HCOOH decomposition on Pt(111) surface: a DFT study

Jessica Scaranto and Manos Mavrikakis*

Department of Chemical and Biological Engineering

University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI, 53706, USA

*corresponding author: emavrikakis@wisc.edu

ABSTRACT

Formic acid (HCOOH) decomposition on transition metal surfaces is important for hydrogen production and for its electro-oxidation in direct HCOOH fuel cells. HCOOH can decompose through dehydrogenation leading to formation of CO₂ and H₂ or dehydration leading to CO and H₂O; because CO can poison metal surfaces, dehydrogenation is typically the desirable decomposition path. Here we report a mechanistic analysis of HCOOH decomposition on Pt(111), obtained from a planewaves Density Functional Theory (DFT-PW91) study. We analyzed the dehydrogenation mechanism by considering the two possible pathways involving the formate (HCOO) or the carboxyl (COOH) intermediate. We also considered several possible dehydration paths leading to CO formation. We studied HCOO and COOH decomposition both on the clean surface and in the presence of other relevant co-adsorbates. The results suggest that COOH formation is energetically more difficult than HCOO formation. In contrast, COOH dehydrogenation is easier than HCOO decomposition. We found that CO₂ is the main product through both pathways and that CO is produced mainly through the dehydroxylation of the COOH intermediate.

Keywords: Pt(111); Formic acid; Dehydrogenation; Dehydration; Formate; Carboxyl; Density Functional Theory.

1. Introduction

Formic acid (HCOOH) is a significant by-product of the conversion of 5-hydroxyl-methyl furfural (HMF) to levulinic acid, a process central to the production of fuels and chemicals from biomass[1]. Converting carbohydrates in biomass to oxygenates and fuels, typically involves several hydrogenation steps, which require purchasing hydrogen[2, 3]. Therefore, generating hydrogen from HCOOH, a byproduct of biomass conversion, can improve the overall process economics. Particularly promising appears to be the *in-situ* hydrogenation of levulinic acid to GVL[4]. In addition, as an energy source, HCOOH has been used in direct formic acid fuel cells (DFAFC)[5-8]. Understanding the fundamental reaction mechanism of HCOOH decomposition on transition metal surfaces would also shed light on the electro-oxidation of HCOOH [5-8].

Platinum (Pt) represents one of the most active transition metals for gas-phase HCOOH decomposition[9, 10], whereas Pt-based catalysts represent common anodes for DFAFC[7, 11-13]. Despite the large number of experimental and theoretical studies performed, the reaction mechanism behind the formation of and selectivity to hydrogen are still not completely understood (see e.g. [14] and references therein).

The decomposition of HCOOH on transition metal surfaces can occur via either dehydrogenation or dehydration[15, 16]: dehydrogenation produces carbon dioxide (CO₂) and hydrogen (H₂), whereas dehydration produces carbon monoxide (CO) and water (H₂O). The former process leads to the desired products, whereas the latter, leading to CO production is accompanied by CO poisoning of these surfaces, resulting in catalytic performance deterioration[17, 18]. H₂ production occurs through two successive dehydrogenation steps followed by recombination of adsorbed atomic H. The first dehydrogenation step leads to the

formation of an intermediate which is either formate (HCOO), via O-H bond breaking in HCOOH, or carboxyl (COOH), via C-H bond breaking in HCOOH.

For HCOOH electro-oxidation on Pt, Chen *et al.*[19, 20] suggested that the mechanism should involve at least three different pathways. In particular, they proposed, that besides the indirect pathway involving CO formation, there are two direct pathways, one through C–H bond breaking of weakly adsorbed HCOOH, and one through the formate intermediate generated via O–H bond breaking in HCOOH. Related to this, Osawa *et al.*[21] concluded that the contribution of the direct electro-oxidation of HCOOH through the COOH intermediate is negligible. In both the gas-phase decomposition and electro-oxidation, the identification of the reactive intermediate is still controversial. Experimental studies on Pt have only identified the HCOO intermediate[20, 22-24], whereas theoretical studies have proposed that CO can be formed from the COOH intermediate[25-27]. Yet, Cuesta *et al.*[28] concluded that HCOO is the key intermediate in the electrocatalytic oxidation of HCOOH, and they argued that CO is formed via HCOO decomposition.

To the best of our knowledge, there are few theoretical studies of HCOOH electro-oxidation and vapor-phase decomposition [26, 29-35]. For vapor-phase decomposition, Gao *et al.*[26] proposed that HCOO is the reactive intermediate and that HCOOH decomposes mainly into CO₂ rather than CO; moreover, they noted that an increase in the surface coverage from 1/9 ML to 1/4 ML leads to an easier HCOOH decomposition. Lin *et al.*[36] found that COOH formation from HCOOH is more difficult than HCOO formation, but COOH decomposition into CO₂ and H is easier than HCOO decomposition.

Here we report a detailed study of gas-phase HCOOH decomposition on Pt(111) using planewave Density Functional Theory (DFT-PW91). We considered HCOOH dehydrogenation

through both HCOO and COOH intermediates and their possible decomposition into CO and CO₂. We investigated the elementary steps involving the decomposition of HCOO and COOH not only on the clean surface but also in the presence of other likely co-adsorbed species, i.e. oxygen (O), hydroxyl (OH), H and CO. Our goal is to elucidate the role of these two key intermediates (i.e. HCOO and COOH) in the formation of both CO₂ and CO.

2. Methods

All calculations were performed using the DACAPO total energy calculation code[37, 38]. The Pt(111) surface was modeled with a 3-atomic layers slab using a (3 x 3) surface unit cell, corresponding to a surface coverage (θ) of 1/9 ML for each adsorbate. The unit cell is periodically repeated in a super cell geometry, and successive slabs are separated by five equivalent layers of vacuum. The calculations were carried out by keeping the Pt atoms fixed in their bulk truncated positions, as surface relaxation effects were found to be very minimal for this surface. Ultrasoft Vanderbilt pseudopotentials[39] were used to describe ionic cores and the Kohn-Sham one-electron valence states were expanded in a basis of plane waves with kinetic energy below 25 Ry. The surface Brillouin zone was sampled at 6 special **k**-points[40]. The exchange-correlation energy and potential were described using the PW91 self-consistent generalized gradient approximation (PW91-GGA)[41, 42]. The value of the calculated lattice constant for bulk Pt is 4.00 Å, which is in reasonable agreement with the experimental value (3.912 Å)[43]. All reported energetics do not account for zero point energy corrections (ZPE).

