

# On the role of adsorbed formate in the oxidation of C<sub>1</sub> species on clean and modified Pd(100) surfaces



Imre Kovács<sup>a,\*</sup>, János Kiss<sup>b,c</sup>, Frigyes Solymosi<sup>b</sup>

<sup>a</sup> University of Dunaújváros, 2401 Dunaújváros, Táncsics M. u. 1/A, Hungary

<sup>b</sup> Department of Physical Chemistry and Materials Science, University of Szeged, 6720 Szeged, Aradi v. tere 1, Hungary

<sup>c</sup> MTA-SZTE Reaction Kinetics and Surface Chemistry Res. Group, University of Szeged, 6720 Szeged, Dóm tér 7, Hungary

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## ABSTRACT

The formation of adsorbed HCOO was confirmed during several catalytic reactions. High concentration of surface HCOO species easily formed by the decomposition of formic acid so its chemical and physical properties have been widely studied on transition metal surfaces. On group VIII and Ib metals HCOO was produced by this way, the lack of HCOO formation on clean Pd(100) was the only exception. The HCOOH/Pd(100) adsorbed layer readily decomposed to CO and H<sub>2</sub> but no HCOO was found by UPS. The presence of formate was also discussed in the oxidation of surface CH<sub>2</sub> groups. We investigated the adsorption of HCOOH and H<sub>2</sub>CO on O(a) pre-covered surfaces. The bands at 4.2, 7.9–8.7, 10.9, and 13.4 eV in the UPS spectra are due to formate species. It is stable up to 300 K in the O(a)+HCOOH(a) reaction and up to 230–240 K in the O(a)+H<sub>2</sub>O(a) reaction. The products were CO<sub>2</sub> and H<sub>2</sub>O, which desorbed with a coincidence peak temperature at 310 K. We can conclude that more adsorbed oxygen is necessary for the formation of HCOO from H<sub>2</sub>CO which is reflected in its lower stability.

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## 1. Introduction

The decomposition of HCOOH on metal and oxide surfaces served as a convenient model reaction for the testing of various theories of catalysis [1–3]. Nowadays, the knowledge of the surface chemistry of adsorbed HCOOH and formate as a reaction intermediate is of great assistance in the elaboration of the mechanism of several important catalytic reactions such as water-gas shift reaction [4,5], synthesis and decomposition of methanol [5,6] and the methanation of CO [7] and CO<sub>2</sub> [8]. There is a great effort to develop an effective and selective catalyst for the decomposition of organic materials to produce H<sub>2</sub>, if possible, free of CO. Regarding the synthesis of methanol Pd is also a promising catalyst, particularly in the production of oxygenated compounds via formate. Recently several papers reported the vapor phase decomposition of HCOOH catalyzed by supported Pt metals [2,3,9–11]. Formic acid is also a good candidate as a H<sub>2</sub> storage compound [11–13]. For fuel cell applications it is important to produce CO free H<sub>2</sub> gas [12].

Formaldehyde (H<sub>2</sub>CO), similarly to formate, can also be an important intermediate in the hydrogenation reactions of carbon

containing molecules [14–17], and even in the interaction of HCOOH with Pt-metals supported on oxides [18–21]. During the interaction between HCOOH and oxide supported catalysts formaldehyde is produced already in the adsorbed layer and in the gas phase. The changes in the amounts of formaldehyde and CO were found to be complementary. Instead of the traditional dehydration mechanism it is suggested that in the HCOOH decomposition the main source of CO gas is the de-oxygenation of HCOOH [21].

It is generally accepted that the support may influence the stability of the intermediates and influence the decomposition pathways. Therefore it is desirable to investigate the surface chemistry of formate and formaldehyde without the disturbing effect of the oxide support.

