Supplemental information for: First -Principles Mechanistic Analysis of Dimethyl Ether Electro-Oxidation on Monometallic Single-Crystal Surfaces

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S1. Free energies of species, zero-point energy corrections, and entropies

Table S1. Free energies, zero-point energies, and entropies of adsorbed species on close-packed facets (fcc(111) and hcp(0001)) of twelve selected metals.

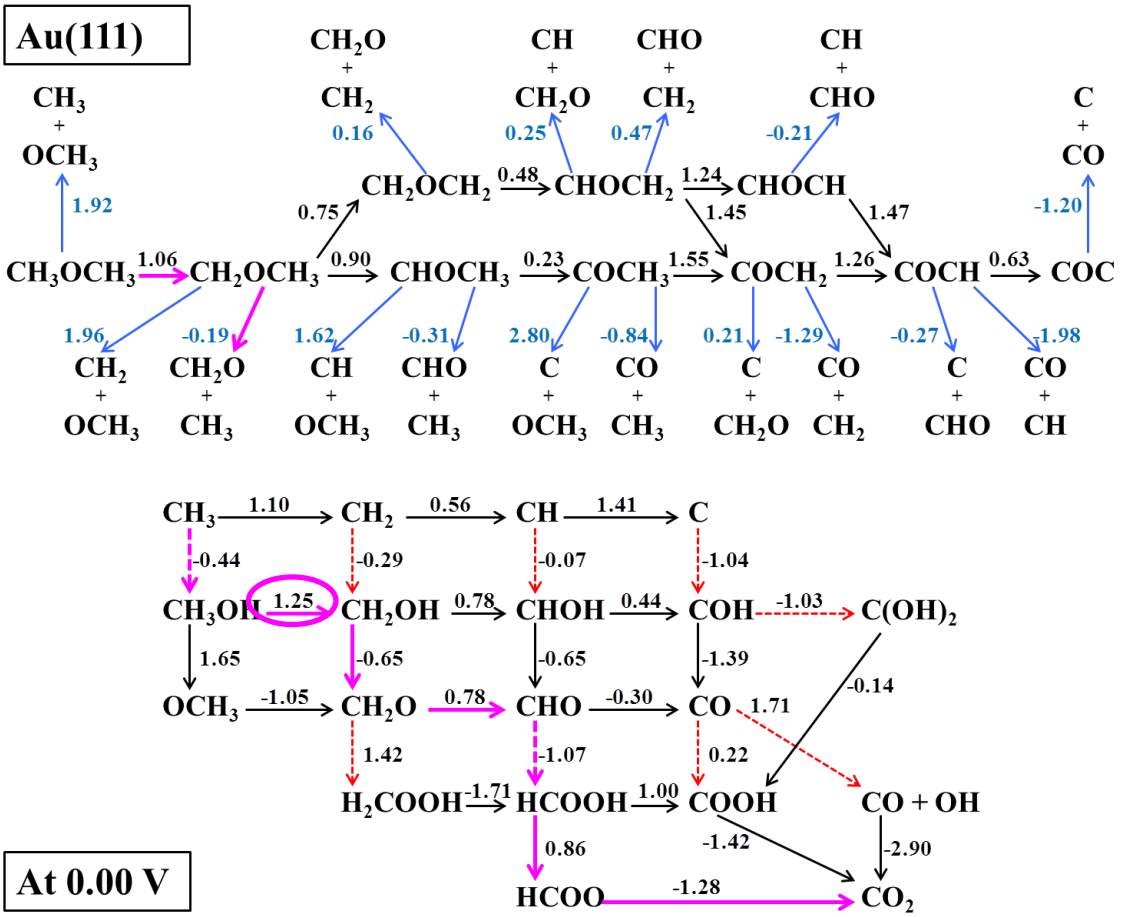
			Free Energies (eV)											
	ZPE (eV)	**S (J/mol-K)**	**Au**	**Ag**	**Cu**	**Pt**	**Pd**	**Ni**	**Ir**	**Rh**	**Co**	**Os**	**Ru**	**Re**
CH_2OCH_3	1.83	93.25	1.45	1.82	1.65	0.59	0.81	1.10	0.60	0.70	1.02	0.50	0.44	0.54
CH_2OCH_2	1.56	59.36	2.20	2.70	2.46	0.56	1.07	1.53	0.65	0.88	1.52	0.70	0.73	1.05
$CHOCH_3$	1.53	70.48	2.35	2.68	2.16	0.84	0.94	1.05	0.59	0.72	0.97	0.48	0.48	0.55
$CHOCH_2$	0.94	44.21	2.68	3.20	2.49	0.34	0.88	1.18	0.24	0.61	1.32	0.28	0.52	0.58
$COCH_3$	1.24	56.11	2.59	3.03	2.04	0.14	0.33	0.41	0.09	0.10	0.39	-0.03	-0.04	-0.09
$COCH_2$	0.94	44.21	4.13	4.60	4.07	1.00	1.33	1.42	0.78	0.79	1.29	0.53	0.63	0.77
CHOCH	0.94	41.73	3.92	4.41	3.46	1.06	1.88	1.77	0.61	1.06	1.74	0.57	0.92	0.74
COCH	0.59	37.26	5.39	5.82	4.35	2.06	2.26	2.36	1.39	1.46	2.01	0.83	1.19	0.95
COC	0.25	28.71	6.02	5.59	4.52	3.13	3.22	2.63	2.56	2.24	2.33	1.94	1.95	1.36
CH_3O	1.06	67.28	1.76	0.98	0.52	1.14	0.93	0.23	0.65	0.30	0.00	0.18	-0.06	-0.46
CH_3	0.90	29.80	0.55	0.80	0.43	-0.25	0.00	-0.11	-0.17	-0.16	-0.24	-0.33	-0.50	-0.63
CH_2OH	1.11	66.26	1.36	1.76	1.56	0.42	0.66	1.04	0.61	0.52	1.19	0.38	0.39	0.43
CH_2	0.59	21.55	1.65	1.93	1.30	0.09	0.33	0.15	-0.01	0.06	0.07	-0.05	0.02	-0.56
CHOH	0.80	33.03	2.14	2.54	1.96	0.53	0.71	0.87	0.16	0.66	0.79	-0.14	0.52	0.39
CHO	0.47	59.96	1.49	1.84	1.54	0.37	0.36	0.49	0.22	0.16	0.57	0.07	0.08	0.04
CH	0.37	11.57	2.22	2.75	1.68	-0.22	0.19	0.09	-0.40	-0.29	0.03	-0.67	-0.35	-0.78
COH	0.49	23.94	2.59	3.06	2.04	0.07	0.25	0.33	-0.01	-0.01	0.29	-0.16	-0.09	-0.19
CO	0.18	40.18	1.19	1.24	0.61	-0.42	-0.66	-0.52	-0.55	-0.59	-0.47	-0.69	-0.65	-0.46
C	0.10	7.31	3.63	4.15	3.01	0.74	0.84	0.92	0.43	0.26	0.72	-0.07	0.31	-0.17
HCOO	0.64	52.39	1.28	0.73	0.44	0.76	0.63	1.05	0.09	0.02	0.17	-0.34	-0.28	-0.35
COOH	0.63	63.69	1.42	1.56	1.22	0.39	0.49	0.48	0.08	0.10	0.47	-0.12	-0.11	0.06
$C(OH)_2$	0.93	49.19	1.56	1.98	1.64	0.14	0.65	0.92	0.25	0.46	0.95	0.21	0.25	0.60
H_2COOH	1.22	71.32	2.13	1.54	1.14	1.48	1.45	0.85	1.14	0.79	0.60	0.42	0.29	0.14
OH	0.35	29.62	1.71	0.98	0.57	1.16	1.04	0.29	0.67	0.54	0.14	0.21	0.05	-0.46
OCH_2OCH_3	1.95	92.10	2.37	1.70	1.34	1.70	1.69	1.06	1.09	1.06	0.84	0.66	0.66	0.43
$HOCHOCH_3$	1.94	109.84	1.91	2.40	2.27	1.06	1.23	1.76	0.97	1.36	1.85	1.21	0.86	1.51

Free energies of closed-shell species are: CH_3OCH_3 (0.39 eV), CH_3OH (0.11 eV), HCOOH (0.42 eV)

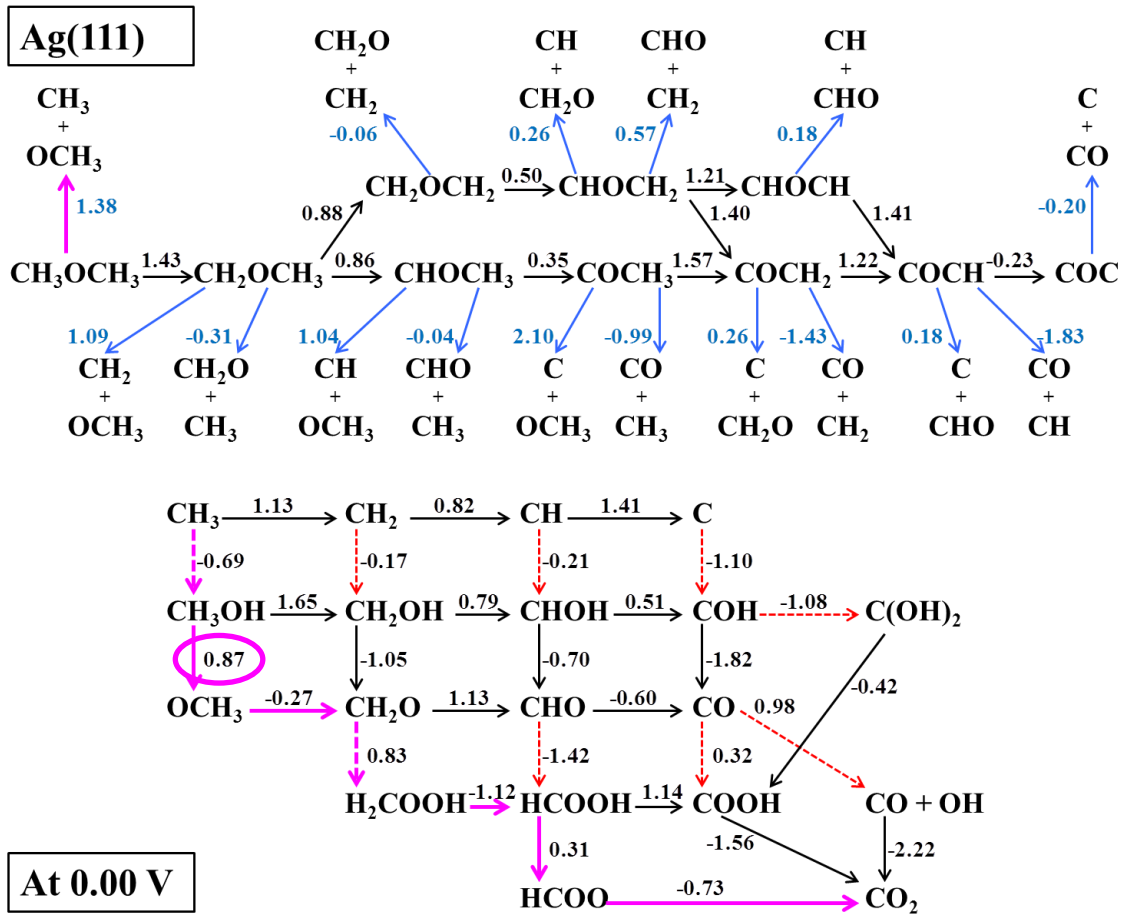
S2. Reaction energetics on different surfaces

Here we present free energy diagrams for each surface. In the first section (Scheme S1-S12), we outline the most-exergonic pathway in pink, with the most difficult electrochemical step circled. In the second section (Scheme S13-S24), the lowest-free-energy pathway is outlined in green, with the most difficult electrochemical step circled. All diagrams are presented at 0.00 V. The black arrows show proton / electron transfer steps, the blue arrows show C-O bond breaking steps, and the red dotted arrows show Heyrovsky-type reaction steps.