The binding energy (BE) of surface intermediates was 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+slab system, the clean slab and the gas-phase intermediate (x), respectively. According to this equation, a negative value of BE_{x} signifies an exothermic adsorption.

The minimum energy paths and the corresponding activation energy barriers of individual elementary steps were determined by using the climbing image nudge elastic band method (CI-NEB)[44-46]. The path for each elementary step was discretized by a total of nine images, including the initial and final states corresponding to the most stable (best) initial and final states, unless otherwise specified. The transition states were verified by the calculation of the corresponding vibrational frequencies and the identification of a single negative curvature mode. The vibrational frequencies of the adsorbate were determined using the harmonic oscillator assumption by diagonalization of the mass-weighted Hessian matrix in internal coordinates[47]. 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

We investigated HCOOH decomposition on the clean Pt(111) surface as described by the following set of elementary steps:

1. $\text{HCOOH}^* + * \rightarrow \text{HCOO}^* + \text{H}^*$
2. $\text{HCOOH}^* + * \rightarrow * \text{COOH} + \text{H}^*$
3. $\text{HCOO}^* + * \rightarrow \text{CO}_2^* + \text{H}^*$
4. $* \text{COOH} + * \rightarrow \text{CO}_2^* + \text{H}^*$
5. $\text{HCOOH}^* + * \rightarrow \text{HCO}^* + * \text{OH}$
6. $\text{HCOO}^* + * \rightarrow \text{HCO}^* + * \text{O}$

We also studied HCOO^* and $^*\text{COOH}$ decomposition in the presence of co-adsorbed O, OH, CO and H species as described in the following steps, including also the recombination of these two intermediates to form HCOOH and CO_2 :

In addition, we analyzed H_2O activation and CO oxidation as described in the following elementary steps:

The detailed energetics of all these above steps will be discussed next. Notably, several of these steps describe the water-gas-shift reaction steps[25], which connect the final products of

the selective and unselective HCOOH decomposition routes.

3.1 Structure, 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 and the computed vibrational frequencies. The experimental vibrational frequencies determined for adsorbed HCOOH and HCOO[48] are also included in Table 1 for comparison.

The calculated vibrational frequencies of adsorbed HCOOH and HCOO agree reasonably well with the experimental frequencies reported by Columbia *et al.*[48]; the calculated vibrational frequencies for 1/4ML of COOH, HCOO and CO are in good agreement with those calculated by Grabow *et al.*[25]. The calculated BEs are in agreement with those reported by Ferrin *et al.*[49] and Herron *et al.*[50]. Focusing on the most important adsorbed species, our BE for HCOOH and HCOO agrees with those reported by Gao *et al.*[26], Hu *et al.*[29]. The BE of COOH agrees with the value indicated by Gao *et al.*[26] while it is weaker with respect to the value found by Hu *et al.*[29]. The BE of CO is stronger with respect to the value of both Gao *et al.*[26] and Hu *et al.*[29]. These differences may be explained by the different computational methodologies including the adopted exchange-correlation functional.

Table 1. Binding energy (BE), site preference, selected geometric parameters and vibrational frequencies ($> 200 \text{ cm}^{-1}$) of HCOOH decomposition intermediates on Pt(111) surface ($\theta = 1/9 \text{ ML}$). Zero of the BE scale corresponds to the slab and gas-phase intermediate at infinite separation from each other.

Species	Site	BE [eV]	X-Pt [Å]	C-O [Å]	O-H [Å]	C-H [Å]	Frequencies [cm^{-1}]
HCOOH*	top-bridge	-0.38	2.32 ^a	1.24 ^d ; 1.31 ^e	1.03	1.10	3044, 2899 (2960 ^f), 1668 (1720 ^f), 1340, 1310 (1230 ^f), 1163, 982 (980 ^f), 674, 655
HCOO*	top-top	-2.33	2.16 ^a	1.27;	--	1.11	2997 (2950 ^f), 1557, 1308, 1304

			2.16 ^a	1.27			(1340 ^f), 962, 744 (790 ^f), 346, 321, 285
*COOH	top	-2.40	2.04 ^b	1.22 ^d ; 1.33 ^e	1.00	--	3453, 1717, 1221, 1135, 658, 600, 514, 262, 254
CO ₂ *	--	-0.06	--	1.18; 1.18	--	--	2453, 1350, 626, 622
*CO	fcc	-1.81	2.13 ^b	1.20	--	--	1842, 324, 270, 270
HCO*	top	-2.36	2.03 ^b	1.21	--	1.11	2870, 1795, 1136, 776, 528, 277, 234
*OH	bridge	-2.03	2.21 ^a	--	0.99	--	3672, 683, 636, 343
H ₂ O*	top	-0.33	2.46 ^a	--	0.99	--	3806, 3702, 1530, 496, 463
H*	top	-2.71	1.57 ^c	--	--	--	2185
O*	fcc	-3.74	2.08 ^a	--	--	--	463

^a O-Pt; ^b C-Pt; ^c H-Pt; ^d C-O; ^e C-OH; ^f HREELS experimental value[48]

Table 1 suggests that HCOO, COOH, HCO, CO, OH, H and O are strongly adsorbed on the surface while HCOOH, CO₂ and H₂O are weakly adsorbed.

HCOOH is adsorbed nearly perpendicular with the carbonyl oxygen pointing to a top site and the hydroxyl group pointing towards a bridge site; the C-H bond in adsorbed HCOOH points away from the surface. HCOO binds to the surface through both its oxygen atoms, in a top – top bidentate configuration; COOH is adsorbed through its carbon atom to a top site and its hydrogen atom pointing towards the surface. H₂O, OH are adsorbed through the oxygen atom while CO and HCO are adsorbed through their carbon atom. H₂O, H and HCO prefer adsorption to a top site, CO and O to an fcc site, and OH to a bridge site. The preferred adsorption geometries for HCOOH, HCOO and COOH are shown in Figure 1.

