Density Functional Theory studies of HCOOH decomposition on Pd(111)

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ABSTRACT

The investigation of formic acid (HCOOH) decomposition on transition metal surfaces is important to derive useful insights for vapor phase catalysis involving HCOOH and for the development of direct HCOOH fuel cells (DFAFC). Here we present the results obtained from periodic, self-consistent, density functional theory (DFT-GGA) calculations for the elementary steps involved in the gas-phase decomposition of HCOOH on Pd(111). Accordingly, we analyzed the minimum energy paths for HCOOH dehydrogenation to $\text{CO}_2 + \text{H}_2$ and dehydration to $\text{CO} + \text{H}_2\text{O}$ through the carboxyl (COOH) and formate (HCOO) intermediates. Our results suggest that HCOO formation is easier than COOH formation, but HCOO decomposition is more difficult than COOH decomposition, in particular in the presence of co-adsorbed O and OH species. Therefore, both paths may contribute to HCOOH decomposition. CO formation goes mainly through COOH decomposition.

Keywords: Density Functional Theory; Formic acid; Pd(111); Decomposition; Formate; Carboxyl.

1. Introduction

The study of formic acid (HCOOH) decomposition on transition metals is important for gaining insights into vapor phase catalysis involving HCOOH[1]. HCOOH represents a byproduct in the production of levulinic acid from HMF[2, 3] and the hydrogen produced in situ from HCOOH degradation may be used to convert levulinic acid into fuels. The study of HCOOH decomposition can also provide important insights for the electro-oxidation of HCOOH at the anode of direct HCOOH fuel cells (DFAFC).

In the early 1960's, Sachtler [et al.](#)[4] investigated the catalytic decomposition of HCOOH vapors on metals using infrared (IR) spectroscopy, adsorption calorimetry and kinetic measurements. They assumed that the decomposition starts with the dissociative adsorption of HCOOH into formate (HCOO) and hydrogen since they observed the presence of adsorbed HCOO with IR. Plotting the catalytic activity of metals in this reaction against the heat of formate formation on each metal, they obtained a volcano plot with the most active metal characterized by an intermediate value of the formate heat of formation. According to their analysis, Pt and Pd represent two of the most promising metals, which is also true for the most active metals used as the anode in DFAFC[5-13].

HCOOH electro-oxidation on Pt is usually explained as a dual-path mechanism[10, 14-19] which was originally proposed by Capon [et al.](#)[20, 21]: the indirect pathway leads to CO formation, followed by its electro-oxidation to CO₂; the direct pathway involves the direct formation of CO₂ (without producing CO). CO production during HCOOH electro-oxidation represents a significant problem for Pt-based fuel cells since the adsorbed CO acts as a poison, limiting the FC operation. Pd-based DFAFC seem to suffer less from CO formation. In fact, using IR, Hoshi [et al.](#) did not detect CO adsorbed on a Pd surface and suggested that Pd single

crystals do not allow CO formation during HCOOH electro-oxidation [22]. Using electromodulated infrared reflectance spectroscopy (EMIRS), Nishimura [et al.](#) did not find CO adsorbed on Pd and PdAu alloy electrodes [23]. Finally, using Fourier Transform Infrared Spectroscopy (FTIR), Arenz [et al.](#) did not observe vibrational features for Pd-CO in their study of HCOOH oxidation on Pt-Pd bimetallic surfaces [24]. However, Wang [et al.](#) observed the presence of CO from HCOOH decomposition Pd electrodes using high-sensitivity *in situ* surface-enhanced IR spectroscopy with attenuated total reflection (ATR-SEIRAS) and suggested that CO formation goes through the reduction of the dehydrogenation product CO₂[25].

The direct CO₂ formation occurs through an active intermediate which derives from HCOOH dehydrogenation and may be either formate (HCOO) or carboxyl (COOH). However, only HCOO intermediate has been observed in experiments on Pt and Pd surfaces, using various techniques, such as low energy electron diffraction (LEED)[26] , IR[15, 16, 23], surface-enhanced infrared absorption spectroscopy (SEIRAS)[27-31] and EMIRS[23, 32] .

To the best of our knowledge, there are few computational studies of HCOOH decomposition on Pd(111) [33-37]: in general, the identification of the reactive intermediate is still controversial; for example, Hu [et al.](#)[34] found HCOO as main intermediate for HCOOH decomposition, whereas Zhang [et al.](#)[37] suggested that both HCOO and COOH are involved in HCOOH dehydrogenation. Here we report a detailed investigation of gas-phase HCOOH decomposition on Pd(111) using Density Functional Theory (DFT-GGA). In this work, we consider not only HCOOH decomposition on the clean surface but also HCOO and COOH decomposition in the presence of co-adsorbed species such as O, OH and CO. The possible steps leading to the formation of CO₂ and CO from both HCOO and COOH have been taken into account, as well as the path for CO production directly from HCOOH. The main goal is to

elucidate the role of the HCOO and COOH intermediates, and to gain insights into the mechanism of CO formation. This study also helps with the understanding of HCOOH electro-oxidation on Pd, which can be further improved by including electrode potential and other corrections accounting for the more complex electro-catalytic environment[38].

