Electronic Binding Energies and Scaling Relations for FCC Transition Metals

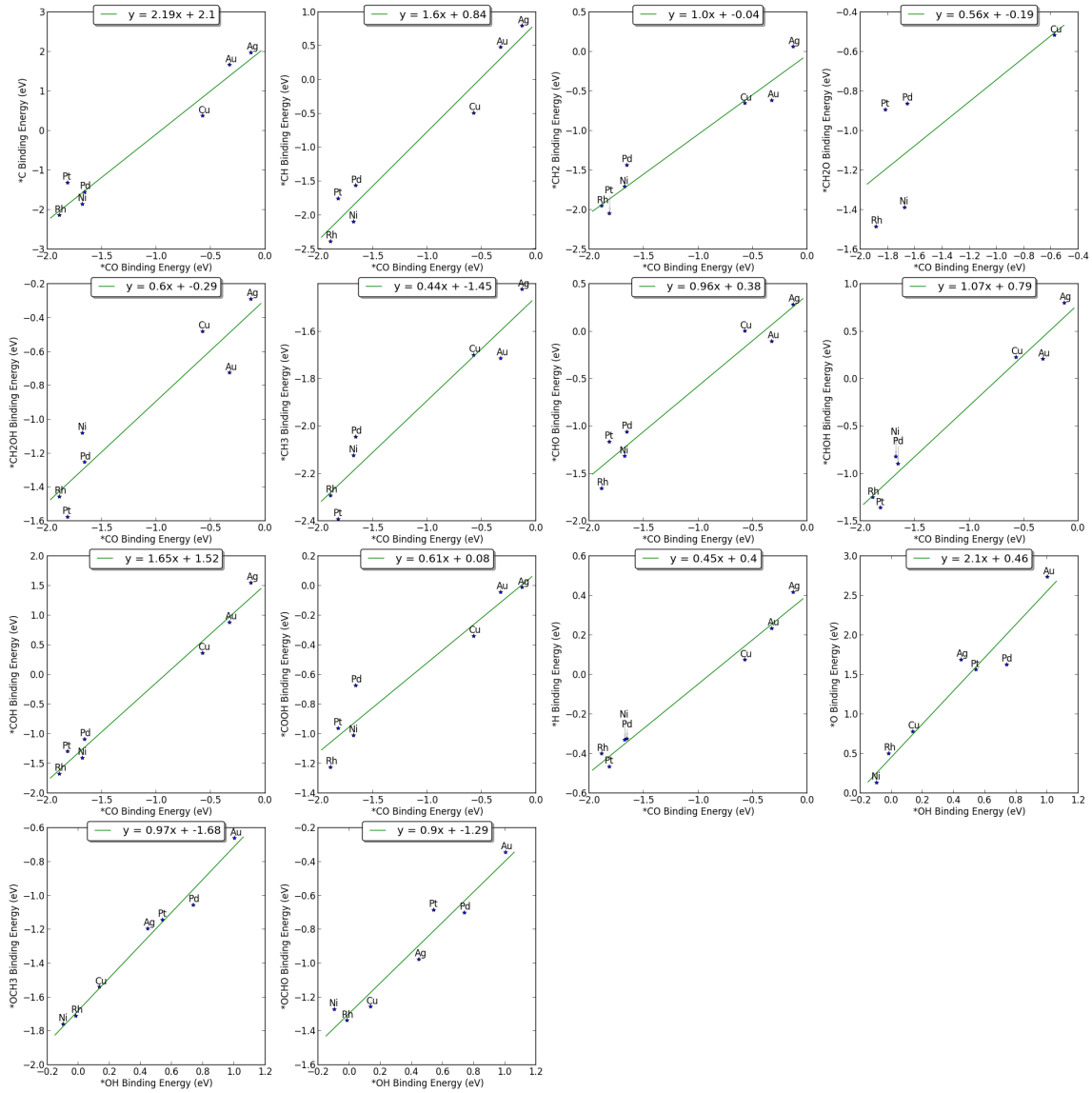


Figure S1. *Scaling relations for CO2RR intermediates on FCC(100) transition metal facets.*

