

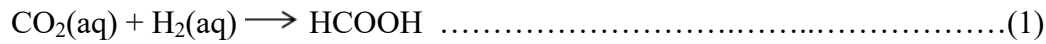
## Supporting Information

### **The origins of Formic acid electrooxidation on selected surfaces of Pt, Pd, and their alloys with Sn**

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### Note 1: Computational methods

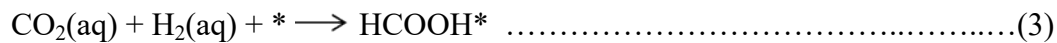
The aqueous-phase free energies are calculated relative to the DFT- derived energies of H<sub>2</sub>O (aq), CO<sub>2</sub>(aq), and H<sub>2</sub>(aq).<sup>1</sup> For example, the free energy of FA is calculated from the reaction:



From which the free energy of HCOOH is calculated as:

$$\begin{aligned} \Delta G_{\text{HCOOH}} &= (E_{\text{HCOOH}} - TS_{\text{HCOOH}} + \text{ZPE}_{\text{HCOOH}}) - (E_{\text{CO}_2} - TS_{\text{CO}_2} + \text{ZPE}_{\text{CO}_2}) - (E_{\text{H}_2} - TS_{\text{H}_2} + \text{ZPE}_{\text{H}_2}) \dots\dots\dots(2) \end{aligned}$$

Where E represent the total energy of a species determined through DFT calculations, T denote the standard temperature (298K), S signify the entropy, and ZPE indicate the calculated zero-point energy for the species. The computation of free energies for other species follows a similar procedure. When determining the free energy of adsorbed species, the total energy of a species and its entropy is evaluated with respect to the gas phase and clean surface. Here is an illustration of the free energy alteration for a reaction involving surface intermediates:



From which the free energy of HCOOH\* is calculated as:

$$\begin{aligned} \Delta G_{\text{HCOOH}} &= (E_{\text{HCOOH}^*} - TS_{\text{HCOOH}^*} + \text{ZPE}_{\text{HCOOH}^*}) - 2(E_{\text{CO}_2} - TS_{\text{CO}_2} + \text{ZPE}_{\text{CO}_2}) - (E_{\text{H}_2} - TS_{\text{H}_2} + \text{ZPE}_{\text{H}_2}) - (E_{\text{surface}} - TS_{\text{surface}} + \text{ZPE}_{\text{surface}}) \dots\dots\dots(4) \end{aligned}$$

Where \* is showing the adsorbed species, E<sub>surface</sub> is the total energy of the clean surface, and the rest of the terms are defined above.

The free energy of adsorption (G) for each species X is defined as:

$$\begin{aligned} G_{\text{ads}}(X) &= (E_X^* + \text{ZPE}_X^* - TS_X^*) - (E_{\text{slab}} + \text{ZPE}_{\text{slab}} - TS_{\text{slab}}) - (E_X + \text{ZPE}_X - TS_X) \dots\dots\dots(5) \end{aligned}$$

Where  $E_X^*$ ,  $E_{\text{slab}}$ , and  $E_X$  are the total energies of the adsorbate X plus slab system, the clean slab, and the gas-phase X, respectively, The  $ZPE^*$ ,  $T.S.^*$  and  $ZPE$ ,  $TS$  are zero-point energy and entropy for the total system (adsorbent and surface) and aqueous phase. The  $ZPE_{\text{slab}}$  and  $TS_{\text{slab}}$  are the zero-point energy and entropy of the clean surface. According to this equation, a negative value of  $E_{\text{ads}}$  signifies exergonic adsorption.

The activation energy is defined as the difference between the energy of the transition state and the reactants.

$$E_a = (E_{\text{ts}} + ZPE_{\text{ts}} - TS_{\text{ts}}) - (E_r + ZPE_r - TS_r) \dots \dots \dots (6)$$

Where  $E_a$ ,  $E_{\text{ts}}$  and  $E_r$  are the activation energy, energy of transition state and energy of reactant respectively, other terms are defined above.

The energy of a reaction, e.g.:  $A + B \rightarrow C + D$ , is defined as:

$$\Delta G^0 = G_C + G_D - G_A - G_B \dots \dots \dots (7)$$

Where  $G_A$ ,  $G_B$ ,  $G_C$ , and  $G_D$  are defined by equation S2.

We employ the computational hydrogen electrode model developed by Norskov to calculate the chemical potential of  $H^+ + e^-$ :<sup>2</sup>

$$\frac{1}{2}G_{\text{H}_2} = G_{(\text{H}^+ + e^-)} \dots \dots \dots (8)$$

This equation is based on the definition of zero potential for the standard hydrogen electrode (SHE) (pH = 0, p= 1 atm, T= 298 K). According to this definition, the reduction potential of reaction 9 is zero ( $\epsilon^0=0$ ), thus the  $\Delta G^0$  of this reaction is also zero by definition ( $\Delta G^0=-nF\epsilon^0$ , n – no. of electrons in the reduction reaction, F – faraday constant,  $\epsilon^0$  – reduction potential).

$$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2 \dots \dots \dots (9)$$

**Note 2: H-COOH cleavage:**

On the monometallic surfaces, the first step (isomerization of the HCOOH) is endergonic on both surfaces, but the C-H bond scission step is exergonic. The reaction energy and activation barriers for the first step are 0.33 eV and 0.70 eV on Pt(111), and 0.26 eV and 0.71 eV on Pd (111)), respectively (Table S4). The energy required for the following C-H cleavage is -0.42 eV and -0.24 eV with barriers of 0.28 eV and 0.22 eV for Pt(111) and Pd(111), respectively (Table S4). This mechanism is described in Figure S4 (e-f).