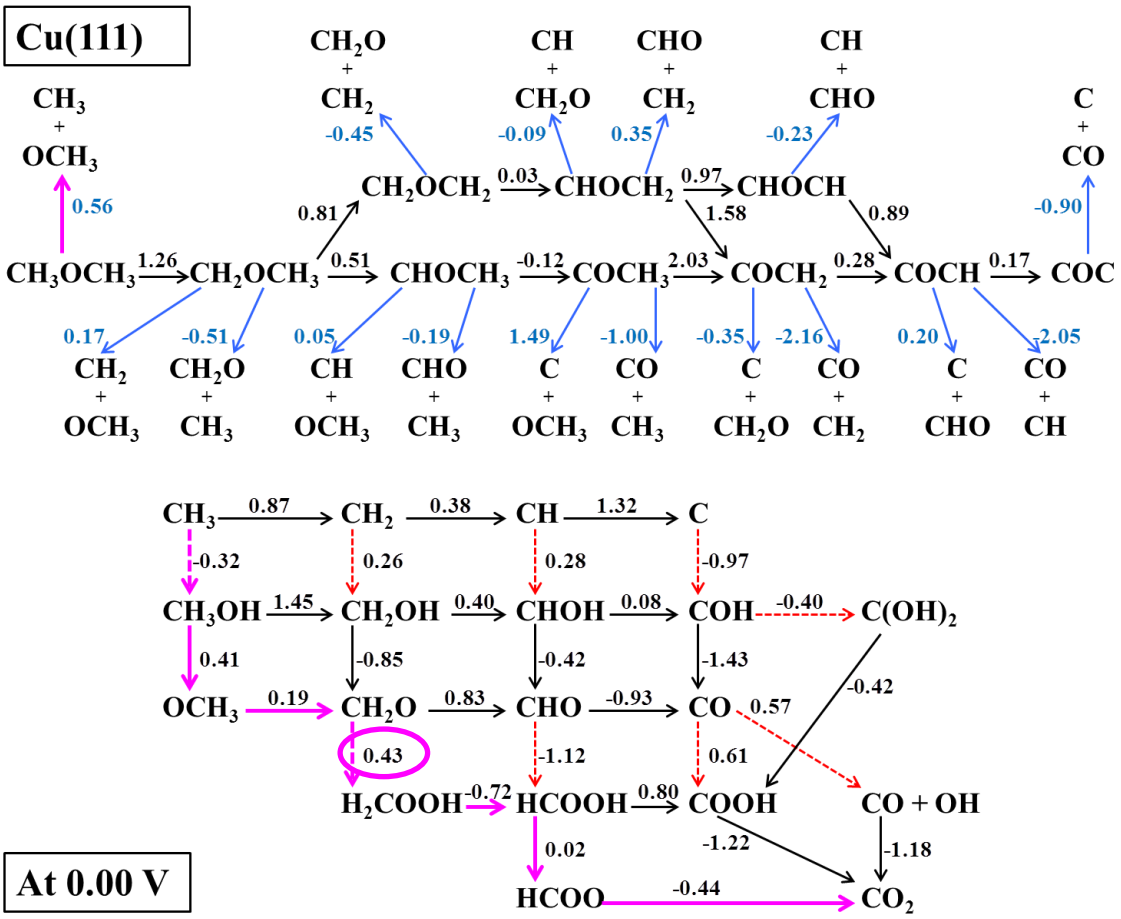
S2.1 Most-Exergonic pathways



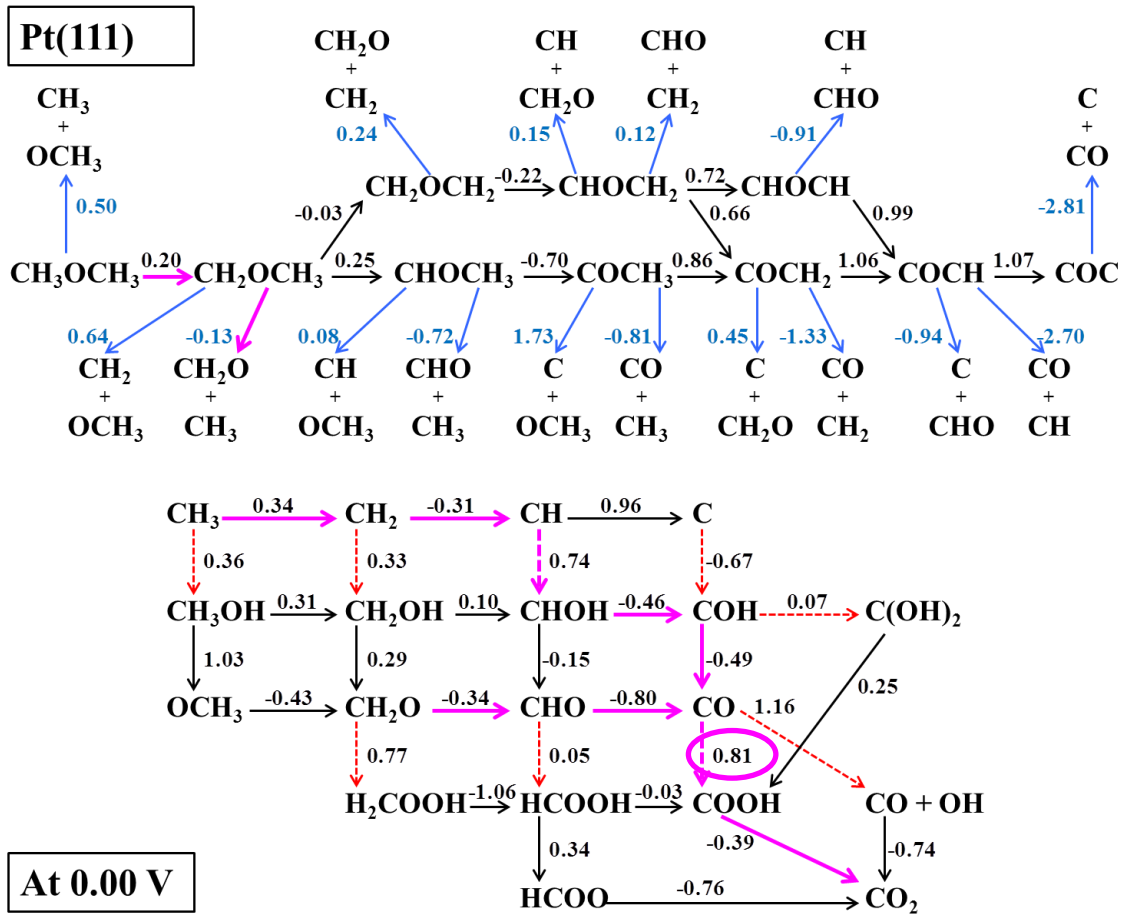
Scheme S1. Most-Exergonic pathway for Au(111) at 0.00 V. All values are in eV.



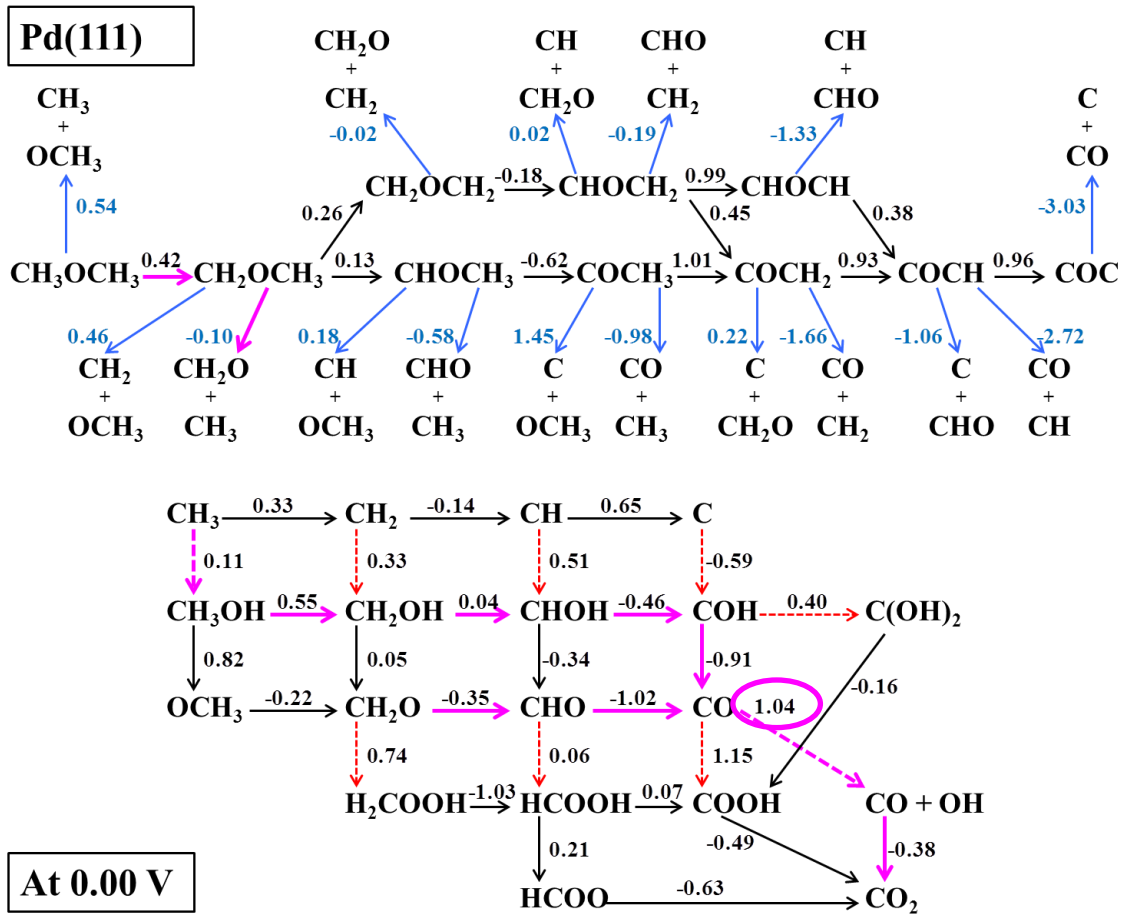
Scheme S2. Most-Exergonic pathway for Ag(111) at 0.00 V. All values are in eV.



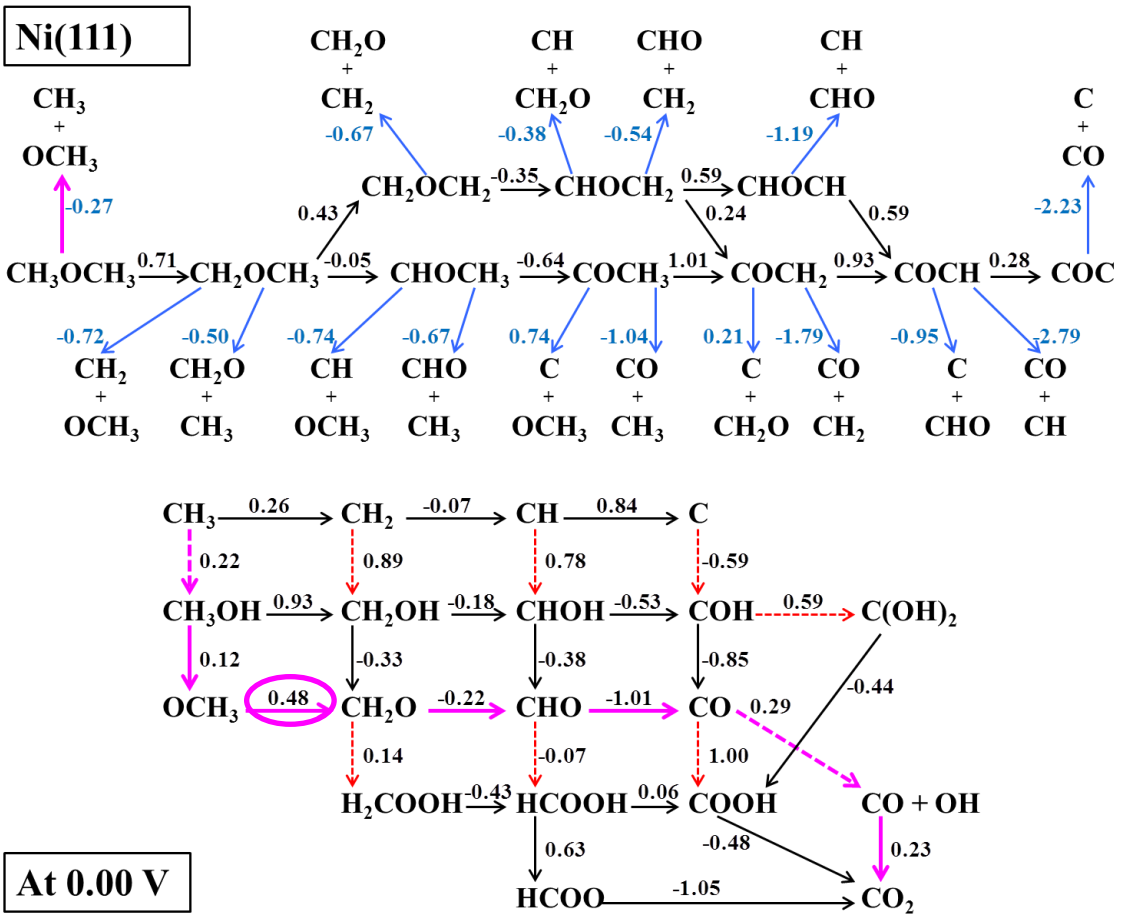
Scheme S3. Most-Exergonic pathway for Cu(111) at 0.00 V. All values are in eV.