Apart from some sporadic works the thermal stability and reaction pathways of adsorbed HCOO [22] and H<sub>2</sub>CO [23,24] on Pd(100) have not been studied in detail. Earlier it turned out that the surface modifiers can alter the stability of these molecules. Pre-adsorbed potassium increased the uptake of formic acid, altered the product distribution of its surface decomposition and induced the formation of formate groups [24]. The pre-adsorbed oxygen on Rh surface also had a stabilizing effect on HCOO [25]. The pre-adsorbed iodine has an inhibition effect on the stability of adsorbed H<sub>2</sub>CO [26]. The results suggested that the electronegative additives

\* Corresponding author.

E-mail address: [amerigo1960@gmail.hu](mailto:amerigo1960@gmail.hu) (I. Kovács).

promote the selective oxidation of CH<sub>2</sub> and CH<sub>3</sub> species on Pd(100) [27].

In the present study we focus on the effects of pre-adsorbed oxygen on the stability of formic acid and formaldehyde on Pd(100). The decomposition products were monitored by thermal desorption spectroscopy (TDS), the surface intermediates were determined by ultraviolet photoelectron spectroscopy (UPS).

## 2. Experimental

The experiments were carried out in a standard ultra-high-vacuum (UHV) chamber with a base pressure of  $5 \times 10^{-10}$  mbar, equipped with facilities for AES, UPS, XPS and quadrupole mass spectrometer. The photoelectrons were detected by an electrostatic hemispherical analyzer (Leybold-Heraeus LHS 10). The photon source for UPS (He I and He II) was pumped differentially. The UPS spectra were recorded with an instrumental resolution of 0.2 eV. All binding energies are referenced to the Fermi level of palladium. TDS measurements were carried out in the same chamber. A heating rate of 14 K/s was used.

The Pd single crystal (Pd(100)) was a product of Material Research Corporation; the purity was 99.99%. The sample could be cooled by a Ta foil connected to a liquid-nitrogen-cooler, and heated resistively by wires. The temperature was measured by a K-type thermocouple spot-welded to the edge of the metal. Sample cleaning was achieved by both Ar<sup>+</sup> sputtering and cycles of oxygen treatments ( $3 \times 10^{-7}$  mbar local pressure, for 10–30 min, with sample temperature at 800–1000 K). HCOOH and H<sub>2</sub>CO were obtained from Merck, H<sub>2</sub>CO as paraformaldehyde; it was further purified by several freeze-pump-thaw cycles and then decomposed by heating. For adsorption it was dosed through a capillary which terminated ca. 1.5 cm from the sample.

The adsorption of oxygen (Messer-Griesheim 99.995%) was carried out at 300 K. The surface concentration of adsorbed oxygen has been determined in separate experiments. This calibration was based on the work of P. Thiel et al. [28]. The appearance of the lower temperature O<sub>2</sub> desorption peak at 800 K was considered as an indication of  $\Theta_o = 0.5$  coverage.

## 3. Results and discussion

### 3.1. Adsorption of HCOOH on clean Pd(100)

In our previous studies we established that HCOOH adsorbs and decomposes on the clean surface, but the formation of adsorbed HCOO as an intermediate could not be confirmed by UPS measurements [24]. The main findings in this topic can be summarized as follows: i.) The thermal desorption from the adsorbed layer resulted in an uncommon desorption of CO and H<sub>2</sub>. Their characteristic desorption temperature,  $T_p$  values suggest a desorption controlled reaction mechanism. ii.) The molecular HCOOH desorption shows that a condensed and a physisorbed layer gave two peaks at 170–175 K and at 200–204 K, respectively. iii.) The He II photoelectron spectra of clean Pd(100) after 10 L HCOOH exposure showed additional features at 6.8, 9.3, 10.3, 11.3, 16.2 eV which can be attributed to the 10a, 2b, the 9a, the 1b, the 8a, 7b and the 6a orbitals, respectively, of molecularly adsorbed HCOOH [Table 1 of Ref. [24]]. Although the thermal decomposition reactions in the chemisorbed layer are unclear, the existence of formate species was not established or it was very unstable on the clean surface. When the UPS feature for molecularly adsorbed HCOOH disappeared, above 230 K, signals were detected at 8.3 and 10.9 eV, which are very probably due to the products (CO) of the surface decomposition. In agreement with this, these signals disappeared above 450 K, which is the temperature of CO desorption. Above the chemisorbed

layer a physisorbed and a condensed HCOOH layer exist at higher coverages.