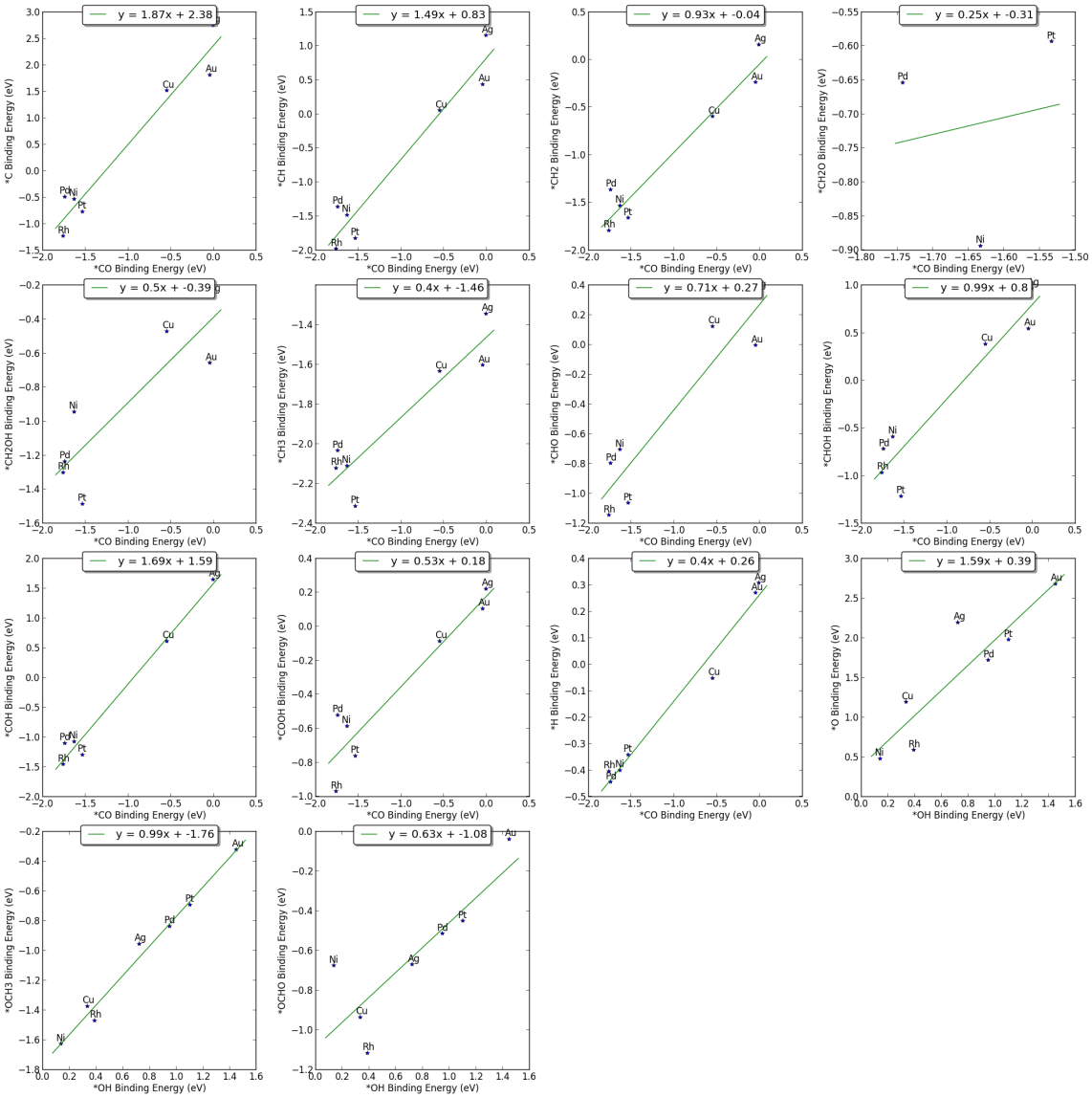


Figure S2. *Scaling relations for CO2RR intermediates on FCC(111) transition metal facets.*