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

3.2 Reaction barriers of elementary steps

The calculated reaction energies and activation energy barriers for all the considered elementary steps are summarized in Table 2. To show the detailed energetic and geometric information of HCOO* and COOH* generation from HCOOH*, the reaction coordinates 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 Figures 4. The transition state structures for reaction 4 and reactions 6-10 are displayed in Figure 5. Also for reaction 5 ($\text{HCOOH}^* + * \rightarrow \text{HCO}^* + * \text{OH}$), and reaction 11 ($\text{HCOO}^* +$

CO $\rightarrow$ HCO + CO₂*), two sequential steps are 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. reactions 12 -20) are displayed in Figures 8 and 9.

Figure 2. Reaction coordinate for O-H bond scission in HCOOH adsorbed on Pt(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 by each inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Platinum, 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 Pt(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 by each inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Platinum, 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 Pt(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 by each inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Platinum, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

O-H = 1.56 Å

C-O = 2.04 Å

C-H = 1.29 Å

C-O = 1.97 Å

C-H = 1.28 Å

C-H = 1.11 Å

Figure 5. Side and top view of the transition state (T.S.) corresponding to Step 4, Step 6, Step 7, Step 8, Step 9 and Step 10: the length of the bond being broken is indicated. Platinum, 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 Pt(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 by each inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Platinum, 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 Pt(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 formed is indicated by each inset. E_f and ΔE denote the calculated activation energy barrier and reaction energy, respectively. Platinum, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

O-H = 1.48 Å

C-O = 1.55 Å

O-H = 1.10 Å

O-H = 1.25 Å

Figure 8. Side and top view of the transition state (T.S.) corresponding to Step 12, Step 13, Step 15 and Step 16: the length of the bond being broken is indicated. Platinum, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

C-O = 2.14 Å

O-H = 1.62 Å

O-H = 1.22 Å

O-H = 1.70 Å

Figure 9. Side and top view of the transition state (T.S.) corresponding to Step 17, Step 18, Step 19 and Step 20: the length of the bond being formed is indicated. Platinum, carbon, hydrogen and oxygen atoms are indicated in blue, dark grey, light grey and red, respectively.

Table 2. Calculated reaction energy (ΔE), activation energy barrier (E_f) for all reaction steps on Pt(111).

Elementary step	ΔE^a	E_f^b
(1) $HCOOH^* + * \rightarrow HCOO^* + H^*$	0.05	0.53
(2) $HCOOH^* + * \rightarrow *COOH + H^*$	-0.25	0.39+0.41
(3) $HCOO^* + * \rightarrow CO_2^* + H^*$	-0.35	1.00
(4) $*COOH + * \rightarrow CO_2^* + H^*$	-0.03	0.67
(5) $HCOOH^* + * \rightarrow HCO^* + *OH$	0.70	0.70+0.42

(6) $\text{HCOO}^* + * \rightarrow \text{HCO}^* + \text{O}^*$	1.59-0.43	1.82
(7) $\text{HCO}^* + * \rightarrow * \text{CO} + \text{H}^*$	-0.59-0.15	0.23
(8) $* \text{COOH} + * \rightarrow * \text{CO} + \text{OH}^*$	0.58-0.19	0.78
(9) $\text{HCOO}^* + \text{O}^* \rightarrow \text{CO}_2^* + * \text{OH}$	-1.07	1.61 ^c
(10) $\text{HCOO}^* + * \text{OH} \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$	-1.07	1.08 ^c
(11) $\text{HCOO}^* + * \text{CO} \rightarrow \text{CO}_2^* + \text{HCO}^*$	0.47	1.16+0.25
(12) $\text{HCOO}^* + * \text{COOH} \rightarrow \text{CO}_2^* + \text{HCOOH}^*$	0.52	0.70
(13) $* \text{COOH} + \text{O}^* \rightarrow \text{CO}_2^* + * \text{OH}$	-0.11	0.12
(14) $* \text{COOH} + * \text{OH} \rightarrow \text{CO}_2^* + \text{H}_2\text{O}^*$	-0.81-0.10	0.00
(15) $* \text{COOH} + \text{H}^* \rightarrow * \text{CO} + \text{H}_2\text{O}^*$	-0.45	0.71
(16) $* \text{COOH} + * \text{CO} \rightarrow \text{CO}_2^* + \text{HCO}^*$	0.81	1.10
(17) $* \text{CO} + \text{O}^* \rightarrow \text{CO}_2^* + *$	-0.78	0.83
(18) $\text{O}^* + \text{H}^* \rightarrow * \text{OH} + *$	-0.20	0.79
(19) $* \text{OH} + * \text{OH} \rightarrow \text{H}_2\text{O}^* + \text{O}^*$	-0.17	0.04
(20) $\text{H}^* + * \text{OH} \rightarrow \text{H}_2\text{O}^* + *$	-0.71	0.19
(21) $\text{H}^* + \text{H}^* \rightarrow \text{H}_2 + 2^*$	0.85 ^d	0.85 ^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.

3.2.1 HCOOH decomposition on the clean Pt(111) surface

$\text{HCOOH}^* + * \rightarrow \text{HCOO}^* + \text{H}^*$ (Step 1). HCOOH dehydrogenation to HCOO begins with the molecule adsorbed in the perpendicular configuration (Figure 2). The reaction is nearly thermo-neutral and has an activation energy barrier of 0.53 eV. O-H distance is equal to 1.03 Å at the B.I.S, 2.95 Å at the B.F.S. and 1.70 Å at the T.S.. There is practically no interaction between the co-adsorbed HCOO (top-top) and H (top) products of this step.

$\text{HCOOH}^* + * \rightarrow * \text{COOH} + \text{H}^*$ (Step 2). HCOOH dehydrogenation to COOH requires the isomerization of the molecule from the perpendicular trans- adsorbed configuration to a

nearly parallel cis- configuration having a nearly zero BE (Figure 3). This re-orientation step has an activation energy barrier of 0.73 eV. The following C-H bond scission is characterized by an increase of the C-H distance by 0.13 Å (I.S. → T.S.) and 1.62 Å (T.S. → B.F.S), is exothermic by 0.66 eV and has an activation energy barrier of 0.39 eV. There is essentially no interaction between the co-adsorbed COOH (top) and H (top) products of this step.

