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The adsorption and decomposition of formic acid on clean and oxygen-dosed Pd(110)

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Abstract. The interaction of formic acid (HCOOH) with Pd(110) was studied using TPD and XPS. At low doses, at an adsorption temperature of 140 K, HCOOH decomposed to yield CO, CO₂, H₂ and H₂O during TPD. CO and H₂ were evolved in desorption-limited peaks at 470 and 320 K, respectively. The CO and H₂O desorptions were saturated at very low doses indicating only a small degree of formate dehydration in such a transient experiment. The CO₂ and H₂ evolution continued to increase with dose and the CO₂ evolved in a decomposition-limited peak at 237 K at low doses which broadened to lower temperature with increasing coverage. This dehydrogenation of HCOOH was of first order with an activation energy of 40 kJ mol⁻¹. At doses above 0.5 L molecularly chemisorbed HCOOH was observed to desorb at 210 K and at still higher doses physisorbed multilayers were present and desorbed at 180 K. XPS confirmed the presence of CO above 250 K and formate below this temperature. When oxygen was pre-dosed the formate was significantly stabilized and its coverage increased, the CO desorption was removed and H₂ was produced at higher temperatures at the expense of the H₂ peak at 320 K.

1. Introduction

In the 1960s the adsorption of HCOOH on transition metals was used as a model reaction to probe the strength of the chemisorption complex and hence to develop the now well-known volcano plot [1]. Since then a lot of work has concentrated not only on the adsorption but also on the decomposition of the molecule [2-6]. With the possibility of HCOOH decomposition into either H₂O and CO or H₂ and CO₂ the selectivity of the catalyst can be studied. The formation of CO₂ and H₂ is generally associated with the presence of the stable intermediate formate (HCOO) on the surface. This complex is believed to be of importance in the oxidation of both HCOOH and CH₃OH and to be involved in the rate-determining steps.

The work described here is concerned with the reactivity of a Pd single crystal of (110) orientation towards HCOOH and the effect of pre-dosed O₂ on the adsorption complex. This study is part of a long-term research programme which aims to understand the reactivity of transition metals such as Pd and Rh as well as the influence of alloying with group IB metals (Cu and Ag) on their catalytic activity.

2. Experimental details

The experiments were performed in a VG single chamber UHV instrument which had been adapted to carry facilities for LEED, XPS, ISS and TPD. The pressure after bake-out was better than 1×10^{-10} mbar. The crystal was cleaned by argon ion bombardment and cycles of oxidation and reduction [8]. The cleanliness of the crystal was assessed by monitoring the thermal desorption pattern of CO which was known to be very sensitive to small amounts of surface carbon [8, 9].

HCOOH was adsorbed at 140 K, and O₂ was dosed at 480 K to ensure atomic adsorption only. The desorption was carried out at constant current which meant that the heating rate varied slightly. In the temperature range of interest it was 3 K s^{-1} . XPS spectra were recorded using Al K α x-irradiation of 180 W. The angle of electron escape was 45°; the pass energy was 44 eV.

3. Results

The masses monitored during the desorption experiments were 46 (HCOOH), 45 (HCOO), 44 (CO₂), 28 (CO), 18 (H₂O) and 2 (H₂). The desorption spectra from increasing doses of HCOOH on Pd(110) are shown in figure 1. At low coverage, the major peaks are CO₂ and H₂O at 237 K while H₂ evolves at 320 K and CO at 470 K, both of which are desorption limited [7-10]. With increasing coverage of HCOOH (0.3 L) two desorption peaks appear at 237 and 210 K. Peaks due to CO₂ and H₂O increase at 237 K and a shoulder develops at 210 K. An exposure of 0.6 L HCOOH to Pd leads to the appearance of a third set of HCOOH desorption peaks at 180 K. The HCOOH peaks at 237 and 210 K are saturated and the most intense peak now is the molecularly desorbing species HCOOH. The H₂ desorption has shifted by 10 K to lower temperatures and its intensity is still increasing. In contrast to the first two HCOOH desorption states this low temperature peak at 180 K does not saturate but increases with the dosage and dominates the peak at 210 K. After the exposure of 0.6 L HCOOH to Pd LEED shows a weak p(1 × 2) pattern which remains unchanged but intensifies with increasing coverage.

