depth, α_m, for the Pd $3d_{5/2}$ photoelectron was 6.89 ML.
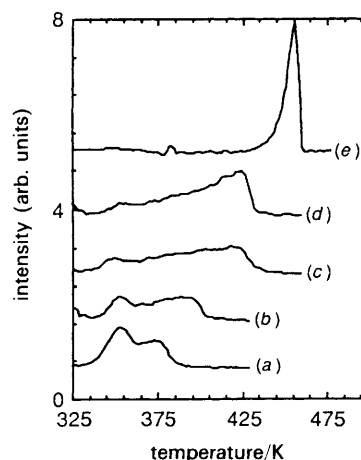
Fig. 3 CO_2 thermal desorption pattern as a function of successive doses of 2.0 L acetic acid onto Pd(110), without in between cleaning of the crystal [(a)–(d)]. In (e), the crystal had been exposed to 12.0 L acetic acid at 473 K before it was cooled down to 325 K for adsorption of 2.0 L acetic acid.

100 K to higher temperatures compared with the first desorption spectrum. The peak was not of the normal Gaussian type, but had a characteristic shape consisting of a steep increase on the low-temperature side and an abrupt drop in intensity once the maximum had been reached. The full width at half maximum (FWHM) was 8–10 K. No other desorbing fragments were seen during this experiment, which was taken as further proof of the existence of acetate on the surface.

Following these experiments, the XPS spectrum showed one C 1s peak at 285.0 eV, which could again be removed by heating the sample in oxygen. LEED analysis gave a (1×1) pattern for the carbon-covered sample.

Acetic Acid Adsorption on the Oxygen Pre-dosed Surface

By analogy with the formic acid experiments reported previously[1] it was of interest to establish how far the presence of oxygen would stabilise the acetate. Fig. 4 shows that at oxygen exposures below 1.0 L, the desorption spectrum resembled that of acetic acid dosed onto the clean sample. Both CO_2 and H_2 were evolved simultaneously between 353 and 385 K in a broad signal. When the oxygen exposure was increased only slightly above this level a drastic change in the desorption behaviour was achieved. The CO_2 desorption signal changed from a broad feature of small peak height to a very narrow desorption peak of much larger height which was superimposed on the desorption pattern from the clean surface. This is illustrated in more detail in Fig. 5. The CO_2 evolution was now accompanied by H_2O desorption which had the same sharp peak shape as CO_2. Both peaks had a FWHM of 6 to 8 K. H_2 was also observed, and it was desorbed in a broad peak which roughly followed the CO_2 evolution from the clean surface. The sharp CO_2 and H_2O peaks shifted from 373 K at 1.1 L O_2 to 393 K at 5.0 L O_2, after which they were fully developed and saturated. The CO_2 peak area was around a factor of 2.5 larger than that of CO_2 being desorbed from the clean surface.

A similar behaviour was obtained by keeping the oxygen exposure constant at 5.0 L and varying the acetic acid dose. Below 0.5 L acetic acid, the CO_2 desorption feature was broad, while at exposures of 2.0 L this changed into the sharp and narrow feature of around 6 K width seen in Fig. 6. Around 0.7 L, a single peak of 10–20 K width was seen, which was intermediate to the CO_2 desorptions from the clean and the oxygen-dosed sample.

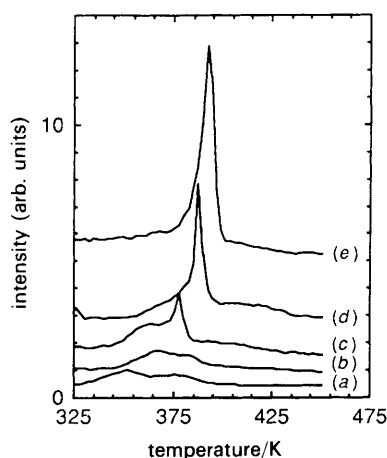The autocatalytic nature of this reaction was further under-