On the bimetallic alloys, Pt<sub>3</sub>Sn(111) and Pd<sub>3</sub>Sn(111), the shift of the FA from the best adsorption site to the active adsorption site consists of two steps:(1) horizontal diffusion from the most stable adsorption site of HCOOH to the top of M-M (M=Pt or Pd) site (Fig. S2(b1-b2)) where the carbonylic oxygen is adsorbed on the top of M. The hydrogen points down to the bridge of Pt-Pt atoms in Pt<sub>3</sub>Sn, and to the top site of Pd atoms in Pd<sub>3</sub>Sn alloy, respectively. This shift requires a very small amount of energy of 0.05 eV and 0.08 eV for Pt<sub>3</sub>Sn(111) and Pd<sub>3</sub>Sn(111), respectively. (2) isomerization of vertical-trans HCOOH to the parallel-cis configuration of HCOOH (Fig S2 (a3-a4)), adsorbed on the bridge site of the M atom, both steps are endergonic, but the second step is the rate-limiting step (Fig S2 (a3-a4)). The reaction energies and activation barriers required for the second step are 0.22 eV and 0.55 eV for Pt<sub>3</sub>Sn(111), 0.20 eV, and 0.66 eV for Pd<sub>3</sub>Sn(111) (Table S4 (reaction 4)). Finally, in the third step, the H-C bond is cleaved. This scission is exergonic, it requires -0.44 eV on Pt<sub>3</sub>Sn(111) (E<sub>a</sub>= 0.22 eV) and -0.04 eV on Pd<sub>3</sub>Sn(111) (E<sub>a</sub>=0.33 eV) (Table S4 (reaction 5)). The potential energy diagram for all three steps is depicted in Fig. S4 (g-h).

On the ternary alloy  $\text{Pt}_3\text{Pd}_3\text{Sn}_2(111)$ , COOH is formed in a two-step process, similar to its formation on the monometallic catalysts. In the first step, HCOOH is rotated from vertical-trans to parallel-trans to a configuration in which it is adsorbed on the bridge site of the Pd-Pt atoms (Fig S2(b3)). This step is endergonic by 0.18 eV. Then, the C-H bond is cleaved, and COOH is produced on the top of the Pt atom (Fig 1(c5)). This step is exergonic by 0.26 eV ( $E_a=0.35$  eV).

**Table S1:** Adsorption energy of all the intermediates on all five surfaces for various configuration and sites.

S.N.	Species	Configuration of adsorbed species	Adsorption site	Energy (eV)				
				Pt (111)	Pd (111)	Pt <sub>3</sub> Sn (111)	Pd <sub>3</sub> Sn (111)	Pt <sub>3</sub> Pd <sub>3</sub> Sn <sub>2</sub> (111)
1	HCOOH	Vertical-trans	atop	-0.90	-0.62	-0.73	-0.72	-0.64 (Pd)
		Parallel-trans	bridge	-0.59	-0.44	-0.43	-0.30	-0.53
		Parallel-cis	bridge	-0.57	-0.36	-0.55	-0.44	-0.60
2	HCOO	Bidentate	bridge	-3.13 (Pt-Pt)	-2.90 (Pd-Pd)	-3.16 (Pt-Pt)	-3.16 (Pd-Pd)	-3.08 (Pt-Pd) -2.98 (Pt-Pd)
		Monodentate	bridge	-2.38	-2.34	-2.95	-2.66 (Sn)	-
3	COOH	Vertical-trans	atop	-3.16	-2.77	-3.07 (Pt)	-2.65 (Pd)	-2.89 (Pt-C) -2.46 (Pd-C)
		Vertical-cis	atop	-3.13	-2.70	-2.95 (Pt)	-2.63 (Pd)	-2.69 (Pt-C) -2.24 (Pd-C)
4	CO <sub>2</sub>	Parallel	bridge	-0.44	-0.28	-0.33 (Pt)	-0.20	-0.07
5	CO	Vertical	atop	-2.06	-1.70	-1.95 (Pt)	-1.47 (Pd)	-1.88 (Pt-C) -1.38 (Pd-C)
		Vertical	hollow	-2.14	-2.32	-2.09	-2.13	-
		Vertical	bridge	-2.04	-	-1.99 (Pt-Pt)	-1.47 (Pd-Pd)	-2.32 (Pt-Pd)
6	OH	Vertical	atop	-2.88	-2.83	-3.25 (Sn)	-3.18 (Sn)	-3.10 (Pt-O) -2.85 (Pd-O)
		Vertical	hollow	-2.99	-3.19	-	-2.85	-
		Vertical	bridge	-2.99	-3.13	-3.25 (Pt-Pt)	-3.30 (Pd-Pd)	-3.32 (Pd-Sn)
7	H <sub>2</sub> O	Parallel	atop	-0.66	-0.46	-0.49	-0.48 (Sn)	-0.18 (Sn) -0.18 (Pd)
8	H	-	atop	-3.77	-3.32	-3.76	-	-3.70 (Pt) -3.13 (Pd)
		-	hollow	-3.69	-3.85	-3.88	-4.07	
		-	bridge	-	-	-	-	-3.96 (Pt-Pd)

**Table S2:** Absorption energy of HCOOH on all five surfaces for vertical-trans, parallel-trans, and parallel-cis configuration.