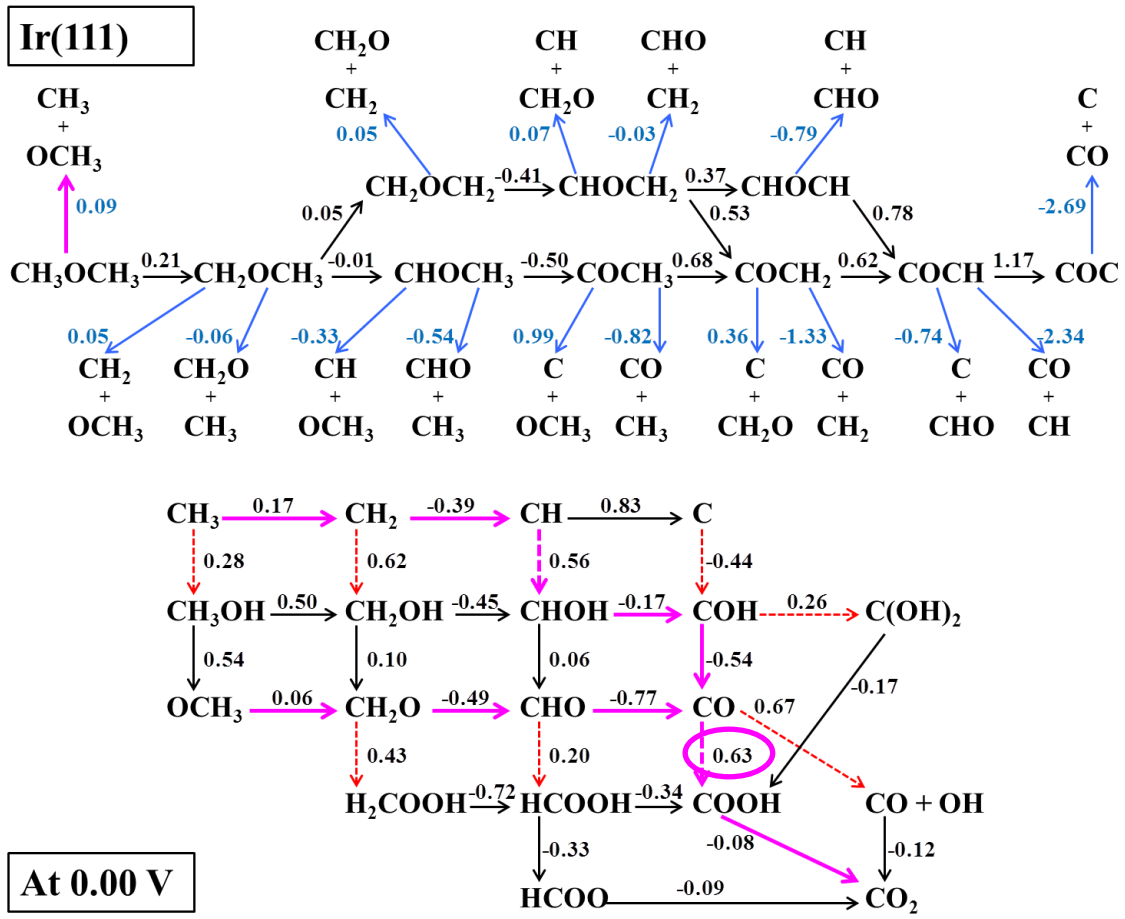
Scheme S4. Most-Exergonic pathway for Pt(111) at 0.00 V. All values are in eV.



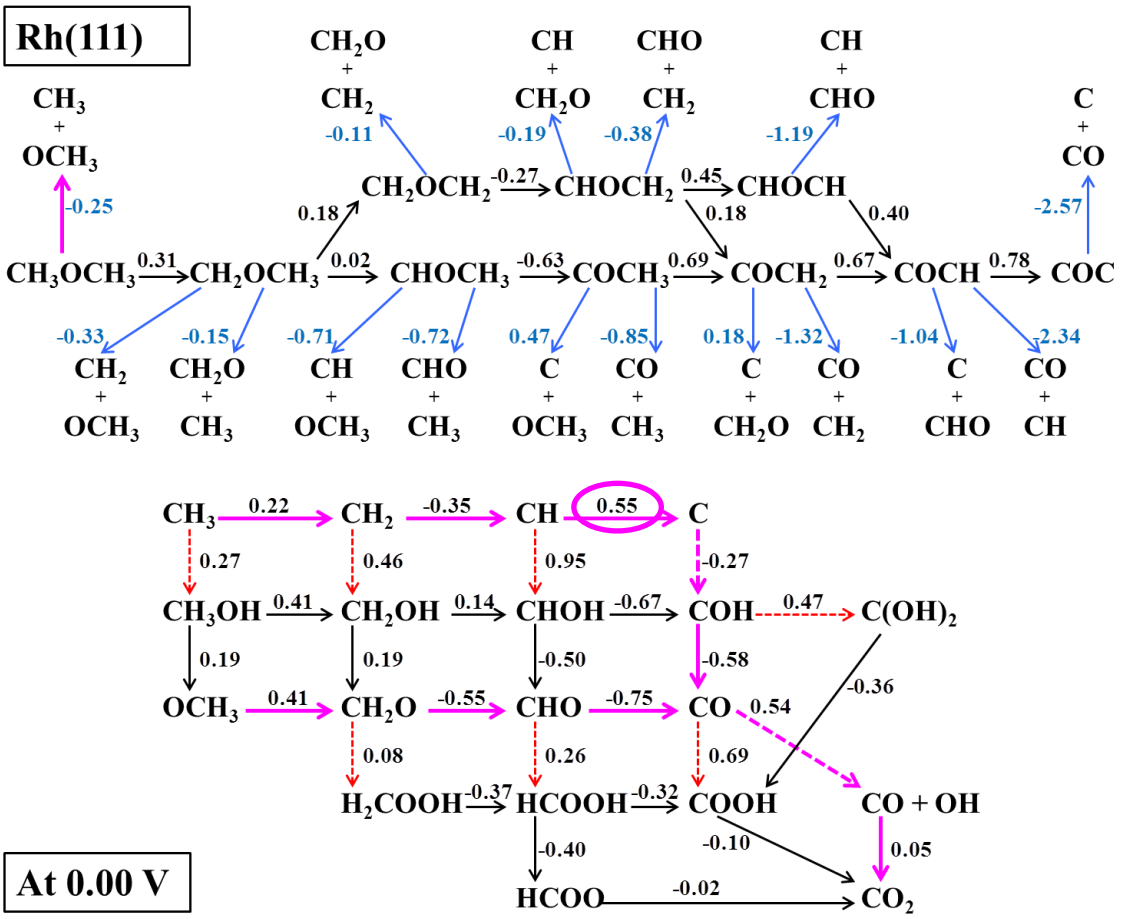
Scheme S5. Most-Exergonic pathway for Pd(111) at 0.00 V. All values are in eV.



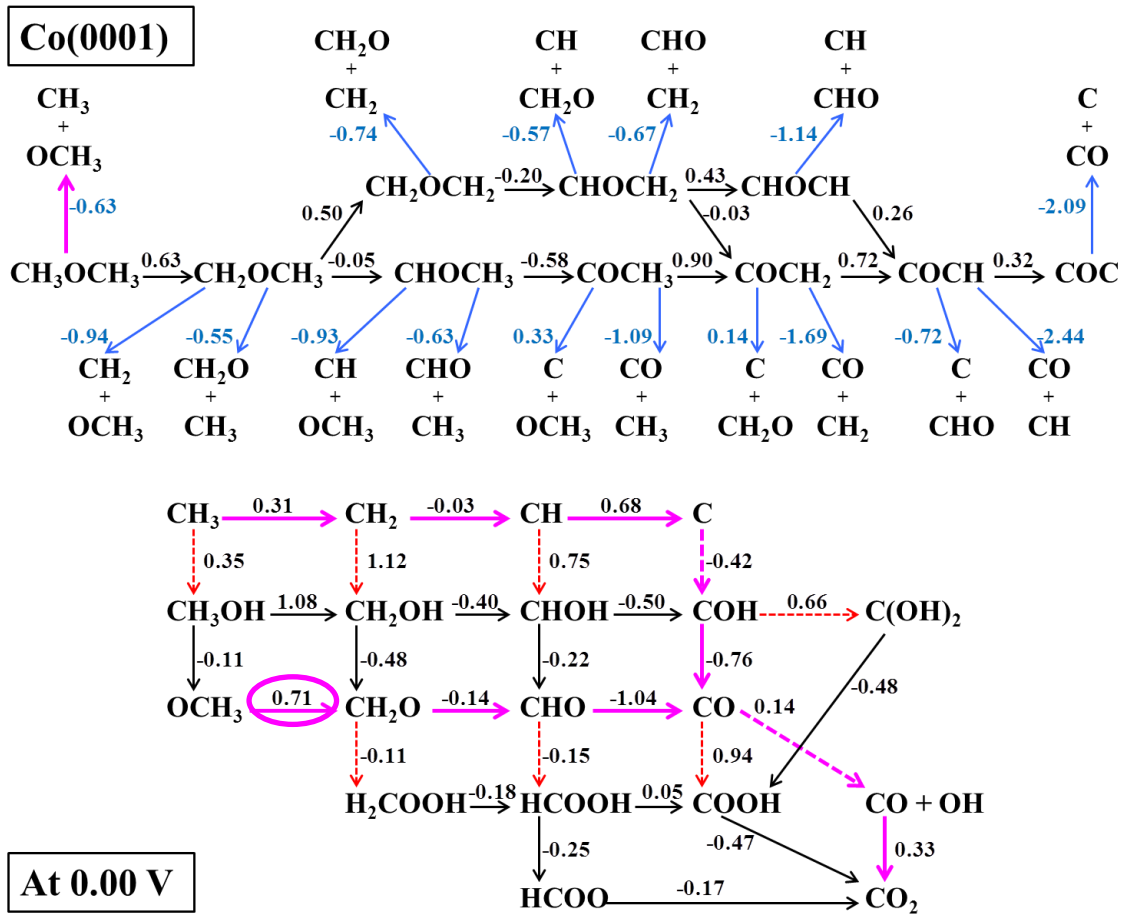
Scheme S6. Most-Exergonic pathway for Ni(111) at 0.00 V. All values are in eV.



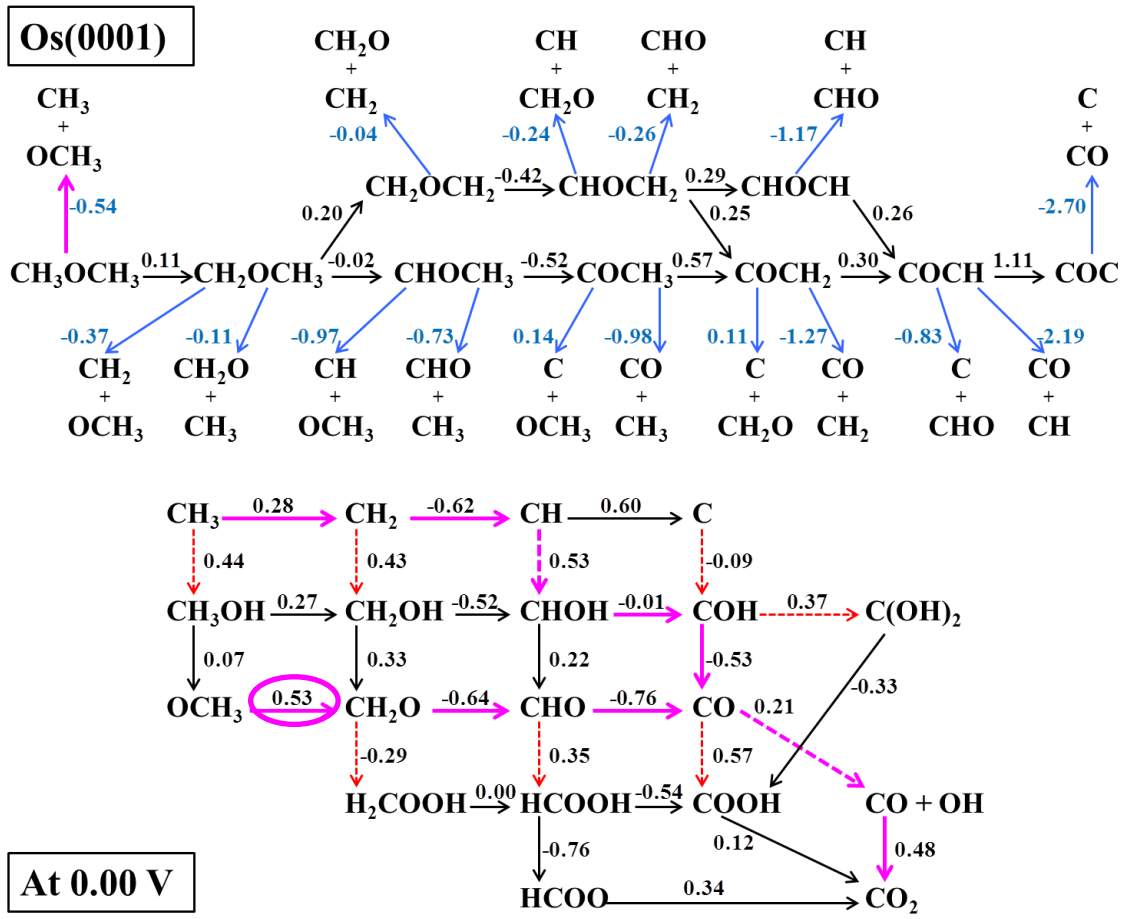
Scheme S7. Most-Exergonic pathway for Ir(111) at 0.00 V. All values are in eV.