lined by an isothermal desorption, which is illustrated in Fig. 7. In this experiment, the heating was stopped at a temperature below the actual desorption maximum. The loss of some initial adsorbate molecules increased the rate so much that the reaction became self-accelerating, and the desorption was completed without any further increase in the temperature.
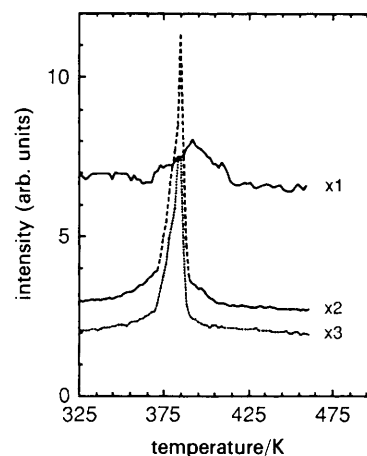

Fig. 5 One thermal desorption spectrum of 2.0 L acetic acid dosed at 325 K onto Pd(110) pre-dosed with 2.0 L O_2 which shows the peak shapes of both H_2O and CO_2 as well as H_2 in more detail. (·····) H_2O, (–––) CO_2, (——) H_2.
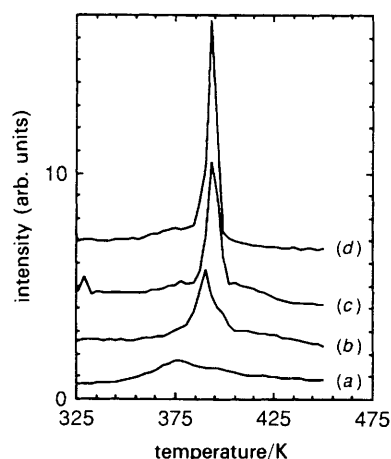

Fig. 6 CO_2 thermal desorption spectra, after increasing amounts of acetic acid were dosed at 325 K onto Pd(110) which had been exposed to 5.0 L O_2 at the same temperature. The acetic acid exposures were (a) 0.3, (b) 0.5, (c) 0.7 and (d) 2.0 L.

Fig. 4 CO_2 thermal desorption spectra of 2.0 L acetic acid dosed at 325 K onto Pd(110) which had been exposed to increasing amounts of O_2 also at 325 K. The oxygen doses were (a) 0, (b) 1.0, (c) 1.1, (d) 2.0 and (e) 5.0 L, and the surface was cleaned between each experiment.
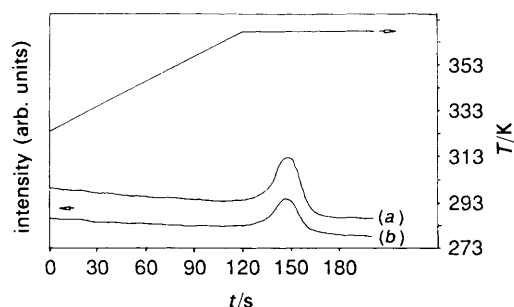

Fig. 7 Isothermal desorption of 3.0 L acetic acid dosed at 325 K onto an oxygen-predosed Pd(110) surface (2.0 L). The heating was kept constant once a sample temperature of 365 K had been reached. (a) CO_2, (b) H_2O.

Following the adsorption of 5.0 L O_2 and 2.0 L acetic acid, the XP spectrum showed the two C 1s peaks to be of increased intensity compared with the clean surface acetate (see Fig. 2). The coverage was calculated to be *ca.* 0.46 ML. In addition to an increase in intensity of the O KLL peak, there was also a broadening of the Pd $3p_{3/2}$ peak from 3.5 to 4.2 eV predominantly to lower E_b. The peak maximum was unchanged at 533.0 eV and the peak area was now increased compared with that of the clean surface peak.