2. Methods

All the calculations have been carried out using the DACAPO total energy calculation code [39, 40]. The Pd(111) surface has been modeled by a 3-atomic layers slab using a (3 x 3) unit cell, corresponding to a surface coverage (θ) of 1/9 ML for each adsorbate per unit cell. Since the surface relaxation has been proved to be negligible for similar systems[41-44], all the calculations have been performed by keeping Pd atoms fixed in their bulk truncated positions. Ultrasoft Vanderbilt pseudopotentials[45] have been adopted to describe core electron interactions and the Kohn-Sham one-electron valence states have been expanded on a basis of plane waves with kinetic energies below 25 Ry. Having checked convergence, the surface Brillouin zone was sampled at 6 special **k**-points[46]. The exchange-correlation energy and potential have been described using the PW91 generalized gradient approximation (PW91-GGA) [47, 48]. The calculated lattice constant for bulk Pd is 3.99 Å, in reasonable agreement with the experimental value (3.89 Å) [49]. All reported energetics do not account for zero point energy corrections (ZPE). In fact, the ZPE was found to have minimal effect on the reaction energies of key elementary steps (e.g. dehydrogenation of HCOOH, HCOO and COOH species)[50].

The binding energy (BE) of surface intermediates has been determined according to the following equation:

$$BE_x = E_{\text{slab}+x} - E_{\text{slab}} - E_x$$

where $E_{\text{slab}+\text{x}}$, E_{slab} and E_{x} are the total energies of the adsorbate-substrate system, the clean slab and the gas-phase intermediate x, respectively. According to the equation, a negative (positive) value of BE_{x} means the adsorption is a favorable (unfavorable) process.

The minimum energy paths and the corresponding activation energy barriers have been calculated using the climbing image nudged elastic band method (CI-NEB) [51-53]. The path for each elementary step has been discretized by a total of nine images, including the initial and final states. Each path has been determined by considering the most stable (best) initial and final states, unless otherwise specified. The transition states were verified by calculating the corresponding vibrational frequencies and identifying a single negative curvature mode.

The vibrational frequencies of adsorbed species were determined using the harmonic oscillator assumption by diagonalization of the mass-weighted Hessian matrix in internal coordinates[54]. Initial, final and transition states are indicated in the text as I.S., F.S. and T.S., respectively. B.I.S. and B.F.S. indicate best initial state and best final state, respectively.

3. Results and Discussion

The elementary steps analyzed for HCOOH decomposition on the clean surface are shown in Scheme 1. Steps considered for the decomposition of HCOO and COOH in the presence of co-adsorbed species are shown in Scheme 2. The following steps for H₂O activation and CO oxidation were also studied:

The detailed energetics of all these steps will be discussed next. Notably, several of these steps describe the water-gas-shift reaction [55], which connect the final products of the selective (dehydrogenation) and unselective (dehydration) HCOOH decomposition routes.

Scheme 1. Reaction network of steps studied for HCOOH decomposition on clean Pd(111). The green and blue arrows indicate HCOO and COOH routes, respectively. The black arrows represent the HCOOH dehydration pathway. The continuous and dashed arrows represent CO₂ and CO formation, respectively.

Scheme 2. Reaction network of steps for HCOO and COOH decomposition on Pd(111), in the presence of co-adsorbed species. The green and blue arrows indicate the HCOO and COOH routes, respectively. The continuous and dashed arrows represent CO₂ and CO formation, respectively.

3.1 Structures, binding energies and vibrational frequencies of reaction intermediates.

The binding energies (BEs) of surface intermediates are reported in Table 1 along with the preferred adsorption sites, selected geometric parameters, the computed vibrational frequencies and the available experimental frequencies for HCOOH and HCOO [26].

The computed vibrational frequencies of HCOOH and HCOO, see Table 1, agree reasonably well with those observed by Zheng [et al.](#) on Pd(111)[26]. Although Zheng [et al.](#)[26] detected another frequency at 1630 cm⁻¹ for adsorbed HCOOH, Wang [et al.](#)[25] assigned an absorption band occurring at ~ 1612 cm⁻¹ to H₂O adsorbed on the Pd surface.

The calculated BEs are close to those reported by Ferrin *et al.*[56] and Herron *et al.*[50]. The BE of HCOOH is almost identical to that found by Hu *et al.*[34]. The BEs of HCOO and COOH are weaker with respect to those found by both Hu *et al.*[34] and Zhang *et al.*[37]. Finally, the BE of CO reproduces well the value reported by Zhang *et al.*[37] while it is stronger than the value from Hu *et al.*[34]. These differences may be explained by the different computational methodologies, e.g. functional and basis set, used in the calculations.

Table 1. Binding energy (BE), site preference, selected geometric parameters and vibrational frequencies ($> 200 \text{ cm}^{-1}$) of HCOOH decomposition intermediates on Pd(111) surface ($\theta = 1/9 \text{ ML}$).