<b>No.</b>	<b>Surface/Configuration</b>	<b>Vertical-trans</b>	<b>Parallel -trans</b>	<b>Parallel-cis</b>
<b>1</b>	<b>Pt111</b>	-0.90	-0.59	-0.57
<b>2</b>	<b>Pd111</b>	-0.62	-0.44	-0.36
<b>3</b>	<b>Pt<sub>3</sub>Sn</b>	-0.73	-0.43	-0.54
<b>4</b>	<b>Pd<sub>3</sub>Sn</b>	-0.72	-0.30	-0.44
<b>5</b>	<b>Pt<sub>3</sub>Pd<sub>3</sub>Sn<sub>2</sub></b>	-0.64	-0.53	-0.60

**Table S3:** Reaction energy ( $\Delta G$ ) for all the steps involved in FAO on across different five surfaces.

No.	Reaction	$\Delta G$ (eV)				
		Pt (111)	Pd (111)	Pt <sub>3</sub> Sn (111)	Pd <sub>3</sub> Sn (111)	Pt <sub>3</sub> Pd <sub>3</sub> Sn <sub>2</sub>
1	$\text{HCOOH} \rightarrow \text{HCOO} + \text{H}^+ + \text{e}^-$	0.24	0.19	0.04	0.04	0.02
2	$\text{HCOOH} \rightarrow \text{COOH} + \text{H}^+ + \text{e}^-$	-0.09	0.02	-0.17	0.24	-0.08
3	$\text{HCOO} \rightarrow \text{CO}_2(\text{g}) + \text{H}^+ + \text{e}^-$	0.66	0.43	0.69	0.69	0.62
4	$\text{HCOO} \rightarrow \text{HCO} + \text{O}$	0.92	0.82	1.08	1.52	1.19
5	$\text{COOH} \rightarrow \text{CO}_2(\text{g}) + \text{H}^+ + \text{e}^-$	1.00	0.60	0.90	0.49	0.72
6	$\text{COOH} \rightarrow \text{CO} + \text{OH}$	0.15	-0.62	-0.15	-0.65	-0.19
7	$\text{CO} + \text{OH} \rightarrow \text{CO}_2(\text{g}) + \text{H}^+ + \text{e}^-$	0.85	1.22	1.05	1.13	0.91
8	$\text{H}_2\text{O} \rightarrow \text{OH} + \text{H}^+ + \text{e}^-$	1.20	0.80	0.77	0.71	0.38



**Table S4:** Reaction energy ( $\Delta G$ ) and activation barrier ( $E_a$ ) for all the multi-steps involved in FAO on all five surfaces.

No.	Reaction	Pt (111)		Pd (111)		Pt <sub>3</sub> Sn (111)		Pd <sub>3</sub> Sn (111)		Pt <sub>3</sub> Pd <sub>3</sub> Sn <sub>2</sub>	
		$\Delta G$ (eV)	$E_a$ (eV)	$\Delta G$ (eV)	$E_a$ (eV)	$\Delta G$ (eV)	$E_a$ (eV)	$\Delta G$ (eV)	$E_a$ (eV)	$\Delta G$ (eV)	$E_a$ (eV)
1	HCOOH-trans (site1) $\rightarrow$ HCOOH-trans (site2)	-	-	-	-	0.05 <sup>a</sup>	-	0.08 <sup>a</sup>	-	0.18 <sup>b</sup>	0.18
2	HCOO (Biden.) $\rightarrow$ HCOO (Monoden.)	-	-	-	-	0.58	0.87	0.50	0.83	0.10	0.10
3	HCOO (Monoden.) $\rightarrow$ CO <sub>2</sub> +H+ + e-	-	-	-	-	0.11	0.11	0.19	0.19	0.52	0.52
4	HCOOH-trans $\rightarrow$ HCOOH-cis	0.33	0.70	0.26	0.71	0.22	0.55	0.20	0.66	-	-
5	HCOOH-cis $\rightarrow$ COOH +H+ + e-	-0.42	0.28	-0.24	0.22	-0.44	0.22	-0.04	0.33	-0.26 <sup>b</sup>	0.35

<sup>a</sup>vertical-trans HCOOH, <sup>b</sup>parallel-trans HCOOH

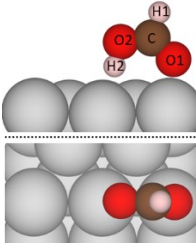
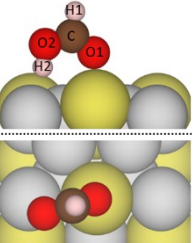
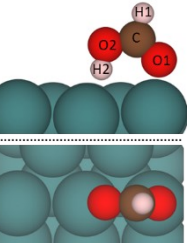
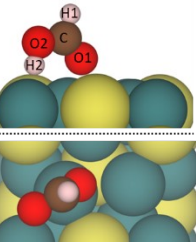
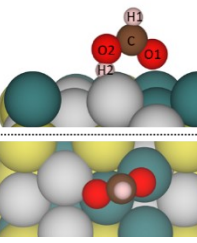
**Table S5:** D-band centre, p-band centre, s-band centre, total d-band centre, difference in ( $\epsilon_d$  and  $\epsilon_p$ )(eV), and difference in ( $\epsilon_d$  and  $\epsilon_s$ )(eV).