5.0 L O_2 adsorbed on Pd(110) gave a clear (2 × 4) LEED pattern once briefly heated at 473 K. The subsequent adsorption of 2.0 L acetic acid at 325 K onto this pre-dosed surface yielded a (1 × 1) pattern on a high background. Upon further inspection some spots due to the previous pattern of oxygen were still observed, but the structure was not as well developed as before.

Although the presence of oxygen changed the desorption pattern it still led to the deposition of carbon which again could be removed by exposing the surface to oxygen. If this carbon was left on the surface and further experiments were carried out on it, the desorption spectrum changed again. Fig. 8 shows the changes that occurred in three consecutive adsorptions and desorptions. The initial sharp CO_2 desorption peak was superimposed on the broader desorption feature typical of the clean surface. The high-temperature side of this was extended to even higher temperatures after the second experiment. Following the third exposure, the autocatalytic desorption feature had decreased in size, the simultaneous evolution of water had nearly vanished and the high-temperature peak had increased in peak height and area (indicated by the black arrow in the figure). This new CO_2 peak was accompanied by H_2 evolution. The higher temperature part of the spectrum resembles that of the desorption from a carbon-covered surface.

Acetic Acid Adsorption followed by Oxygen Exposure

The autocatalytic desorption feature was further investigated by reversing the order of dosing, that is acetic acid was adsorbed onto the clean surface after which oxygen was dosed. Fig. 9 shows that the CO_2 and H_2O peaks increased in intensity and were sharper than the desorptions from the clean surface, but of lower intensity than the features produced on the oxygen pre-dosed surface. H_2 evolution was also observed, and it appeared in two forms. One part followed the broad CO_2 evolution, and one more intense and sharp
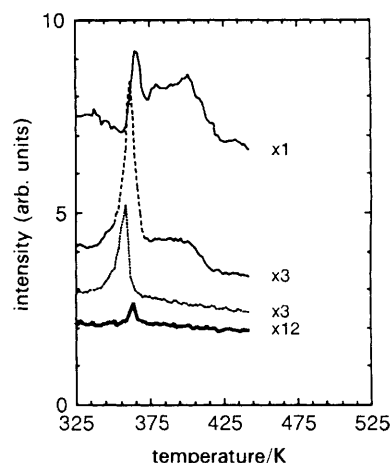
Fig. 9 The thermal desorption spectrum following reverse dosing: 5.0 L acetic acid were dosed onto Pd(110) at 325 K, followed by 2.0 L O_2. (– – –) CO_2, (——) H_2, (· · · ·) H_2O, (——) CH_3CO_2H.

feature started once the H_2O intensity had dropped back to its background level. This H_2 evolution was accompanied by acetic acid desorption. The H_2O desorption peak followed the initial outlines of the CO_2 peak and was hence of the same shape as the one produced on the oxygen pre-dosed surface. The peak shape of CO_2 did not have the sharp drop on the high-temperature side, but a slower decay of the signal, which in conjunction with the other evolutions seems to indicate that this peak is associated with two overlapping events. The overall decomposition profile appears to be due to two processes, the first giving coincident CO_2 and H_2O evolution, while the second yields CO_2, H_2 and some acetic acid; thus the CO_2 curve is an envelope of both decompositions. Another important change in reversing the order of dosing was the temperature at which the CO_2 and H_2 peaks evolved. For the oxygen pre-dosed surface this was between 373 and 393 K, while for the reverse dosing the set of peaks appeared at 360 K.