The effect of pre-dosing O₂ on the desorption of a 0.6 L dose of HCOOH is illustrated in figure 2. At the lowest dose of 0.5 L O₂ which corresponds to a p(1 × 3) LEED pattern the CO₂ peak is shifted to higher temperatures and the H₂ desorption consists of a peak with shoulder to higher temperatures. Once the O₂ coverage is increased to 1.0 L (the LEED structure is now c(2 × 6)) the CO₂ peak maximum is shifted to even higher temperatures, and the corresponding peak is increased in intensity. The main two CO₂ desorptions now occur at 290 and 240 K. The presence of O₂ not only alters the CO₂ desorption but also removes the CO evolution at 470 K. Furthermore, more H₂O is now seen to desorb at lower temperatures, that is below 200 K, compared with the behaviour on clean Pd, and the lower temperature H₂ desorption at 320 K has been suppressed while the shoulder at 350 K has increased in intensity.

The XPS regions of interest were those of O 1s and C 1s of which the former overlaps with Pd 3p. This made differentiating between differently adsorbed oxygen species impossible; therefore we will discuss only the C 1s spectra. At low coverage, a broad feature of low intensity is seen between 285 and 290 eV which cannot be resolved into separate peaks. With increasing coverage this changes into a distinct peak at 289.0 eV. The condensed phase of HCOOH on Pd is shifted even further and

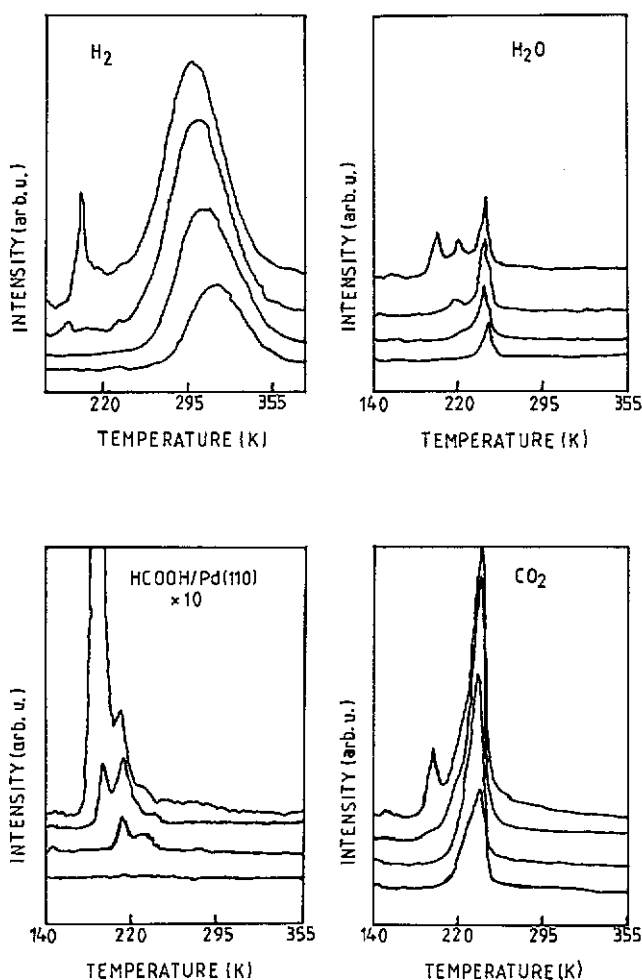


Figure 1. Thermal desorption spectra of increasing amounts of HCOOH adsorbed on Pd(110) at 140 K. The heating rate was 3 K s⁻¹; the doses were 0.15, 0.3, 0.6 and 1.5 L. CO which evolved at 470 K is not shown here.

has a single peak at 290.0 eV. When this phase is heated to 170 K there is a drastic reduction in intensity and a broad envelope is seen at lower binding energy. This spectrum resembles that of the surface of low HCOOH coverage. On further heat treatment the shoulder at the higher binding energy disappears and a single peak at 286.0 eV appears which is maximized at 230 K and identified as carbon originating from CO adsorbed on Pd. The pre-dosing of 2.0 L O₂ followed by 0.5 L HCOOH leads to the development of a C 1s peak at 286.9 eV which is stable up to 270 K.