### 3.2. Adsorption of HCOOH on O-saturated ( $\Theta_o = 0.5$ ) Pd(100)

The characteristic features of the coadsorbed layer significantly changed compared to the clean surface. No desorption of HCOOH was detected at low exposure even after zooming in on the relevant region. This indicates that this chemisorbed layer totally decomposes (Fig. 1). At higher exposures the TDS spectra of the parent molecule show a new peak developing at 324 K which saturates and shifts to 305 K. The weak feature at 350–450 K is very probably an experimental artefact from the sample holder. Above 0.5 L exposure a new peak developed around 190 K which moved to 200 K, it can be attributed to the physisorbed state of HCOOH. A condensed multilayer appeared at 170–175 K after above 5 L exposures. The appearance of gas phase HCOOH above 300 K can be attributed to the formate-hydrogen recombination or formate disproportionation (see below).



The products of thermal decomposition show CO<sub>2</sub> and H<sub>2</sub>O evolution, while H<sub>2</sub> and CO desorption was suppressed (Fig. 2). The peaks below 250 K correspond to fragments of the parent molecule. Above this temperature the peaks at 325 K, both in H<sub>2</sub>O and CO<sub>2</sub> desorption spectra, are of the same origin. In addition, HCOOH desorption was detected at this temperature. We suppose that the adsorbed formate layer formed in the HCOOH dissociation decomposes further on the oxygen pre-adsorbed surface. We cannot exclude (in accordance with Ref. [31]) the formate disproportionation (formate + formate) reaction:

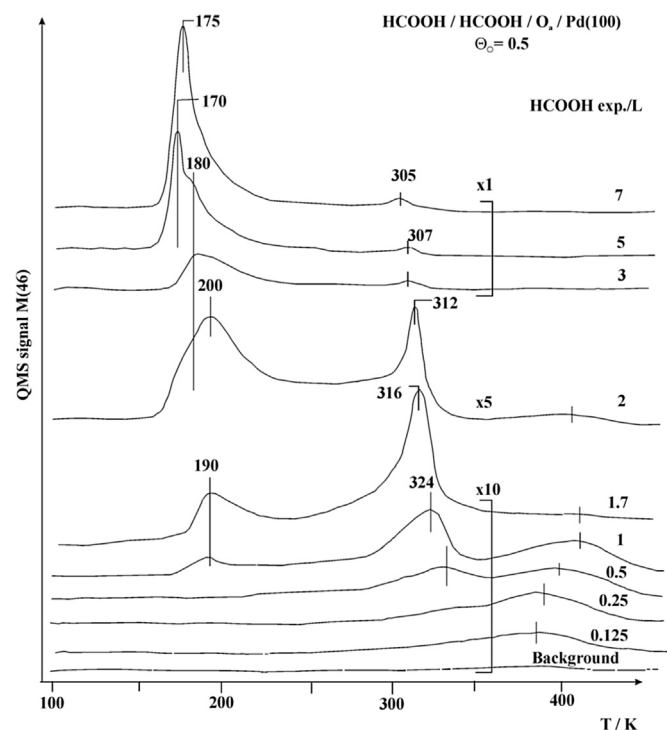


Fig. 1. HCOOH desorption after its adsorption on O-saturated Pd(100) ( $\Theta_o = 0.5$ ). The HCOOH exposures are indicated.

