Supplementary Information for

Formic Acid Electrooxidation on Pt or Pd Monolayer on Transition Metal Single-Crystals: A First-Principles Structure Sensitivity Analysis

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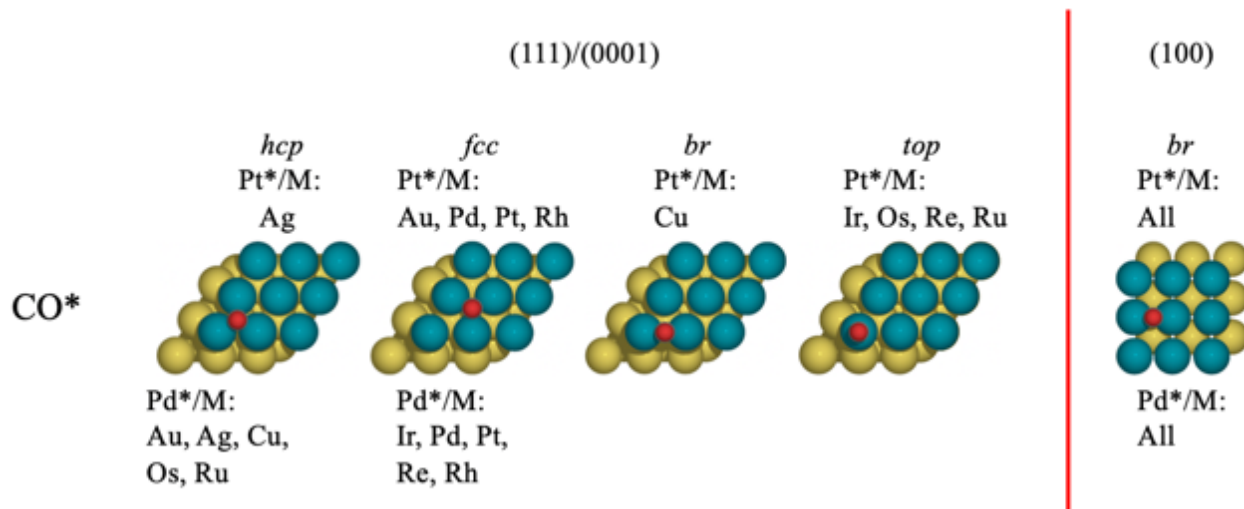
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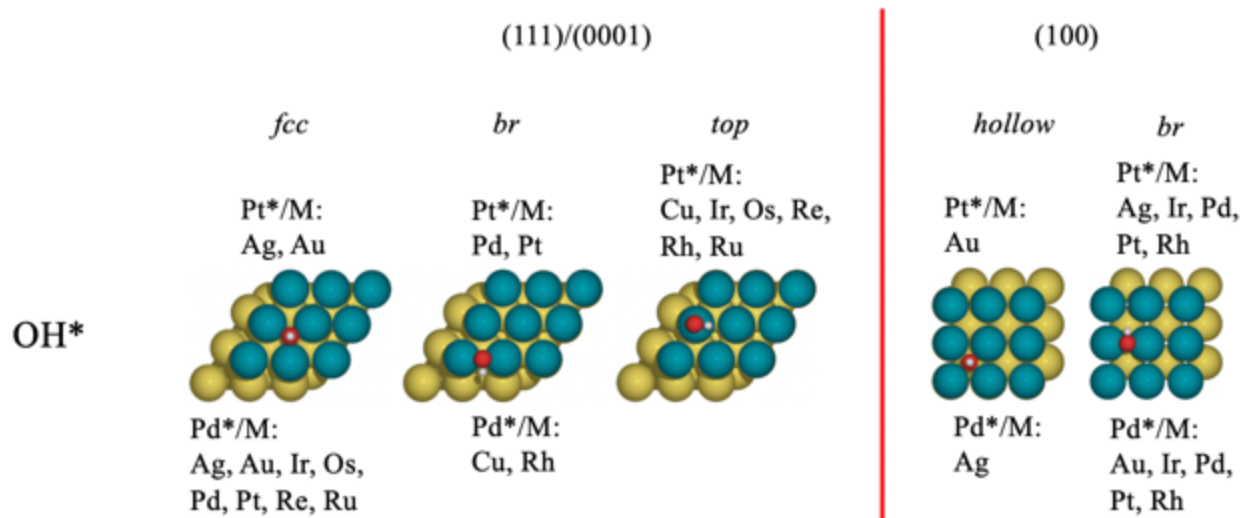[#]Current address: Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza 12613, Egypt

