

ADSORPTION OF FORMIC ACID ON CLEAN AND OXYGEN COVERED Pt(111)

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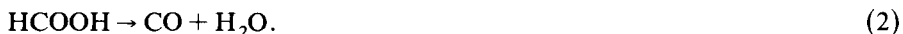
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The adsorption of HCOOH on Pt(111) and Pt(111)–O surfaces has been studied by high resolution electron energy loss spectroscopy and thermal reaction desorption spectroscopy. At 130 K, multilayer HCOOH is molecularly adsorbed in the strongly hydrogen-bonded α -polymorphic form which evaporates at 170 K, leaving a bridge-bonded formate species in the highly symmetric C_{2v} configuration. Preadsorbed oxygen enhances the Bronsted basicity of the Pt(111) surface, raising the yield of formate six- to seven-fold. Reaction with the Pt(111)–O surface produced H_2O which desorbed at 180 K. Formate decomposition occurred exclusively by dehydrogenation to $H_2 + CO_2$ at 260 K. No evidence for any other decomposition products was found.

1. Introduction

The decomposition of HCOOH over materials of catalytic interest may occur by either dehydrogenation [Eq. (1)] or dehydration [Eq. (2)], and, consequently, has been studied extensively to test catalyst specificity [1]:



In addition, these reactions have attracted further interest as a possible intermediate in the commercially important water–gas shift reaction for the reduction of H_2O to H_2 , i.e. a shift from (2) to (1).

In catalysis, where the reaction is usually performed with pressures in excess of several Torr, it is typically found that oxides catalyze predominantly the dehydration reaction whereas transition metals, which are commonly in the form of poorly defined powders, are more active towards dehydrogenation. On metal surfaces which may be described as clean in the modern surface physics sense, the specificity is less clear. For example, on freshly evaporated nickel films [2] and a Ni(110) single crystal [3,4], both CO and CO_2 are produced. The thermal reaction desorption spectroscopy (TRDS) work of Madix and co-workers [3,4] has shown that on Ni(110), this does not arise from two competing reactions, but instead is due to a bimolecular dehydration to a stable intermediate with the stoichiometry of the normally unstable formic

anhydride. At higher temperature this intermediate decomposes to H_2 , CO_2 and CO with a $CO_2:CO$ ratio of 1:1. Direct evidence for the stable anhydride has been claimed by infrared spectroscopy (IRS) [5]. However, this study also claimed that the same intermediate was formed on copper films whereas TRDS [6] and vibrational electron energy loss spectroscopy (EELS) [7] find only a formate intermediate. A W(001) surface [8] was more aggressive and decomposed the first doses of HCOOH to H, C and O residues which desorbed as H_2 and CO, leaving O chemisorbed on the surface. Larger doses on the surface covered with these residues produced a stable formate which decomposed to CO_2 at 580 K. For platinum, a catalytic molecular beam study on the evaporated films at 1400 K [9] has identified the main products as CO_2 and H_2 along with $\sim 15\%$ CO as a minor product, suggesting a possible complexity in the reaction over this catalyst as well. A Pt(110) surface has been shown to be very active towards formic acid decomposition, yielding a CO_2 pulse peaking at 265 K [10]. However, no further details of this reaction were given in this report.

The present EELS and brief TRDS experiments with HCOOH were performed as part of a wider study of the interaction of the range of oxygen-containing organic molecules (carboxylic acids, anhydrides, aldehydes, ketones and alcohols) on Pt(111) and Pt(111)-O surfaces. More particularly, the present study has sought to identify both the nature of the intermediate in HCOOH decomposition on Pt(111) and the role of adsorbed oxygen in promoting the Bronsted basicity of the surface.