Species	Site	BE [eV]	X-Pd [Å]	C-O [Å]	O-H [Å]	C-H [Å]	Frequencies [cm^{-1}]
HCOOH*	top-bridge	-0.41	2.33 ^a	1.24 ^d ; 1.32 ^e	1.02	1.10	3041, 2937, 1691 (1704 ^f), 1342, 1294 (1243 ^f), 1142, 988 (947 ^f), 668, 643
HCOO*	top-top	-2.34	2.18 ^a	1.27; 1.27	--	1.11	2965 (2904 ^f), 1558, 1314 (1342 ^f), 1303, 973, 736 (792 ^f), 320, 317, 295
*COOH	top	-2.22	2.00 ^b	1.24 ^d ; 1.34 ^e	0.99	--	3596, 1653, 1218, 1130, 671, 581, 458, 283, 246
CO ₂ *	--	-0.05	--	1.18	--	--	2449, 1348, 622, 615
*CO	fcc	-1.99	2.09 ^b	1.19	--	--	1868, 311, 299, 298
HCO*	fcc	-2.26	2.11 ^b	1.26	--	1.11	2890, 1478, 1088, 634, 437, 263, 254
*OH	fcc	-2.16	2.22 ^a	--	0.98	--	3790, 353, 352, 334
H ₂ O*	top	-0.31	2.45 ^a	--	0.99	--	3824, 3717, 1531, 413, 380
H*	fcc	-2.83	1.82 ^c	--	--	--	988
O*	fcc	-3.73	2.05 ^a	--	--	--	444

^a O-Pd; ^b C-Pd; ^c H-Pd; ^d C-O; ^e C-OH; ^f Experimental value[26]

Table 1 indicates that HCOOH and H₂O are weakly adsorbed, whereas CO₂ is only physisorbed.

HCOOH is adsorbed nearly perpendicularly with the carbonyl oxygen bound to a top surface site and the hydroxyl group pointing towards a bridge site; HCOO interacts through its

oxygen ends, in a top – top bidendate configuration; COOH is adsorbed through its carbon atom to a top site and its hydrogen atom pointing towards the surface. H₂O and OH are adsorbed through the oxygen atom while CO and HCO are adsorbed through the carbon atom. H₂O prefers adsorption to a top site while H, CO, HCO, O and OH to an fcc site. The preferred adsorption modes for HCOOH, HCOO and COOH are depicted in Figure 1; the calculated geometric parameters for adsorbed HCOO agree well with the experimental data obtained from LEED[26] and previous DFT computed values[26], as shown in Table 2.

Figure 1. Side and top views of the most stable configuration of HCOOH, HCOO and COOH adsorbed on Pd(111) at $\theta = 1/9$ ML. Palladium, carbon, hydrogen and oxygen atoms are indicated with blue, dark grey, light grey and red spheres, respectively.

Table 2. Calculated and experimental geometric parameters for HCOO adsorbed on Pd(111)^a.

Parameter	DFT	LEED[26]
O-Pd	2.18	2.16 ± 0.06
O-C-O plane to the surface	90	90 ± 2
O-C-O	130	130 ± 5
C-O	1.27	1.26 ± 0.05
C-H	1.11	-

^a Bond length and bond angle are given in Å and °, respectively.

3.2 Reaction barriers of elementary steps

The calculated reaction energies and activation energy barriers for all the elementary steps studied are summarized in Table 3. To show the detailed energetic and geometric information of HCOO and COOH formation from HCOOH, the reaction coordinate for step 1 ($\text{HCOOH}^* + * \rightarrow \text{HCOO}^* + \text{H}^*$) and step 2 ($\text{HCOOH}^* + * \rightarrow * \text{COOH} + \text{H}^*$) are shown in Figures 2 and 3, respectively. For reaction 3 ($\text{HCOO}^* \rightarrow \text{CO}_2^* + \text{H}^*$), two sequential steps are needed, (i.e. a rotation step followed by a bond-breaking step), and the reaction coordinates are shown in Figure 4. The transition state structures for step 4 and steps 6-10 are displayed in Figure 5; the reaction coordinates are reported in the Supporting Information (Figures S1-S6). Also for step 5 ($\text{HCOOH}^* + * \rightarrow \text{HCO}^* + * \text{OH}$), and step 11 ($\text{HCOO}^* + * \text{CO} \rightarrow \text{HCO}^* + \text{CO}_2^*$), a sequence of two steps is needed, and the reaction coordinates are shown in Figures 6 and 7, respectively. Finally, the transition state structures for all the remaining steps (i.e. steps 12-20) are displayed in Figures 8 and 9; the reaction coordinates are reported in the Supporting Information (Figures S7-S15).

Figure 2. Reaction coordinate for step 1 ($\text{HCOOH}^* + * \rightarrow \text{HCOO}^* + \text{H}^*$) on Pd(111). Insets provide side and top views of B.I.S. (= best initial state), T.S. (= transition state) and B.F.S. (= best final state); the length of the bond being broken is indicated in each inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Palladium, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

Figure 3. Reaction coordinate for step 2 ($\text{HCOOH}^* + * \rightarrow * \text{COOH} + \text{H}^*$) on Pd(111). Insets provide side and top views of B.I.S. (= best initial state), T.S. (= transition state), F.S. (= final state), I.S. (= initial state) and B.F.S. (= best final state); the length of the bond being broken is indicated in the inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Palladium, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

Figure 4. Reaction coordinate for step 3 ($\text{HCOO}^* \rightarrow \text{CO}_2^* + \text{H}^*$) on $\text{Pd}(111)$. Insets provide side and top views of B.I.S. (= best initial state), T.S. (= transition state), F.S. (= final state) and B.F.S. (= best final state); the length of the bond being broken is indicated in the inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Palladium, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