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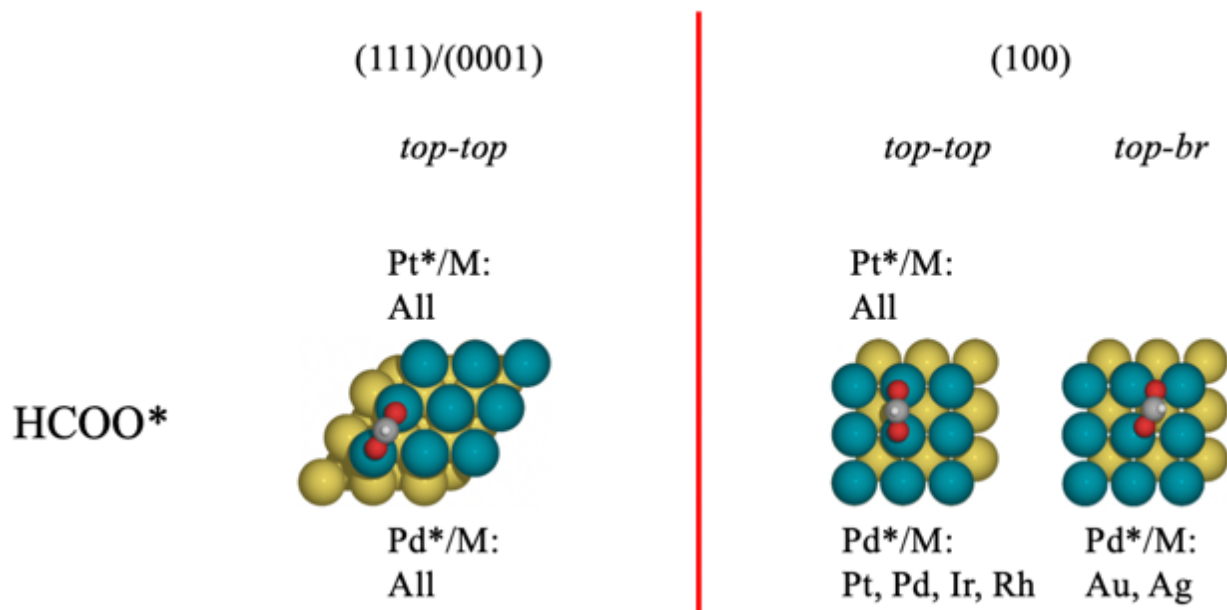
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Figure S1. Top views of preferred adsorption sites and configurations of CO* on a (3×3) unit cell for close-packed and open facets. From the left to the right, the insets depict the adsorption of CO* on the close-packed facets: the first inset represents the *hcp* hollow site, the second inset represents the *fcc* hollow site, the third inset represents the *bridge* site, and the fourth represents the *top* site. The last inset to the right represents CO* adsorption on the open facet. In the insets, the green spheres represent either the Pt or Pd monolayer atoms, while the yellow spheres underneath represent the host transition metal (M), including Pt or Pd. The list of Pt*/M surfaces that subscribe to a given inset is given above the insets, while the list of Pd*/M surfaces that subscribe to a given inset is given below. On the (100) facet, CO* only adsorbs on the bridge site on all surfaces studied. Adsorption sites remain the same on a (2×2) unit cell, with the following exceptions on the close-packed facets: Pt*/Au, Pt, Pt*/Pd, Pd, Pd*/Pt, Pd*/Re, and Pd*/Rh prefer the *hcp* hollow site, while Pt*/Rh prefers the *bridge* site; and the following exceptions for the (100) facet: Pt*/Ir prefers the *top* site.