2. Experimental

A brief description of the electron optics, which was developed for the EELS work, has already been given [11]. The electron monochromator and rotatable analyzer were mounted in the front portion of a Vacuum Generators chamber which also contained conventional LEED optics, side electron gun for Auger analysis and Riber quadrupole mass spectrometer. Base pressures of $(1-2) \times 10^{-10}$ Torr were obtained routinely. All EELS data were obtained by sampling the specularly reflected beam and therefore may be expected to be dominated by dipole excitations, at least for the modes which involve predominantly the motion of C and O atoms. It has been noted previously [11] that modes involving H may, but not necessarily, be excited by short-range impact scattering. In the present study, off-specular identification of the scattering mechanism was not performed. After initial interation of the beam focus and scattering geometry to optimize the elastic intensity, final tune-up of the resolution was mainly a function of beam alignment which was controlled by a comprehensive electrostatic deflection system. During final tune-up, a 25 meV region centered on the elastic peak was scanned, displayed and erased once a second on a Tracor Northern signal averager. In this way, the resolution could

be rapidly (a few minutes) and routinely tuned to 6–7 meV with a space-charge limited current to the crystal of $\sim 3 \times 10^{-10}$ A. Since this yielded an elastic count rate of $(2\text{--}4) \times 10^5$ counts s^{-1} which saturated the channel electron multiplier, all spectra were recorded with the incident current reduced to give a standardized elastic count rate of 10^5 counts s^{-1} . EELS data was obtained with a 4.1 eV beam (uncorrected for contact potential difference) at an angle of incidence of 45° . Spectra were taken by ramping the analyzer pass-energy in a constant resolution mode at $\sim 8 \text{ cm}^{-1} \text{ s}^{-1}$ and recorded directly from the ratemeter output.

A Pt(111) specimen, 8 mm diameter \times 1 mm, was cut from a boule supplied by Materials Research Corporation, mechanically polished and finally flash electropolished ($\sim 10 \text{ A cm}^{-2}$ for 2–4 s) in a 20% aqueous KCN solution. The crystal was mounted by spotwelding at one end to a piece of platinum foil which was crimped over liquid nitrogen cooled tantalum heater wires. Final cleaning was done in situ by extensive heating to 1500 K in up to 10^{-6} Torr of oxygen, until Auger showed no impurities within the limit of reliable detectability by the LEED retarding grid optics. Crystal temperature was monitored from a chromel–alumel thermocouple spotwelded to the back of the crystal.

Prior to each adsorption experiment, the surface was cleaned by flashing to 1300 K in $\sim 5 \times 10^{-8}$ Torr oxygen until a 300 L exposure of oxygen during the cool-down to 140 K produced a thermal desorption pulse at ~ 650 K characteristic of a saturated Pt(111)–O surface. It was often found that 2–3 such cycles were necessary to produce the desired surface. Another such exposure to oxygen produced an EELS band at 470 cm^{-1} due to the $\nu(\text{PtO})$ mode of dissociatively adsorbed oxygen. This band is similar to the one seen at 490 cm^{-1} by Gland et al. [12]. A clean Pt(111) surface was prepared, after the oxygen cleanup, by cooling to ~ 120 K, flashing to ~ 600 K to desorb tramp CO and H_2 and recooling to the desired temperature. HCOOH was adsorbed at < 130 K.

Both O_2 and thoroughly degassed HCOOH were introduced into the vacuum system through a moveable 2 mm diameter glass-lined molecular beam doser which was estimated (from CO adsorption data) to enhance the flux of noncondensable gases as the crystal surface by a factor of 6 over that from the background.

Sets of TRDS data were recorded in a single experiment by multiplexing the required mass peaks with a quadrupole mass spectrometer at 0.1 s intervals. The mass spectrometer was operated in a particle counting mode so that the ion-counts could be stored directly in successive channels of the Tracor Northern signal averager. The crystal was heated with a fixed a.c. potential which gave an approximately linear heating rate over the intermediate temperature region. Since the abscissa becomes linear in time, the temperature was also recorded during the heating cycle.

3. Results

3.1. Thermal reaction desorption spectroscopy (TRDS)

Molecular HCOOH desorption from a multilayer (estimated to be 3–5 monolayers from the calibrated beam doser) on Pt(111) produced a pulse with $T_p = 170$ K (T_p = peak desorption temperature) (fig. 1a) in good agreement with the data from Ag(110) [13]. A second state seen in the Ag(110) work as 190 K and attributed to monolayer molecular adsorption could not be resolved in the present work possibly due to the multiplexer resolution.