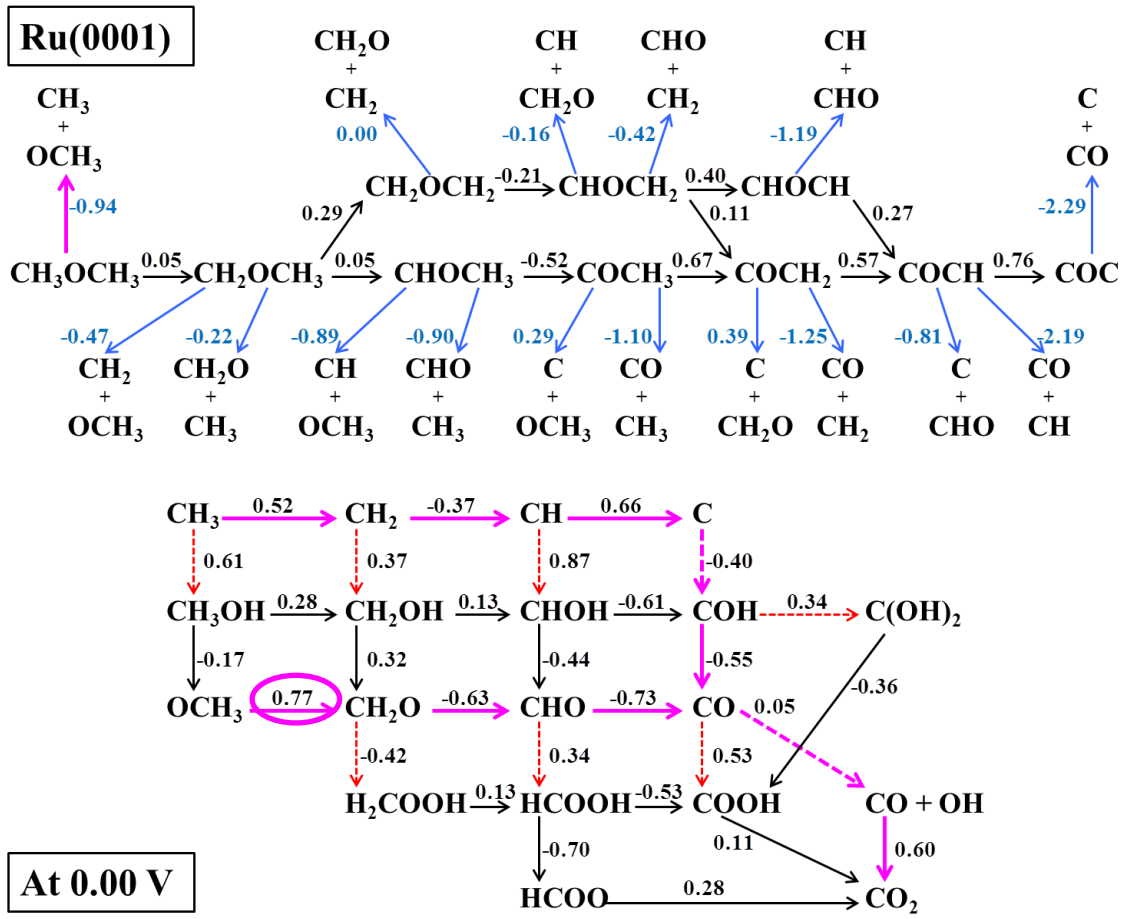
Scheme S8. Most-Exergonic pathway for Rh(111) at 0.00 V. All values are in eV.



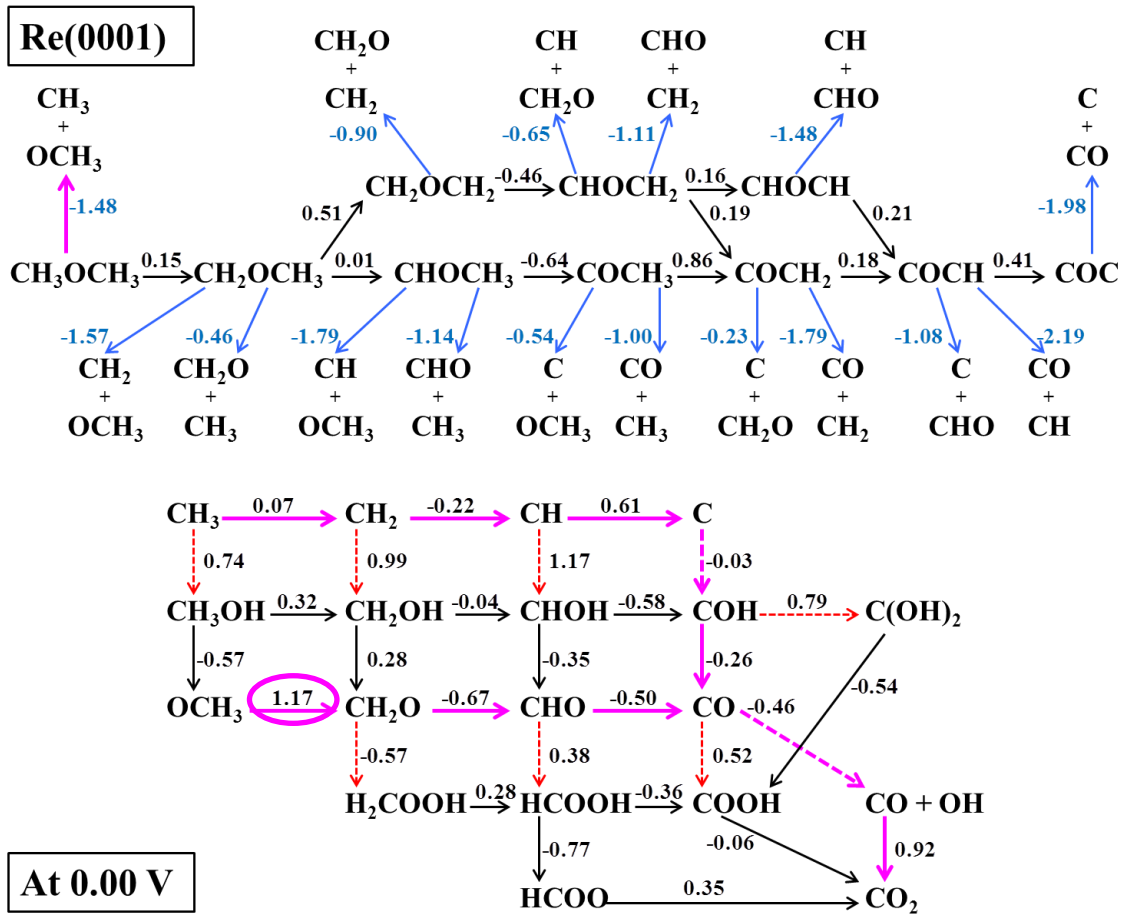
Scheme S9. Most-Exergonic pathway for Co(0001) at 0.00 V. All values are in eV.



Scheme S10. Most-Exergonic pathway for Os(0001) at 0.00 V. All values are in eV.

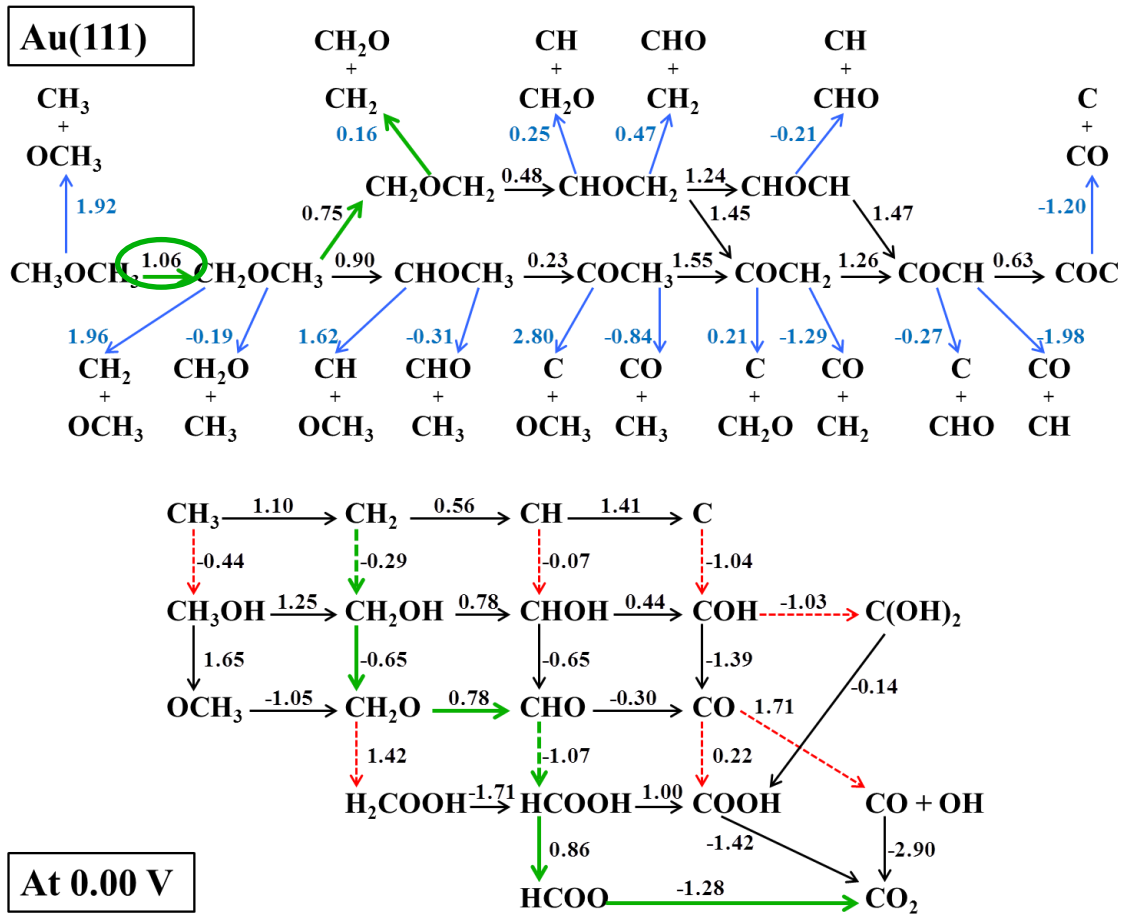


Scheme S11. Most-Exergonic pathway for Ru(0001) at 0.00 V. All values are in eV.

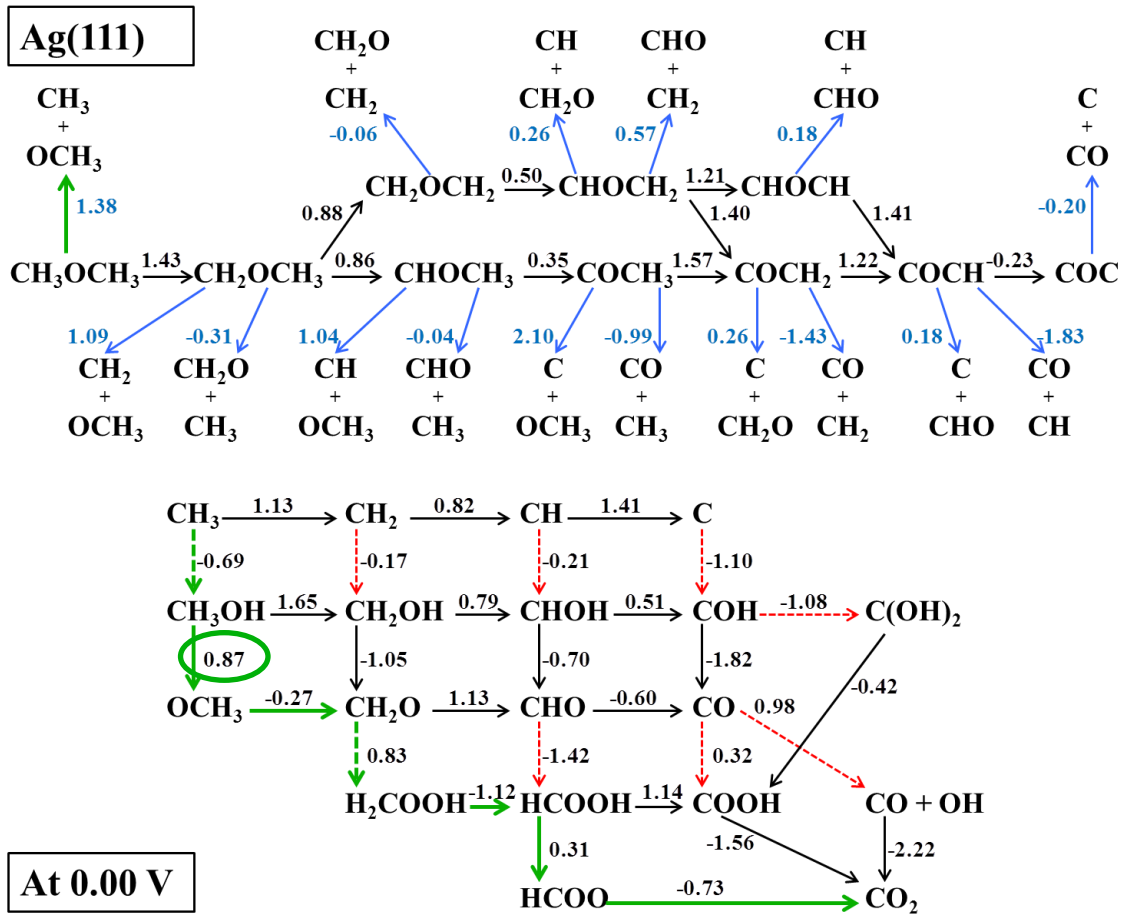


Scheme S12. Most-Exergonic pathway for Re(0001) at 0.00 V. All values are in eV.