	(111)/(0001)			(100)	
	fcc	*br*	*top*	*hollow*	*br*
OH*	Pt*/M: Ag, Au	Pt*/M: Pd, Pt	Pt*/M: Cu, Ir, Os, Re, Rh, Ru	Pt*/M: Au	Pt*/M: Ag, Ir, Pd, Pt, Rh
	Pd*/M: Ag, Au, Ir, Os, Pd, Pt, Re, Ru	Pd*/M: Cu, Rh		Pd*/M: Ag	Pd*/M: Au, Ir, Pd, Pt, Rh

Figure S2. Top views of preferred adsorption sites and configurations of OH* on the (3×3) unit cell for close-packed and open facets. From the left to the right, the insets depict the adsorption of OH* on the close-packed facets: the first inset represents the *fcc* hollow site, the second inset represents the *bridge* site, and the third represents the *top* site. The last two insets to the right represent OH* adsorption on the open facet on the *hollow* and *bridge* sites (left and right, respectively). In the insets, the green spheres represent either the Pt or Pd monolayer atoms, while the yellow spheres underneath represent the host transition metal (M), including Pt or Pd. The list of Pt*/M surfaces that subscribe to a given inset is given above the insets, while the list of Pd*/M surfaces that subscribe to a given inset is given below. Adsorption sites remain the same for the (2×2) unit cell, with the following exceptions on the close-packed facets: Pt*/Ag, Pt*/Au, Pd*/Ir, Pd*/Os, Pd, Pd*/Ru prefer the *bridge* site; and the following exceptions for the (100) facet: Pt*/Au prefers the *bridge* site.
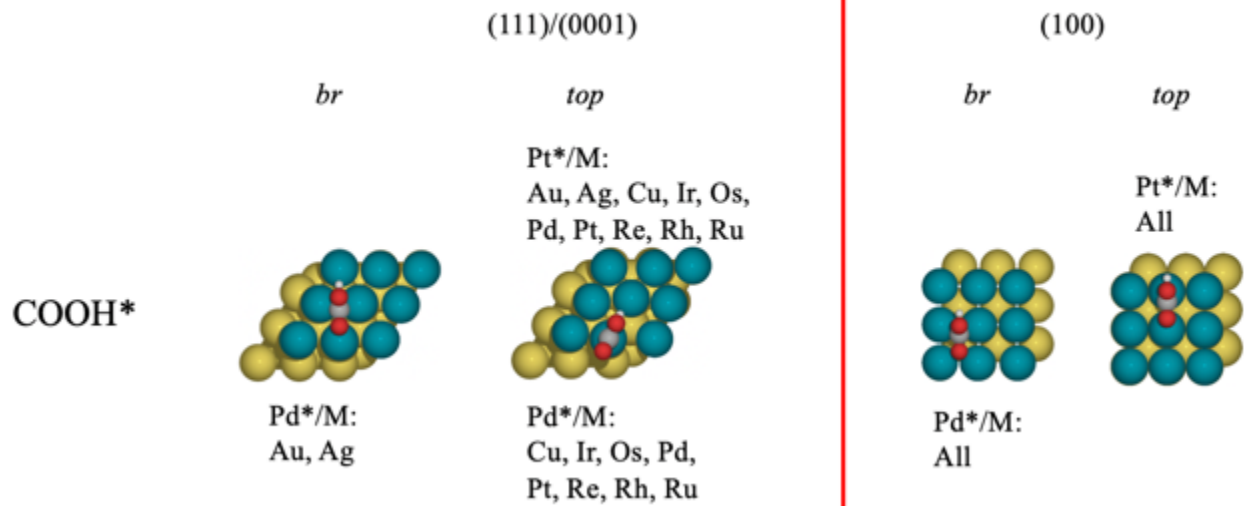
Figure S3. Top views of preferred adsorption sites and configurations of COOH* on the (3×3) unit cell for close-packed and open facets. From the left to the right, the insets depict the adsorption of COOH* on the close-packed facets: the first inset represents the *bridge* site, and the second represents the *top* site. The last two insets to the right represent COOH* adsorption on the open facet on the *bridge* and *top* sites (left and right, respectively). The site type refers to the site to where the carbon atom of COOH* binds. In the insets, the blue spheres represent either the Pt or Pd monolayer, while the yellow spheres underneath represent the host transition metal (M), including Pt or Pd. The list of Pt*/M surfaces that subscribe to a given inset is given above the insets, while the list of Pd*/M surfaces that subscribe to a given inset is given below. Adsorption sites remain the same for the (2×2) unit cell, with the following exceptions on the (100) facet: Pd*/Ir and Pd*/Rh prefer the *top* site, while Pt*/Ag prefers the *bridge* site.