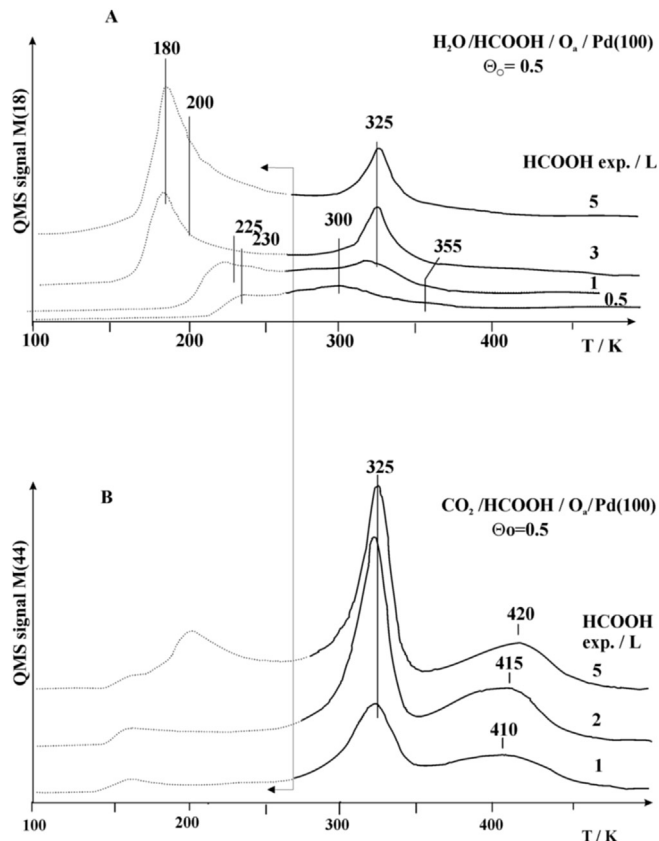
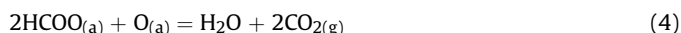


Fig. 2. Thermal desorption of H<sub>2</sub>O (A) and CO<sub>2</sub> (B) from the HCOOH + O co-adsorbed layer. The initial oxygen coverage was constant,  $\Theta_{\text{O}} = 0.5$ , the HCOOH exposures are indicated. The dotted lines are very probably fragments of HCOOH molecules.



The main products, H<sub>2</sub>O and CO<sub>2</sub>, desorb with the same peak temperature. At this temperature only reaction limited desorption can produce these sharp peaks around 325 K in Fig. 2AB. After these reactions the surface coverage decreased and little CO and surface O react to form CO<sub>2</sub> at 410–420 K. For comparison it should be noted that the adsorbed CO<sub>2</sub> desorbs from clean Pd(100) at 135 and 185 K [29]. Molecularly adsorbed H<sub>2</sub>O desorbs with  $T_{\text{p}} = 173$  K, while on oxygen precovered Pd(100) this temperature is 256 K [30].

The UPS signals of the coadsorbed layer can be seen in Fig. 3. The peaks at 4.9, 8.7, 11.9 and 14.6 eV binding energies correspond to adsorbed HCOOH. The slight shifts and/or developing new peaks at 4.2, 7.9, 10.7 and 13.4 eV are attributed to formate species. They were present up to 360 K. The same UPS signals for formate were detected on clean Rh(111) [25]. The observed photoemissions from formate species disappeared above 360 K on oxygen pre-covered surface. We note that there was no UPS signal of adsorbed HCOOH above 258 K. Adsorbed CO<sub>2</sub> was not detected but CO<sub>2</sub> evolution was observed in gas phase ( $T_{\text{p}} = 325$  K) which confirms the disproportionation of formate. The slight difference between these CO<sub>2</sub> (H<sub>2</sub>O) and HCOOH peak temperatures indicates rearrangements in the adsorbed species which cause the retarded desorption step. In contrast to the clean surface, the adsorbed CO orbitals ( $1\pi+5\sigma$  and  $4\sigma$ ) with binding energy of 8.3 and 10.9 eV, respectively, developed at higher temperatures (above 300 K). It means that a small part of formate decomposes forming CO which

