Supplementary Information for:

Theoretical insight on reactivity trends in CO_2 electroreduction across transition metals

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1. Optimized configuration of solvated intermediates

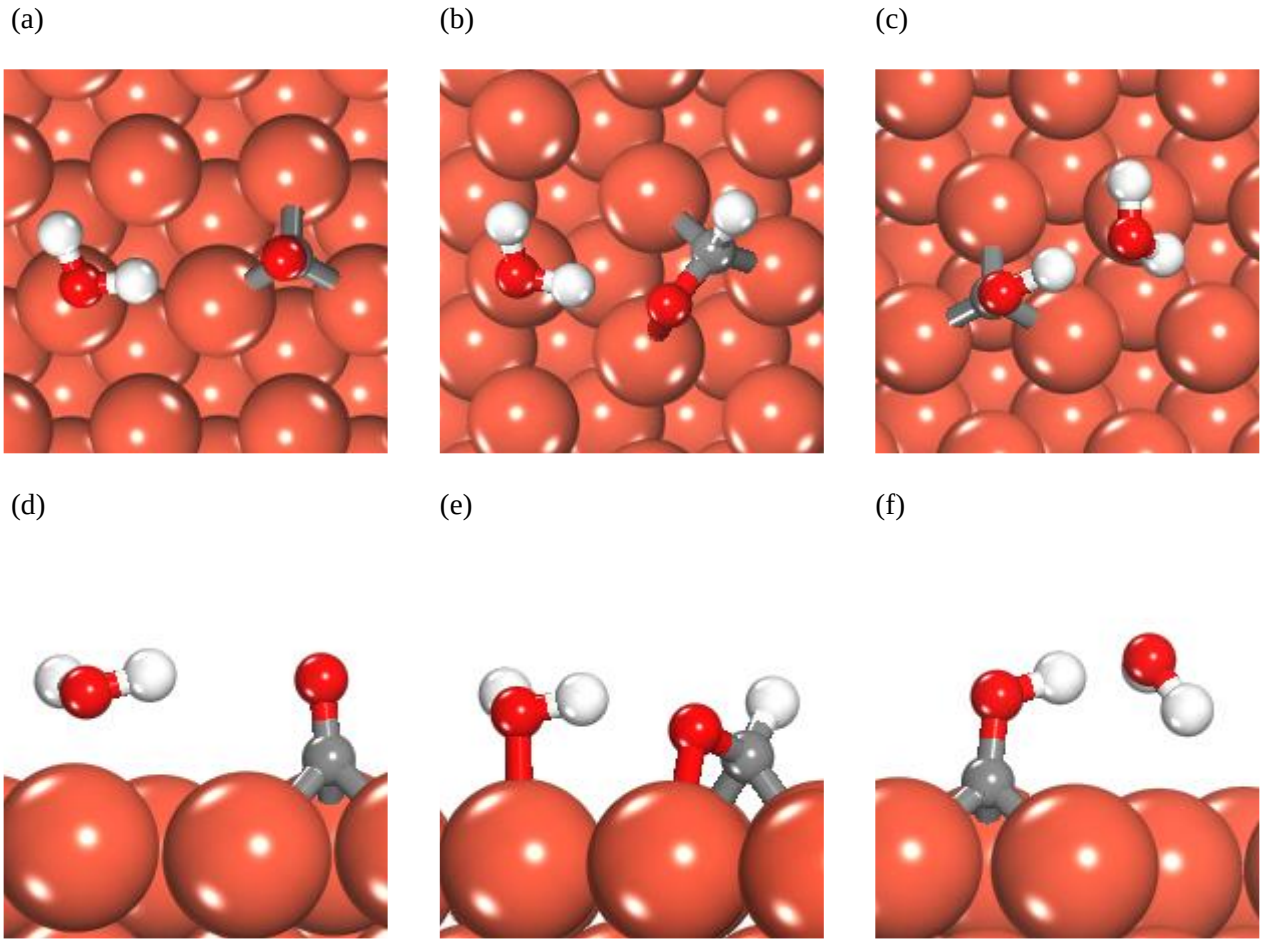


Figure S 1. Top and side view of the optimized configuration of explicitly solvated surface bound intermediates: CO* (a & d), CHO* (b & e) and COH* (c & f) on Cu (111) surface. (Orange = copper, gray = carbon, red = oxygen and white = hydrogen)