Figure S4. Top views of preferred adsorption sites and configurations of HCOO* on the (3×3) unit cell for close-packed and open facets. From the left to the right, the insets depict the adsorption of HCOO* on the close-packed facets: the only inset represents the bidentate *top-top* adsorption structure. The last two insets to the right represent HCOO* adsorption on the open facet on the *top-top* and *top-bridge* sites (left and right, respectively). The site type refers to the site to where both oxygen atoms of HCOO* bind. In the insets, the blue spheres represent either the Pt or Pd monolayer, while the yellow spheres underneath represent the host transition metal (M), including Pt or Pd. The list of Pt*/M surfaces that subscribe to a given inset is given above the insets, while the list of Pd*/M surfaces that subscribe to a given inset is given below. On the close-packed facet, HCOO* only adsorbs as bidentate on a *top-top* configuration on all surfaces studied. Adsorption sites remain the same for the (2×2) unit cell, with the following exceptions on the (100) facet: Pd*/Ag prefers a *bridge-bridge* site.

Table S1. Free energies of key intermediates relative to HCOOH(g) at 0.00 V when adsorbed on close-packed and open facets of Pt*/M at 1/4 ML coverage of species on a (2×2) unit cell. For CO*+OH* and CO*+H₂O(g), energies are given at infinite separation between the involved species. For COOH*, HCOO*, and CO*+OH*, stoichiometry is balanced with protons and electrons, which are not written explicitly here. For each metal facet, among all isomeric intermediates, the most stable isomer is indicated with a bold entry. The close-packed facet for the hcp metals Os, Ru, and Re is (0001); no open facet was studied for these metals (entry --). Additionally, Pt*/Cu(100) is not included in this trends study (entry --).The entry for Pt represents pure monometallic Pt surfaces. Surfaces are arranged from weaker to stronger stabilization of the state CO*+H₂O(g) on the close-packed facets. The final state of $CO_2(g)+2(H^++e^-)$ is surface-independent, and is calculated to be -0.26 eV relative to HCOOH(g) at 0.00 V.

| Pt*/M	Free energy (eV) relative to HCOOH(g) at 0.00 V							
M	COOH*		HCOO*		CO*+OH*		CO*+H₂O(g)	
	(111/0001)	(100)	(111/0001)	(100)	(111/0001)	(100)	(111/0001)	(100)
Cu	0.63	--	1.40	--	1.84	--	**-0.17**	--
Ru	0.50	--	0.77	--	1.24	--	**-0.37**	--
Os	0.42	--	0.62	--	1.01	--	**-0.48**	--
Rh	0.38	0.09	0.78	0.50	1.02	0.00	**-0.58**	**-1.01**
Ir	0.35	0.10	0.63	0.29	0.87	0.07	**-0.63**	**-0.92**
Re	0.21	--	0.01	--	0.36	--	**-0.71**	--
Pt	0.04	-0.23	0.38	0.31	0.14	-0.59	**-1.11**	**-1.35**
Pd	0.09	-0.25	0.51	0.33	0.17	-0.69	**-1.19**	**-1.43**
Ag	0.35	-0.33	0.92	0.45	0.24	-1.19	**-1.19**	**-1.62**
Au	0.04	-0.42	0.52	0.25	-0.29	-1.32	**-1.47**	**-1.71**

Table S2. Free energies of key intermediates relative to HCOOH(g) at 0.00 V when adsorbed on close-packed and open facets of Pd*/M at 1/4 ML coverage of species on a (2×2) unit cell. For CO*+OH* and CO*+H2O(g), energies are given at infinite separation between the involved species. For COOH*, HCOO*, and CO*+OH*, stoichiometry is balanced with protons and electrons, which are not written explicitly here. For each metal facet, among all isomeric intermediates, the most stable isomer is indicated with a bold entry. The close-packed facet for the hcp metals Os, Ru, and Re is (0001); no open facet was studied for these metals (entry --). Additionally, Pd*/Cu(100) is not included in this trends study (entry --).The entry for Pd represents pure monometallic Pd surfaces. Surfaces are arranged from weaker to stronger stabilization of the state CO*+H2O(g) on the close-packed facets. The final state of $CO_2(g)+2(H^++e^-)$ is surface-independent, and is calculated to be -0.26 eV relative to HCOOH(g) at 0.00 V.