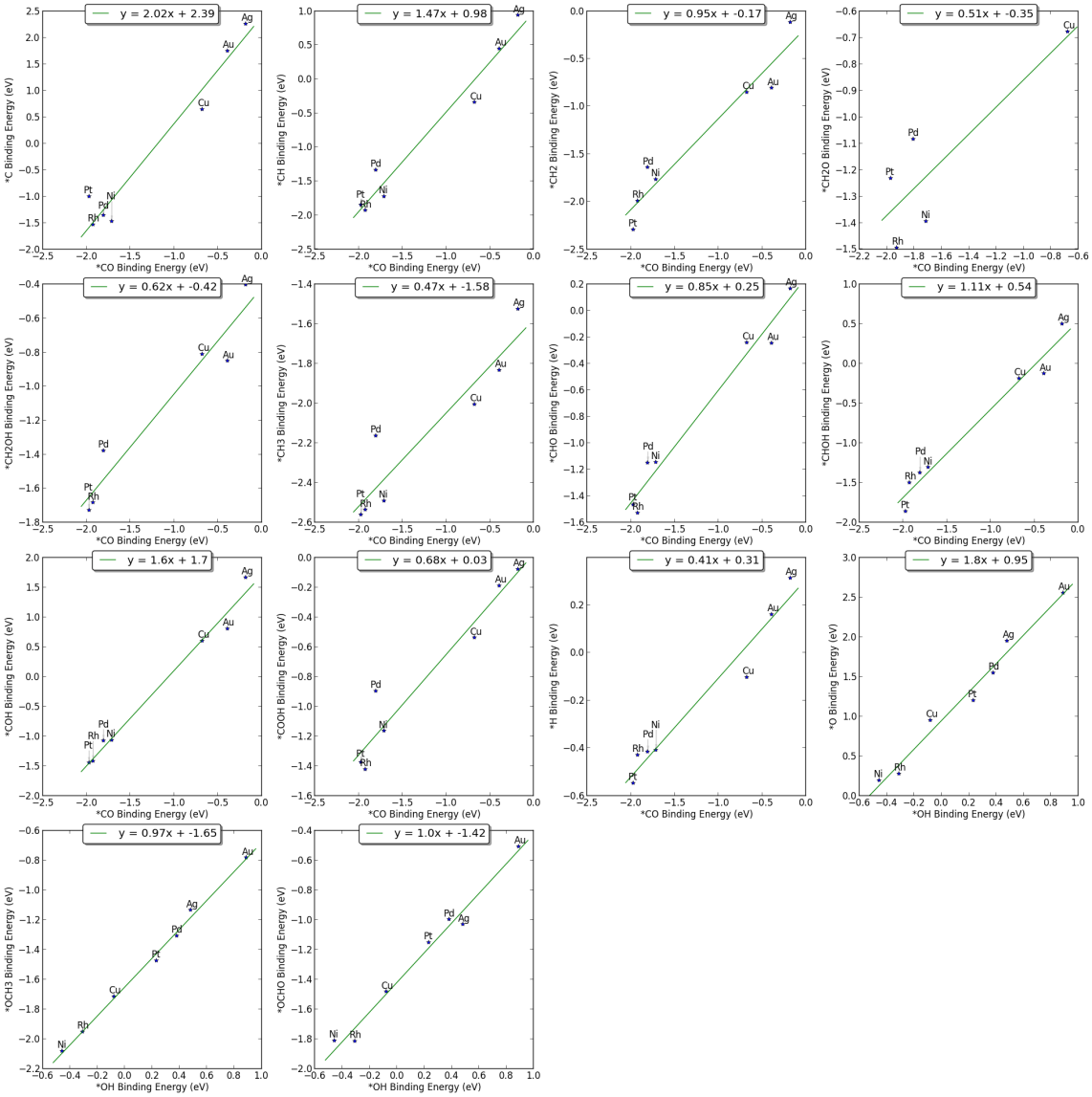


Figure S3. *Scaling relations for CO2RR intermediates on FCC(211) transition metal facets.*

In Figures S1, S2, and S3, scaling relations for the electronic binding energies of 14 CO2RR intermediates are plotted against the electronic binding energies of *CO or *OH. Calculations for the (211) facet use data from the same underlying calculations as Peterson et al. (2012)[1], but numbers are reported to give a consistent reference. All electronic binding energies are referenced to formation energies based on calculations of gas phase CO, H_2O, and H_2.

Details of Binding Energies on *CO covered Pt(111)

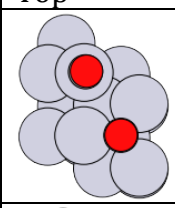
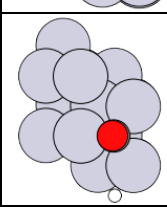
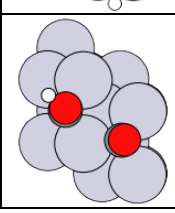
Calculations for binding energies of *CHO, *COH, *COOH, and *H on *CO-covered Pt(111) surface used different calculation parameters and methodology (minima hopping) than the low coverage binding energies. We summarize the calculation parameters in the table below:

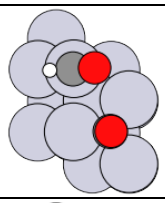
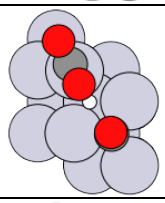
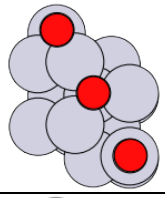
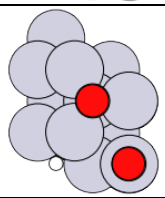
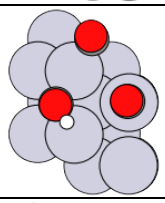
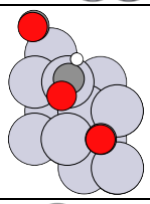
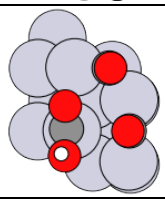
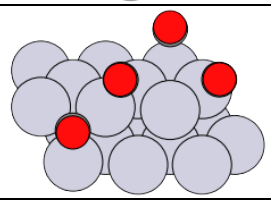
Slab Size	# of *CO Initially	Initial Coverage of *CO	Coverage of Adsorbates	*k*-points
2×2	0	0	0.125	6×6×1
2×2	1	0.25	0.375	6×6×1
2×2	2	0.5	0.625	6×6×1
3×2	4	0.67	0.75	4×6×1

Table S1. *Table of calculation parameters for high *CO coverage calculations on Pt(111).*

It is important to note that in Figure 1 of the main text, the green triangles are labeled with coverages corresponding to the "Coverage of Adsorbates" column in Table S1. In Figure 3 of the main text, the plot titles of "*CO Coverage" correspond to the "Initial Coverage of *CO" in Table S1. We find that this methodology reports a more relevant and realistic coverage that is consistent within a given figure.