The decomposition products (H_2 , H_2O and CO_2) from a monolayer of HCOOH on a Pt(111)–O surface are shown in figs. 1b–1d. Little or no molecular desorption occurred with this exposure thereby avoiding possible confusion from HCOOH fragment ions. Desorption-limited pulses of H_2O ($T_p = 180$ K) and H_2 ($T_p = 370$ K) can be correlated with desorption from an otherwise clean Pt(111) surface [14,15]. In the latter case, the high observed T_p can be associated further with desorption from a low coverage of the β_2 phase of chemisorbed hydrogen. The appearance of CO_2 ($T_p = 260$ K), which does not chemisorb on transition metals, must occur by a reaction-limited surface decomposition of what EELS will show to be an adsorbed formate (section 2.31). Desorption-limited CO ($T_p = 470$ K) was also seen during TRDS. However, adsorbed CO was not seen by EELS, indicating that the CO seen during TRDS must arise from the Pt support, edge or back of the Pt(111) crystal. A similar dose of HCOOH on clean Pt(111) produced similar pulses of H_2 and CO_2 but with reduced intensity. In particular, $T_p(CO_2)$ was unaltered with the lower coverage, indicating first-order decomposition kinetics.

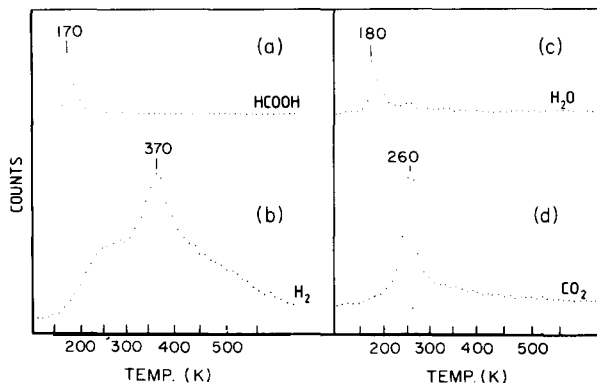


Fig. 1. TRDS for HCOOH adsorbed on Pt(111) surface at 130 K: (a) HCOOH (46) from a thick (three to five monolayers) deposit on clean Pt(111). (b)–(d) H_2 (2), H_2O (18) and CO_2 (44) from approximately one monolayer of HCOOH on a Pt(111)–O surface. The heating rate was 10 K s^{-1} .

3.2. EELS

3.2.1, Adsorption of HCOOH on Pt(111) – O

Condensation of sufficient HCOOH (3 – 5 monolayers) onto the Pt(111) – O surface at 130 K to conceal the new bands of the chemisorbed species resulted in the spectrum shown in fig. 2 which is assigned according to table 1 [16]. This spectrum is characterized by strong specular reflection of the elastic peak, suggesting good epitaxy with the Pt(111) substrate. This may be due to the layer structure of solid HCOOH which arises from strong intermolecular hydrogen bonding. This strong hydrogen bonding leads to the large upward and downward shifts of the $\pi(\text{OH})$ (970 cm^{-1}) and $\nu(\text{OH})$ ($\sim 2900\text{ cm}^{-1}$) modes from their monomer frequencies (636 and 3570 cm^{-1} , respectively). The $\delta(\text{OH})$ mode is expected to be similarly shifted but is either too weak or strongly coupled with $\nu(\text{C}=\text{O})$ and $\delta(\text{C}-\text{H})$ modes. The splitting of the $\nu(\text{C}=\text{O})$ mode into two bands has been attributed to tautomerism in the α -polymorph [15], although the lower frequency mode is unusually weak in the present case. The alternative β -polymorph has only a single $\nu(\text{C}=\text{O})$ band at 1600 cm^{-1} and is clearly not formed on the Pt(111) surface. Previous, lower resolution EELS from solid HCOOH on Cu(001) [7] and Ag(110) [12] failed to detect some of the modes seen in the present work. A difference in assignment also arises. Whereas the strong 960 cm^{-1} was first assigned to the $\nu(\text{C}-\text{O})$ mode [7] and later to the in-plane $\delta(\text{OH})$ mode [12], the present assignment prefers the out-of-plane $\pi(\text{OH})$ mode on the basis of the large upward frequency shift to be expected from the strong hydrogen bonding. This assignment is also consistent with good epitaxy of a layer structure $(\text{HCOOH})_n$ on Pt(111) since this would lead to the out-of-plane, $\pi(\text{OH})$ mode (B_1 symmetry), along with the