$HCOO^* + * \rightarrow CO_2^* + H^*$ (Step 3). HCOO dehydrogenation goes through two successive steps; HCOO first reorients itself to a configuration in which H points down towards the surface, followed by a H-C bond-breaking step (Figure 4). The first step has an activation energy barrier of 1.00 eV, while the second step is spontaneous. CO₂ generation from HCOO is exothermic by 0.35 eV. The final products of this step: CO₂ (nearly desorbed) and H (top) do not interact with each other.

$*COOH + * \rightarrow CO_2^* + H^*$ (Step 4). The dehydrogenation of COOH is nearly thermo-neutral and has an activation energy barrier of 0.67 eV. The O-H distance (Figure 5) is 1.00 Å (B.I.S.), 1.56 Å (T.S.) and 3.27 Å (B.F.S.). In the final state, CO₂ (nearly desorbed) and H (top) have no interactions.

$HCOOH^* + * \rightarrow HCO^* + *OH$ (Step 5). Similarly to COOH formation, the C-OH bond scission in HCOOH requires an isomerization of HCOOH from the perpendicular trans-adsorbed configuration to a nearly parallel cis- configuration similar to that found for Step 2, as discussed above (Figure 6). The activation energy barrier for the isomerization is 0.77 eV. The C-OH bond scission is characterized by an increase of the C-OH distance of 0.49 Å (I.S. → T.S.) and 0.94 Å (T.S. → B. F. S.) and is endothermic by 0.28 eV, with an activation energy barrier of 0.70 eV. The coadsorbed products of this step (HCO (top) and OH (top)) attract each other by about 0.30 eV.

$HCOO^* + * \rightarrow HCO^* + O^*$ (Step 6). The C-O bond scission in HCOO is endothermic by 1.59 eV and requires an activation energy barrier of 1.82 eV. The C-O distance (Figure 5) increases from 1.27 Å (B.I.S) to 2.04 Å (T.S) and to 3.37 Å at the F.S.. The co-adsorbed products of this step (HCO (top) and O (hcp)) repel each other by about 0.40 eV. This final state is 0.43 eV less stable than the most stable coadsorbed state of these species (B.F.S.), where HCO and O are interacting by occupying adjacent sites.

$HCO^* + * \rightarrow *CO + H^*$ (Step 7). The decomposition of HCO into CO and H is exothermic by 0.59 eV and has an activation energy barrier of 0.23 eV. The C-H distance (Figure 5) changes from 1.11 Å (B.I.S.) to 1.29 Å (T.S.) and to 3.08 Å (F.S.). In this F.S., which is 0.15 eV less stable than the B.F.S., coadsorbed CO (top) and H(top) have an interaction energy of 0.25 eV.

$*COOH + * \rightarrow *CO + *OH$ (Step 8). This reaction step is endothermic by 0.58 eV and has an activation energy barrier of 0.78 eV. The C-O distance in C-OH (Figure 5) increases by 0.64 Å (B.I.S. $\rightarrow$ T.S.) and 0.99 Å (T.S. $\rightarrow$ F.S.). The coadsorbed CO (top) and OH (top) repel each other by about 0.10 eV. The B.F.S. is 0.19 eV more stable than the F.S..

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

$HCOO^* + O^* \rightarrow CO_2^* + *OH$ (Step 9). H is transferred from an adsorbed formate to a coadsorbed O atom in this step. The co-adsorbed HCOO (top-top) and O (hcp) repel each other by about 0.40 eV. The C-H bond scission in HCOO is exothermic by 1.07 eV and has an activation energy barrier of 1.61 eV. The C-H distance (Figure 5) changes from 1.11 Å (B.I.S.) to 1.28 Å (T.S.), to 3.50 Å (B.F.S.). In the final state, products CO₂ (nearly desorbed) and OH (top) attract each other by 0.14 eV.

$HCOO^* + ^*OH \rightarrow CO_2^* + H_2O^*$ (Step 10). H is transferred from an adsorbed formate to a coadsorbed OH in this step. Coadsorbed HCOO (top-top) and OH (top) attract each other by about 0.15 eV. The C-H bond scission in HCOO and O-H bond making in H₂O has an activation energy barrier of 1.08 eV and is exothermic by 1.07 eV. The T.S. (Figure 5) corresponds to the O-Pt bond breaking followed immediately by transfer of H from HCOO to OH. The final coadsorbed products (CO₂ (nearly desorbed) and H₂O (top)) do not interact with each other.

$HCOO^* + CO^* \rightarrow CO_2^* + HCO^*$ (Step 11). As written, this reaction occurs through two sequential steps. There is a negligible interaction between coadsorbed HCOO (top-top) and CO (hcp). Before the C-H bond scission, there is the formation of a stable complex HCOOCO: the activation energy barrier for O-C bond formation is 1.23 eV (Figure 7). The subsequent decomposition of this complex into CO₂ and HCO has an activation energy barrier of 0.25 eV and is characterized by an increase in the C-O distance by 0.53 Å (I.S. → T.S.) and 1.92 Å (T.S. → B.F.S.). The overall process is endothermic by 0.47 eV. In the final state, CO₂ nearly desorbed) and HCO (top) attract each other slightly.

$HCOO^* + ^*COOH \rightarrow HCOOH^* + CO_2^*$ (Step 12). This is a H transfer step from an adsorbed carboxyl to a coadsorbed formate. The co-adsorption of HCOO (top-top) and COOH (top) leads to a destabilization of 0.12 eV. The O-H bond scission in COOH and the simultaneous O-H bond making leading to the formation of HCOOH is endothermic by 0.52 eV and has an activation energy barrier of 0.70 eV. The O-H distance (Figure 8) in COOH is equal to 0.99 Å (B.I.S.), 1.48 Å (T.S.) and 3.03 Å (B.F.S.) The final state includes coadsorbed CO₂ (top) and HCOOH (top-top) which are destabilized by 0.30 eV with respect to their adsorption at infinite separation.

$*COOH + O^* \rightarrow CO_2^* + *OH$ (Step 13). This is a H transfer step from an adsorbed carboxyl to a coadsorbed O. Coadsorbed COOH (top) and O (fcc) do not interact with each other. The O-H bond scission in COOH is exothermic by 0.11 eV and is nearly spontaneous with an activation energy barrier of 0.12 eV. The O-H distance (Figure 8) increases by 0.10 Å (B.I.S. $\rightarrow$ T.S.) and 0.57 Å (T.S. $\rightarrow$ B.F.S.). In the final state, products CO₂ (top) and OH (bridge) repel each other by about 0.10 eV.