For each coverage and for each adsorbate (including the no additional adsorbate case), a global optimization method[2,3] was employed (minima hopping at 2000K initial temperature and 25 iterations) to find the global minimum. The minimum binding energy configurations, and binding energies are detailed below.

Slab Size	# of *CO initially	Additional Adsorbate	Electronic Binding Energy (eV)	Configuration
2×2	0	CO	-1.48	Hollow
2×2	0	H	-0.32	Hollow
2×2	0	COH	-1.30	Hollow
2×2	0	CHO	-1.06	Top
2×2	0	COOH	-0.76	Top
2×2	1	CO	-1.17	
2×2	1	H	-0.11	
2×2	1	COH	-0.86	

2×2	1	CHO	-0.83	
2×2	1	COOH	-0.25	
2×2	2	CO	-0.85	
2×2	2	H	-0.06	
2×2	2	COH	-0.57	
2×2	2	CHO	-0.39	
2×2	2	COOH	0.42	
3×2	4	none	0.00	

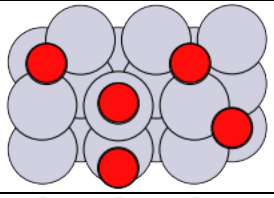
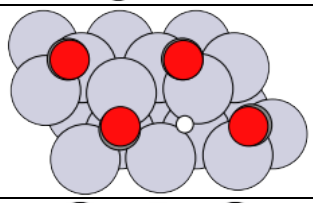
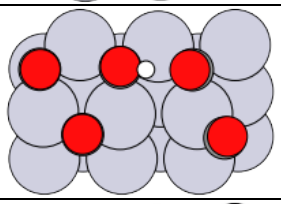
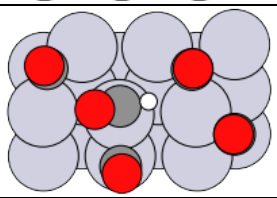
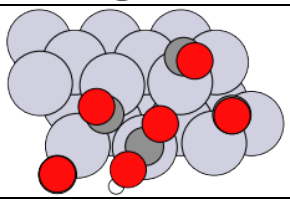
3×2	4	CO	1.06	
3×2	4	H	0.47	
3×2	4	COH	1.11	
3×2	4	CHO	0.98	
3×2	4	COOH	1.37	

Table S2. *Table of electronic binding energies and minimum energy configurations for key adsorbates on *CO-covered Pt(111).*

Free Energy Diagrams for CO_2 Reduction on FCC(111) Surfaces

Below, we plot free energy diagrams for the CO2RR to single-carbon products on fcc(111) transition metal surfaces. Adsorbed *CH_2O is not stable on many of these surfaces, and gas phase "CH_2O" is used to denote surfaces for which this is the case. These diagrams show some likely paths for the CO2RR on these surfaces, but they are not representative of every possible reaction pathway that can reach these products. For example, *CHOH shown below comes from a proton-electron transfer to the C-end of *COH, but it can also be made from a proton-electron transfer to the O-end of *CHO.

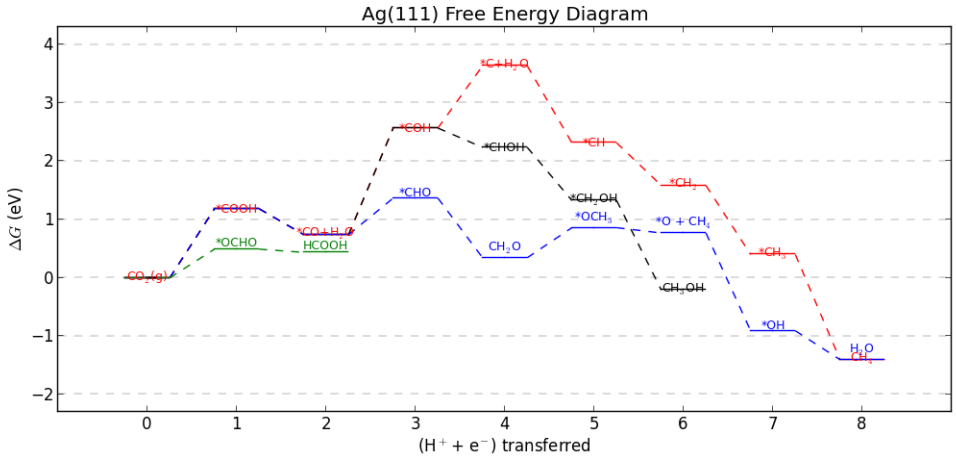


Figure S4. *Free energy diagram for the CO2RR to single-carbon products on Ag(111)*