O-H = 1.55 Å

C-O = 2.15 Å

C-H = 1.24 Å

C-O = 1.97 Å

C-H = 1.32 Å

C-H = 1.30 Å

Figure 5. Side and top view of the transition state (T.S.) corresponding to Step 4 ($*\text{COOH} + * \rightarrow \text{CO}_2^* + \text{H}^*$), Step 6 ($\text{HCOO}^* + * \rightarrow \text{HCO}^* + \text{O}^*$), Step 7 ($\text{HCO}^* + * \rightarrow *\text{CO} + \text{H}^*$), Step 8 ($*\text{COOH} + * \rightarrow *\text{CO} + \text{OH}^*$), Step 9 ($\text{HCOO}^* + \text{O}^* \rightarrow \text{CO}_2^* + *\text{OH}$) and Step 10 ($\text{HCOO}^* + *\text{OH} \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$) on Pd(111). The length of the bond being broken is indicated. Palladium, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

Figure 6. Reaction coordinate for step 5 ($\text{HCOOH}^* + * \rightarrow \text{HCO}^* + *\text{OH}$) on Pd(111). Insets provide side and top views of B.I.S. (= best initial state), T.S. (= transition state), F.S. (= final state), I.S. (= initial state) and B.F.S. (= best final state); the length of the bond being broken is indicated in the inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Palladium, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

Figure 7. Reaction coordinate for step 11 ($\text{HCOO}^* + \text{*CO} \rightarrow \text{HCO}^* + \text{CO}_2$) on Pd(111). Insets provide side and top views of B.I.S. (= best initial state), T.S. (= transition state), F.S. (= final state), I.S. (= initial state) and B.F.S. (= best final state); the length of the bond being broken is indicated in the inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Palladium, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

O-H = 1.29 Å

C-O = 1.52 Å

O-H = 1.10 Å

O-H = 1.27 Å

Figure 8. Side and top view of the transition state (T.S.) corresponding to Step 12 ($\text{HCOO}^* + \text{*COOH} \rightarrow \text{HCOOH}^* + \text{CO}_2^*$), Step 13 ($\text{*COOH} + \text{O}^* \rightarrow \text{CO}_2^* + \text{*OH}$), Step 15 ($\text{*COOH} + \text{H}^* \rightarrow \text{*CO} + \text{H}_2\text{O}^*$) and Step 16 ($\text{*COOH} + \text{*CO} \rightarrow \text{CO}_2^* + \text{HCO}^*$) on Pd(111). The length of the bond being broken is indicated. H being involved in the transfer is indicated for Step 12. Palladium, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

$$C-O = 2.15 \text{ \AA}$$

$$O-H = 1.64 \text{ \AA}$$

$$O-H = 1.17 \text{ \AA}$$

$$O-H = 1.75 \text{ \AA}$$

Figure 9. Side and top view of the transition state (T.S.) corresponding to Step 17 ($*CO + O^* \rightarrow CO_2^* + *$), Step 18 ($O^* + H^* \rightarrow *OH + *$), Step 19 ($*OH + *OH \rightarrow H_2O^* + O^*$) and Step 20 ($H^* + *OH \rightarrow H_2O^* + *$) on Pd(111). The length of the bond being formed or broken is indicated. Palladium, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

Table 3. Reaction energy (ΔE), activation energy barrier (E_f) for all elementary steps on Pd(111).

Elementary step	ΔE^a	E_f^b
(1) $HCOOH^* + * \rightarrow HCOO^* + H^*$	0.10	0.60
(2) $HCOOH^* + * \rightarrow *COOH + H^*$	-0.03	0.34+0.38

(3) $\text{HCOO}^* + * \rightarrow \text{CO}_2^* + \text{H}^*$	-0.47	0.93
(4) $*\text{COOH} + * \rightarrow \text{CO}_2^* + \text{H}^*$	-0.32	0.70
(5) $\text{HCOOH}^* + * \rightarrow \text{HCO}^* + *\text{OH}$	0.98	0.88+0.44
(6) $\text{HCOO}^* + * \rightarrow \text{HCO}^* + \text{O}^*$	1.40	1.95
(7) $\text{HCO}^* + * \rightarrow *\text{CO} + \text{H}^*$	-1.16	0.14
(8) $*\text{COOH} + * \rightarrow *\text{CO} + \text{OH}^*$	-0.07	0.80
(9) $\text{HCOO}^* + \text{O}^* \rightarrow \text{CO}_2^* + *\text{OH}$	-0.66	1.46 ^c
(10) $\text{HCOO}^* + *\text{OH} \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$	-1.09	1.22+0.24
(11) $\text{HCOO}^* + *\text{CO} \rightarrow \text{CO}_2^* + \text{HCO}^*$	0.93	1.54+0.08
(12) $\text{HCOO}^* + *\text{COOH} \rightarrow \text{HCOOH}^* + \text{CO}_2^*$	0.28	0.39
(13) $*\text{COOH} + \text{O}^* \rightarrow \text{CO}_2^* + *\text{OH}$	-0.35	0.05
(14) $*\text{COOH} + *\text{OH} \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$	-0.63-0.22	0.00
(15) $*\text{COOH} + \text{H}^* \rightarrow *\text{CO} + \text{H}_2\text{O}^*$	-0.83	1.20
(16) $*\text{COOH} + *\text{CO} \rightarrow \text{CO}_2^* + \text{HCO}^*$	1.24	1.52
(17) $*\text{CO} + \text{O}^* \rightarrow \text{CO}_2^* + *$	-0.52	1.40
(18) $\text{O}^* + \text{H}^* \rightarrow *\text{OH} + *$	-0.30	1.12
(19) $*\text{OH} + *\text{OH} \rightarrow \text{H}_2\text{O}^* + \text{O}^*$	-0.30	0.03
(20) $\text{H}^* + *\text{OH} \rightarrow \text{H}_2\text{O}^* + *$	-0.51	0.63
(21) $\text{H}^* + \text{H}^* \rightarrow \text{H}_2 + 2*$	1.09 ^d	1.09 ^d