Discussion

The adsorption and decomposition of acetic acid is described by the following steps:

$$CH_3CO_2H_{(g)} \rightarrow CH_3CO_2H_{(a)} \tag{1}$$

$$CH_3CO_2H_{(a)} \rightarrow CH_3CO_{2(a)} + H_{(a)} \tag{2}$$

$$CH_3CO_{2(a)} + H_{(a)} \rightarrow CH_3CO_2H_{(g)} \tag{3}$$

$$H_{(a)} + H_{(a)} \rightarrow H_{2(g)} \tag{4}$$

$$2CH_3CO_2H_{(a)} + O_{(a)} \rightarrow H_2O_{(g)} + 2CH_3CO_{2(a)} \tag{5}$$

$$CH_3CO_{2(a)} \rightarrow CO_{2(g)} + CH_{3(a)} \tag{6}$$

$$CH_{3(a)} \rightarrow C_{(a)} + 3H_{(a)} \tag{7}$$

$$2H_{(a)} + O_{(a)} \rightarrow H_2O_{(g)} \tag{8}$$

The first step of this mechanism is acetate formation. The data do not indicate at what temperature dissociation occurs [step (2)], but it certainly occurs below 280 K, since H_2 evolution in a desorption-limited peak is seen just after that temperature [step (4)]. In the presence of O, though, the H atoms combine with O to form water which leaves the surface during the dosing of acetic acid at 325 K [step (5)]. The remaining acetate molecules which decompose to CO_2 and adsorbed methyl [step (6)] are bound in one stable state. Adsorbed methyl is not stable in this temperature range and preferentially dehydrogenates to leave carbon on the surface [step (7)]. CO desorption was not detected at any stage. Only
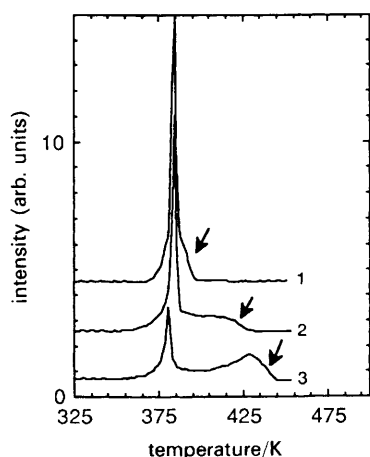

Fig. 8 CO_2 thermal desorption pattern for three successive doses of 2.0 L O_2, followed by 2.0 L acetic acid onto Pd(110) at 325 K without in between cleaning of the crystal. '1' represents the first, '2' the second and '3' the last experiment. The black arrows mark the peak of interest.
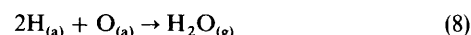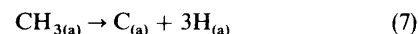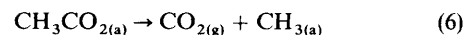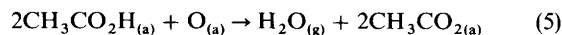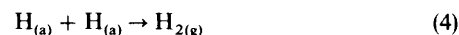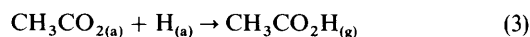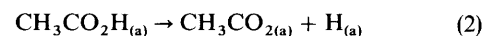
one decomposition path appears to exist for acetate on Pd(110) under these conditions [step (6)], in contrast to the results of Davis and Barteau on Pd(111).[7,8]

The presence of acetate on the surface has been confirmed by XPS. The two distinct carbon peaks are indicative of an intermediate containing two carbon atoms. The assignment of the adsorbed intermediate as acetate rather than adsorbed acetic acid or acetaldehyde has been done on the basis of the desorbing species, but can also be further proved by comparison with the XPS data of Bowker et al.[5] They studied all these three species adsorbed on Cu(110). Although they all show two peaks in the C 1s region, the peaks originating from acetic acid are shifted by 1–2 eV to higher E_b (290.1 and 286.6 eV) and have a separation of 3.5 eV. Acetaldehyde yields peaks at lower E_b (287.1 and 284.9 eV), which are separated by 2.2 eV. Acetate on Cu has two peaks at 288.2 and 285.0 eV, which are almost identical to the ones found on Pd(110). The O 1s peak is located at 531.6 eV. If it is assumed that the oxygen atoms in acetate on Pd would yield a similar position then that would also explain the broadening of the Pd $3p_{3/2}$ peak to lower E_b.