	$\epsilon_d$ (eV)	$\epsilon_p$ (eV)	$\epsilon_s$ (eV)	<b>Total d-band centre (eV)</b>	$\epsilon_d - \epsilon_p$ (eV)	$\epsilon_d - \epsilon_s$ (eV)
Pt	- 2.47	-3.62	-4.52	-2.51	1.15	2.05
Pd	- 2.14	-3.75	-4.74	-2.23	1.61	2.60
Pt <sub>3</sub> Sn	- 2.57	-3.92	-4.65	-2.58	1.35	2.08
Pd <sub>3</sub> Sn	- 2.30	-4.10	-5.04	-2.34	1.80	2.74
Pt <sub>3</sub> Pd <sub>3</sub> Sn <sub>2</sub>	- 2.55 (Pt)	-4.17	-5.00	-2.41	1.62	2.45
	-2.30 (Pd)				1.87	2.70

**Table S6:** Bader charge analysis for all five surfaces: Average charge and charge transfer from Sn to M (M=Pt,Pd).

Pt (111)		Pt <sub>3</sub> Sn (111)		Pd (111)		Pd <sub>3</sub> Sn (111)		Pt <sub>3</sub> Pd <sub>3</sub> Sn <sub>2</sub> (111)			
Atom	$\langle Q \rangle$ (e)	Atom	$\langle Q \rangle$ (e)	Atom	$\langle Q \rangle$ (e)	Atom	$\langle Q \rangle$ (e)	Atom	$\langle Q \rangle$ (e)	Atom	$\langle Q \rangle$ (e)
Pt	9.99	Pt	11.04	Pd	9.99	Pd	10.51	Pt	11.56	Pd	10.81
$\Delta \langle Q \rangle = 1.04 e$				$\Delta \langle Q \rangle = 0.51 e$				$\Delta \langle Q \rangle = 1.56 e$		$\Delta \langle Q \rangle = 0.81 e$	

**Table S7:** Charge transfer between catalyst surfaces and adsorbate.

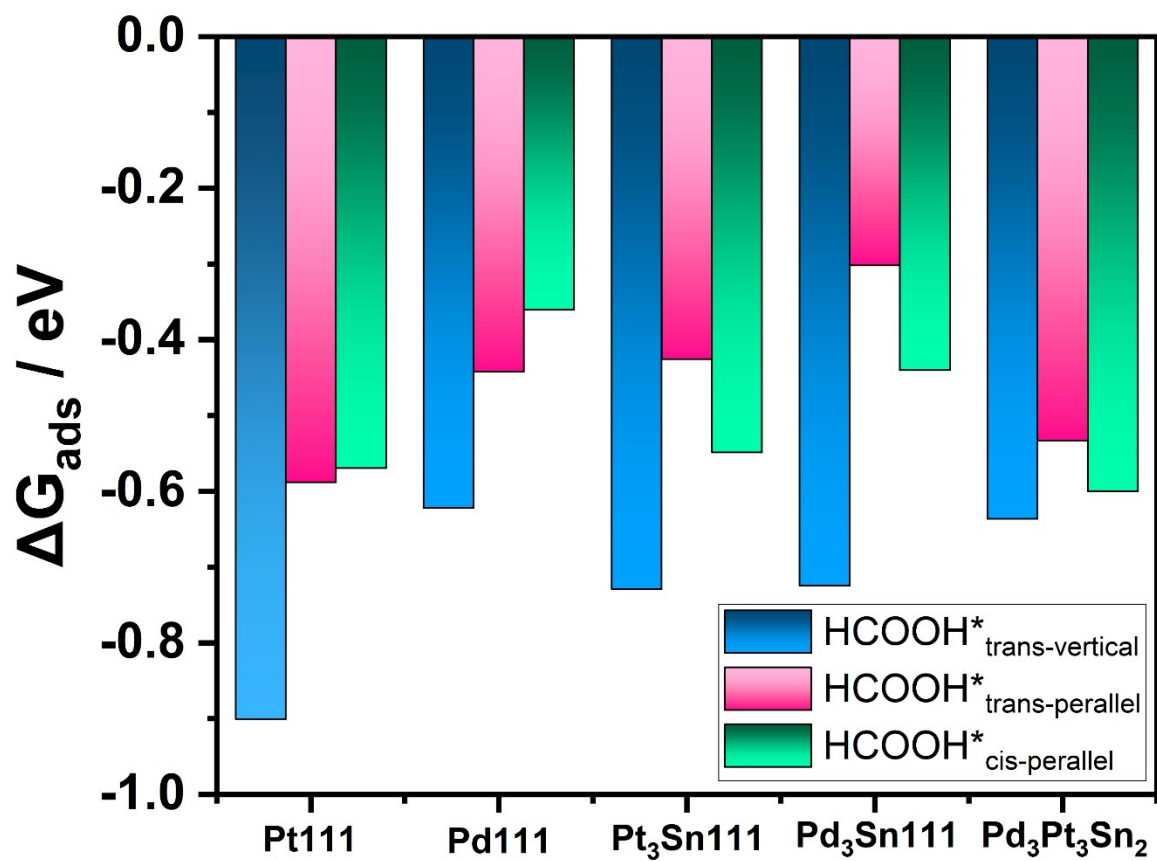
Atom s	 <b>Pt (111)</b>	 <b>Pt<sub>3</sub>Sn (111)</b>	 <b>Pd (111)</b>	 <b>Pt<sub>3</sub>Sn (111)</b>	 <b>Pt<sub>3</sub>Pd<sub>3</sub>Sn (111)</b>
	$\Delta q$ (e <sup>-</sup> )	$\Delta q$ (e <sup>-</sup> )	$\Delta q$ (e <sup>-</sup> )	$\Delta q$ (e <sup>-</sup> )	$\Delta q$ (e <sup>-</sup> )
C	-0.01	0.02	0.016	0.04	0.022
O1	-0.14	0.109	-0.09	-0.07	-0.08
O2	0.149	0.155	0.139	0.12	0.124
H1	0.005	-0.05	-0.05	-0.05	-0.04
H2	0	0	0	0	0

**Table S8:** Comparison of adsorption energy for PBE and RPBE functional by including DFT-D2 for the most stable configuration of all the intermediates involved in FAO on Pt(111), Pd(111) and Pt<sub>3</sub>Pd<sub>3</sub>Sn<sub>2</sub>(111) surfaces. The zero-point energy correction are not considered for given value.