^a If the final state (F.S.) is not the best final state (B.F.S), then ΔE is reported as $\Delta E(\text{NEB}) - (\text{F.S.} - \text{B.F.S.})$

^b If the initial state (I.S.) is not the best initial state (B.I.S.), then E_f is reported as $E_f(\text{NEB}) + (\text{I.S.} - \text{B.I.S.})$

^c The path was discretized by a total of eleven images.

^d ΔE and E_f were computed from the two adsorbed H atoms at infinite separation since H_2 dissociation on Pd(111) is found to be a nearly spontaneous process[57].

3.2.1 HCOOH decomposition on the clean Pd(111) surface

$\text{HCOOH}^* + * \rightarrow \text{HCOO}^* + \text{H}^*$ (*Step 1*). This step, which starts from HCOOH adsorbed in the most stable perpendicular trans- configuration, is slightly endothermic (~ 0.10 eV) and requires an activation energy of 0.60 eV (Figure 2). The O-H distance increases from 1.02 Å (B.I.S) to 2.62 Å (B.F.S.) and is equal to 1.70 Å at the T.S.. The final co-adsorbed state, with

HCOO (top-top) and H (fcc), includes a destabilization of ~ 0.2 eV with respect to the co-adsorption at infinite separation.

$HCOOH^* + * \rightarrow *COOH + H^*$ (Step 2). Before decomposing to carboxyl, adsorbed HCOOH reorients from the perpendicular trans- configuration to a nearly parallel cis- configuration (Figure 3). This re-orientation needs an activation energy of 0.72 eV. The subsequent C-H bond scission, which is characterized by an increase of the corresponding distance by 0.29 Å (I.S. $\rightarrow$ T.S.) and 1.14 Å (T.S. $\rightarrow$ B.F.S) is exothermic by 0.41 eV and has an activation energy barrier of 0.34 eV. A destabilization of 0.2 eV with respect to the co-adsorption at infinite separation is attributed to the interaction between co-adsorbed COOH (top) and H (fcc).

$HCOO^* + * \rightarrow CO_2^* + H^*$ (Step 3). Before formate's decomposition, one O-Pd bond is broken, which leads to the formation of a monodentate HCOO: the activation energy barrier associated to this process is 0.93 eV (Figure 4). The C-H bond length changes from 1.11 Å (B.I.S) to 1.12 Å (T.S.) up to 1.25 Å (F.S.). The subsequent C-H bond scission is a spontaneous process. The overall step is exothermic by 0.47 eV. The final CO₂ (almost desorbed) and H (fcc) are co-adsorbed with negligible interaction.

$*COOH + * \rightarrow CO_2^* + H^*$ (Step 4). The dehydrogenation of COOH requires an activation energy of 0.70 eV and is exothermic by 0.32 eV (Figure S1). The O-H distance (Figure 5) changes from 0.99 Å (B.I.S.) to 3.66 Å (B.F.S.) through a value of 1.55 Å (T.S.). The final CO₂ (almost desorbed) and H (fcc) are co-adsorbed with no interaction energy.

$HCOOH^* + * \rightarrow HCO^* + *OH$ (Step 5). Before decomposing, HCOOH transforms itself from the perpendicular adsorbed configuration to a nearly parallel configuration having a substantially smaller binding energy (Figure 6). This step has an activation energy barrier of 0.75

eV. The subsequent C-O bond scission which is characterized by an increase of the corresponding distance of 0.84 Å (I.S. → T.S.) and 0.56 Å (T.S. → B.F.S.) is endothermic by 0.54 eV and requires an activation energy of 0.88 eV. The final co-adsorbed HCO (top) and OH (fcc/bridge) have no interaction energy.

$HCOO^* + * \rightarrow HCO^* + O^*$ (Step 6). This step is endothermic by 1.40 eV and needs an activation energy of 1.95 eV (Figure S2). The C-O distance (Figure 5) increases from 1.27 Å (B.I.S) to 3.18 Å (B.F.S) and has a value of 2.15 Å at the T.S. The co-adsorption of HCO (fcc/bridge) and O (fcc) is repulsive by about 0.1 eV with respect to the co-adsorption at infinite separation.