$*COOH + *OH \rightarrow CO_2^* + H_2O^*$ (Step 14). This is a H transfer step from an adsorbed carboxyl to a coadsorbed OH. The coadsorbed COOH (top) and OH (bridge) do not interact with each other. This step is exothermic by 0.81 eV and is practically spontaneous. The O-H distance in COOH increases by 0.59 Å between the B.I.S. and the F.S.. The products in the final state (CO₂ (top) and H₂O (top)) do not interact with each other. However, there is a 0.10 eV more stable coadsorbed configuration (B.F.S.), due to CO₂ and H₂O interacting in adjacent sites.

$*COOH + H^* \rightarrow CO^* + H_2O^*$ (Step 15). This step involves the attack of carboxyl by a coadsorbed H atom, with the simultaneous release of a H₂O molecule. The initial state corresponds to the final state of the dehydrogenation of HCOOH into COOH+H. The C-OH bond scission in COOH is exothermic by 0.45 eV and has an activation energy barrier of 0.71 eV. The C-O distance (Figure 8) increases by 0.22 Å (B.I.S. $\rightarrow$ T.S.) and 2.94 Å (T.S. $\rightarrow$ B.F.S.) The final state involves the coadsorption of CO (fcc) and H₂O (top), which stabilize each other only mildly.

$*COOH + CO^* \rightarrow CO_2^* + HCO^*$ (Step 16). This step involves a H transfer from a carboxyl to a coadsorbed CO. Co-adsorbed COOH (top) and CO (top) repel each other by about 0.30 eV. The simultaneous O-H bond scission in COOH and O-H bond making in HCOO is endothermic by 0.81 eV and has an activation energy barrier of 1.10 eV. The breaking O-H bond

length (Figure 8) is equal to 0.99 Å (B.I.S.), 1.25 Å (T.S.) and 2.00 Å (B.F.S.). The final state involves coadsorbed CO₂ (top) and HCO (top) which repel each other by about 0.30 eV.

3.2.3 CO oxidation and H₂O formation steps

$*CO + O^* \rightarrow CO_2^* + *$ (Step 17). The co-adsorption of CO (fcc/bridge) and O (fcc) includes a repulsive interaction of about 0.10 eV, with respect to the adsorption of these two species at infinite separation from each other. C-O bond formation is exothermic by 0.78 eV and has an activation energy barrier of 0.83 eV. The OC-O bond length (Figure 9) decreases from 3.62 Å (B.I.S.) to 2.14 Å (T.S.) and to 1.18 Å at the B.F.S..

$O^* + H^* \rightarrow *OH + *$ (Step 18). The co-adsorbed O (fcc) and H (top) do not interact with each other. The O-H bond formation is exothermic by 0.20 eV and has an activation energy barrier of 0.79 eV. The O-H distance (Figure 9) decreases by 1.69 Å (B.I.S. → T.S.) and 0.63 Å (T.S. → B.F.S.).

$*OH + *OH \rightarrow H_2O^* + O^*$ (Step 19). This is the OH disproportionation reaction step. The co-adsorption of OH (fcc/bridge) and OH (top) leads to a large stabilization of 0.50 eV with respect to their adsorption at infinite separation. The simultaneous O-H bond scission in one of the OH groups and the O-H bond making in the other OH group is exothermic by 0.17 eV and is a nearly spontaneous process. The breaking O-H bond length (Figure 9) increases by 0.17 Å (B.I.S. → T.S.) and 0.98 Å (T.S. → B.F.S.). The final state has H₂O (top) and O (fcc) co-adsorbed, but not interacting with each other.

$H^* + *OH \rightarrow H_2O^* + *$ (Step 20). Co-adsorbed H (top) and OH (top) attract each other by 0.07 eV. The O-H bond formation is exothermic by 0.71 eV and has an activation energy

barrier of 0.19 eV. The O-H distance (Figure 9) changes from 2.87 Å (B.I.S.), to 1.70 Å (T.S.) and to 0.99 Å (B.F.S.).

Based on Table 3 we can suggest that the formation of HCOO starting from adsorbed HCOOH (Step 1) is easier than COOH formation (Step 2), in agreement with the calculations of Gao *et al.*[26] and Hu *et al.*[29], even though our activation energy barriers are smaller, perhaps due to the different method used for identifying the transition state (T.S. search). The second dehydrogenation step leading to the formation of CO₂ occurs more easily starting from the COOH intermediate (Step 4) than from the HCOO intermediate (Step 3), which is in agreement with previous results by Grabow *et al.*[25], Yoo *et al.*[32] and Qi *et al.*[35]. Our calculated activation energy barriers are close to those determined by Grabow *et al.*[25] and are smaller with respect to those computed by Gao *et al.*[26], probably as consequence of the different T.S. search method. Moreover, we found that the dehydrogenation of HCOO to CO₂ occurs through the formation of a monodentate HCOO intermediate which agrees with the work of Gao *et al.*[26], Qi *et al.*[35] and Hu *et al.*[29]; however, our barriers are smaller especially for the decomposition of the monodentate HCOO which occurs spontaneously in our work. In general, we found a behavior for the two dehydrogenation steps similar to that reported by Lin *et al.*[36], suggesting that the HCOO is the only intermediate observed experimentally in HCOOH decomposition since it is formed more easily than COOH but it decomposes more difficultly than COOH. However, our values of activation energy barrier for the first dehydrogenation of HCOOH are smaller than those determined by Lin *et al.*[36], very likely due to the different unit cells utilized in these studies.

The presence of co-adsorbed O or OH species on Pt(111) makes the dehydrogenation of HCOO more difficult with respect to the same process on the clean surface (Steps 9 and 10 vs.

Step 3). By contrast, the presence of co-adsorbed O or OH species favors the dehydrogenation of COOH into CO₂ (Steps 13 and 14 vs. Step 4). The dehydrogenation of HCOO or COOH is easier through uni-molecular decomposition than through bi-molecular reaction with co-adsorbed CO (Step 11 vs. Step 3 and Step 16 vs. Step 4). The trend of these results is the same as that reported by Grabow *et al.*[25].