| Pd*/M	Free energy (eV) relative to HCOOH(g) at 0.00 V							
M	COOH*		HCOO*		CO*+OH*		CO*+H$_2$O(g)	
	(111/0001)	(100)	(111/0001)	(100)	(111/0001)	(100)	(111/0001)	(100)
Cu	0.70	--	1.02	--	1.12	--	**-0.53**	--
Ru	0.57	--	0.52	--	0.59	--	**-0.68**	--
Re	0.33	--	-0.08	--	0.12	--	**-0.68**	--
Os	0.52	--	0.40	--	0.48	--	**-0.69**	--
Rh	0.48	0.35	0.52	0.37	0.41	0.15	**-0.87**	**-0.83**
Ir	0.39	0.39	0.33	0.31	0.22	0.21	**-0.91**	**-0.75**
Pt	0.17	0.12	0.23	0.29	-0.28	-0.21	**-1.27**	**1.08**
Pd	0.18	0.01	0.33	0.29	-0.29	-0.36	**-1.37**	**-1.20**
Ag	0.32	0.03	0.56	0.30	-0.44	-0.38	**-1.45**	**-1.20**
Au	0.14	-0.02	0.32	0.26	-0.62	-0.39	**-1.52**	**-1.26**
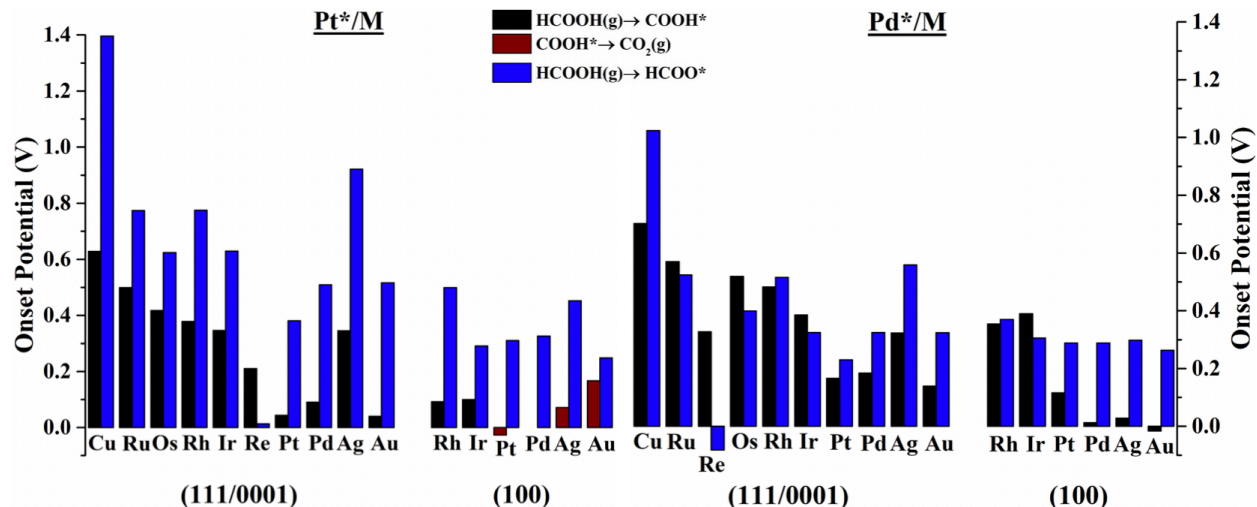
Figure S5. Onset potentials for both direct mechanisms on the close-packed and open facets of Pt*/M (left panel) and Pd*/M (right panel), as calculated on the (2×2) unit cell. For each surface, the left bar represents the onset potential for the direct oxidation via the carboxyl mechanism, while the right bar represents the onset potential for the direct oxidation via the formate mechanism. Negative onset potentials indicate spontaneous paths at 0.00 V. Bars are colored according to the potential determining step (PDS) as represented by the legend. For each elementary step listed in the legend, stoichiometry is implicitly balanced with protons and electrons. Surfaces are arranged from left to right according to their stabilization of CO*, from weaker to stronger, as they appear in Table S1 and Table S2. The entries for Pt in the left panel represent the monometallic Pt surfaces, and the entries for Pd in the right panel represent the monometallic Pd surfaces.
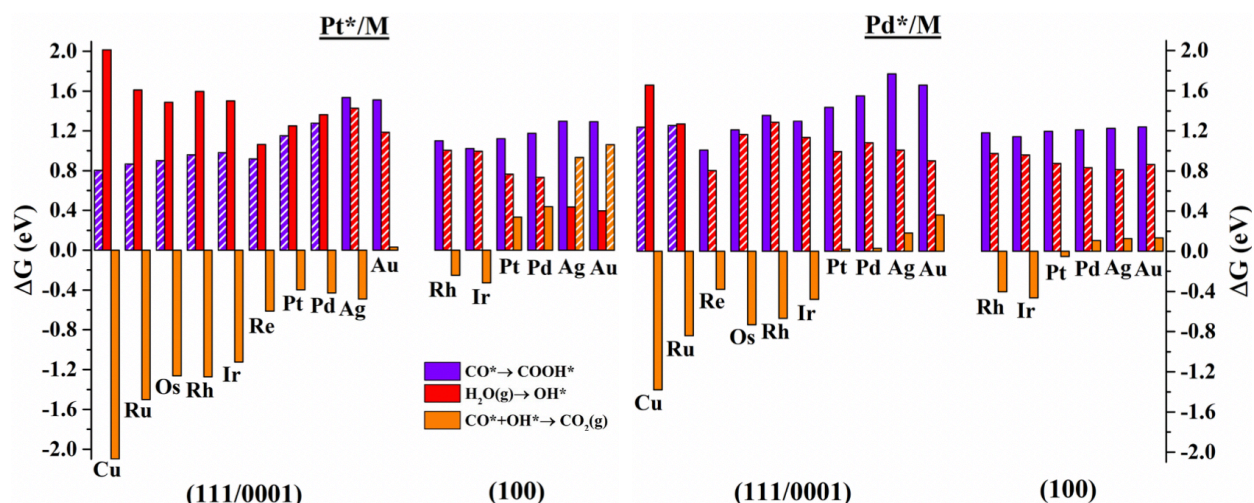