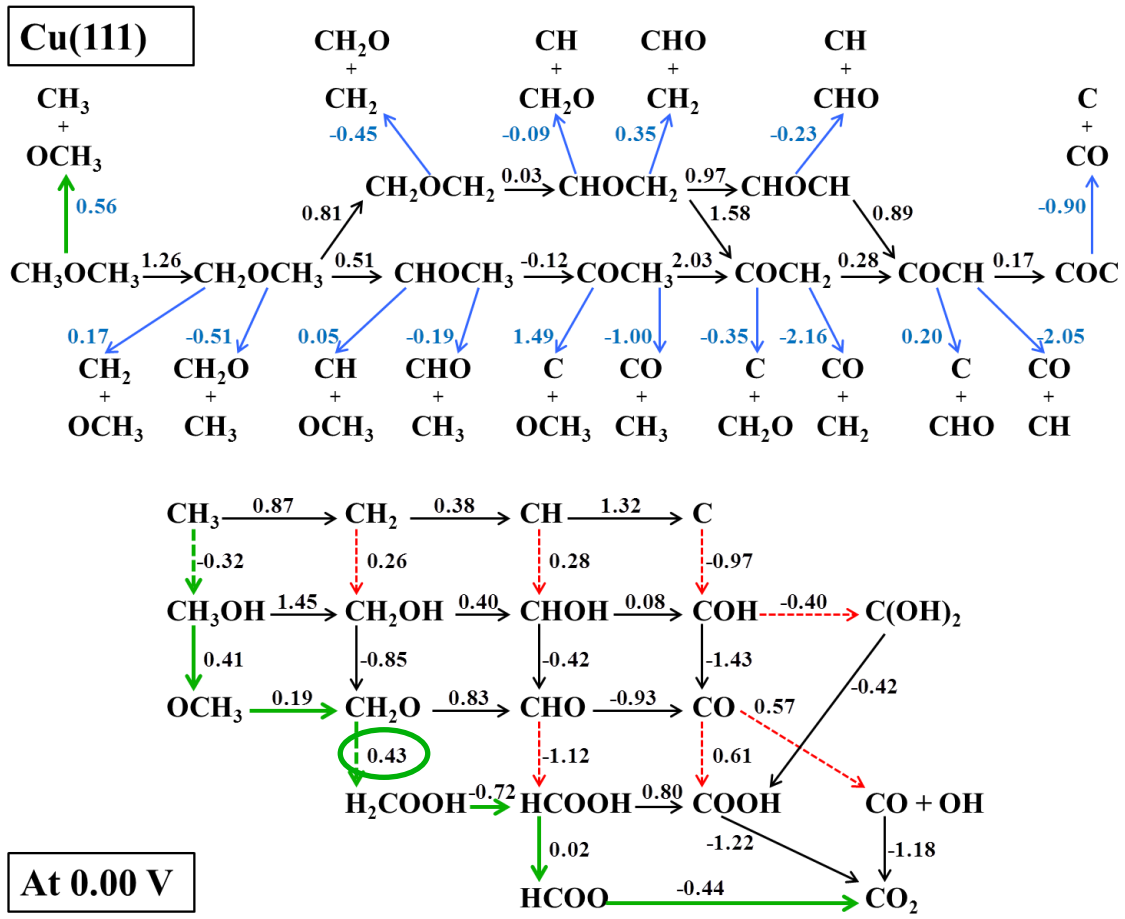
S2.2 Lowest-Free-Energy Pathways



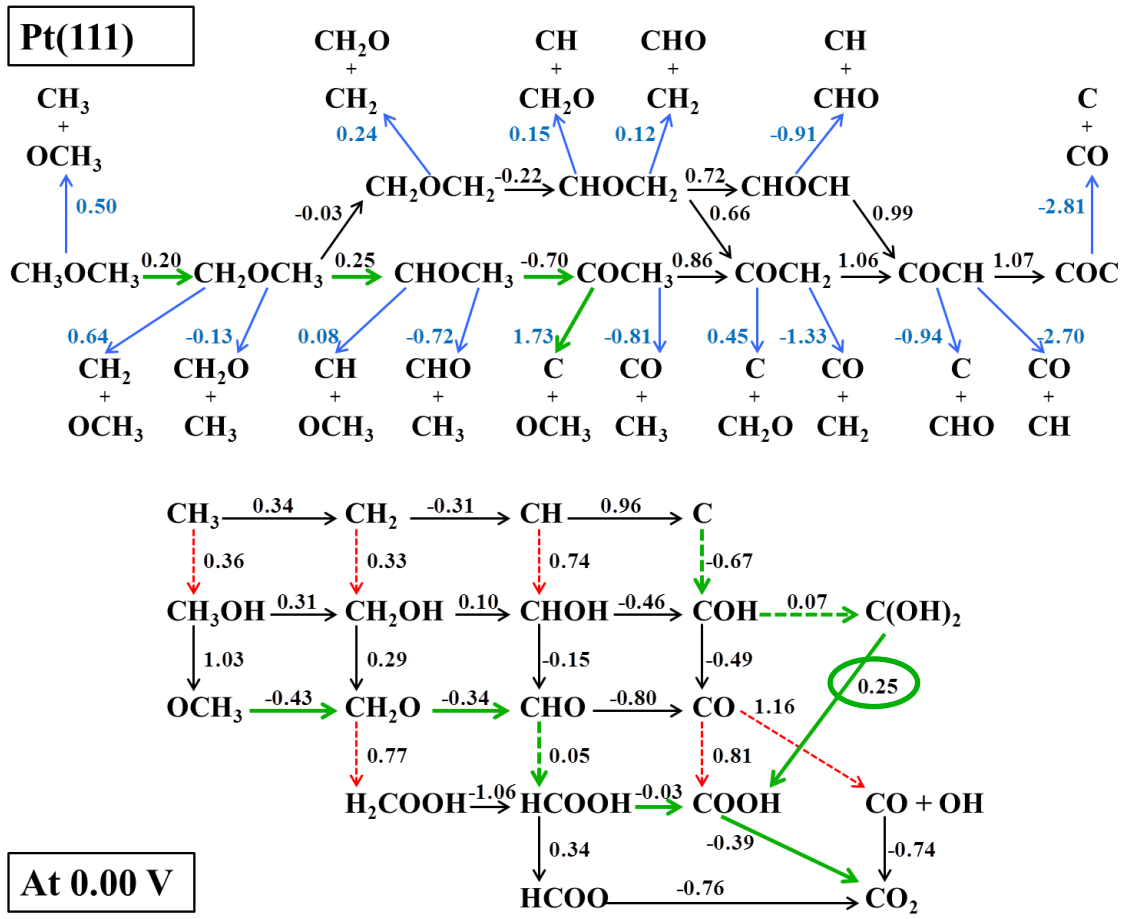
Scheme S13. Lowest-free-energy pathway for Au(111) at 0.00 V. All values are in eV.



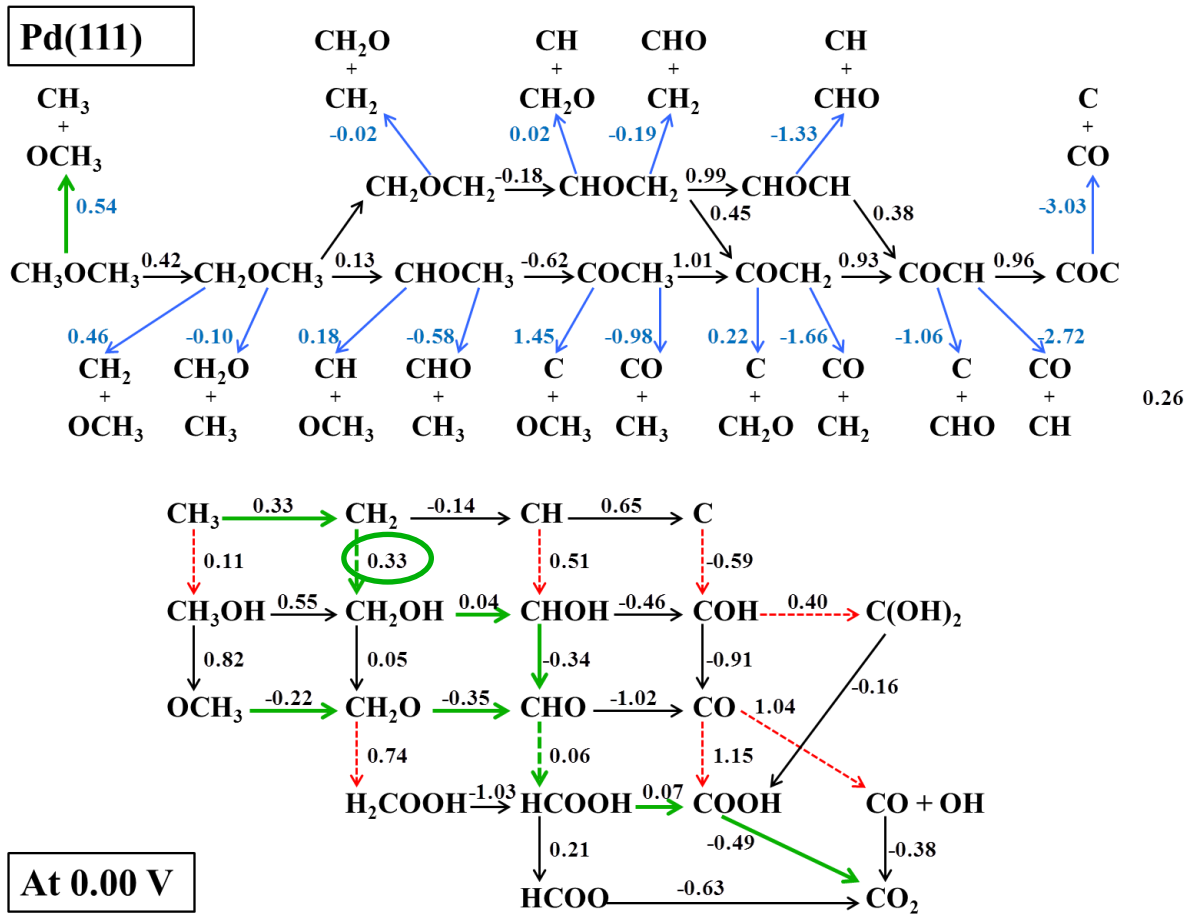
Scheme S14. Lowest-free-energy pathway for Ag(111) at 0.00 V. All values are in eV.