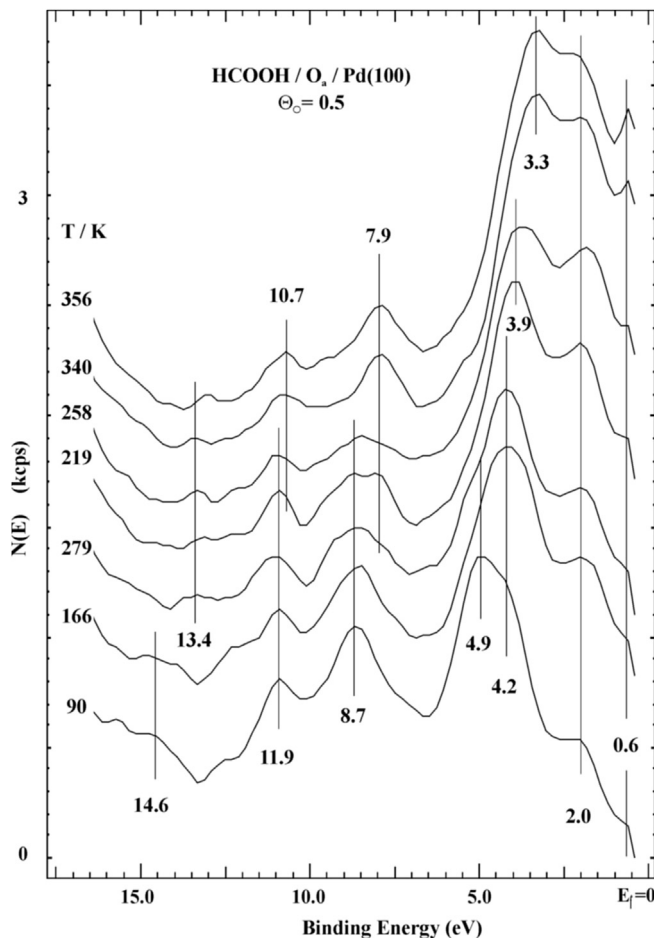
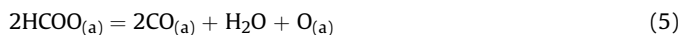


Fig. 3. He II excited photoelectron spectra of the HCOOH + O co-adsorbed layer heated at different temperatures. The 5 L HCOOH was exposed on the  $\Theta_{\text{O}} = 0.5$  covered Pd(100) surface.

reacts with adsorbed oxygen and was released as CO<sub>2</sub> around 410–420 K.



### 3.3. Adsorption of H<sub>2</sub>CO on clean Pd(100)

The adsorption of H<sub>2</sub>CO on clean Pd(100) was studied and published earlier [26]. Here we briefly summarize the obtained results. The H<sub>2</sub>CO desorption spectra after formaldehyde adsorption show a weakly held (condensed) H<sub>2</sub>CO state with  $T_{\text{p}}$  values between 120 and 155 K. This peak gained intensity and another broad desorption state developed between 200 and 300 K can be attributed to the chemisorbed states. The part of chemisorbed formaldehyde layer decomposes to H<sub>(a)</sub> and CO<sub>(a)</sub>, which are released in the gas phase at their characteristic desorption temperatures,  $T_{\text{p}} = 320$ –350 K and  $T_{\text{p}} = 490$  K, respectively. The adsorption of H<sub>2</sub>CO on clean Pd(100) surface produces two intensive peaks at 8.1 and 10.8 eV in the UPS spectra which correspond to the MO-s of adsorbed CO. The signal at 13.7 eV suggests the presence of condensed H<sub>2</sub>CO.