4. Discussion

A comparison of the intensities of the desorbing species reveals that following the first dose the HCOOH molecules on Pd are not stable, but are decomposed and desorbed as H₂, CO, CO₂ and H₂O. The coincident evolution of CO₂ and H₂O indicates that both of these products derive from a common intermediate; it is also likely that CO_(a)

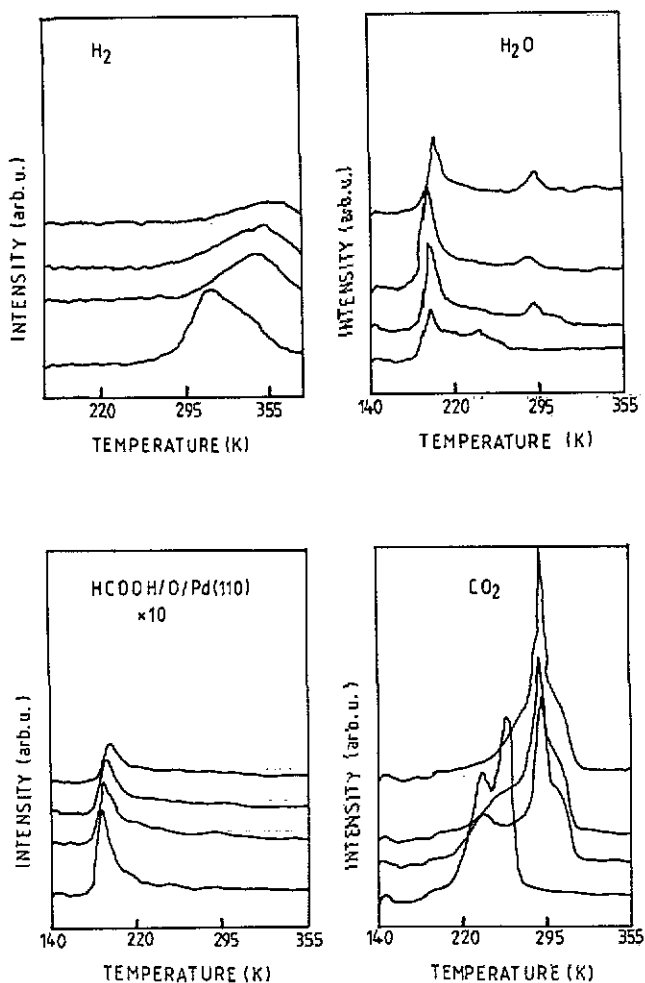
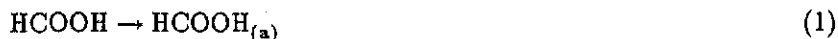


Figure 2. Thermal desorption spectra of 0.6 L HCOOH dosed at 140 K onto Pd(110) which had been exposed to increasing amounts of O₂ at 480 K. The heating rate was 3 K s⁻¹; the O₂ doses were 0.5, 1.0, 2.0 and 5.0 L.

and H_(a) are formed at the same time, but are retained on the surface because they are strongly bound. It is proposed that the common intermediate for all of these products is the formate species HCOO, since it is likely that HCOOH will dehydrogenate at the acid group upon or near to the adsorption temperature (even Ag and Cu can induce such dissociation [3, 5]).



The decomposition of HCOO then takes two routes implying a common rate-determining step for dehydrogenation and dehydration.