Figure S6. Free energy change of elementary steps involved in CO* removal on the close-packed and open facets of Pt*/M (left panel) and Pd*/M (right panel), as calculated on the (2×2) unit cell. Violet corresponds to formation of COOH* from CO*, red corresponds to water activation to form OH*, and orange corresponds to CO* oxidation to CO_2(g) via OH*. For each surface, the hatched bar represents the potential determining step (PDS) for the indirect mechanism. For each elementary step listed in the legend, stoichiometry is implicitly balanced with water, protons and electrons. Surfaces are arranged from left to right according to their stabilization of CO*, from weaker to stronger, as they appear in Table S1 and Table S2. The entries for Pt in the left panel represent the monometallic Pt surfaces, and the entries for Pd in the right panel represent the monometallic Pd surfaces.
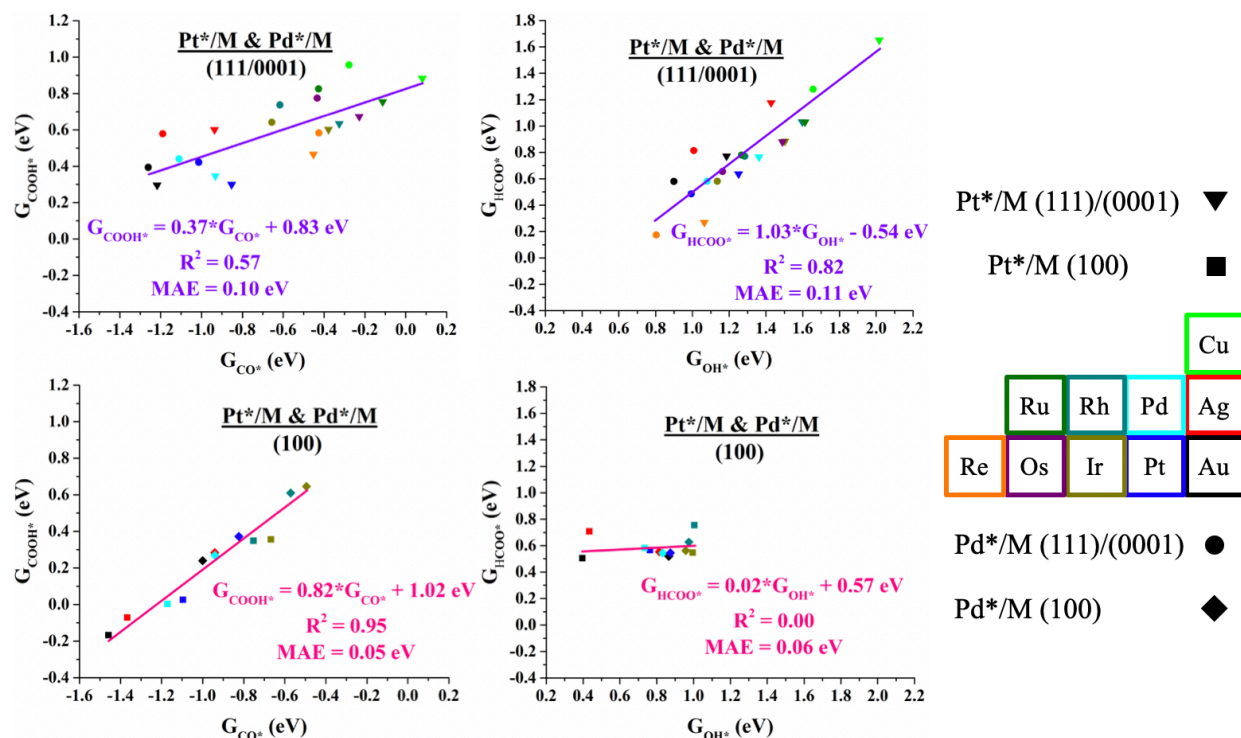
Figure S7. Scaling relations for the free energy of CO* (G_{CO*}) and the free energy of COOH* (G_{COOH*}) (left panel), and the free energy of OH* (G_{OH*}) and the free energy of HCOO* (G_{HCOO*}) (right panel) adsorbed on Pt*/M and Pd*/M for the close-packed (violet lines in top two correlations) and open facets (pink lines in bottom two correlations), as calculated at 1/4 ML coverage on the (2×2) unit cell. All free energies are calculated relative to the free energies of gas-phase CO_2, H_2, and H_2O. Below each correlation are the r-squared value (R^2) and the mean absolute error (in eV). Notice that both correlations are not drawn to the same scale. Close-packed Pt*/M surfaces are represented by inverted triangles, open Pt*/M facets are represented by squares, close-packed Pd*/M surfaces are represented by circles, and open Pd*/M surfaces are represented by diamonds. The colors of these symbols follow the colors of the boxes surrounding the elements, arranged as they appear in the periodic table.