### 3.4. Adsorption of $\text{H}_2\text{CO}$ on O-saturated ( $\Theta_o = 0.5$ ) Pd(100)

Thermal desorption spectra of  $\text{H}_2\text{CO}$  (Fig. 4) show similar peak-structures as in the case of the clean surface [26]. Physisorbed layer desorbs with  $T_p = 120$  and  $141$  K. The TDS peaks (due to chemisorbed layer) between  $200$  and  $300$  K are more pronounced, with  $T_p$  values at  $210$  and  $265$  K. The dashed curve represents a TPD curve from the clean surface for comparison. On oxygen pre-covered surface the peak temperature due to the chemisorbed layer ( $T_p = 265$  K) is close to that of its corresponding decomposition products ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) although they appeared at somewhat higher temperature,  $T_p = 285$  K (Fig. 5). The picture is very similar to the  $\text{HCOOH}/\text{HCOO}$  case.

The thermal stability of the  $\text{H}_2\text{CO} + \text{O}_{(a)}$  co-adsorbed layer was also investigated by UPS (Fig. 6). The spectrum collected at  $95$  K shows intense peaks at  $4.4$ ,  $7.9$ ,  $9.8$ ,  $10.6$ ,  $11.4$ , and  $14.0$  eV. It is a very complex spectrum, which can be interpreted as overlapping MO bands of condensed  $\text{H}_2\text{CO}$ , and adsorbed  $\text{HCOO}$ . The existence of formate ( $13.4$  eV) is pronounced at  $228$  K (see the insertion in Fig. 6). The peaks at  $10.8$ ,  $7.9$  and  $4.2$  eV due to formate are also visible. The stronger UPS signal at  $11.7$  eV could be attributed to the surface formaldehyde. From  $250$  to  $290$  K adsorbed CO can be detected. The observed products, their formation temperatures and UPS signals support our idea, namely that formate can be formed in the surface reaction of formaldehyde and pre-adsorbed oxygen.

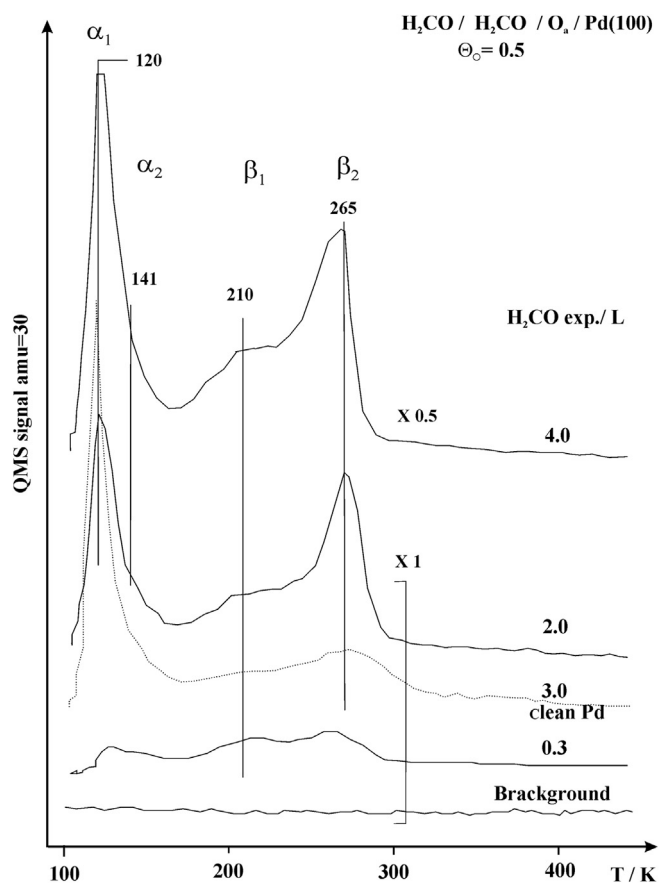
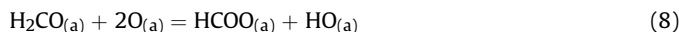


Fig. 4.  $\text{H}_2\text{CO}$  desorption after its adsorption on O-saturated Pd(100) ( $\Theta_o = 0.5$ ). The exposures are indicated. For comparison, the dotted line represents one spectrum from the clean Pd(100) after 3 L exposure.