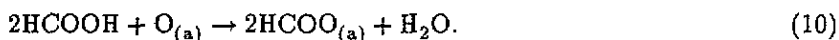


or



The dehydrogenation indicated in step 3 was found to be of first order, with an activation energy of 40 kJ mol⁻¹. The CO₂ which is formed simultaneously is not stable on Pd above 90 K [10]. If formed from pre-dosed O₂ and adsorbed CO, CO₂ desorbed in several peaks at 400, 390, 300, 230 and 200 K, in accordance with similar observations already described in the literature [11]. Consequently, we propose that the evolution of CO₂ as shown in figures 1 and 2 derives from the decomposition of HCOO and is not a product of CO oxidation. Furthermore, it is suggested that once the reactive sites for intermediate formation are filled (probably by formation of half a monolayer of formate—hence the p(1 × 2) LEED pattern) the remaining HCOOH is adsorbed intact and does not dissociate. This would account for the increases in all the peaks at 210 K. Above 0.3 L HCOOH the decomposed amount does not change much. Once the surface is completely covered any incoming HCOOH condenses on the already adsorbed layer. These species are now physisorbed and are desorbed at 180 K. The intensity of this HCOOH peak is proportional to the exposure and does not saturate.

When O₂ is pre-dosed the main change in the spectra is the increase in the intensity as well as in the stability of the HCOO intermediate and the evolution of water at low temperature. This derives from the oxidative dehydrogenation at the hydroxyl group.



The presence of oxygen atoms has enhanced the adsorption of HCOOH by creating new adsorption sites. Similarly, it has prevented the decomposition of HCOOH into CO and has favoured the formation of H₂O. The peak at 190 K results from the desorption of H₂O formed according to step 10 [12]. Further experiments are being carried out using deuterated formic acid to establish the origin of the H₂ peak at 350 K.

All the XPS results confirm the conclusions drawn from the TPD experiments. At low doses no single carbon-containing species can be isolated. With increasing coverage a broad peak develops which is characteristic of condensed HCOOH. This peak position compares well with that of multilayers of DCOOH on Cu(110) as determined by Bowker *et al* [5]. The condensed layers can be desorbed at 170 K which then leaves a single adsorbate layer on the surface the spectrum of which is very similar to that of a low dose of HCOOH on Pd. Further heat treatment leads to the development of a single peak. The carbon-containing species which disappears during the heat treatment is formate. The single peak left on the surface is CO which agrees with the results of Sanders *et al* [10] who also detected CO with FT-RAIRS on a Pd(100) surface after heating a layer of HCOOH to 190 K.

After pre-dosing O₂ the C 1s peak appears in a position different from both those of CO and HCOOH which indicates the presence of a new carbon-containing species. The high binding energy of carbon in physisorbed formic acid is associated with a high oxidation state or more generally speaking with little extra-atomic relaxation. For both CO and HCOO the oxidation states of the carbon atoms differ from that of carbon in HCOOH; also the close proximity to the Pd crystal will enhance the screening that the C 1s core holes experience and hence lead to peak positions at lower binding energies.

Finally, it should be mentioned that Pd is very reactive towards HCOOH. On Cu(110) it was necessary to heat the crystal to well above room temperature in order to decompose HCOO [5]; using Ag(110) it was not possible to produce HCOO without pre-dosing O₂ [6].

References

- [1] Fahrenfort J, van Reijen L L and Sachtler W M H 1960 *The Mechanism of Heterogeneous Catalysis* ed J H deBoer (Amsterdam: Elsevier) p 23
- [2] Sexton B A 1979 *Surf. Sci.* **88** 319
- [3] Ying D H S and Madix R J 1980 *J. Catal.* **61** 48
- [4] Barteau M A, Bowker M and Madix R J 1980 *Surf. Sci.* **94** 303
- [5] Bowker M and Madix R J 1981 *Surf. Sci.* **102** 542
- [6] Sexton B A and Madix R J 1981 *Surf. Sci.* **105** 177
- [7] Behm R J, Christmann K and Ertl G 1980 *J. Chem. Phys.* **73** 2984
- [8] Goschnick J 1987 *PhD Thesis* Berlin, p 75
- [9] Conrad H, Ertl G and Latta E E 1974 *J. Catal.* **35** 363
- [10] Sander D and Erley W 1990 *J. Vac. Sci. Technol. A* **8** 3357
- [11] Matsushima T 1989 *Chem. Phys. Lett.* **155** 313
- [12] Brosseau R, Ellis T H and Morin M 1990 *J. Vac. Sci. Technol. A* **8** 2454