$HCO^* + * \rightarrow *CO + H^*$ (Step 7). The decomposition of HCO is exothermic by 1.16 eV and requires an activation energy of 0.14 eV (Figure S3). The C-H distance (Figure 5) changes from 1.11 Å (B.I.S.) to 1.24 Å (T.S.) up to 2.96 Å (B.F.S.). In the co-adsorbed state, CO (fcc) and H (fcc) destabilize each other by ~0.1 eV with respect to co-adsorption at infinite separation.

$*COOH + * \rightarrow *CO + *OH$ (Step 8). This step is slightly exothermic by 0.07 eV and has an activation energy barrier of 0.80 eV (Figure S4). The C-O distance (Figure 5) increases by 0.63 Å (B.I.S. → T.S.) and 1.47 Å (T.S. → B.F.S.). The co-adsorption of CO (fcc) and OH (fcc/bridge) leads to a small stabilization with respect to co-adsorption at infinite separation.

3.2.2 HCOO and COOH decomposition in the presence of co-adsorbed species

$HCOO^* + O^* \rightarrow CO_2^* + *OH$ (Step 9). Co-adsorbed HCOO (top-top) and O (fcc) do not interact with each other. The C-H bond scission (Figure 5), with the corresponding distance changing from 1.11 Å (B.I.S.) to 1.32 Å (T.S.) up to 3.82 Å (B.F.S.), is exothermic by 0.66 eV

and requires an activation energy of 1.46 eV (Figure S5). The final state involves CO₂ (almost desorbed) and OH (fcc), which do not interact with each other.

$HCOO^* + ^*OH \rightarrow CO_2^* + H_2O^*$ (Step 10). The initial state for the elementary step involves the co-adsorption of HCOO (top-top) and OH (bridge) with no interaction energy. However, this configuration is 0.24 eV less stable than the best one on the surface. The following C-H bond scission (Figure 5) has an activation energy barrier of 1.22 eV and is exothermic by 1.09 eV (Figure S6). The C-H distance changes from 1.10 Å (I.S.) to 3.09 Å (B.F.S.) and is equal to 1.30 Å at the T.S. The final co-adsorbed state has CO₂ (almost desorbed) and H₂O (top), stabilizing each other by ~0.1 eV.

$HCOO^* + CO^* \rightarrow CO_2^* + HCO^*$ (Step 11). Before C-H bond scission starts, a stable complex HCOOCO is formed: the activation energy barrier for O-C bond formation is 1.64 eV (Figure 7). The decomposition of that complex into CO₂ and HCO requires an activation energy of 0.08 eV and leads to an increase of the C-O distance by 0.46 Å (I.S. → T.S.) and 1.62 Å (T.S. → B.F.S.). The overall process is endothermic by 0.93 eV. The final state involves CO₂ (almost desorbed) and HCO (top), which repel each other by ~0.1 eV.

$HCOO^* + ^*COOH \rightarrow HCOOH^* + CO_2^*$ (Step 12). The co-adsorption of HCOO (top-top) and COOH (top) is characterized by a slight destabilization with respect to the co-adsorption at infinite separation. The H transfer from COOH to HCOO (indicated by the underscore) is endothermic by 0.28 eV and needs an activation energy of 0.39 eV (Figure S7). The O-H distance (Figure 8) in COOH is equal to 0.99 Å (B.I.S.), 1.29 Å (T.S.) and 2.88 Å (B.F.S.). The final CO₂ (top) and HCOOH (top-top) are co-adsorbed with a destabilization of about 0.15 eV with respect to their co-adsorption at infinite separation.

$*COOH + O^* \rightarrow CO_2^* + *OH$ (Step 13). The co-adsorption of COOH (top) and O (fcc) is characterized by a stabilization of about 0.1 eV with respect to co-adsorption at infinite separation: the interaction between the two intermediates leads to a weakening of the COO-H bond. The subsequent O-H bond scission is exothermic by 0.35 eV and is a nearly spontaneous process requiring an activation energy of 0.05 eV (Figure S8). The O-H distance (Figure 8) increases by 0.09 Å (B.I.S. $\rightarrow$ T.S.) and 0.71 Å (T.S. $\rightarrow$ B.F.S.). The final CO₂ (top) and OH (fcc) are co-adsorbed with no interaction energy.

$*COOH + *OH \rightarrow CO_2^* + H_2O^*$ (Step 14). The co-adsorption of COOH (top) and OH (fcc) leads to a stabilization of about 0.1 eV with respect to their co-adsorption at infinite separation. The O-H bond scission is exothermic by 0.63 eV and is spontaneous with an increase of the corresponding distance by 0.60 Å (Figure S9). The final state, has CO₂ (top) and H₂O (bridge) co-adsorbed, but we could find a more stable co-adsorbed state (by 0.22 eV).

$*COOH + H^* \rightarrow CO^* + H_2O^*$ (Step 15). The initial configuration is the same as the final state of HCOOH dehydrogenation. The C-OH bond scission is exothermic by 0.83 eV and requires an activation energy of 1.20 eV (Figure S10). The C-OH distance (Figure 8) changes by 0.19 Å (B.I.S. $\rightarrow$ T.S.) and 2.91 Å (T.S. $\rightarrow$ B.F.S.) The final CO (fcc) and H₂O (top) are co-adsorbed with a stabilization of about 0.1 eV with respect to their co-adsorption at infinite separation.