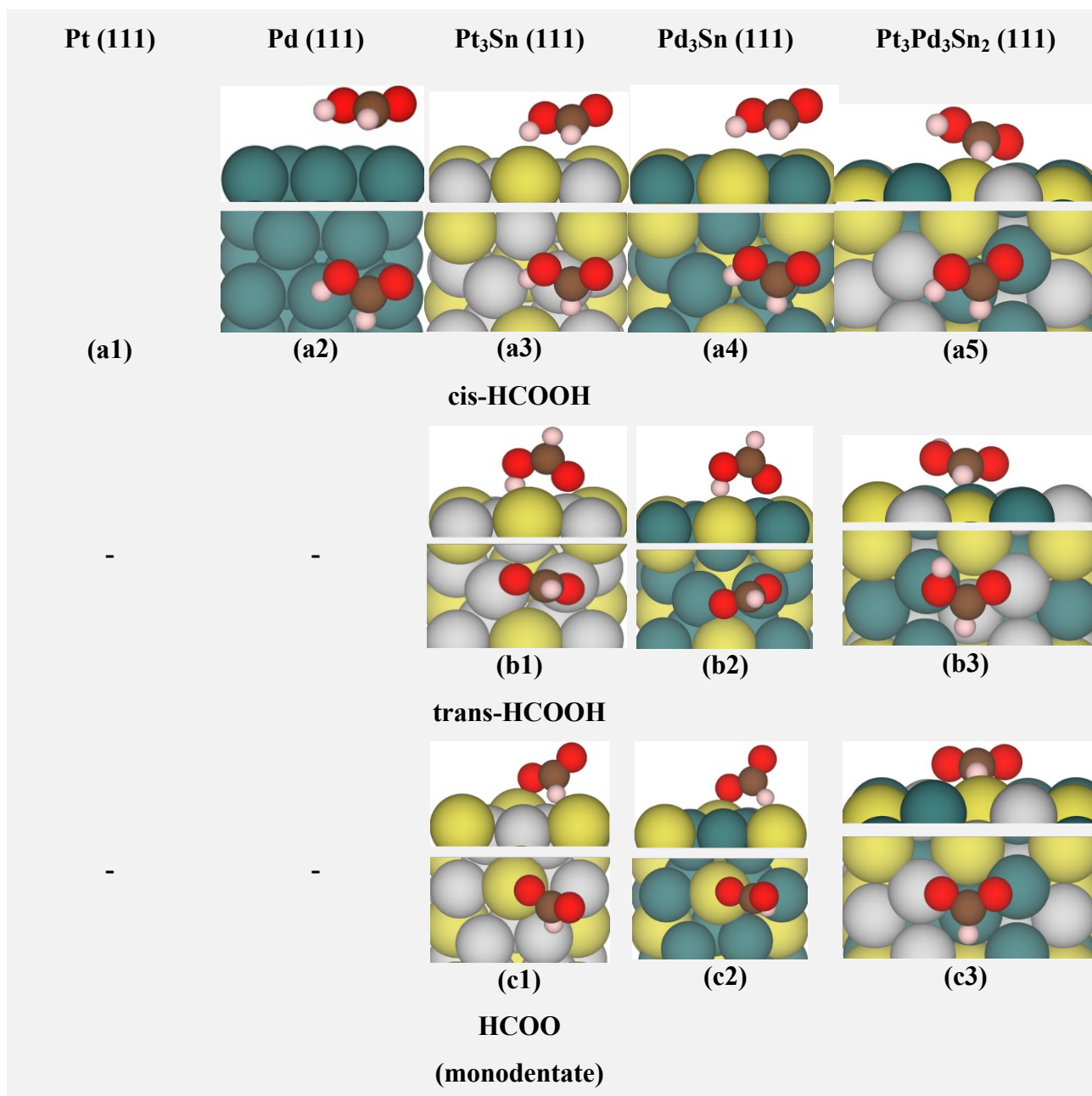
Species	Eads (eV)/unit surface					
	Pt (111)		Pd (111)		Pt <sub>3</sub> Pd <sub>3</sub> Sn <sub>2</sub>	
	PBE +DFT-D2	RPBE +DFT-D2	PBE +DFT-D2	RPBE +DFT-D2	PBE +DFT-D2	RPBE +DFT-D2
<b>HCOOH</b>	-0.88	-1.92	-0.61	-0.25	-0.64	-0.39
<b>COOH</b>	-3.23	-4.25	-2.82	-2.26	-2.46	-2.72
<b>HCOO</b>	-3.27	-4.21	-3.03	-2.80	-3.08	-2.90
<b>CO<sub>2</sub></b>	-0.45	-1.65	-0.29	-0.10	-0.07	0.00
<b>CO</b>	-2.20	-2.69	-2.40	-2.00	-2.32	-2.17
<b>OH</b>	-3.12	-2.77	-3.31	-2.86	-3.32	-3.22
<b>H</b>	-3.92	-3.77	-4.01	-3.82	-3.96	-3.77
<b>H<sub>2</sub>O</b>	-0.74	-0.47	-0.54	-0.30	-0.18	0.08