Above room temperature, the stability of the acetate species present on the surface is very much dependent on its environment. The acetate on the clean surface decomposes between 350 and 375 K. The presence of this high-temperature feature is not thought to be an indication of a second or a differently adsorbed acetate species related to the clean surface, but a consequence of the deposition of carbon during acetate decomposition. The experiments on the carbon-covered surface show that carbon enhances the stability of the acetate. Thus, the desorption from the clean surface is a dynamic process in that the surface composition changes continuously. The first acetate molecule of a total ensemble of n entities experiences predominantly the influence of $(n-1)$ other acetate molecules, the second one is influenced by $(n-2)$ acetate molecules and one carbon atom. However, by the time the last molecule decomposes it experiences the effect of $(n-1)$ carbon atoms. The high-temperature peak of the CO_2 desorption reflects this situation.

Initially, the desorption occurs from the clean surface. Once the first molecules have decomposed and the first carbon atoms have been deposited, these can diffuse and influence the desorption of further acetate. Following a couple of repeated desorption experiments without intermediate cleaning, carbon atoms are deposited all over the crystal and the acetate decomposition on the clean surface has been suppressed and replaced with a desorption pattern typical of a carbon-covered surface, with high-temperature CO_2 and H_2 evolutions (as high as 450 K).

Oxygen pre-dosing also leads to a stabilisation of the adsorbed intermediate, but additionally there is a drastic change in the decomposition profile. During the acetic acid adsorption, oxygen on the surface reacts with the acid hydroxy hydrogen to form water. The surface coverage of oxygen after this is therefore lower than would be predicted from the actual exposure. This explains why, at low O_2 doses, the autocatalytic decomposition does not take place, since acetate decomposition begins on an essentially clean surface. When higher coverages of oxygen atoms are adsorbed on the surface there are more than can be removed by acetic acid to form water stoichiometrically. The excess oxygen is then co-adsorbed with the acetate and can react with hydrogen atoms from the methyl groups during acetate decomposition, as shown by the evolution of water coincident with CO_2 [steps (6) and (8)]. The increased presence of oxygen on the surface results in further stabilisation of the acetates, showing a shift in peak temperature up to 393 K and the 'surface explosion'. For a fixed oxygen dose of 2.0 L, increasing doses of acetic

acid again show autocatalytic acetate decomposition at 393 K. Direct proof of the autocatalytic nature of the decomposition is given by the data (see Fig. 7).

These results can be compared with those for Rh(111) and Rh(110). In fact, in many ways the Pd(110) surface looks like Rh(111), in that the acetate is stable on the surface during adsorption at 325 K and the decomposition temperatures are similar [353 K here vs. 380 K on Rh(111)].[9] In contrast, Rh(110) decomposes acetic acid completely at room temperature giving CO_2 and H_2 during adsorption.[3] Stabilisation and autocatalytic decomposition of the acetate are also observed on both Rh surfaces, in fact a range of atomic species on Rh(110) induce autocatalytic decomposition (carbon and nitrogen atoms as well as oxygen).[9]

When the order of adsorption is reversed, a combination of the effects observed on the clean, the oxygen pre-dosed and the carbon-covered surfaces is seen. The CO_2 peak is shifted to lower temperatures than for oxygen pre-dosing and it is broadened and of lower intensity. However, it still resembles the autocatalytic desorption feature, and it is also superimposed on the desorption associated with acetate on the clean surface. However, the desorption of both H_2O and H_2 is seen as sharp features which are separated by around 4 K in peak temperature, the H_2 evolving after H_2O. This would mean, then, that the CO_2 evolution is an envelope containing CO_2 from the decomposition of two different acetate species and since these are slightly shifted in temperature from each other, the peak appears broader than expected. Both these acetates appear 'explosive' (H_2O and H_2 peak widths at half maximum are 8–10 K). The lower temperature state appears intimately connected with oxygen atoms (hence all hydrogen from the acetate decomposition is converted to H_2O), whereas the high-temperature peak appears not to be associated with oxygen (no water evolution). Note that for this second peak, significant amounts of acetic acid desorption were seen, but not for the lower temperature peak, presumably due to the availabilty of free hydrogen atoms needed for step (3) above. These are not available for the lower temperature acetate, since the hydrogen atoms are mopped up by oxygen. The broader CO_2/H_2 evolution centred around 390 K is again most likely to be associated with acetates stabilised by carbon on the surface. These results indicate that the stability of the acetate and its decomposition are strongly influenced by the environment the acetate experiences. Differently influenced acetate molecules can coexist on the surface, and although they lead to a similar decomposition pattern, their different stabilities make it possible to distinguish between them in the TPD spectrum.