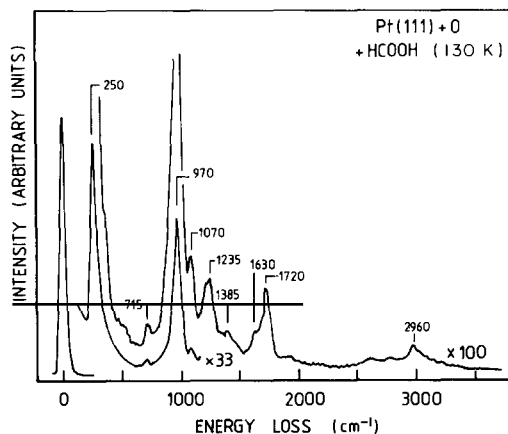


Fig. 2. EELS from a thick (three to five monolayers) layer of solid HCOOH on a Pt(111)–O surface at 130 K.

Table 1
Assignment of vibrational bands for solid HCOOH and annealed formate on Pt(111)

Mode	Frequency (cm^{-1})	
	Solid HCOOH	Adsorbed formate
lattice	250	
$\nu(\text{PtO})$		360
$\delta(\text{OCO})$	715	780
$\pi(\text{OH})$	970	
$\pi(\text{CH})$	1070	
$\nu(\text{CO})$	1235	
$\nu_s(\text{OCO})$		1330
$\delta(\text{CH})$	1385	
$\nu(\text{C}=\text{O})$	1630	
$\nu(\text{C}=\text{O})$	1720	
$\nu(\text{OH})$	Broad, centered	
$\nu(\text{OH})$	Near 2900	
$\nu(\text{CH})$	2960	2920
$2\pi(\text{OH})$	1920	
$\nu(\text{PtO}) + \nu_s(\text{OCO})$		1690
$2\nu_s(\text{OCO})$		2670

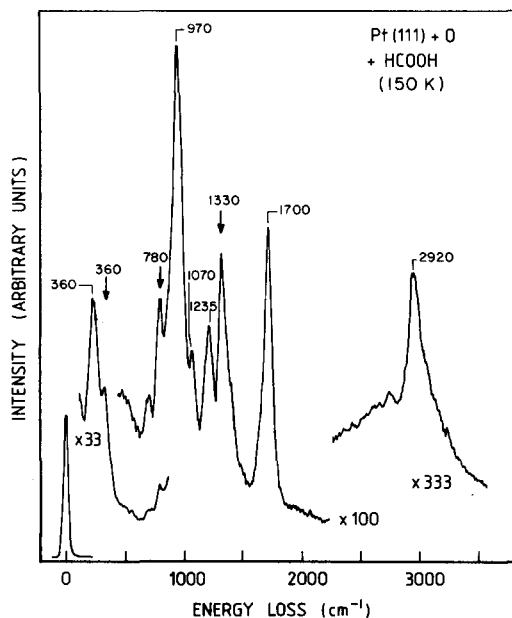


Fig. 3. EELS from HCOOH adsorbed on a Pt(111)-O surface at 150 K. The arrows indicate the new bands of the adsorbed formate species coexisting with solid HCOOH.

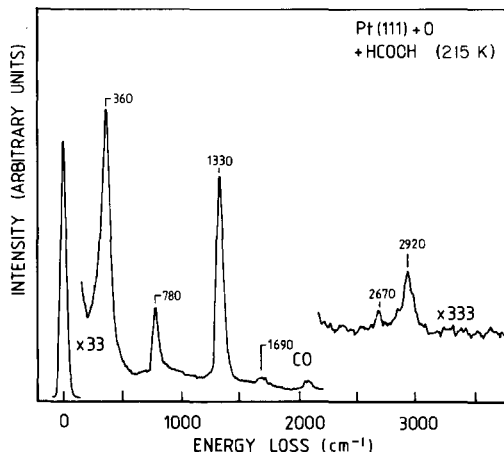


Fig. 4. EELS obtained by heating a thick layer of solid HCOOH on a Pt(111)–O surface to 215 K. Excess HCOOH and H₂O have been desorbed leaving only the spectrum of the annealed formate.