The formation of CO from HCOOH and HCOO through the Steps 5-7 is difficult because of the large activation energy barrier associated to the HCO formation (Steps 5 and 6); we note in passing that this step is found to have a barrier of 0.88 eV by Qi *et al.*[35]. In contrast, CO formation through COOH is easier, both on the clean surface (Step 8) and in the presence of co-adsorbed H (Step 15). This result agrees with the finding of Gao *et al.*[26]. CO oxidation to CO₂ requires a modest activation energy barrier, in good agreement with that reported by Lin *et al.*[36], Eichler *et al.*[51] and Grabow *et al.*[25].

Finally, the formation of OH may occur from reaction between co-adsorbed O and H (Step 18) or from COOH decomposition on the clean surface (Step 8) or from COOH decomposition in the presence of co-adsorbed O (Step 13). The produced OH may easily react to form H₂O following Steps 19 and 20. The calculated reaction energies for OH and H₂O formation are in reasonable agreement with experiments[52]. The activation energy barrier for H₂O formation agrees well with results from Phatak *et al.*[53], Grabow *et al.*[25], Ford *et al.*[54] and Michaelides *et al.*[55], while the barrier for OH formation is slightly smaller, except with respect to the value of Ford *et al.*[54].

3.3 Potential energy surface for HCOOH decomposition on the clean Pt(111) surface

The potential energy surface (PES) for HCOOH dehydrogenation and dehydration through the HCOO and COOH intermediates on the clean Pt(111) surface is shown in Figure 10 where both the two possible adsorption states, i.e. co-adsorption and infinite separation, 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 above, pathway (b) should be easier in the presence of co-adsorbed O and OH species due to the lower activation energy for COOH dehydrogenation then.

The PES shows that adsorbed HCOO is less stable than adsorbed COOH. As discussed above, we found that the formation of the HCOO intermediate is easier than the formation of COOH intermediate, a direct consequence of the necessary isomerization of HCOOH from its perpendicular trans- configuration to its parallel cis- configuration. However, our data suggest that the dehydrogenation of the HCOO intermediate is more difficult than the dehydrogenation of the COOH intermediate. In general, the COOH pathway appears to be energetically easier than the HCOO pathway. The formation of CO_2 is more favorable than CO formation for both pathways and the production of CO should go mainly through COOH decomposition. In fact, we suggest that the adsorbed HCOO is converted completely into CO_2 while adsorbed COOH may produce both CO_2 and CO. Our results may, therefore, indicate that HCOO could be the only intermediate that can be observed in HCOOH decomposition experiments: HCOO is easier to make and more difficult to decompose than COOH on Pt(111).

Figure 10. Potential energy surface of reaction mechanisms for HCOOH decomposition on the clean Pt(111) surface. Zero of the energy axis corresponds to HCOOH at infinite separation from Pt(111) slab. The red and the blue lines indicate the HCOO and COOH paths respectively. Solid red line: $\text{HCOOH}^* \rightarrow \text{HCOO}^* \rightarrow \text{CO}_2^*$ (step 1 and 3); solid blue line $\text{HCOOH}^* \rightarrow \text{COOH}^* \rightarrow \text{CO}_2^*$ (step 2 and 4); dashed red line: $\text{HCOOH}^* \rightarrow \text{HCOO}^* \rightarrow \text{HCO}^* \rightarrow \text{CO}^*$ (step 1, 6 and 7); dashed blue line: $\text{HCOOH}^* \rightarrow \text{COOH}^* \rightarrow \text{CO}^*$ (step 2 and 8).

Symbol § represents infinite separation. The dashed line in the $\text{CO}_2 + 2\text{H}$ state indicates that CO_2 is physisorbed.

4. Conclusion

We carried out periodic, self-consistent (GGA-PW91), Density Functional Theory calculations to study the HCOOH decomposition on Pt(111) through the formate and carboxyl pathways. We considered the paths for the formation of both CO_2 and CO and we analyzed the possible reaction mechanisms by accounting for decomposition steps on both the clean surface and in the

presence of co-adsorbed O, OH, H or CO. Our results suggest that the formation of HCOO is easier than that of COOH, mainly because the dehydrogenation to COOH requires first the isomerization of HCOOH from an adsorbed perpendicular trans- configuration to the adsorbed parallel cis- configuration. However, HCOO dehydrogenation is more difficult than COOH decomposition and proceeds through the formation of a monodentate HCOO intermediate. Based on the derived Potential Energy Surface alone, we conclude that the COOH pathway is energetically more favorable than the HCOO pathway also because the COOH intermediate is more stable than the HCOO intermediate on Pt(111). According to our data, the production of CO is less favorable than the dehydrogenation to CO₂ product. CO₂ is primarily generated through the COOH intermediate, since HCOO dehydrogenation is characterized by a large activation energy barrier. The presence of co-adsorbed O and OH favors COOH dehydrogenation to CO₂ while the opposite is true for the HCOO dehydrogenation. The reaction of COOH and HCOO with co-adsorbed CO is less favorable than the decomposition of the two intermediates on the clean surface. We further suggest that HCOO should be easier to identify in experiments than COOH, as it is easier to make and more difficult to decompose HCOO on Pt(111). Yet, our forthcoming study combining experimental reaction data with the DFT results presented here and a comprehensive microkinetic model should be able to shed more light on mechanistic questions such as rate controlling steps, surface coverages, and paths carrying the majority of the dehydrogenation versus dehydration reaction fluxes.

Acknowledgements

This manuscript is dedicated to Prof. Gabor Somorjai, whose pioneering work has been inspirational to both coauthors. We thank Y. Bai for his useful comments on the manuscript.

Fraction of this research was supported as part of the Institute for Atom-efficient Chemical Transformations (IACT), an Energy Frontiers Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (BES). This work was also partially supported by a DOE-BES, Office of Chemical Sciences (grant DE-FG02-05ER15731). The computational work was performed in part using supercomputing resources from the following institutions: EMSL, a National scientific user facility at Pacific Northwest National Laboratory (PNNL); the Center for Nanoscale Materials at Argonne National Laboratory (ANL); and the National Energy Research Scientific Computing Center (NERSC). EMSL is sponsored by the Department of Energy's Office of Biological and Environmental Research located at PNNL. CNM, and NERSC are supported by the U.S. Department of Energy, Office of Science, under contracts DE-AC02-06CH11357, and DE-AC02-05CH11231, respectively.