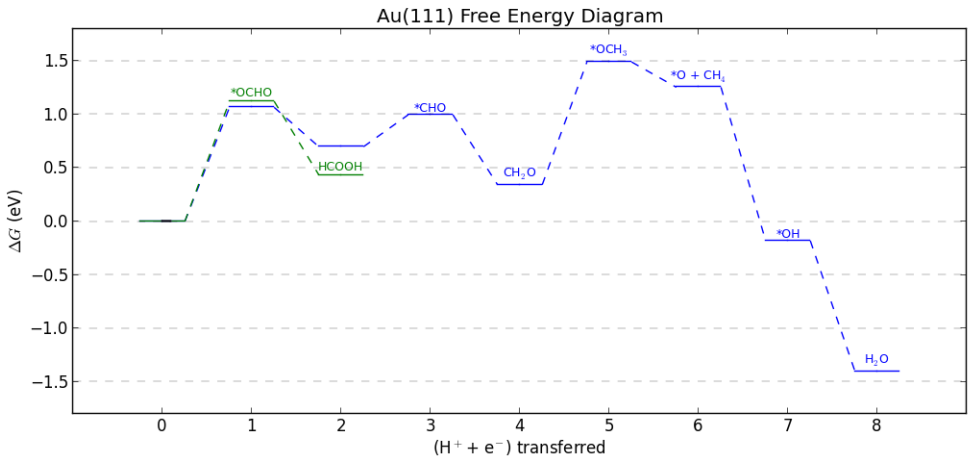


Figure S5. *Free energy diagram for the CO2RR to single-carbon products on Au(111). Pathways involving *COH are inaccessible due to the instability of *COH on Au(111), which is calculated to spontaneously dissociate into *CO and *H.*

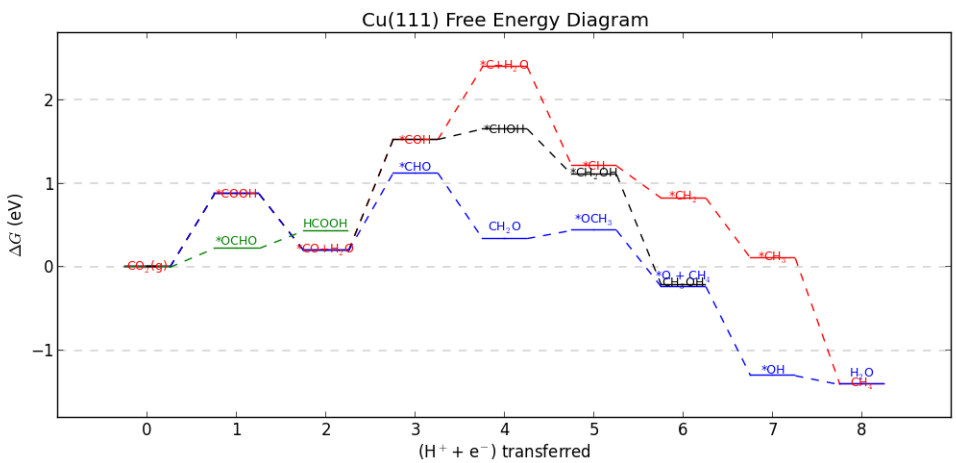


Figure S6. *Free energy diagram for the CO2RR to single-carbon products on Cu(111)*

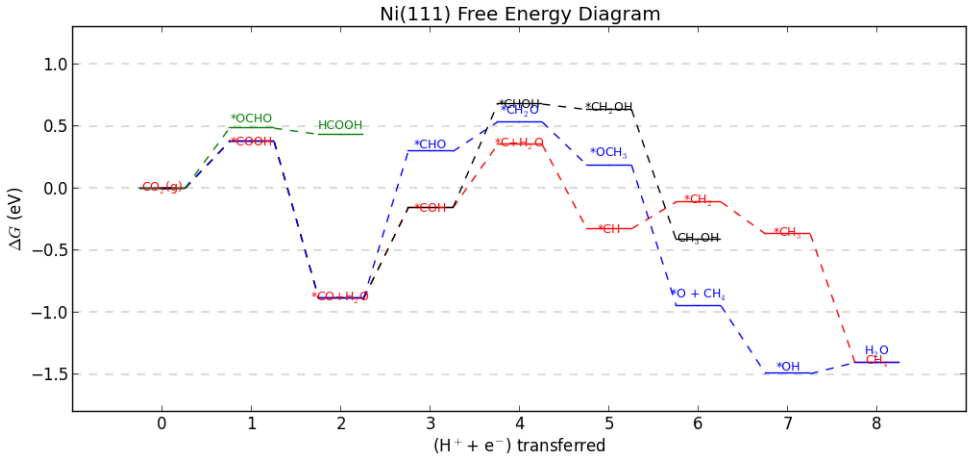


Figure S7. *Free energy diagram for the CO2RR to single-carbon products on Ni(111)*