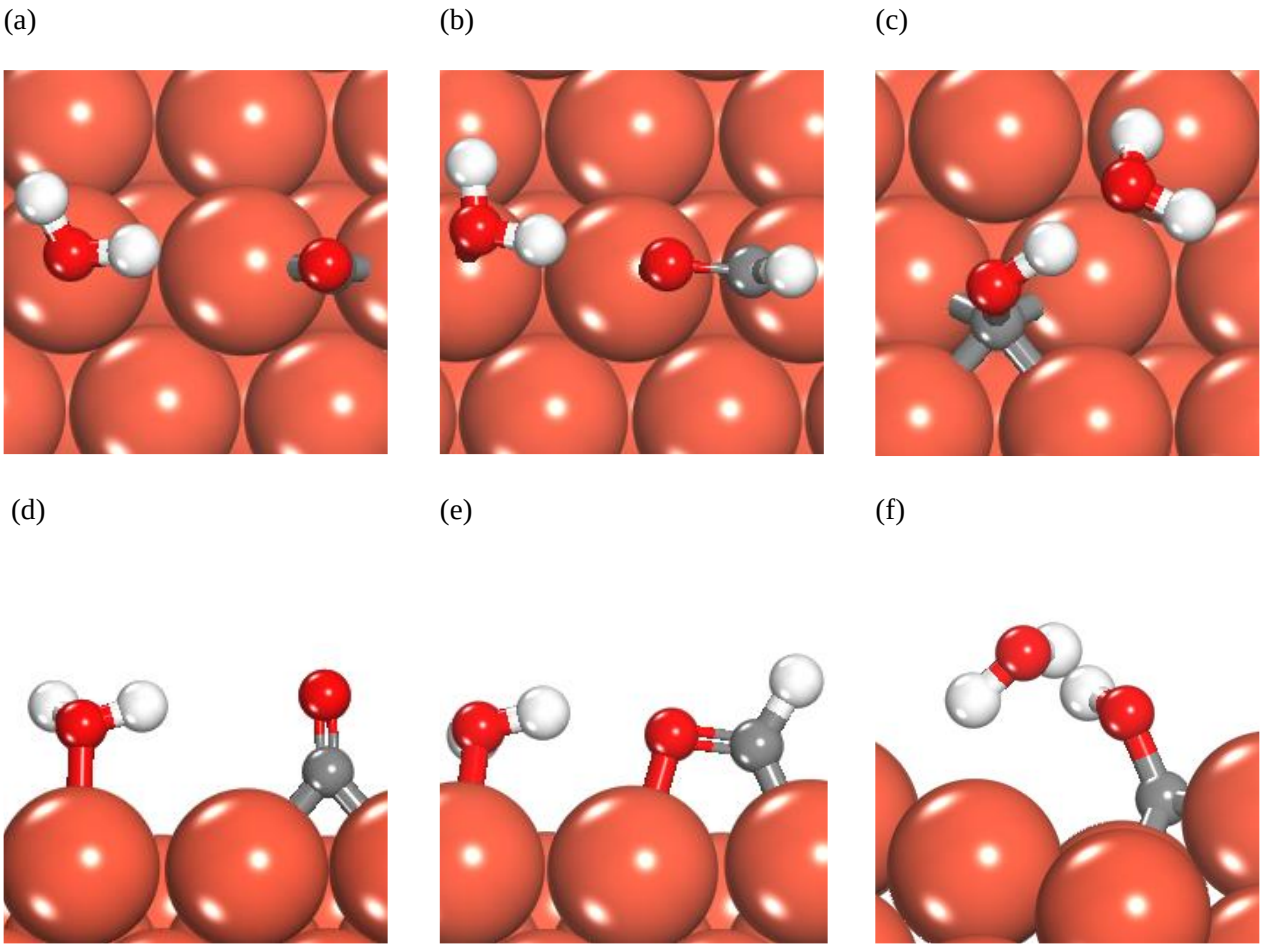
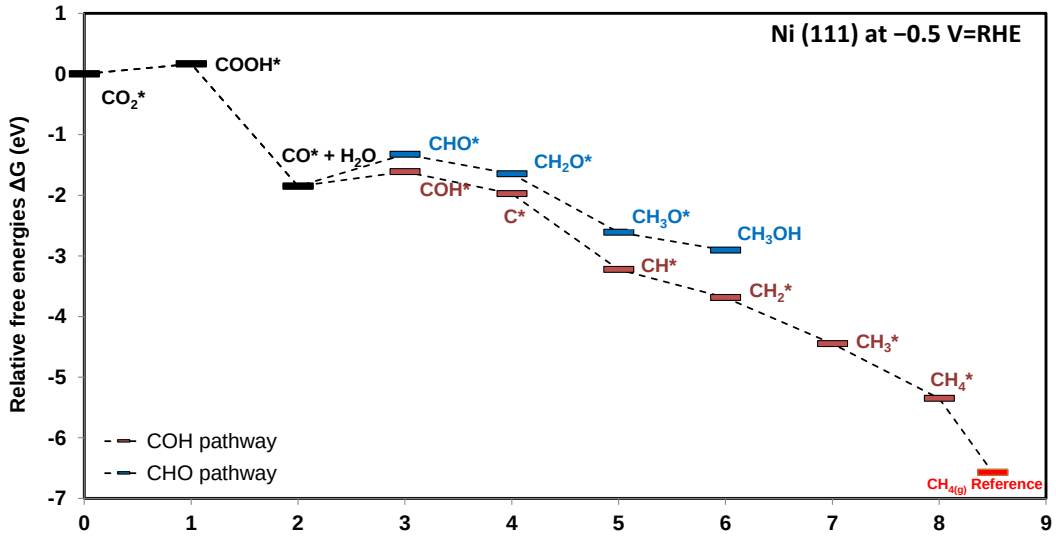