Madix and Falconer[10,11] who studied the adsorption of formic and acetic acid on Ni(110) found that both acids decomposed to yield CO_2 and H_2 in narrow peaks of 6 K width. They were the first people to describe the autocatalytic behaviour of these acids on a metal single crystal. Their model to explain this behaviour assumes that at low coverage the adsorbed species are held in sites far apart. Once the coverage increases, islands start to grow. Owing to the anisotropy of the (110) surface, an ordering of the adsorbate molecules takes place. There is an attractive interaction between the adsorbates which further stabilises them. In order for the decomposition to take place, free metal sites are necessary which at higher coverage are not immediately available. This delays the decomposition further. Once the first molecules have decomposed, the free sites act as catalytic centres for further decompositions and the reaction becomes self-accelerating. Further evidence for this model came from their study of low exposures which showed the decomposition to take place at a temperature of 58 K below the autocatalytic decomposition. The peak width was increased to 21

K. Above a critical exposure, this low-temperature desorption was saturated and sharp decomposition took place.

A major important requirement which we have found for explosive decomposition, a requirement not reported by Madix and Falconer, is for the presence of a co-adsorbed atom to induce the explosion. For Pd(110) reported here, oxygen atoms co-adsorbed with the acetate induce the explosion and on Rh(110) we have found that the presence of carbon or nitrogen on the surface does the same thing. Autocatalytic decompositions were not found on the clean Rh(110), (111) or Pd(110) surfaces. The reason why a co-adsorbate atom is required is not completely clear, but may relate to surface ordering. It is likely that the acetate layer on the clean surface is not very well ordered [Fig. 10(a)], having mismatches in the adsorption site of the acetate as it sticks randomly on the surface with the molecular plane being parallel with [110]. When an adatom is bound to the surface it usually forms a well ordered layer due to strong electronic interactions through the conduction band of the metal. It may be that the acetic acid is adsorbed in an ordered fashion by interactions (either repulsive, or attractive) with these adatoms [Fig. 10(b)]. This then places acetates adjacent to each other and these impede decomposition by steric hindrance (increased activation barrier). This fits with our proposed mathematical model[3] which gives the desorption rate, R, as

$$R = 2kD/N_s^{1/2}[\theta_N \pi a(1 - \theta)]^{1/2}$$

where k is the rate constant $[= A \exp(-E_d/RT)]$, D is the density of reactive sites at the reaction boundary, θ_N is the coverage of nucleation sites expressed as the ratio of the number of nucleation sites, N, over the total number of sites involved N_S, θ is the surface coverage of adsorbates and a is the area of the sample.

Of course, the surface is not so homogeneous as illustrated in Fig. 10 during the decomposition, and as Fig. 8 shows, several differently stabilised acetates can be adsorbed on one and the same surface and these are probed by TPD. Every spectrum contains the CO_2/H_2 desorptions associated with the clean surface. Thus, there are likely to be islands of atomic adsorbate density and of relatively clean surface.