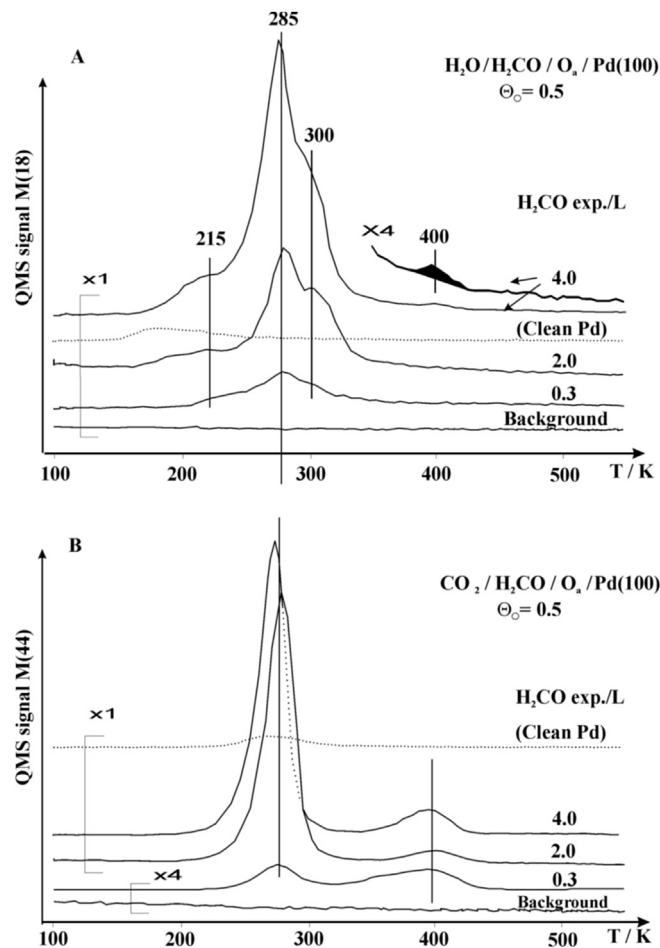


Fig. 5. Thermal desorption of  $\text{H}_2\text{O}$  (A) and  $\text{CO}_2$  (B) from the  $\text{H}_2\text{CO} + \text{O}$  co-adsorbed layer. The initial oxygen coverage was constant,  $\Theta_o = 0.5$ , the  $\text{H}_2\text{CO}$  exposures are indicated. For comparison, the dashed lines represent spectra from the clean Pd(100) after 3 L exposure.

### 3.5. Comparisons

Taking into account the data presented in 3.2 and 3.4, we can compare the similarities and differences. Both parent molecules, adsorbed formic acid and formaldehyde reacting with pre-adsorbed oxygen, produce formate and OH groups. Further reactions in the chemisorbed layer changed the products distribution, and while hydrogen and carbon monoxide desorbed from the clean Pd surface, from oxygen pre-covered surfaces  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were detected. It is interesting that they decompose with a coincidence peak temperature, at  $325$  and  $285$  K from  $\text{HCOOH} + \text{O}$  and  $\text{H}_2\text{CO} + \text{O}$  coadsorbed layers, respectively, suggesting a common reaction or reactions. The sharp peaks also suggest a two dimensional surface explosion, first introduced by R. Madix in Ref. [32]. It is also interesting that in both cases the highest desorption peak of the parent molecules are  $265$  K and  $305$  K, for  $\text{H}_2\text{CO}$  and  $\text{HCOOH}$ , respectively,  $10$ – $20$  K lower than the corresponding  $\text{CO}_2$  and  $\text{H}_2\text{O}$  main peaks.