**Table S9:** Adsorption energy ( $E_{\text{ads}}$ ) of the co-adsorbed species (HCOOH and OH).

Surfaces	$E_{\text{ads}}$ (eV)	
	Co-adsorption of HCOOH and OH	Sum of individual adsorption of HCOOH and OH
Pt (111)	-4.00	-4.00
Pd (111)	-3.88	-3.92
Pt <sub>3</sub> Sn (111)	-4.09	-4.07
Pd <sub>3</sub> Sn (111)	-4.02	-4.21
Pt <sub>3</sub> Pd <sub>3</sub> Sn <sub>2</sub> (111)	-4.24	-4.24

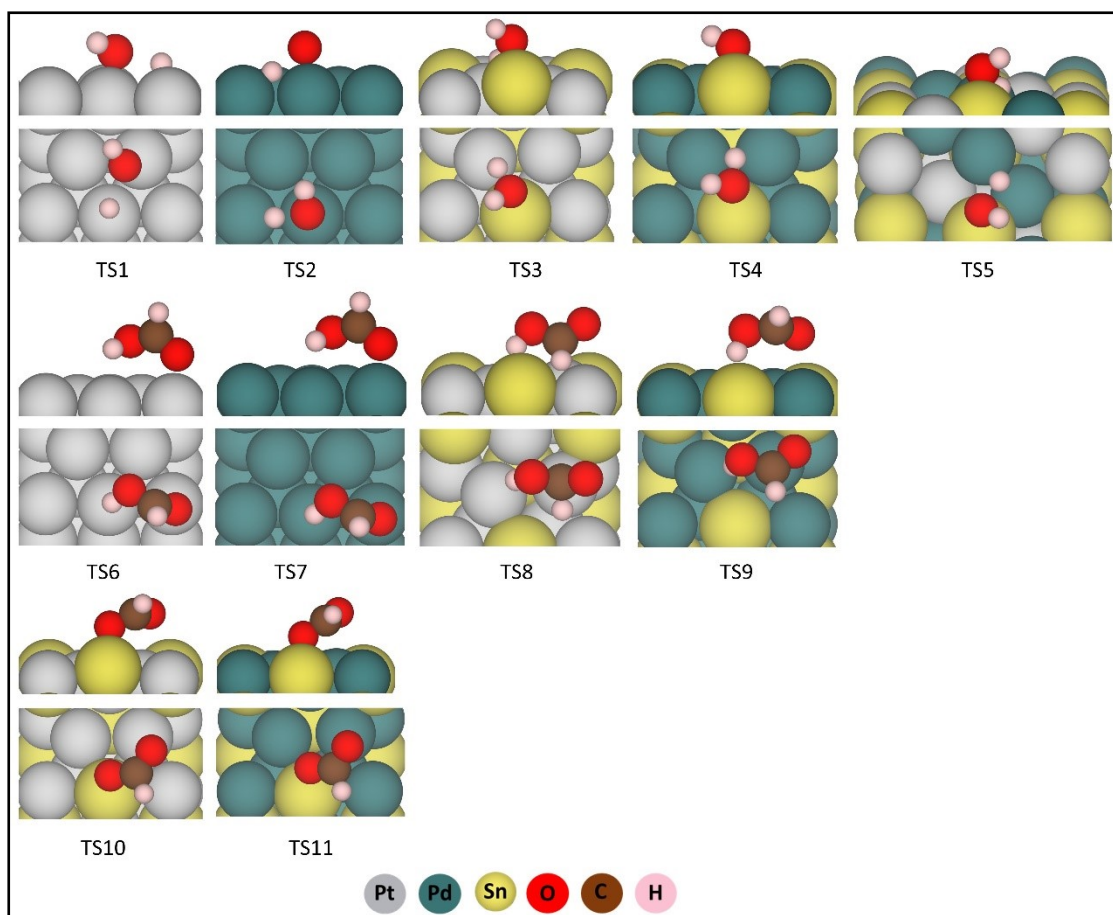


**Fig S1:** Comparison of adsorption energy of HCOOH on all five surfaces for vertical-trans, parallel-trans, and parallel-cis configuration.

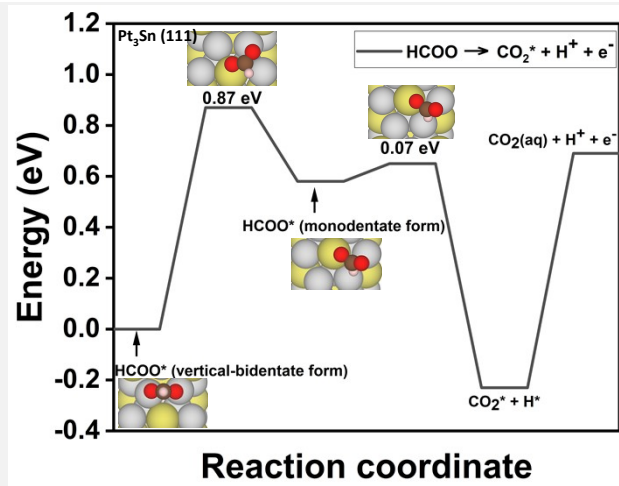
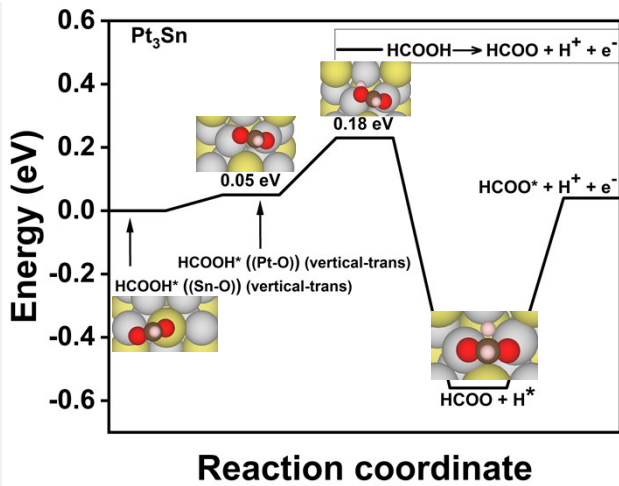