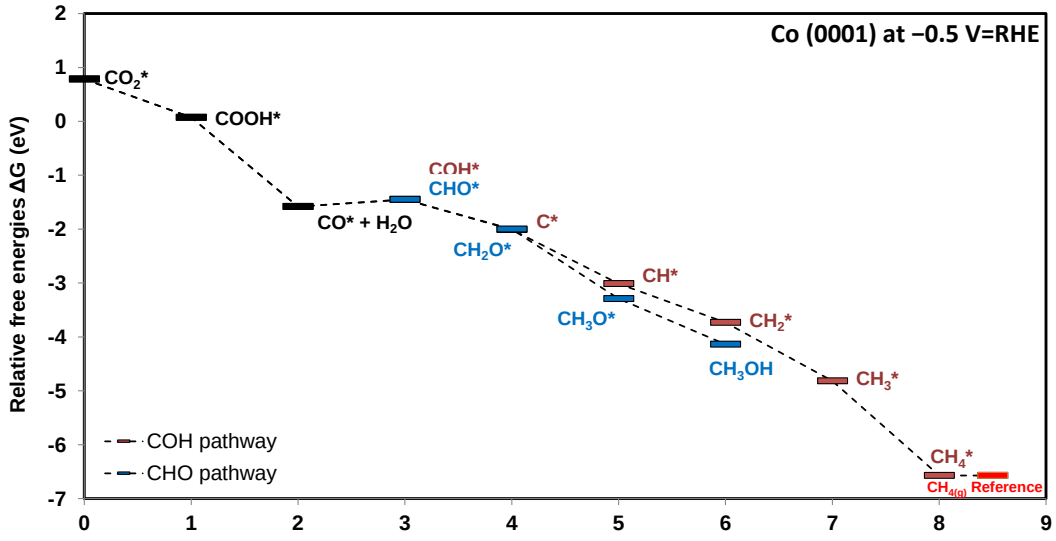
Figure S 2. Top and side view of the optimized configuration of explicitly solvated surface bound intermediates: CO* (a & d), CHO* (b & e) and COH* (c & f) on Cu (211) surface. (Orange = copper, gray = carbon, red = oxygen and white = hydrogen)