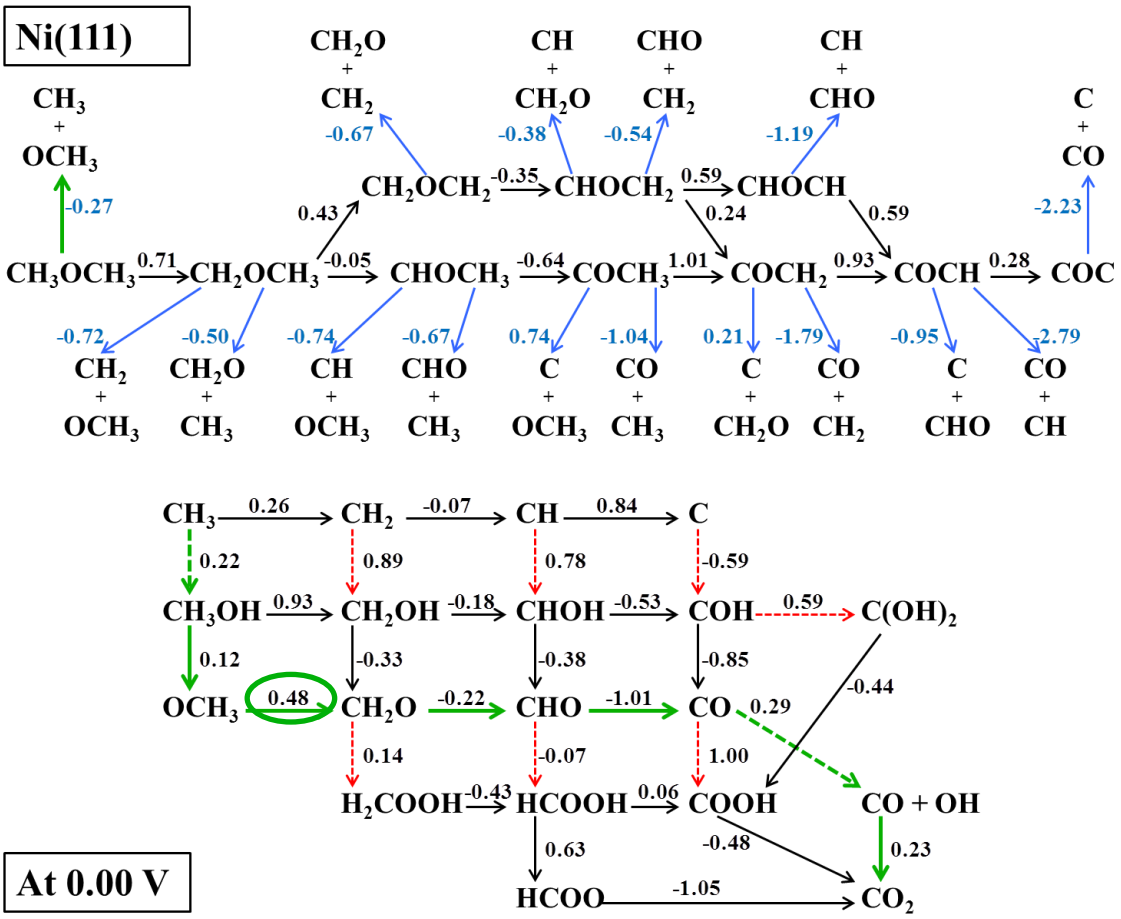
Scheme S15. Lowest-free-energy pathway for Cu(111) at 0.00 V. All values are in eV.



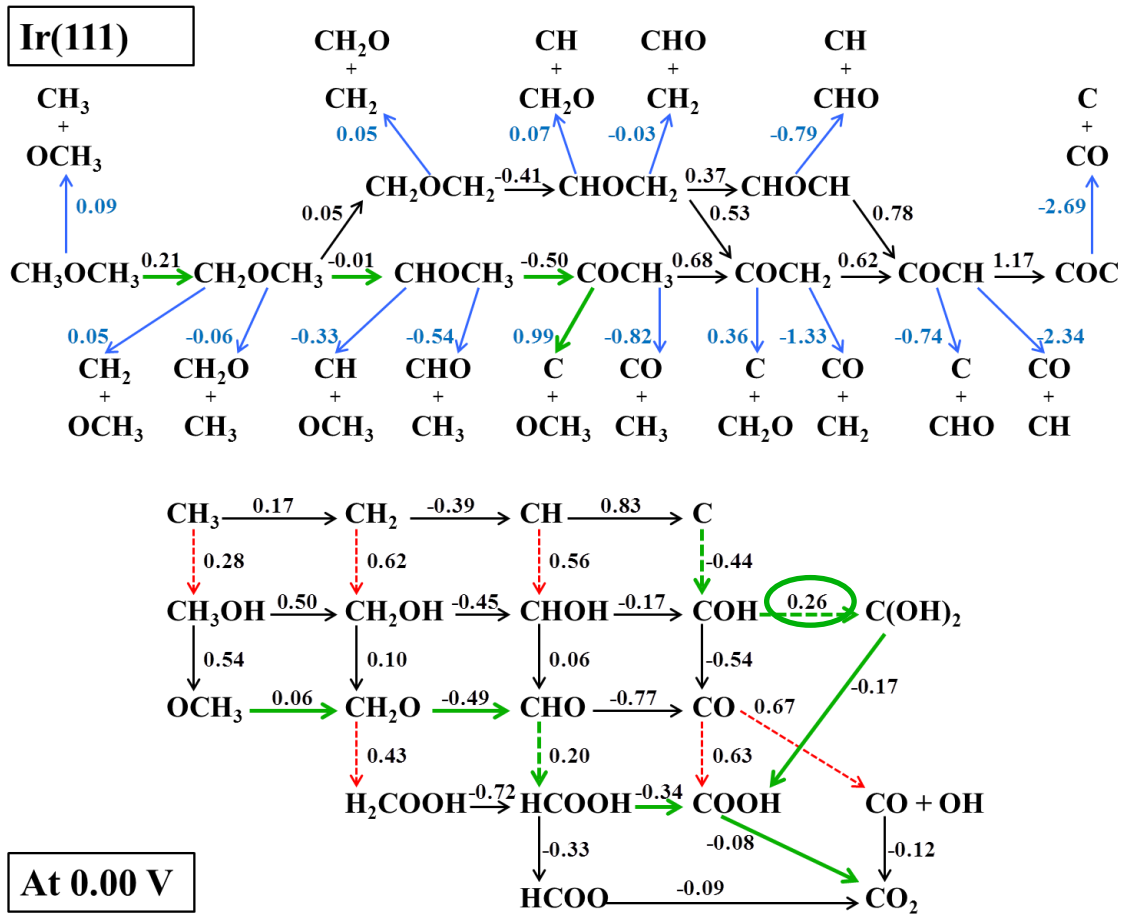
Scheme S16. Lowest-free-energy pathway for Pt(111) at 0.00 V. All values are in eV.



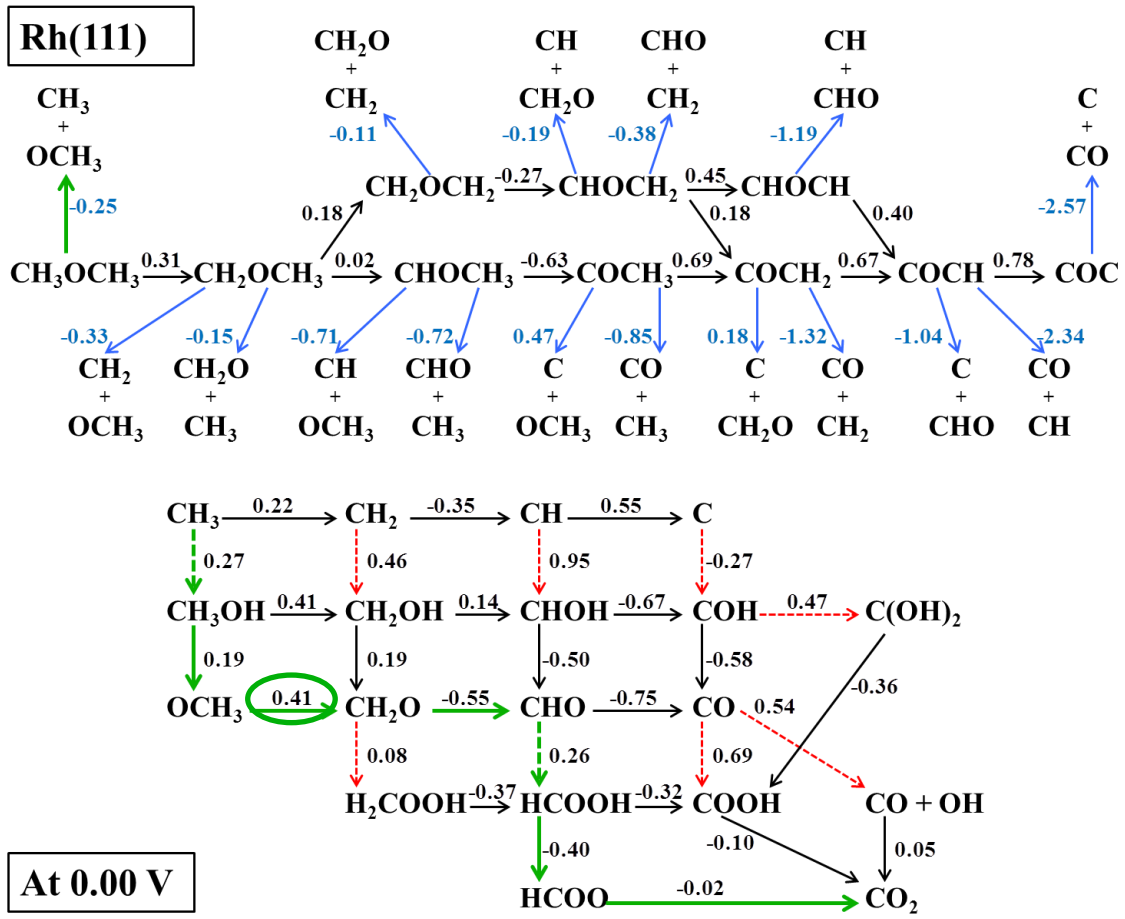
Scheme S17. Lowest-free-energy pathway for Pd(111) at 0.00 V. All values are in eV.



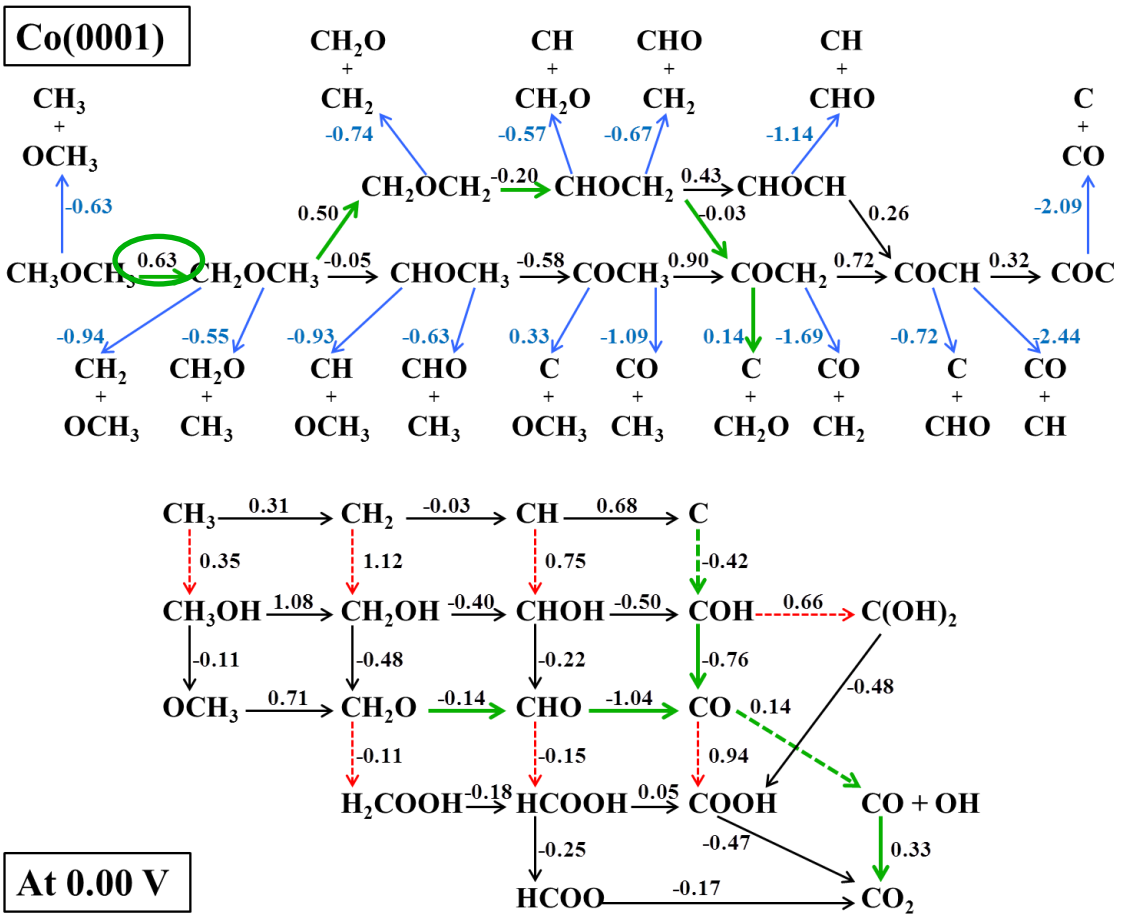
Scheme S18. Lowest-free-energy pathway for Ni(111) at 0.00 V. All values are in eV.