Table S3. Parameters for the scaling relations (as calculated on the (3×3) unit cell) of G_{CO*} versus G_{COOH*}, and G_{OH*} versus G_{HCOO*} on the close-packed facets of, separately, Pt*/M and Pd*/M, and the open facets of, separately, Pt*/M and Pd*/M.

		Slope	Intercept (eV)	R^2	MAE (eV)
Pt*/M (111/0001)	G_{CO*} vs G_{COOH*}	0.43	0.86	0.74	0.07
	G_{OH*} vs G_{HCOO*}	0.53	0.16	0.28	0.21
Pd*/M (111/0001)	G_{CO*} vs G_{COOH*}	0.51	1.09	0.77	0.08
	G_{OH*} vs G_{HCOO*}	0.79	-0.25	0.63	0.12
Pt*/M (100)	G_{CO*} vs G_{COOH*}	1.08	1.22	0.93	0.08
	G_{OH*} vs G_{HCOO*}	0.70	0.02	0.96	0.05
Pd*/M (100)	G_{CO*} vs G_{COOH*}	0.97	1.21	0.99	0.02
	G_{OH*} vs G_{HCOO*}	0.13	0.40	0.05	0.03

Figure S8. Calculated phase diagrams for FAO on close-packed facets at 0.0 V and at 0.6 V, and open facets at 0.0 V and at 0.6 V of Pt*/M and Pd*/M, as calculated at 1/4 ML coverage on the (2×2) unit cell. Linear scaling relations of Figure S7 were used to construct this diagram. The free energy of the most endergonic step is signified by the color code explained in the right hand side bar. The pink lines divide the phase space into regions by the nature of the most endergonic step. Surfaces are scattered on the phase space (inverted triangles for close-packed facets of Pt*/M, squares for open facets of Pt*/M, circles for close-packed facets of Pd*/M, and diamonds for open facets of Pd*/M; the colors of these symbols follow the colors of the boxes surrounding the elements, arranged as they appear in the periodic table) according to their values of the reactivity descriptors, as calculated with DFT. Because of the approximate nature of the underlying scaling relations, the rigorously calculated ΔG_{RDS} for specific surfaces (see Table S1 and Table S2) could differ from what is shown here.