2. Reaction energy path for CO_2 ER to methane and methanol

(a)



(b)



(c)

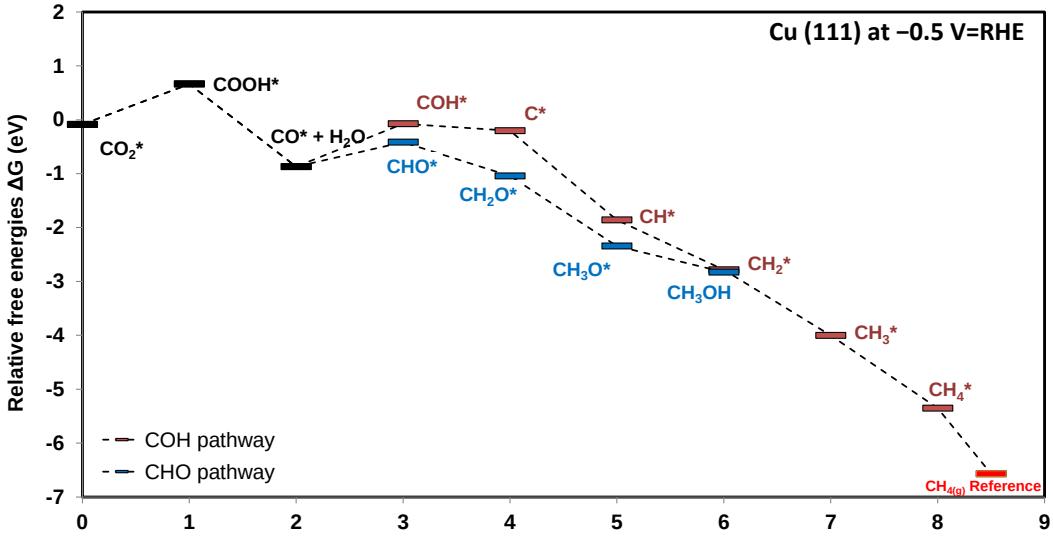


Figure S 3. Relative free energy diagram for CO_2 to methane and methanol via the CHO* (**blue**) and COH* (**brown**) path at U = −0.5 V-RHE on (a) Ni (111), (b) Co (0001), (c) Cu (111).

3. Effect of the XC functional (PBE and RPBE) on the binding energy and overpotential (U_L) of CO* reduction

(a) (b)