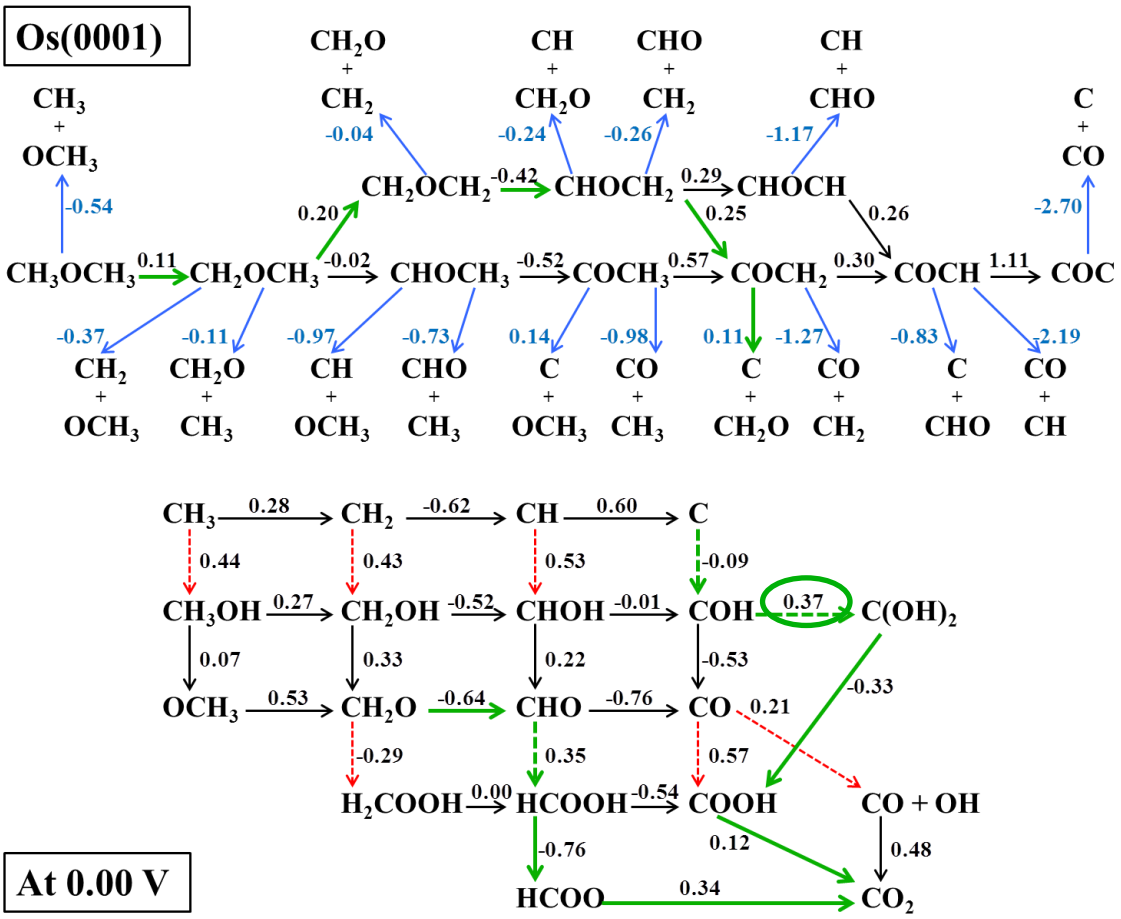
Scheme S19. Lowest-free-energy pathway for Ir(111) at 0.00 V. All values are in eV.



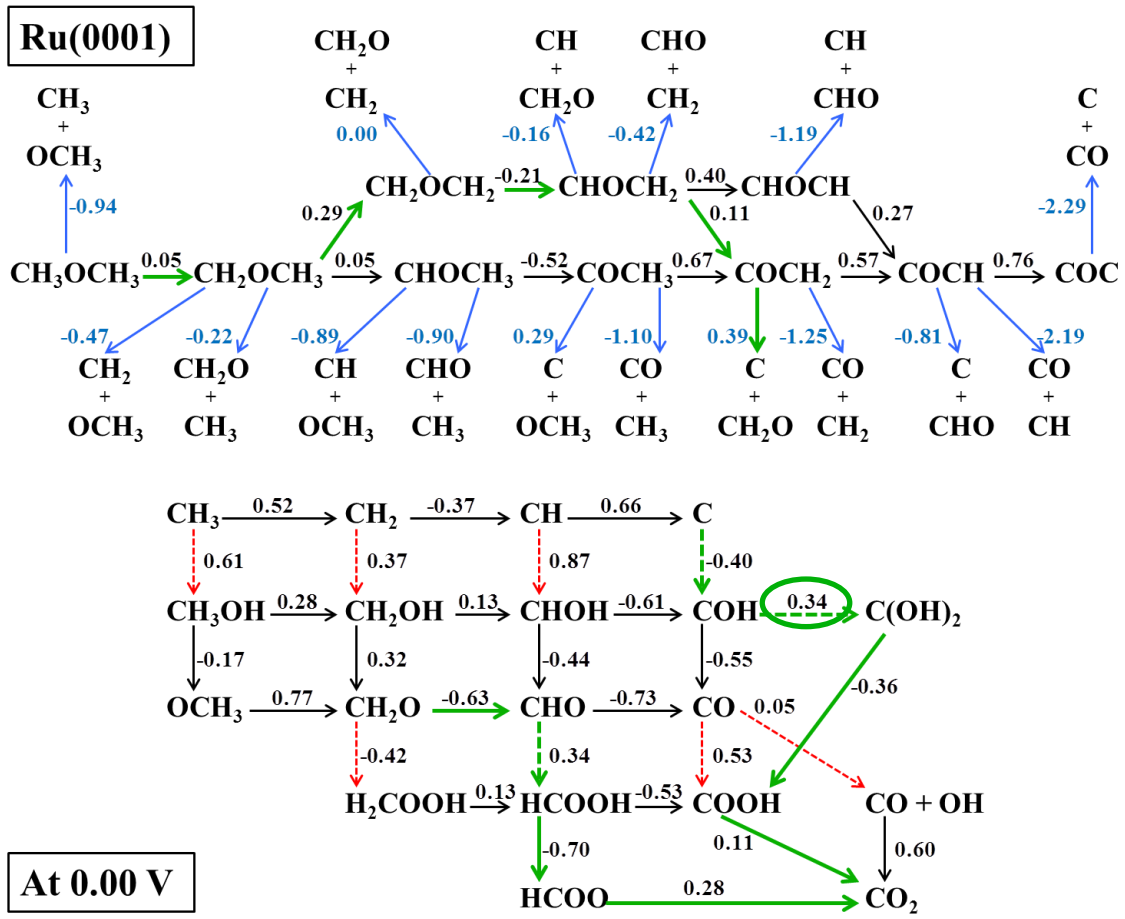
Scheme S20. Lowest-free-energy pathway for Rh(111) at 0.00 V. All values are in eV.



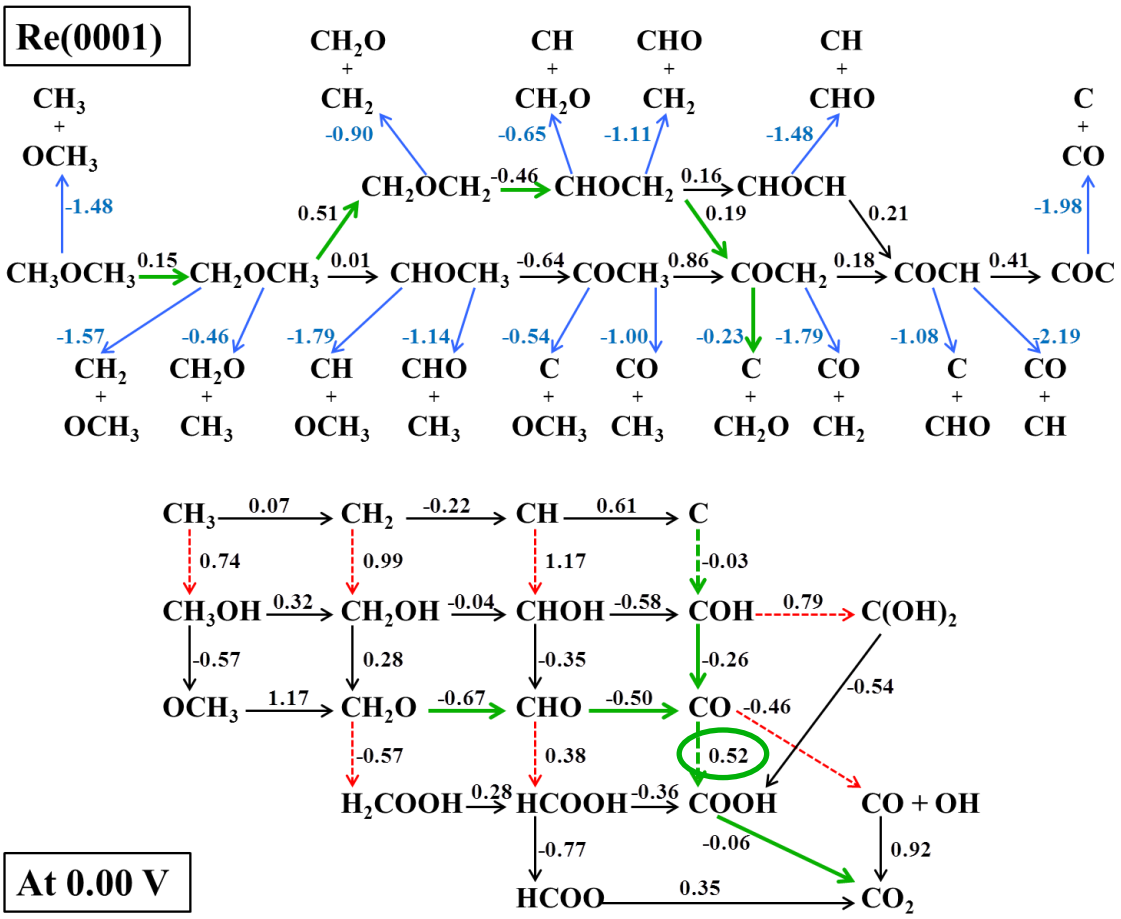
Scheme S21. Lowest-free-energy pathway for Co(0001) at 0.00 V. All values are in eV.



Scheme S22. Lowest-free-energy pathway for Os(0001) at 0.00 V. All values are in eV.



Scheme S23. Lowest-free-energy pathway for Ru(0001) at 0.00 V. All values are in eV.



Scheme S24. Lowest-free-energy pathway for Re(0001) at 0.00 V. All values are in eV.

S3. Linear Free Energy Correlations

In this section, we show the linear scaling relationships that were used in constructing the theoretical phase space. First, in Figure S1 we demonstrate that there is a weak correlation between C and O binding energies on the surfaces studied. We use this result to motivate our choosing of 2 descriptors, the free energy of adsorbed CO and the free energy of adsorbed OH, rather than a single universal descriptor.

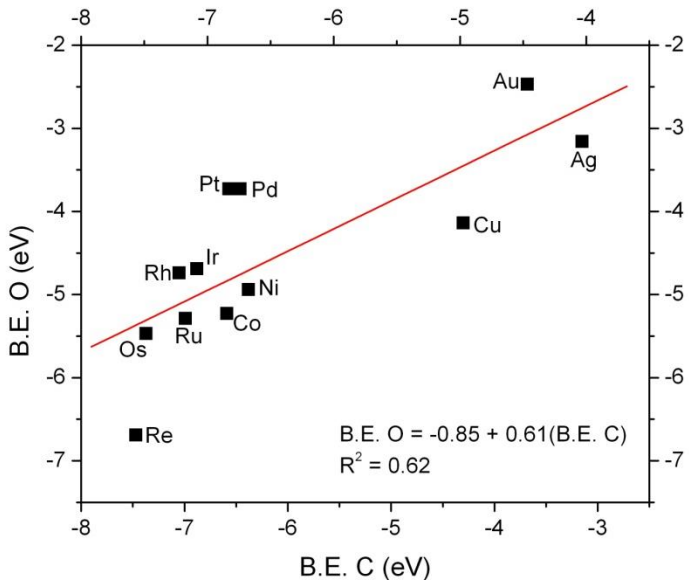


Figure S1. Binding energy of O versus binding energy of C on close-packed facets of metals.

In the following figures, we present the linear scaling relationships between the free energies of adsorbed intermediates versus the free energies of adsorbed CO and OH. For species which bind through at least 1 carbon atom, we use the free energy of CO as the independent variable used in the correlation (Figures S2 – S7). For species which bind through an oxygen atom, we use the free energy of OH as the independent variable used in the correlation (Figure S8).