$\pi(\text{C-H})$ mode, with dynamic dipoles normal to the image plane of Pt(111). According to the dipole surface selection rule, this would lead to enhanced intensity of these modes over the remaining modes (A_1 and B_2 symmetry) as a comparison with non epitaxial solid HCOOH [17] confirms.

If HCOOH is condensed onto the Pt(111)–O surface at 150 K, new bands at 360, 780 and 1330 cm^{-1} coexist with the $(\text{HCOOH})_n$ spectrum (fig. 3). After a flash to 215 K, the molecular HCOOH evaporates leaving only the chemisorbed species (fig. 4). This species is identified with an adsorbed formate (table 1) due to the absence of bands due to $-\text{OH}$ indicative of deprotonation of the acid and the similarity of the EELS bands to the infrared spectra of inorganic formate coordination compounds [18]. The prominent bands seen here are similar to those reported previously for formate adsorbed on Cu(001) [7] and Ag(110) [13]. As discussed by Sexton [7], the symmetry of formate adsorbed on a structureless (jellium) infinite metal surface can be determined by application of the surface selection rule for dipole excitations. Briefly, this selection rule requires that for a mode to couple to the incident electron (or photon), the dynamic dipole must have a component perpendicular to the surface. Thus, the absence of the normally intense $\nu_{\text{as}}(\text{OCO})$ mode (expected near 1600 cm^{-1}), which has B_1 symmetry, is clear indication that the formate is adsorbed with symmetry no lower than $C_s(1)$, i.e. with O–O parallel to the surface. That the formate is more probably adsorbed in the more highly symmetric C_{2v} configuration hinges on the absence of the sole B_2 mode, viz. the out-of-plane $\pi(\text{CH})$ deformation. By comparison, in the infrared spectrum of the formate anion this mode is seen near 1070 cm^{-1} but is weak with an intensity only 6% that of the $\nu_s(\text{OCO})$ mode [19]. In the present EELS spectrum

of the adsorbed formate it is estimated that a band in this clear region of the spectrum with an intensity 1% of the $\nu_s(\text{COO})$ mode would have been detected easily. Although CH modes may be excited by short-range impact scattering [11] and therefore not subject to the surface selection rule the absence of an active $\pi(\text{CH})$ mode is taken as evidence that the formate is adsorbed in the highly symmetric C_{2v} configuration. Thus, the local symmetry of the clean structured Pt(111) surface (C_{6v}) is lowered to C_{2v} by the adsorbed formate.

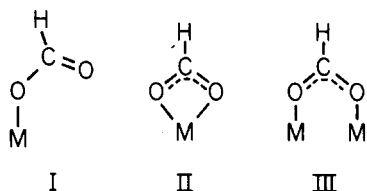
On Cu(001) [7] and Ag(110) [13], the adsorbed formate exhibited a temperature dependent orientation. For example, on Cu(001), the $\nu_{\text{as}}(\text{OCO})$ mode became active reversibly at lower temperatures whereas the opposite effect was seen irreversibly on Ag(110). No comparable effect was seen on Pt(111), i.e. the C_{2v} configuration of the annealed formate was maintained at all temperatures from its appearance with the evaporation of excess HCOOH at ~ 180 K until decomposition occurred at 260 K. The formate bands merely decrease in unison and no new features were seen in the spectrum. In particular, the intensity of the tramp CO band near 2100 cm^{-1} increased by $< 2\%$ of the saturated linear $\nu(\text{CO})$ band of the half-monolayer Pt(111)-CO $\alpha(4 \times 2)$ structure [20]. This demonstrates clearly that the CO seen with TRDS did not arise from the front central region of the Pt(111) crystal that was exposed to HCOOH and probed by the EELS beam.

3.2.2. Adsorption of HCOOH on clean Pt(111)

Adsorption and evaporation of excess HCOOH from a clean Pt(111) surface at 180 K produced the same EELS bands seen for the Pt(111)-O surface, but with only 15% the intensity. Correlating intensities, this amounts to 6–7 times more adsorption on the Pt(111)-O surface compared with the clean surface.