References

- [1] J.J. Bozell, CHEMISTRY Connecting Biomass and Petroleum Processing with a Chemical Bridge, *Science*, 329 (2010) 522-523.
- [2] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Heterogeneous Catalytic Transfer Hydrogenation and Its Relation to Other Methods for Reduction of Organic-Compounds, *Chemical Reviews*, 85 (1985) 129-170.
- [3] B. Loges, A. Boddien, F. Gartner, H. Junge, M. Beller, Catalytic Generation of Hydrogen from Formic acid and its Derivatives: Useful Hydrogen Storage Materials, *Topics in Catalysis*, 53 (2010) 902-914.
- [4] S.G. Wettstein, J.Q. Bond, D.M. Alonso, H.N. Pham, A.K. Datye, J.A. Dumesic, RuSn bimetallic catalysts for selective hydrogenation of levulinic acid to gamma-valerolactone, *Applied Catalysis B-Environmental*, 117 (2012) 321-329.
- [5] Y.M. Zhu, S.Y. Ha, R.I. Masel, High power density direct formic acid fuel cells, *Journal of Power Sources*, 130 (2004) 8-14.
- [6] K.J. Jeong, C.A. Miesse, J.H. Choi, J. Lee, J. Han, S.P. Yoon, S.W. Nam, T.H. Lim, T.G. Lee, Fuel crossover in direct formic acid fuel cells, *Journal of Power Sources*, 168 (2007) 119-125.
- [7] X.W. Yu, P.G. Pickup, Recent advances in direct formic acid fuel cells (DFAFC), *Journal of Power Sources*, 182 (2008) 124-132.
- [8] N.V. Rees, R.G. Compton, Sustainable energy: a review of formic acid electrochemical fuel cells (vol 15, pg 2095, 2011), *Journal of Solid State Electrochemistry*, 16 (2012) 419-419.
- [9] M.A. Barteau, Linear Free-Energy Relationships for C1-Oxygenate Decomposition on Transition-Metal Surfaces, *Catalysis Letters*, 8 (1991) 175-184.
- [10] W.M.H. Sachtler, Fahrenfort.J, The catalytic decomposition of formic acid vapour on metals, *Proceedings, 2nd International Congress on Catalysis, Technip, Paris, 1960*, pp. p. 831.
- [11] X.W. Yu, P.G. Pickup, Screening of PdM and PtM catalysts in a multi-anode direct formic acid fuel cell, *Journal of Applied Electrochemistry*, 41 (2011) 589-597.
- [12] A.C. Chen, P. Holt-Hindle, Platinum-Based Nanostructured Materials: Synthesis, Properties, and Applications, *Chemical Reviews*, 110 (2010) 3767-3804.
- [13] N.M. Markovic, P.N. Ross, Surface science studies of model fuel cell electrocatalysts, *Surface Science Reports*, 45 (2002) 121-229.
- [14] K. Jiang, H.X. Zhang, S. Zou, W.B. Cai, Electrocatalysis of formic acid on palladium and platinum surfaces: From fundamental mechanisms to fuel cell applications, *Physical Chemistry Chemical Physics*, 16 (2014) 20360-20376.
- [15] S. Enthaler, J. von Langermann, T. Schmidt, Carbon dioxide and formic acid-the couple for environmental-friendly hydrogen storage?, *Energy & Environmental Science*, 3 (2010) 1207-1217.
- [16] M.R. Columbia, P.A. Thiel, The Interaction of Formic-Acid with Transition-Metal Surfaces, Studied in Ultrahigh-Vacuum, *Journal of Electroanalytical Chemistry*, 369 (1994) 1-14.
- [17] K. Kunimatsu, H. Kita, Infrared Spectroscopic Study of Methanol and Formic-Acid Adsorbates on a Platinum-Electrode .2. Role of the Linear Co(a) Derived from Methanol and Formic-Acid in the Electrocatalytic Oxidation of Ch3oh and Hcooh, *Journal of Electroanalytical Chemistry*, 218 (1987) 155-172.
- [18] D.S. Corrigan, M.J. Weaver, Mechanisms of Formic-Acid, Methanol, and Carbon-Monoxide Electrooxidation at Platinum as Examined by Single Potential Alteration Infrared-Spectroscopy, *Journal of Electroanalytical Chemistry*, 241 (1988) 143-162.
- [19] Y.X. Chen, M. Heinen, Z. Jusys, R.J. Behm, Bridge-bonded formate: Active intermediate or spectator species in formic acid oxidation on a Pt film electrode?, *Langmuir*, 22 (2006) 10399-10408.
- [20] Y.X. Chen, M. Heinen, Z. Jusys, R.J. Behm, Kinetics and mechanism of the electrooxidation of formic acid - Spectroelectrochemical studies in a flow cell, *Angewandte Chemie-International Edition*, 45 (2006) 981-985.