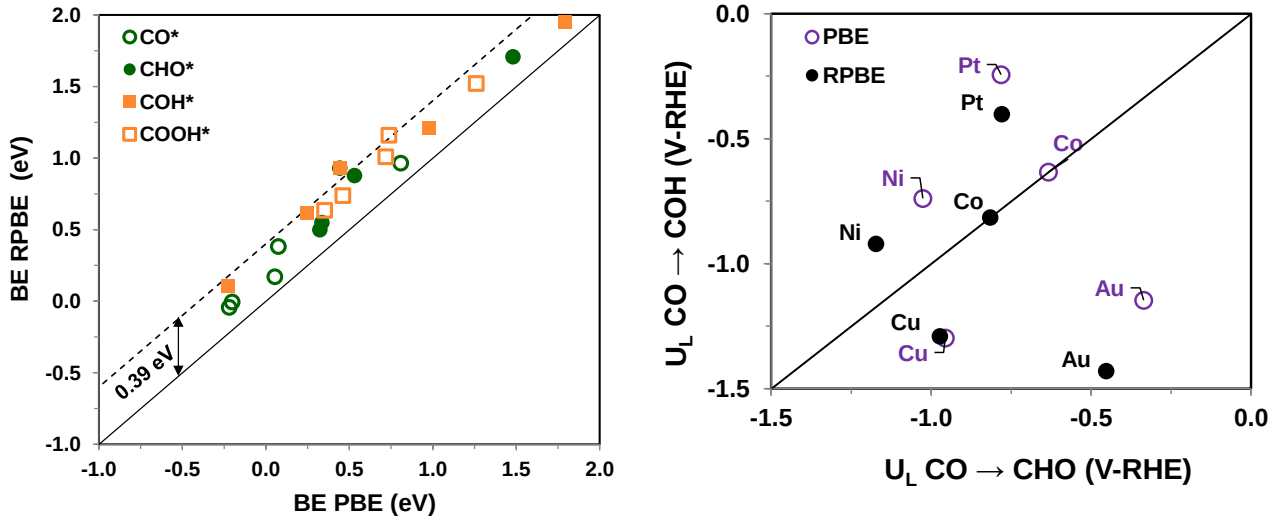


Figure S 4. (a) Binding energies (BE) of four CO_2 ER intermediates (COOH*, CO*, CHO* and COH*) and (b) explicitly calculated overpotential (U_L) for the electroreduction of CO*→COH* versus CO*→CHO* computed using PBE (○) and RPBE (●) XC functional on the close-packed surface facets of transition metals – Pt, Ni, Co Cu and Au. Solid line denotes parity at which $y=x$. Dashed line denotes the average weakening in the binding energy of surface intermediates when the RPBE functional is used.

4. Details of binding energy (BE) correlations

$$BE_{COH^{*}\,or\,CHO^{*}} = M\ BE_{CO^{*}} + N \quad \textbf{(1)}$$

	Correlation	Slope (M)	Intercept (N)	R^2
$BE_{COOH^{*}} = f(BE_{CO^{*}})$	Unsolvated, close-packed	0.665	0.635	0.852
	Unsolvated, stepped	0.555	0.560	0.829
$BE_{CHO^{*}} = f(BE_{CO^{*}})$	Unsolvated, close-packed	0.800	0.511	0.857
	Unsolvated, stepped	0.738	0.501	0.822
	Solvated, close-packed	0.653	0.509	0.935
	Solvated, stepped	0.603	0.780	0.892
$BE_{COH^{*}} = f(BE_{CO^{*}})$	Unsolvated, close-packed	1.493	0.298	0.949
	Unsolvated, stepped	1.377	0.755	0.947
	Solvated, close-packed	1.175	0.800	0.947
	Solvated, stepped	1.073	1.266	0.925

5. Estimated overpotential (U_L) using scaling correlations

$$U_{L(scaled)} = \frac{(1-M)\ BE_{CO^{*}} - N + (G_{CO^{*}}^{CORR} - G_{COH^{*}\,or\,CHO^{*}}^{CORR}) - E_H + ½\ G_{H2(g)}}{e^{-}} \quad \textbf{(2)}$$

TM	U_L CO* → CHO*	U_L CO* → COH*	U_L CO* + H_2O → CHO* + H_2O	U_L CO* + H_2O → COH* + H_2O
Co (0001)	-0.76	-0.60	-0.76	-0.88
Ni (111)	-0.84	-0.49	-1.04	-0.98
Cu (111)	-0.63	-1.01	-0.65	-1.27
Pt (111)	-0.79	-0.44	-0.83	-0.80
Au (111)	-0.48	-1.30	-0.34	-1.45
Co (102)	-0.68	-1.00	-0.83	-0.91
Ni (211)	-0.86	-0.97	-1.13	-0.99
Cu (211)	-0.55	-1.38	-0.75	-1.26
Pt (211)	-0.84	-0.81	-0.82	-0.80
Au (211)	-0.53	-1.49	-0.52	-1.44