4. Discussion

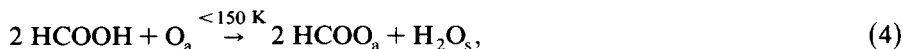
Adsorption of HCOOH on both clean and oxygen covered Pt(111) surfaces produced a formate species which is adsorbed in the highly symmetric C_{2v} configuration, i.e. the two-fold symmetry axis is perpendicular to the image plane of the Pt(111) surface. In organic coordination chemistry, three types of carboxylate ligands have been recognized [18], viz. monodentate (I), bidentate (II) and bridged (III) which can usually be distinguished on the basis of the splitting, Δ , between the $\nu_s(\text{OCO})$ and $\nu_{\text{as}}(\text{OCO})$ modes: In the formate anion,



$\Delta = 201 \text{ cm}^{-1}$ and is similar to the splitting seen in III. For I, $\nu_s(\text{OCO})$ becomes more single bond-like whereas $\nu_{as}(\text{OCO})$ becomes more carbonyl-like and typically $\Delta > 300 \text{ cm}^{-1}$. On the other hand, it is usually found that for II $\Delta < 80 \text{ cm}^{-1}$. The equivalence to the two oxygen atoms in the C_{2v} configuration on Pt(111) clearly eliminates I. In the absence of an active $\nu_{as}(\text{OCO})$ mode, Δ cannot be measured; but since the observed $\nu_s(\text{OCO})$ (1330 cm^{-1}) is only slightly lower than that of the free formate anion (1361 cm^{-1}), it is more probable that the formate is adsorbed in a bridged configuration similar to III. For comparison, the $\nu_s(\text{OCO})$ mode in bidentate acetate inorganic complexes, like II, is raised $\sim 50 \text{ cm}^{-1}$ from the equivalent band in the acetate anion [18]. The bridge-bonded structure of adsorbed formate was maintained at all temperatures until decomposition to CO_2 and H_2 occurred with a maximum rate at 260 K. Essentially no CO was produced on the well-defined part of the Pt(111) surface.

The interaction of HCOOH with a Pt(111) surface can be described by simple acid-base concepts in the Lowey–Bronsted sense [21]. Although the clean Pt(111) surface possesses a measurable activity for the deprotonation of HCOOH to its conjugate base (the adsorbed formate species), this activity could be enhanced six- to seven-fold by increasing the basicity of the surface with a chemisorbed layer of oxygen.

For the Pt(111)–O surface, the adsorption and decomposition scheme may be written thus



It can also be presumed that some deprotonation occurs directly on Pt(111) sites.



During decomposition, no evidence could be found for an intermediate other than formate. The desorption of H_2O_s released by reaction (4) at 180 K correlates with the desorption of H_2O from a clean Pt(111) surface [14]. This desorption temperature is of significance since the reaction of H_2O with a Pt(111)–O surface has been shown to produce an adsorbed hydroxyl species which decomposes to adsorbed oxygen and H_2O at 215 K [14], i.e. 35 K higher than desorption from the clean Pt(111) surface. This demonstrates that ad-

sorbed hydroxyl is not a product of HCOOH reaction with Pt(111)–O, thereby releasing each adsorbed oxygen to produce two formate species according to eq. (4).

5. Summary

(1) Multilayer HCOOH condenses on a Pt(111) surface, with strong inter-molecular hydrogen bonding, in the α -polymorphic form which desorbs at 180 K.

(2) Adsorption of formic acid on a Pt(111) surface produces a chemisorbed bridge-bonded formate species in the highly symmetric C_{2v} configuration.

(3) The yield of formate (as judged from the EELS band intensities) is increased six- to seven-fold by increasing the Bronsted basicity of the surface with chemisorbed oxygen.

(4) The reaction of HCOOH with Pt(111)–O produces H_2O as a by-product which desorbs at 180 K.

(5) Adsorbed formate decomposes with a peak rate at 260 K exclusively by dehydrogenation to H_2 and CO_2 and without the formation of any new surface species.

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