**Fig S2:** Top and side view for the configuration of the intermediates involved in multi-step process for FAO, a1-a5 represent parallel cis-configuration of formic acid on all five surfaces, b1 and b2 represent vertical trans and b3 represent parallel trans-configuration of HCOOH, c1-c3 represents the monodentate configuration of HCOO.

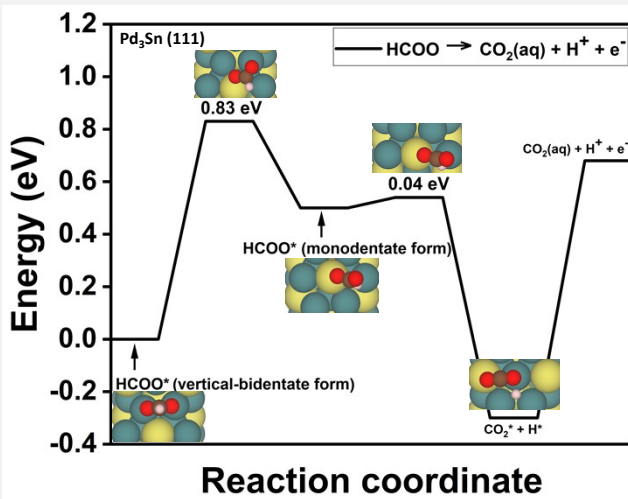




**Fig S3:** Top and side view of the geometry of the TS for water (TS1-TS5), and TS for HCOOH vertical-trans to HCOOH parallel-cis rotation (TS6-TS9) involved in FAO, and TS for the HCOO bidentate to monodentate rotation (TS10-TS11).

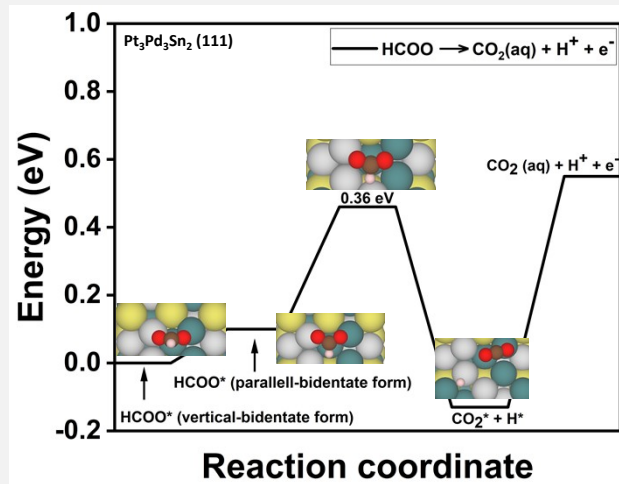


(a)  $\text{HCOOH} \rightarrow \text{HCOO} + \text{H}^+ + \text{e}^-$

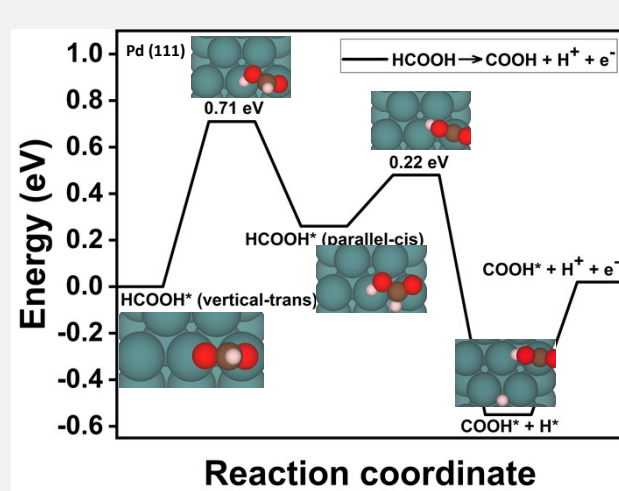
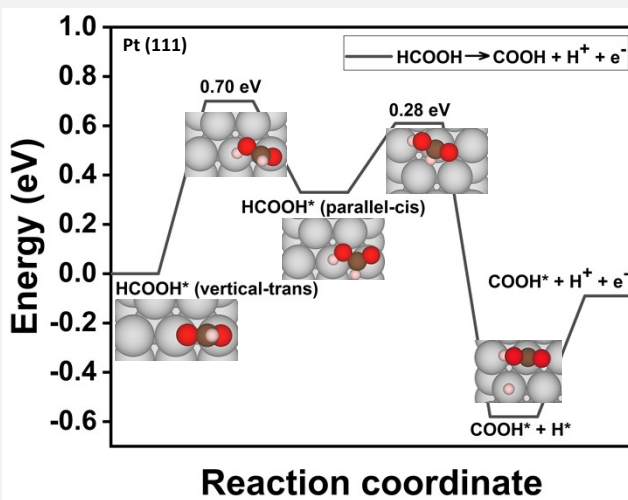