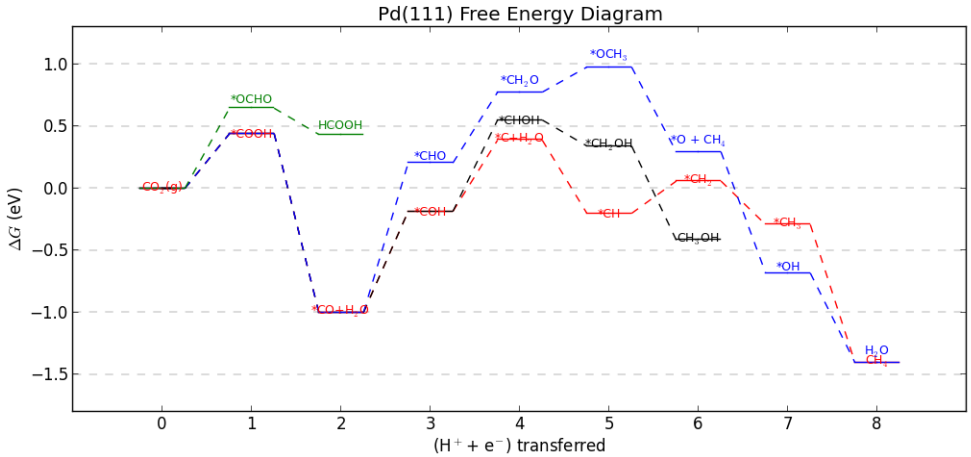


Figure S8. *Free energy diagram for the CO2RR to single-carbon products on Pd(111)*

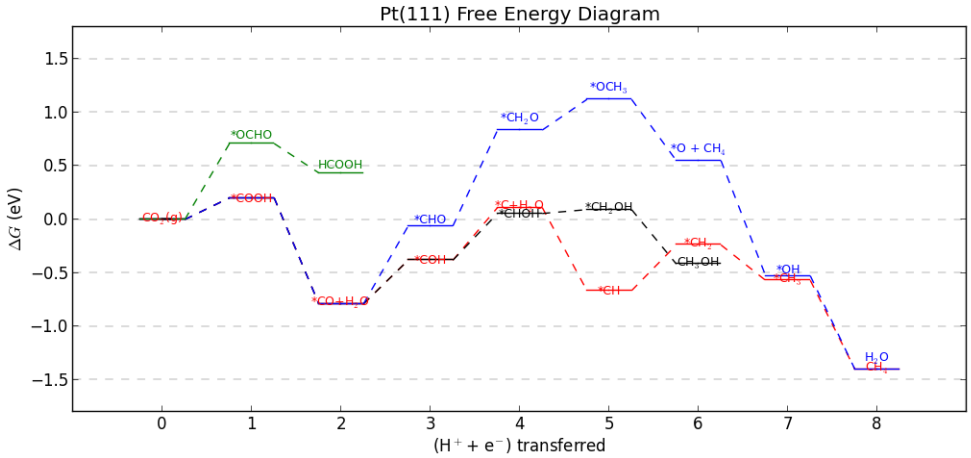


Figure S9. *Free energy diagram for the CO2RR to single-carbon products on Pt(111)*

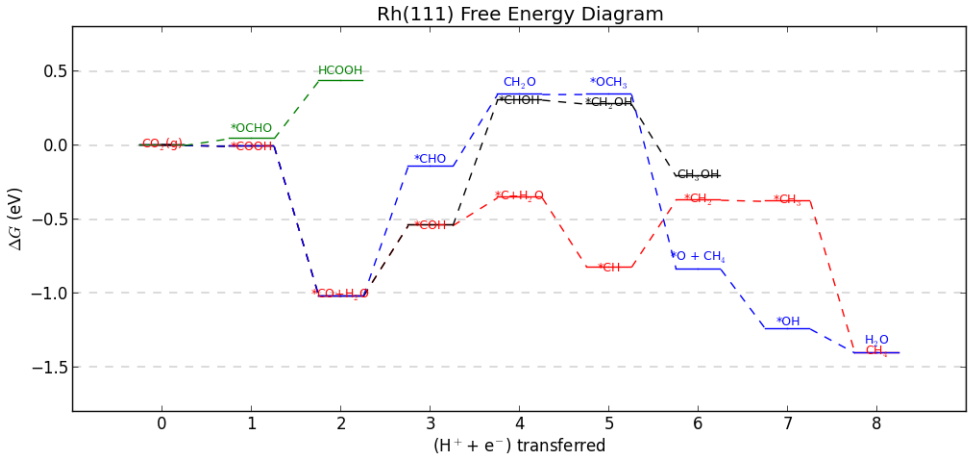


Figure S10. *Free energy diagram for the CO2RR to single-carbon products on Rh(111)*

Full CO2RR Activity Maps

For clarity, the activity maps in Figure 4 in the main paper only show elementary steps for CO2RR that are potential-limiting at some *CO binding energy. The full activity map including all steps are shown in Figure S11.

