Supporting Information for
Oxygen-induced changes to selectivity-determining steps in electrocatalytic CO_2 reduction

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Table 1: Chemical potentials of non-adsorbed molecules at 25°C, including electronic potential energy, zero-point energy, enthalpic temperature correction and entropy contribution. CH_3OH was calculated at the fugacity where liquid-vapor equilibrium is reached. CH_4 and H_2 were treated as ideal gas and were calculated at the atmosphere pressure. H_2 (ref) is used for evaluating the chemical potential of $(H^+ + e^-)$ by CHE model.

Molecule	Fugacity Pa	E_{elec} eV	ZPE eV	$\int C_p dT$ eV	$-TS$ eV	μ eV
CH_3OH	13020	-657.181	1.370	0.118	-0.790	-656.484
CH_4	101325	-220.739	1.194	0.104	-0.575	-220.016
H_2 (ref)	101325	-32.032	0.275	0.091	-0.403	-32.071

Table 2: Free energy corrections of adsorbates at 25°C, including zero-point energy, enthalpic temperature correction and entropy contribution. All values are reported in eV.

Adsorbate	ZPE	$\int C_p dT$	$-TS$	$G - E_{\text{elec}}$
CH_3O*	1.108	0.096	-0.186	1.018
O*	0.072	0.027	-0.040	0.058

Table 3: Electronic potential energies and free energies of surfaces Cu(111), $Cu_2O(111)$ and Cu(110)-(2×1)O at 25°C. All values are reported in eV.

	$E_{\mathrm{elec}}[*]$	$G_{\mathrm{elec}}[*]$	$E_{\mathrm{elec}}[\mathrm{CH_3O}*]$	$G[\mathrm{CH_3O}*]$	$E_{\mathrm{elec}}[\mathrm{O}*]$	$G[O*]$
Cu(111)	-30275.01	-30275.01	-30710.92	-30710.86	-30915.91	-30914.89
$Cu_2O(111)$	-45196.10	-45196.10	-45632.72	-45632.66	-45836.97	-45835.95
Cu(110)-(2×1)O	-44396.86	-44396.86	-44832.56	-44832.50	-45036.67	-45035.65

Table 4: Binding energies of O on Cu(111) surface with specified coverage of OH and CO spectators co-adsorbed.

	Coverage ML	$E_{\mathrm{elec}}[\mathrm{O}*+x\mathrm{OH}]$ eV	$E_{\mathrm{elec}}[x\mathrm{OH}+*]$ eV	$E_{\mathrm{B}}[\mathrm{O}]$ eV	$\Delta E_{\mathrm{B}}[\mathrm{O}]$ eV
OH	0	-45632.716	-45196.104	1.087	0.000
	1/9	-46086.150	-45649.451	1.000	-0.087
	2/9	-46539.453	-46102.742	0.988	-0.099
	3/9	-46992.589	-46555.974	1.084	-0.003
	4/9	-47445.277	-47009.356	1.778	0.691
CO	0	-45632.716	-45196.104	1.087	0.000
	1/9	-46224.573	-45787.906	1.033	-0.055
	2/9	-46816.394	-46379.867	1.172	0.085
	3/9	-47408.116	-46971.514	1.097	0.010
	4/9	-47999.766	-47563.237	1.171	0.084

Table 5: Binding energies of CH_3O on Cu(111) surface with a certain coverage of OH and CO spectators co-adsorbed.

	Coverage ML	$E_{\mathrm{elec}}[\mathrm{CH_3O} * + x\mathrm{OH}]$ eV	$E_{\mathrm{elec}}[x\mathrm{OH} + *]$ eV	$E_{\mathrm{B}}[\mathrm{CH_3O}]$ eV	$\Delta E_{\mathrm{B}}[\mathrm{CH_3O}]$ eV
OH	0	-45836.969	-45196.104	0.300	0.000
	1/9	-46290.321	-45649.448	0.294	-0.007
	2/9	-46743.632	-46102.719	0.253	-0.047
	3/9	-47196.954	-46556.107	0.319	0.019
	4/9	-47649.886	-47009.356	0.635	0.335
CO	0	-45836.969	-45196.104	0.300	0.000
	1/9	-46428.845	-45787.954	0.275	-0.025
	2/9	-47020.717	-46379.867	0.316	0.016
	3/9	-47612.358	-46971.641	0.449	0.148
	4/9	-48203.550	-47563.247	0.863	0.563

Table 6: Vibrational modes of adsorbates on copper surface, from [**?**].

O*			**CH_3O***		
mode #	energy meV	freq cm^{-1}	mode #	energy meV	freq cm^{-1}
0	39.3	317.0	0	8.8	71.0
1	49.5	399.5	1	18.3	147.6
2	54.7	441.5	2	20.8	167.9
			3	25.4	205.1
			4	37.2	300.4
			5	38.1	307.4
			6	128.0	1032.5
			7	141.2	1138.6
			8	143.0	1153.4
			9	179.3	1446.5
			10	180.4	1455.1
			11	180.7	1457.4
			12	367.1	2960.5
			13	373.1	3009.0
			14	375.4	3027.9

Table 7: Vibration modes of non-adsorbed molecules. Note that the lowest six (in the case of CH_3OH, CH_4) or five (H_2) modes are ignored, as these are translational and rotational degrees of freedom treated with standard statistical mechanics techniques for ideal gases.

CH_3OH			**CH_4**			**H_2**		
mode #	energy meV	freq cm^{-1}	mode #	energy meV	freq cm^{-1}	mode #	energy meV	freq cm^{-1}
0	7.9i	63.8i	0	17.8i	143.4i	0	14.6	117.6
1	3.9	31.7	1	16.9i	136.6i	1	19.2	154.8
2	6.4	51.8	2	14.0i	112.6i	2	21.3	172.1
3	10.9	88.0	3	10.7i	86.2i	3	31.6	254.5
4	12.2	98.2	4	10.1	81.5	4	40.1	323.6
5	13.7	110.7	5	16.2	130.3	5	549.2	4429.8
6	39.0	314.4	6	159.8	1289.1			
7	124.3	1002.8	7	160.2	1291.8			
8	130.3	1050.8	8	160.6	1295.1			
9	140.5	1133.4	9	186.9	1507.4			
10	164.2	1324.3	10	187.5	1512.2			
11	177.8	1434.0	11	372.1	3001.5			
12	180.3	1454.1	12	387.1	3121.8			
13	181.5	1464.2	13	387.2	3123.1			
14	366.3	2954.6	14	387.5	3125.6			
15	373.4	3011.5						
16	383.0	3089.2						
17	479.1	3864.2						