- [21] M. Osawa, K. Komatsu, G. Samjeske, T. Uchida, T. Ikeshoji, A. Cuesta, C. Gutierrez, The Role of Bridge-Bonded Adsorbed Formate in the Electrocatalytic Oxidation of Formic Acid on Platinum, *Angewandte Chemie-International Edition*, 50 (2011) 1159-1163.
- [22] M.B. Jensen, U. Myler, P.A. Thiel, Local and Collective Structure of Formate on Pt(111), *Surface Science*, 290 (1993) L655-L661.
- [23] Y.X. Chen, S. Ye, M. Heinen, Z. Jusys, M. Osawa, R.J. Behm, Application of in-situ attenuated total reflection-Fourier transform infrared spectroscopy for the understanding of complex reaction mechanism and kinetics: Formic acid oxidation on a Pt film electrode at elevated temperatures, *Journal of Physical Chemistry B*, 110 (2006) 9534-9544.
- [24] N.R. Avery, Adsorption of Formic-Acid on Clean and Oxygen Covered Pt(111), *Applied Surface Science*, 11-2 (1982) 774-783.
- [25] L.C. Grabow, A.A. Gokhale, S.T. Evans, J.A. Dumesic, M. Mavrikakis, Mechanism of the water gas shift reaction on Pt: First principles, experiments, and microkinetic modeling, *Journal of Physical Chemistry C*, 112 (2008) 4608-4617.
- [26] W. Gao, J.A. Keith, J. Anton, T. Jacob, Oxidation of formic acid on the Pt(111) surface in the gas phase, *Dalton Transactions*, 39 (2010) 8450-8456.
- [27] W. Gao, J.A. Keith, J. Anton, T. Jacob, Theoretical Elucidation of the Competitive Electro-oxidation Mechanisms of Formic Acid on Pt(111), *Journal of the American Chemical Society*, 132 (2010) 18377-18385.
- [28] A.C. Cuesta, G. Osawa, Masatoshi; Gutierrez, C., Mechanism of the Electrocatalytic Oxidation of Formic Acid on Metals, *Acs Catalysis*, 2 (2012) 11.
- [29] C.T.S.-W.C. Hu, K.-Y.; Huang W., Reaction pathways derived from DFT for understanding catalytic decomposition of formic acid into hydrogen on noble metals, *International Journal of Hydrogen Energy*, 37 (2012) 10.
- [30] H.F. Wang, Z.P. Liu, Formic Acid Oxidation at Pt/H₂O Interface from Periodic DFT Calculations Integrated with a Continuum Solvation Model, *Journal of Physical Chemistry C*, 113 (2009) 17502-17508.
- [31] M. Neurock, M. Janik, A. Wieckowski, A first principles comparison of the mechanism and site requirements for the electrocatalytic oxidation of methanol and formic acid over Pt, *Faraday Discussions*, 140 (2008) 363-378.
- [32] J.S. Yoo, F. Abild-Pedersen, J.K. Nørskov, F. Studt, Theoretical analysis of transition-metal catalysts for formic acid decomposition, *ACS Catalysis*, 4 (2014) 1226-1233.
- [33] Y. Qi, J. Gao, D. Zhang, C. Liu, Comparative theoretical study of formic acid decomposition on PtAg(111) and Pt(111) surfaces, *RSC Advances*, 5 (2015) 21170-21177.
- [34] W. Zhong, D. Zhang, New insight into the CO formation mechanism during formic acid oxidation on Pt(111), *Catalysis Communications*, 29 (2012) 82-86.
- [35] Y. Qi, J. Li, D. Zhang, C. Liu, Reexamination of formic acid decomposition on the Pt(111) surface both in the absence and in the presence of water, from periodic DFT calculations, *Catalysis Science & Technology*, (2015).
- [36] C.H. Lin, C.L. Chen, J.H. Wang, Mechanistic Studies of Water-Gas-Shift Reaction on Transition Metals, *Journal of Physical Chemistry C*, 115 (2011) 18582-18588.
- [37] B. Hammer, L.B. Hansen, J.K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, *Physical Review B*, 59 (1999) 7413-7421.
- [38] J. Greeley, J.K. Nørskov, M. Mavrikakis, Electronic structure and catalysis on metal surfaces, *Annual Review of Physical Chemistry*, 53 (2002) 319-348.
- [39] D. Vanderbilt, Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism, *Physical Review B*, 41 (1990) 7892-7895.
- [40] D.J. Chadi, M.L. Cohen, Special Points in the Brillouin Zone, *Physical Review B*, 8 (1973) 5747-5753.

- [41] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, Molecules, Solids, and Surfaces - Applications of the Generalized Gradient Approximation for Exchange and Correlation, *Physical Review B*, 46 (1992) 6671-6687.
- [42] J.A. White, D.M. Bird, Implementation of Gradient-Corrected Exchange-Correlation Potentials in Car-Parrinello Total-Energy Calculations, *Physical Review B*, 50 (1994) 4954-4957.
- [43] CRC Handbook of Chemistry and Physics, CRC Press, New York, 1996.
- [44] A. Ulitsky, R. Elber, A New Technique to Calculate Steepest Descent Paths in Flexible Polyatomic Systems, *Journal of Chemical Physics*, 92 (1990) 1510-1511.
- [45] G. Mills, H. Jonsson, G.K. Schenter, Reversible Work Transition-State Theory - Application to Dissociative Adsorption of Hydrogen, *Surface Science*, 324 (1995) 305-337.
- [46] G. Henkelman, B.P. Uberuaga, H. Jonsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, *Journal of Chemical Physics*, 113 (2000) 9901-9904.
- [47] J. Greeley, M. Mavrikakis, A first-principles study of surface and subsurface H on and in Ni(1 1 1): diffusional properties and coverage-dependent behavior, *Surface Science*, 540 (2003) 215-229.
- [48] M.R. Columbia, A.M. Crabtree, P.A. Thiel, The Temperature and Coverage Dependences of Adsorbed Formic-Acid and Its Conversion to Formate on Pt(111), *Journal of the American Chemical Society*, 114 (1992) 1231-1237.
- [49] P. Ferrin, M. Mavrikakis, Structure Sensitivity of Methanol Electrooxidation on Transition Metals, *Journal of the American Chemical Society*, 131 (2009) 14381-14389.
- [50] J.A. Herron, J. Scaranto, P. Ferrin, S. Li, M. Mavrikakis, Trends in Formic Acid Decomposition on Model Transition Metal Surfaces: A Density Functional Theory study, *ACS Catalysis*, 4 (2014) 4434-4445.
- [51] A. Eichler, J. Hafner, Reaction channels for the catalytic oxidation of CO on Pt(111), *Surface Science*, 433 (1999) 58-62.
- [52] E.M.C. Karp, C.T.; Studt, F.; Abild-Pedersen, F.; Norskov, J.K, The energetics of oxygen adatoms, hydroxyl species and water dissociation on Pt(111), *Journal of Physical Chemistry C*, just accepted (2012).
- [53] A.A. Phatak, W.N. Delgass, F.H. Ribeiro, W.F. Schneider, Density Functional Theory Comparison of Water Dissociation Steps on Cu, Au, Ni, Pd, and Pt, *Journal of Physical Chemistry C*, 113 (2009) 7269-7276.
- [54] D.C. Ford, A.U. Nilekar, Y. Xu, M. Mavrikakis, Partial and complete reduction of O(2) by hydrogen on transition metal surfaces, *Surface Science*, 604 (2010) 1565-1575.
- [55] A. Michaelides, P. Hu, Catalytic water formation on platinum: A first-principles study, *Journal of the American Chemical Society*, 123 (2001) 4235-4242.