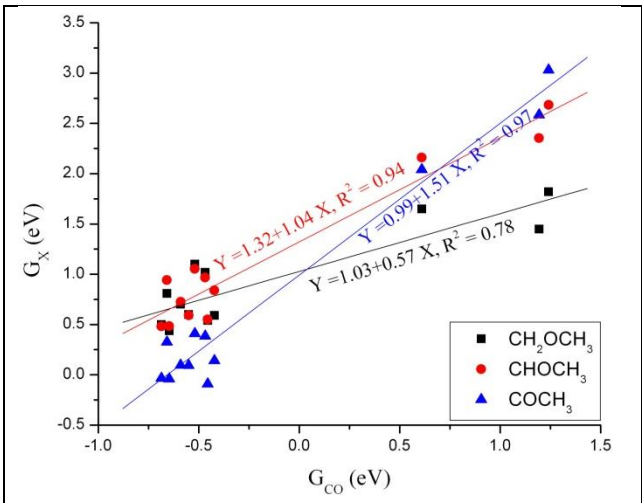


Figure S2. Free energy of adsorbed CH_xOCH_3 species versus free energy of adsorbed CO

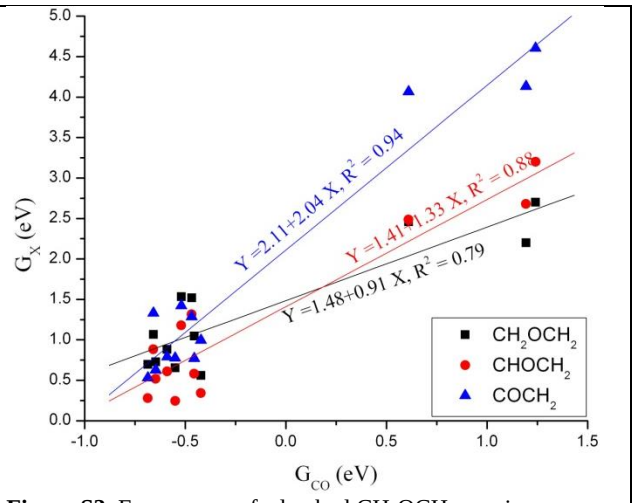


Figure S3. Free energy of adsorbed CH_xOCH_2 species versus free energy of adsorbed CO

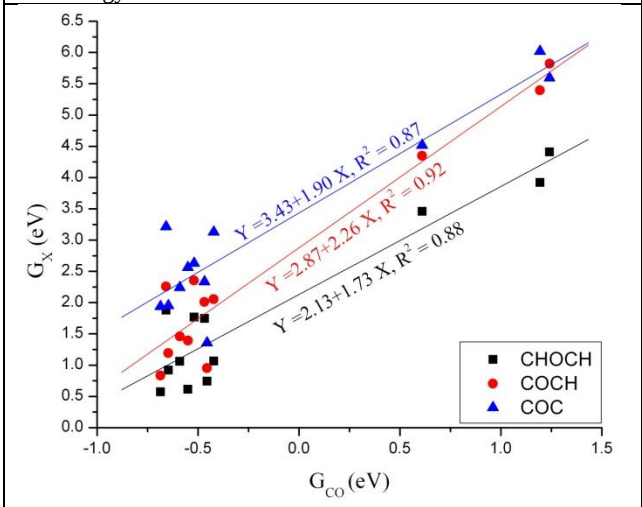


Figure S4. Free energy of adsorbed CHOCH, COCH, and COC versus free energy of adsorbed CO

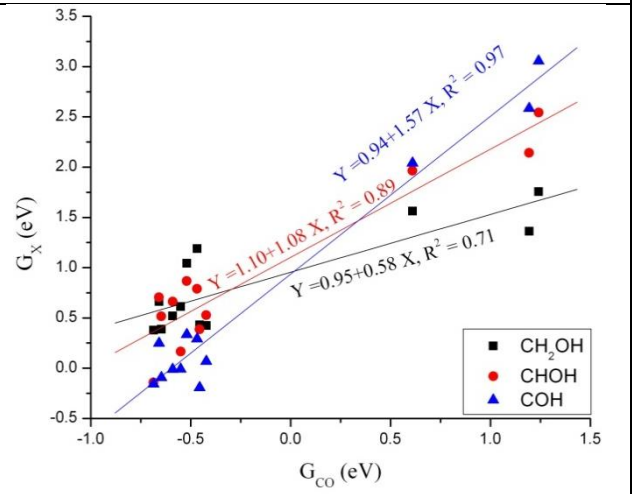


Figure S5. Free energy of adsorbed CH_2OH, CHOH, and COH versus free energy of adsorbed CO

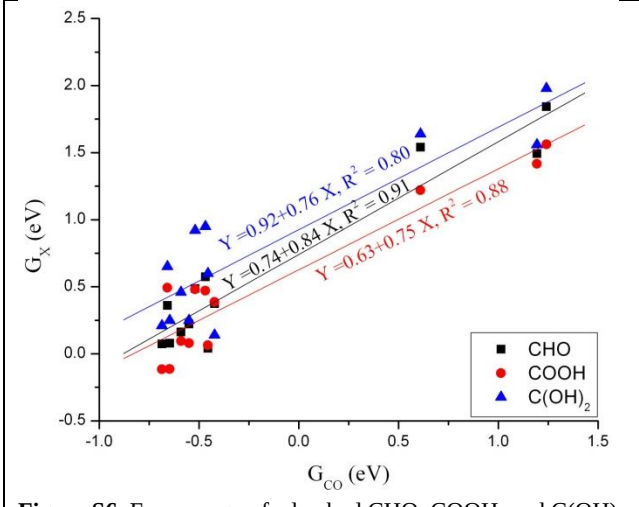


Figure S6. Free energy of adsorbed CHO, COOH, and $C(OH)_2$ versus free energy of adsorbed CO

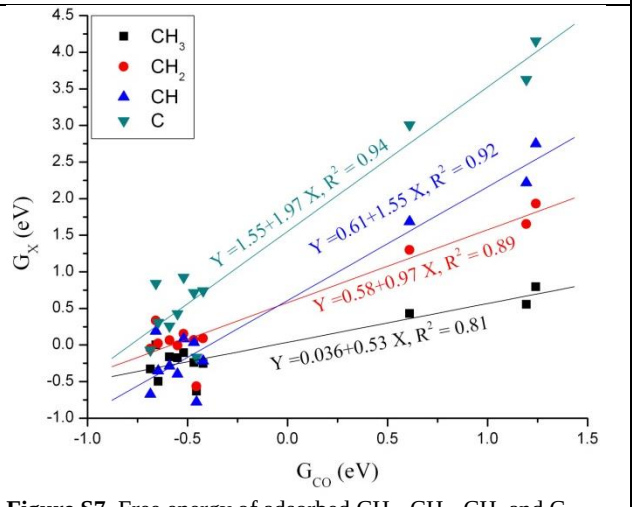


Figure S7. Free energy of adsorbed CH_3, CH_2, CH, and C versus free energy of adsorbed CO

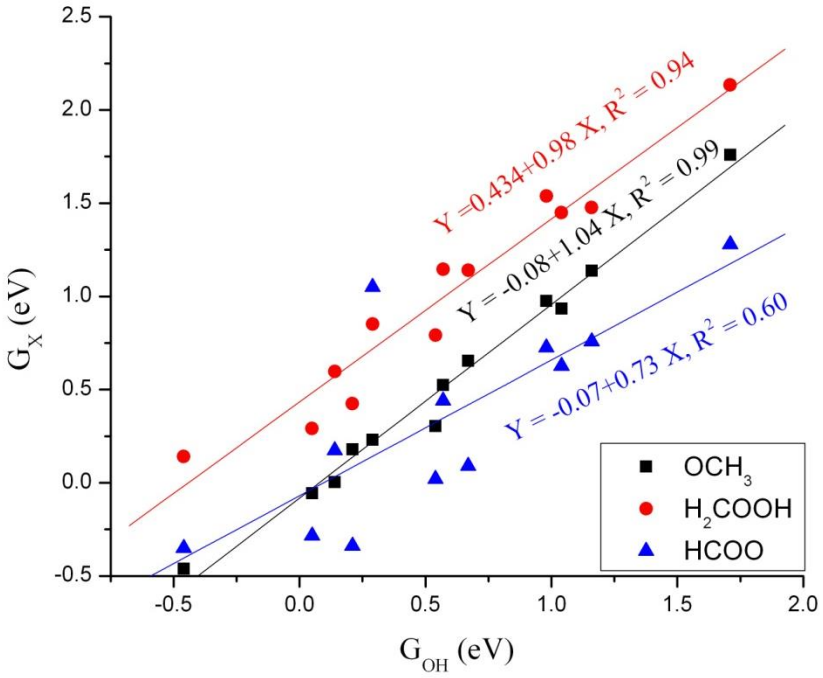


Figure S8. Free energy of adsorbed OCH_3, H_2COOH, and HCOO versus free energy of adsorbed OH

S4. Theoretical Phase Diagram at 0.35 V

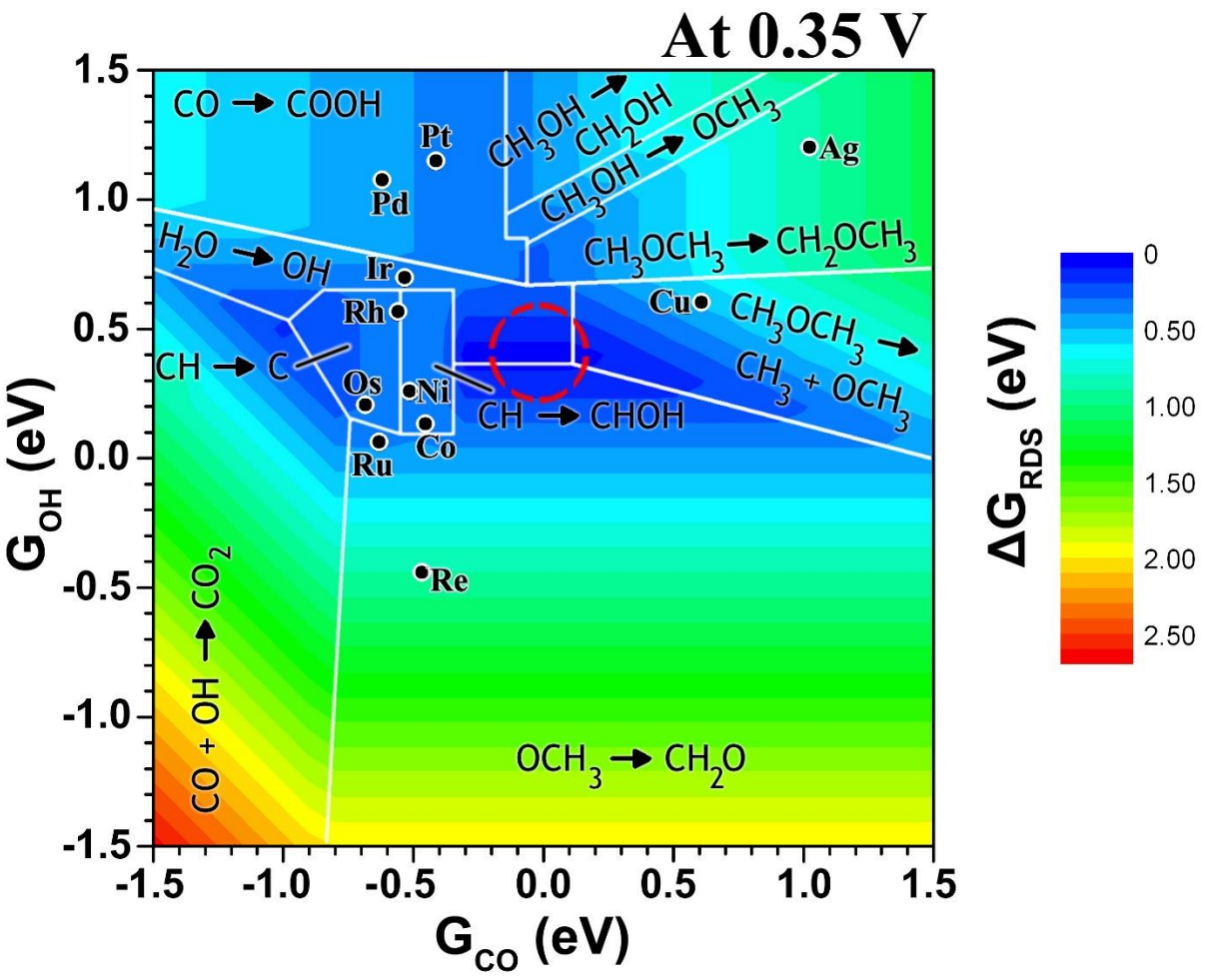


Figure S9. Theoretical phase-diagram showing free energy of reaction for most energetically difficult step (ΔG_{RDS}) within the most-exergonic pathway formulation at 0.35 V. Shown are regions with the same most endergonic reactions (note: proton/electron pairs and water are not written explicitly in the reactions). Monometallic catalysts are plotted for comparison/optimization, but most endergonic reaction identities (and ΔG_{RDS}) may differ from more rigorous DFT results presented in the main paper. Error is introduced due to the approximate nature of the scaling relations used to construct this diagram. Blue color is region of highest activity (circled in red), while red is the least active region. An analogous plot constructed at 0.0 V and 0.60 V is provided in the main text.