$*COOH + CO^* \rightarrow CO_2^* + HCO^*$ (Step 16). Co-adsorbed COOH (top) and CO (fcc) in the initial state have no interaction. The O-H bond scission is endothermic by 1.24 eV and requires an activation energy barrier of 1.52 eV (Figure S11). The O-H distance (Figure 8) changes from 0.99 Å (B.I.S.) to 1.27 (T.S.) up to 2.15 (B.F.S.). The final state involves co-

adsorption of CO₂ (top) and HCO (top) which repel each other by 0.3 eV, compared to their co-adsorption at infinite separation.

3.2.3 CO oxidation and H₂O formation

$*CO + O^* \rightarrow CO_2^* + *$ (*Step 17*). CO (hcp) and O (fcc) are co-adsorbed in the initial state with no interaction energy. The C-O bond formation is exothermic by 0.52 eV and needs an activation energy of 1.40 eV (Figure S12). The C-O distance (Figure 9) decreases from 4.30 Å (B.I.S.) to 2.15 Å (T.S.) down to 1.18 Å (B.F.S.).

$O^* + H^* \rightarrow *OH + *$ (*Step 18*). The co-adsorption of O (fcc) and H (hcp) leads to a destabilization of about 0.1 eV with respect to their co-adsorption at infinite separation. The O-H bond formation is exothermic by 0.30 eV and requires an activation energy of 1.12 eV (Figure S13). The O-H distance (Figure 9) decreases by 1.72 Å (B.I.S. → T.S.) and 0.66 Å (T.S. → B.F.S.).

$*OH + *OH \rightarrow H_2O^* + O^*$ (*Step 19*). The co-adsorption of OH (top) and OH (top) results in a stabilization of about 0.2 eV with respect to their co-adsorption at infinite separation. The O-H bond scission is exothermic by 0.30 eV and is a nearly spontaneous process (Figure S14). The O-H distance (Figure 9) increases by 0.13 Å (B.I.S. → T.S.) and 0.93 Å (T.S. → B.F.S.). In the final state, H₂O (top) and O(fcc) are co-adsorbed with a stabilization of more than 0.1 eV with respect to their co-adsorption at infinite separation.

$H^* + *OH \rightarrow H_2O^* + *$ (*Step 20*). The co-adsorption of H (fcc) and OH (fcc/bridge) occurs with no interaction energy. The O-H bond formation is exothermic by 0.51 eV and has an activation energy barrier of 0.63 eV (Figure S15). The O-H (Figure 9) distance is equal to 3.45 Å (B.I.S.), 1.75 Å (T.S.) and 0.99 Å (B.F.S.).

Table 3 shows that, starting from HCOOH adsorbed in the perpendicular configuration, O-H bond scission (Step 1) is easier than C-H bond scission (Step 2); a strong repulsion between the final co-adsorbed products is observed in both cases. Further, CO₂ formation from HCOO (Step 3) is more difficult than CO₂ formation from COOH (Step 4) in agreement with the results of Yoo [et al.](#)[36]. The behavior of the two dehydrogenation paths, with HCOO formation being easier than COOH formation and HCOO decomposition being more difficult than COOH decomposition, is in agreement with findings from Lin [et al.](#)[58] who investigated WGS on different metal surfaces. In general, all our dehydrogenation barriers (Steps 1 – 4) are smaller than those reported by Hu [et al.](#)[34] and Zhang [et al.](#)[37], perhaps because different transition state search methods have been used. The activation energy barrier found for HCOO decomposition is related to the formation of monodentate adsorbed HCOO which involves an O-Pd bond scission followed by C-H bond scission (see Figure 4a). The formation of the monodentate HCOO intermediate before the C-H bond scission takes place agrees well with findings from both Hu [et al.](#)[34] and Zhang [et al.](#)[37].

The reaction between HCOO and O or OH (Step 9 and 10) leads to activation energy barriers for C-H bond scission higher than that needed for HCOO dehydrogenation on the clean surface. By contrast, the presence of co-adsorbed O and OH facilitates COOH dehydrogenation (Step 13 and 14): this could be partially explained by the attractive interaction between the starting co-adsorbed species in the case of COOH+O and COOH+OH. This stabilization is due to the acidity of the H atom in the COOH intermediate, in analogy with the acidic behavior of the hydroxyl hydrogen of formic acid which has been reported in several studies by Madix *et al.* (see e.g. ref.[59-62]). The different behavior of COOH and HCOO intermediates in presence of O and OH species is also in agreement with the behavior of ethanol on Pd as reported by Hibbitts *et*

al.[63]. The reaction between HCOO or COOH and CO, resulting in the formation of CO₂ and HCO (Step 11 and 16), is unfavorable and is characterized by a repulsion between the co-adsorbed products. The recombination of HCOO and COOH (Step 12), which occurs through O-H bond scission, is slightly endothermic and requires a small activation energy.