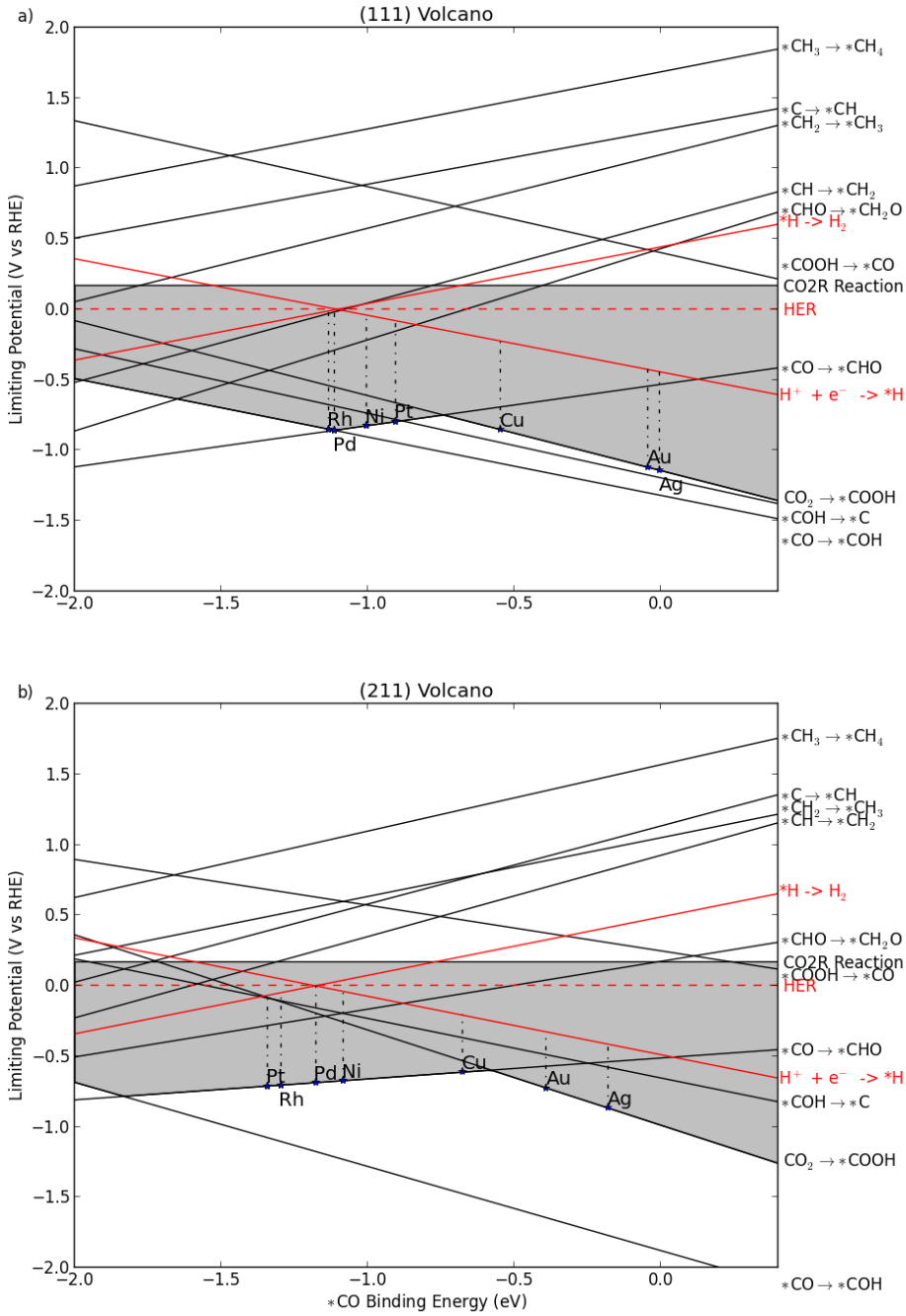


Figure S11. *Full CO2RR activity maps for the (111) and (211) facets of various fcc transition metals. Between *CO binding energies of -2.0 eV and 0.5 eV on both facets, only three steps are ever potential-limiting.*