The high temperature  $\text{HCOOH}$  desorption (at  $305$ – $324$  K) observed after  $\text{HCOOH}$  adsorption on oxygen covered Pd(100) due to formate disproportionation was found on oxygen modified Cu(110) surface too [31,33–35] but it was not detected on clean and oxygen covered Rh(111) [25].

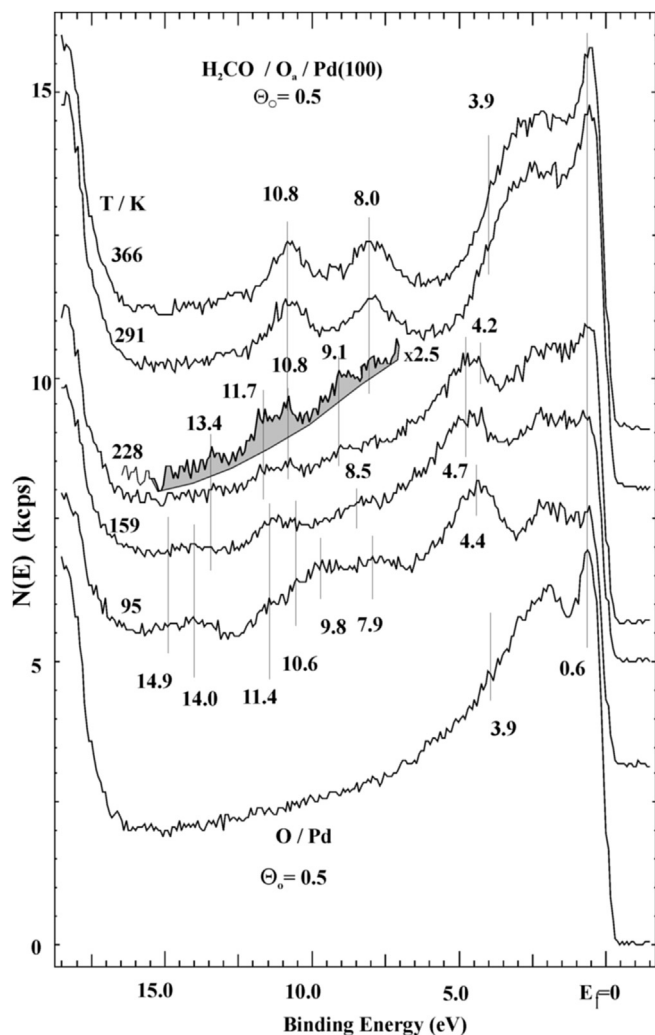


Fig. 6. He II excited photoelectron spectra from the co-adsorbed layer heated to different temperatures. The 5 L  $\text{H}_2\text{CO}$  was exposed on the  $\Theta_o = 0.5$  oxygen covered Pd(100) surface. The spectrum collected at 228 K is zoomed.

#### 4. Conclusions

Our results can be summarized as follows:

1. Pre-adsorbed oxygen promoted the formation of formate from HCOOH as well as from  $\text{H}_2\text{CO}$ .
2. Adsorbed formate is stable in the co-adsorbed layer.

3. Disproportionation of formate forming HCOOH and  $\text{CO}_2$  is a pronounced reaction pathway beside the oxidation of formate.
4. The thermal decomposition of HCOOH happens in a mutual reaction,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  desorb with a common peak temperature on oxygen pre-covered Pd(100).
5. In both systems the precovered oxygen reacts in similar manner, giving the same products, but as the H to C ratio is different in formic acid and formaldehyde and the oxygen consumption is also different, consequently some more oxygen atoms remain to stabilize the surface layer. According to the mechanism, the formation of HCOO from formaldehyde needs two adsorbed oxygen atoms, unlike in the case when HCOOH is the precursor. In accordance the formate is more stable in HCOOH case. The characteristic desorption temperatures, appeared at somewhat higher temperature (by ca. 30 K).

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