(c)  $\text{HCOO} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^-$

(b)  $\text{HCOO} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^-$



(d)  $\text{HCOO} \rightarrow \text{CO}_2 + \text{H}^+ + \text{e}^-$



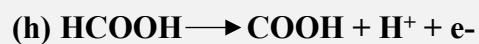
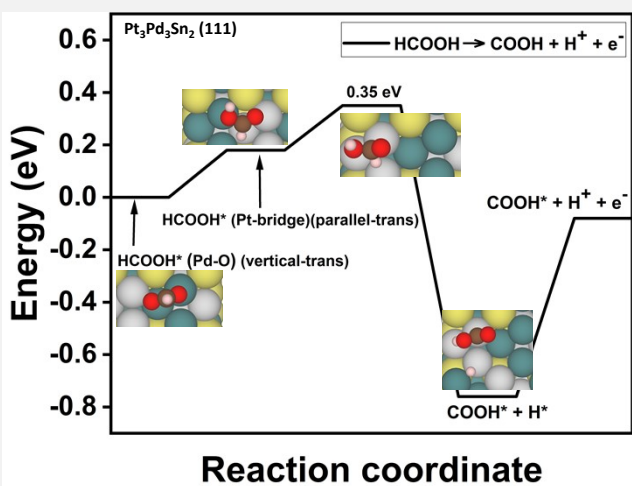
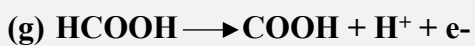
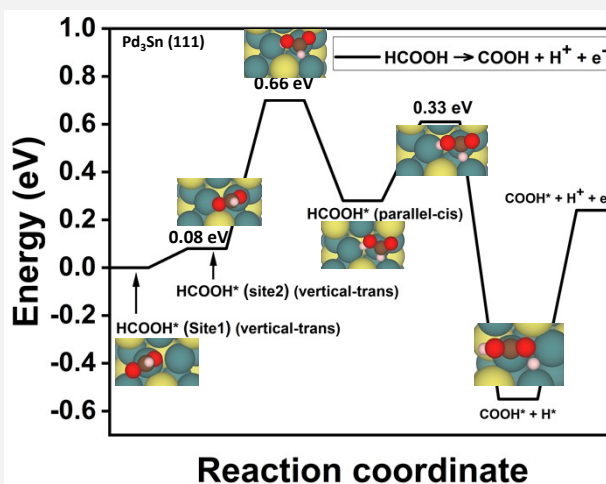
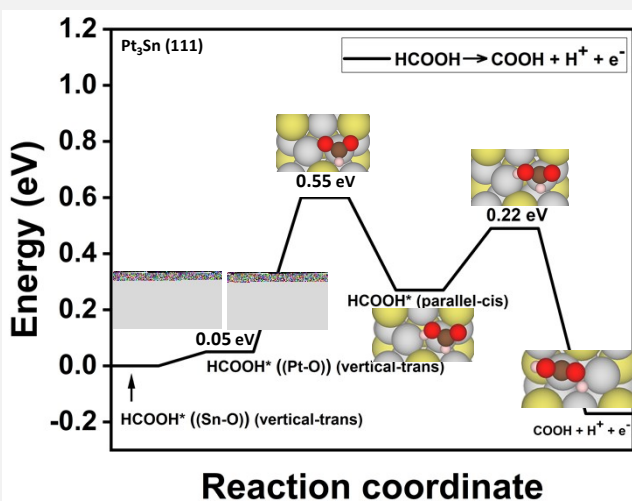
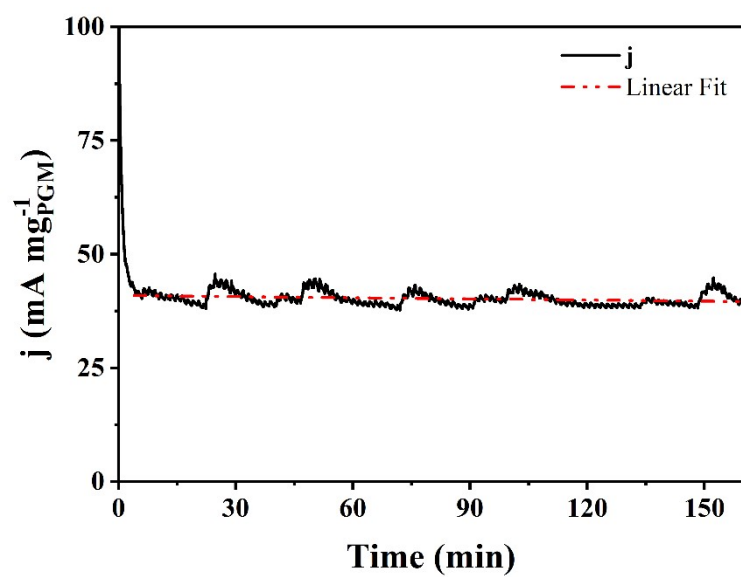


Fig S4: Free energy diagram for reaction involves in two and three-step process.



**Fig. S5.**  $j$  vs.  $t$  plot of FA oxidation at 0.9 V on  $\text{Pt}_3\text{Pd}_3\text{Sn}_2/\text{C}$ . (catalyst loading of  $0.5 \text{ mg cm}^{-2}$ ; electrolyte  $0.5 \text{ M H}_2\text{SO}_4$  containing  $0.5 \text{ M FA}$ )

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