Including Adsorbate-Adsorbate Effects in Scaling Relations

As mentioned in the main text, at high *CO coverage, the binding energy of *COOH and *COH deviate from the scaling relation by a somewhat significant amount – at 0.625ML coverage, *COOH binding is weaker than the scaling would suggest by 0.39 eV and *COH binding is stronger than the scaling would suggest by 0.51 eV. We can incorporate these deviations by allowing the scaling relation themselves to shift according to the deviation (*COOH becomes less stable relative to *CO and *COH becomes more stable relative to *CO). The result of this shift is shown in the activity map below:

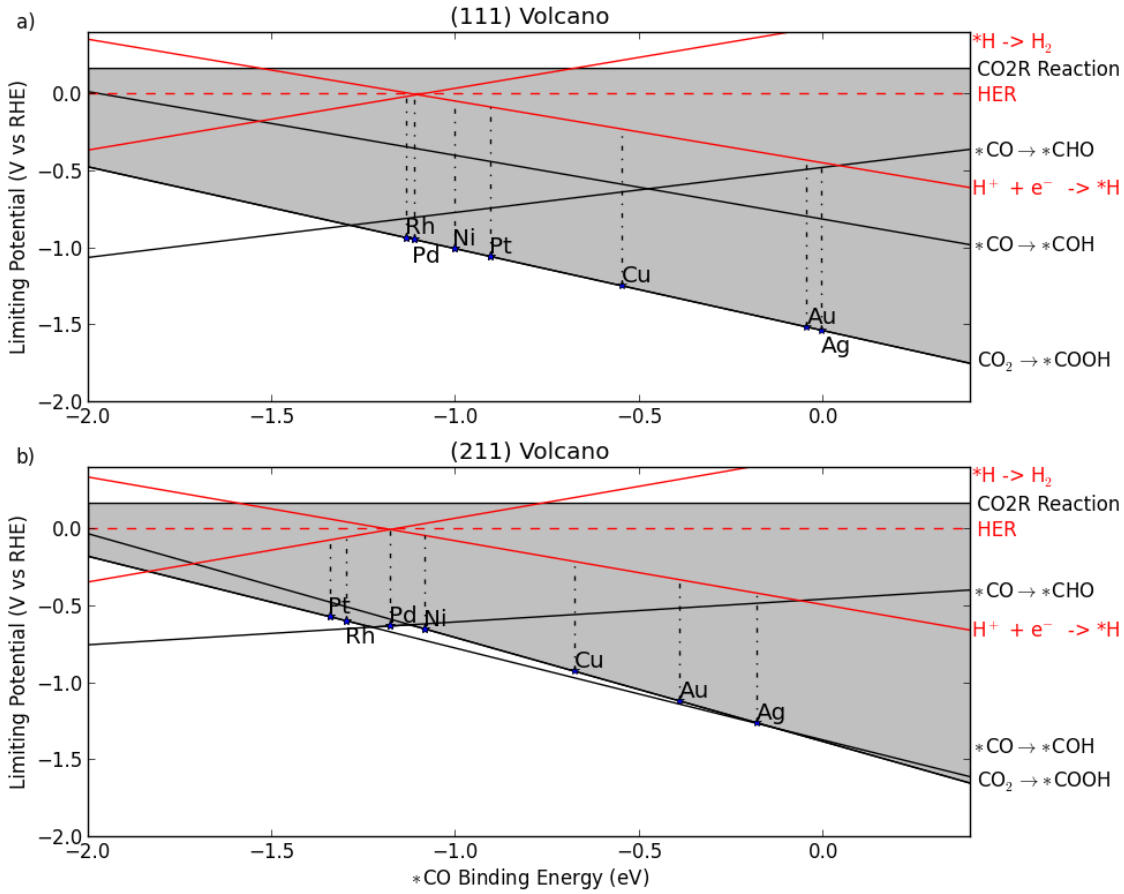


Figure S12. *CO2RR activity maps for the (111) and (211) facets of various fcc transition metals incorporating deviations from linear scaling at high *CO coverage for *COOH and *COH.*

The first point to notice about Figure S12 is that Cu, Au, and Ag do not bind *CO strongly enough to obtain this high coverage, so it is unlikely they would most likely follow the activity maps shown by Figure 4. Secondly, for the (111) facet at high *CO coverage, CO_2 activation appears to be much more difficult than *CO activation to *COH. A coverage of *CO that would effect this significant of a shift would be unlikely to exist at steady state due to the difficulty of replenishing *CO from the CO_2

activation step being so heavily punished at high *CO coverage. The true picture for the CO2RR on these strong-binding terraces lies somewhere between the extremes painted by Figure 4 and Figure S12. Limiting potentials for the (211) facets of Pt, Ni, Pd, and Rh do not change significantly.

References

1. A. A. Peterson and J. K. Nørskov, *J. Phys. Chem. Lett.*, 2012, **3**, 251–258.

2. A. A. Peterson, *Top. Catal.*, 2013.

3. S. Goedecker, *J. Chem. Phys.*, 2004, **120**, 9911–7.