It can only be speculated that both electronic and specific site requirements determine the actual stability of the acetate. For instance, Davis and Barteau[7] carrying out similar experiments on Pd(111), found with HREELS that there was no difference between low-temperature desorbed acetate on the clean or the oxygen-dosed surface, but that the high-temperature desorbed acetate on the oxygen-dosed surface had lower vibrational frequencies. They attributed this to the withdrawal of electrons by the oxygen atoms present which led to an increase in the work function of Pd by 0.6 eV. This is a satisfactory reason for explaining the increased stability

of acetate in the presence of oxygen and is likely to be applicable to Pd(110) as well, but it does not account for the auto-catalytic nature of the desorption. The influence of oxygen on the acetate stability may have both electronic and simple site-blocking character. In the case of carbon, there is certainly a site-blocking effect involved, although on Rh(110) it can also produce the autocatalytic decomposition. This is apparently not the case here. The source of these differences is probably the degree of order in the carbon layer on the two surfaces.

It is well known that the stability of adsorbed carboxylate species is associated with the metal–oxygen and metal–hydrogen bond strengths. Furthermore, Davis and Barteau[7] pointed out that oxygen generally has a stabilising influence on group 8–10 metals, but that the actual stability is very dependent on the metal and on the chain length of the adsorbate. In addition, the experiments described here have highlighted the importance of lateral interactions which are known to influence the rate of adsorption and desorption in catalytic reactions. It is evident that there are similarities between the reaction of acetic acid on Pd(111) and Pd(110). On Pd(111), Davis and Barteau[8] see no autocatalytic decomposition on a p(2 × 2) oxygen dosed surface, although the mechanism of decomposition is somewhat different with acetic acid desorption dominating. The reason for this difference is not clear, but may be related to the relatively low coverage of oxygen (0.25 ML). As shown in Fig. 4, low doses of oxygen do not produce the explosion due to clean-off of the atomic adsorbate during reaction.

The maximum dose of oxygen employed here which yields the c(2 × 4) structure produces a coverage of 0.5 ML.[12,13] From the literature quoted it must also be assumed that the Pd surface under these conditions is reconstructed. He et al.[12] suggested that in the presence of oxygen the substrate rearranged to a (1 × 2) surface. In fact, Dhanak et al.[13] managed to isolate this structure by oxygen exposure followed by careful reduction a 310 K. They also established that this missing row reconstruction was stable up to 355 K. For lower oxygen coverages, a (1 × 3) reconstruction was found, which in the absence of oxygen was stable up to 370 K. He et al.[12] pointed out that the reconstructions were stable as long as oxygen was present on the surface. Once its desorption started the substrate would revert back to a (1 × 1) structure. Although narrow desorption peaks are often associated with reconstructions, the oxygen desorption from Pd is not narrow. Even if the Pd substrate is reconstructed under the layer of oxygen atoms and acetate molecules, we would expect it to remain in that state until sufficient oxygen has been removed for the reconstruction to be lifted. The oxygen atoms are here lost through reaction with hydrogen atoms, and from the isothermal experiment it is known that this reaction goes to completion once initiated. Furthermore, for higher coverages of oxygen, the CO_2 desorption is shifted to higher temperatures, which is contrary to the stabilities of the clean and reconstructed surfaces. Although we cannot exclude the possibility that a reconstruction of Pd takes place, the data support the view that the 'surface explosions' are driven by a different mechanism, as outlined in this paper, rather than by a reconstruction.
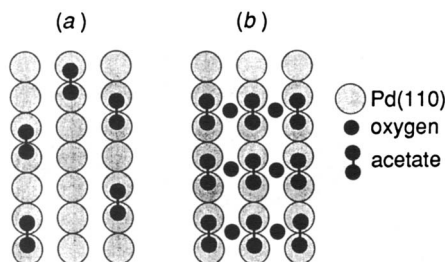
Fig. 10 A schematic representation of the order of acetate molecules on Pd(110) (a) and on the oxygen-dosed surface (b). This model assumes that the adsorption on the clean surface is random, while the presence of a co-adsorbate induces ordering, and that the acetate is in a bridged configuration.

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