The production of CO from HCOOH (Step 5 and 7) through HCO formation is difficult because of the large activation energy barrier to decompose HCOOH into HCO and OH (Step 5), which is similar to what we found for HCOO dissociation into HCO and O (Step 6): the barrier for C-OH bond scission in HCOOH is smaller than that found by Zhang *et al.*[37] due perhaps to the different TS search methods used. Even if CO production from HCO is favorable (Step 7), this route seems to be unlikely since all the possible paths considered for HCO formation (Step 5, 6 and also 11 and 16) are characterized by high activation energies. By contrast, CO formation through COOH (Step 8) is easier. In particular, the direct COOH decomposition into CO is easier than H-assisted COOH decomposition (Step 15). The subsequent CO oxidation (Step 17) is a difficult step because of the large activation energy barrier, which is in agreement with that calculated by García-Mota *et al.*[64] and Eichler[65] and slightly larger with respect to the measurements reported by Engel *et al.*[66].

Finally, the formation of OH may occur either through the reaction between co-adsorbed O and H (Step 18) or through COOH decomposition on the clean surface (Step 8) or in presence of co-adsorbed O (Step 13). The produced OH could react to form H₂O through Steps 14, 19 and 20. The values of the activation energy barriers for OH and H₂O formation are in reasonable agreement with the values reported by Phatak *et al.*[67], though they are larger than those obtained by Ford *et al.*[68], likely due to the different unit cell size used.

3.3 Potential energy surface of HCOOH decomposition on clean Pd(111)

The potential energy surface (PES) for HCOOH dehydrogenation and dehydration through HCOO and COOH intermediates on the clean Pd(111) surface is shown in Figure 10; both the co-adsorption and infinitely separated states are indicated. Figure 10 includes the following pathways: (a) $\text{HCOOH}^* \rightarrow \text{HCOO}^* \rightarrow \text{CO}_2^*$ (step 1 and 3); (b) $\text{HCOOH}^* \rightarrow \text{COOH}^* \rightarrow \text{CO}_2^*$ (step 2 and 4); (c) $\text{HCOOH}^* \rightarrow \text{HCOO}^* \rightarrow \text{HCO}^* \rightarrow \text{CO}^*$ (step 1, 6 and 7) and (d) $\text{HCOOH}^* \rightarrow \text{COOH}^* \rightarrow \text{CO}^*$ (step 2 and 8). As reported in Section 3.2, the presence of co-adsorbed O and OH species facilitates COOH dehydrogenation, whereas it makes HCOO decomposition into CO_2 and H more difficult.

The PES shows that, based on the computed total energy, adsorbed COOH is more stable than adsorbed HCOO. However, HCOO formation is easier than COOH formation because of the lower stability of HCOOH adsorbed in the nearly parallel configuration, which is the precursor state for COOH formation. Further, HCOO decomposition is more difficult than COOH decomposition. These two findings may suggest that formate may accumulate on the surface, which is in agreement with relevant experimental findings (see e.g. ref[4]). Depending on experimental conditions, both intermediates may contribute to HCOOH decomposition. CO_2 formation is preferred to CO formation in both formate- and carboxyl-mediated routes. The production of CO, however, should mainly proceed through COOH decomposition. In fact, one can argue that, based on the PES alone, adsorbed HCOO would be converted into CO_2 while adsorbed COOH may decompose into both CO_2 and CO. The higher activation energy barriers characterizing HCOO decomposition compared to COOH decomposition, both on the clean surface and in presence of co-adsorbed species, such as O and OH, may explain why only HCOO intermediate has been observed in experiments, as discussed in the introduction.

Figure 10. Potential energy surface for reaction paths leading to HCOOH decomposition on the clean Pd(111) surface. Red and the blue lines indicate the HCOO and COOH paths respectively. Solid red line: $\text{HCOOH}^* \rightarrow \text{HCOO}^* \rightarrow \text{CO}_2^*$ (steps 1 and 3); solid blue line $\text{HCOOH}^* \rightarrow \text{COOH}^* \rightarrow \text{CO}_2^*$ (steps 2 and 4); dashed red line: $\text{HCOOH}^* \rightarrow \text{HCOO}^* \rightarrow \text{HCO}^* \rightarrow \text{CO}^*$ (steps 1, 6 and 7); dashed blue line: $\text{HCOOH}^* \rightarrow \text{COOH}^* \rightarrow \text{CO}^*$ (steps 2 and 8). Symbol ξ means infinite separation. The dashed line in the $\text{CO}_2 + 2\text{H}$ state indicates that CO_2 is physisorbed.

4. Conclusion

Periodic, self-consistent (GGA-PW91), Density Functional Theory calculations have been performed to investigate HCOOH decomposition on Pd(111) surface through HCOO and COOH intermediates. Possible elementary reaction steps have been studied both on the clean surface and

in the presence of co-adsorbed species such as O, OH and CO. DFT results suggest that HCOO formation is easier than COOH formation, but HCOO decomposition is more difficult than COOH decomposition. We conclude that depending on reaction conditions, both HCOO and COOH routes may contribute to HCOOH decomposition. CO₂ formation is in general preferred to CO formation, the latter occurring mainly through COOH decomposition on the clean surface. Co-adsorbed O and OH facilitate CO₂ formation from COOH; by contrast, these co-adsorbed species make CO₂ formation from HCOO more difficult. The effect of high coverage of co-adsorbed CO on the reaction mechanisms is currently under consideration. Finally, a comparison between DFT-derived microkinetic modeling results and experimental reaction kinetics data, should shed further light into the detailed reaction mechanism for HCOOH decomposition over a range of relevant experimental reaction conditions.

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