Electronic Supplementary Information for

Computational Screening of Homo and Hetero Transition Metal Dimer Catalysts for Reduction of CO_2 to C_2 Products with High Activity and Low Limiting Potential

Dachang Chen[a,b], Zhiwen Chen[b], Zhuole Lu[b], , Ju Tang[a], Xiaoxing Zhang[a,d*], Chandra Veer Singh[b,c*]

[a] School of Electrical Engineering and Automation, Wuhan University, Wuhan 430072, China

[b] Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, M5S 3E4, Canada

[c] Department of Mechanical and Industrial Engineering, University of Toronto, Toronto, Ontario, M5S 3G8, Canada

[d] Hubei Key Laboratory for High-efficiency Utilization of Solar Energy and Operation Control of Energy Storage System, Hubei University of Technology, Wuhan 430068, China

[*]Corresponding author, E-mail: xiaoxing.zhang@outlook.com; chandraveer.singh@utoronto.ca

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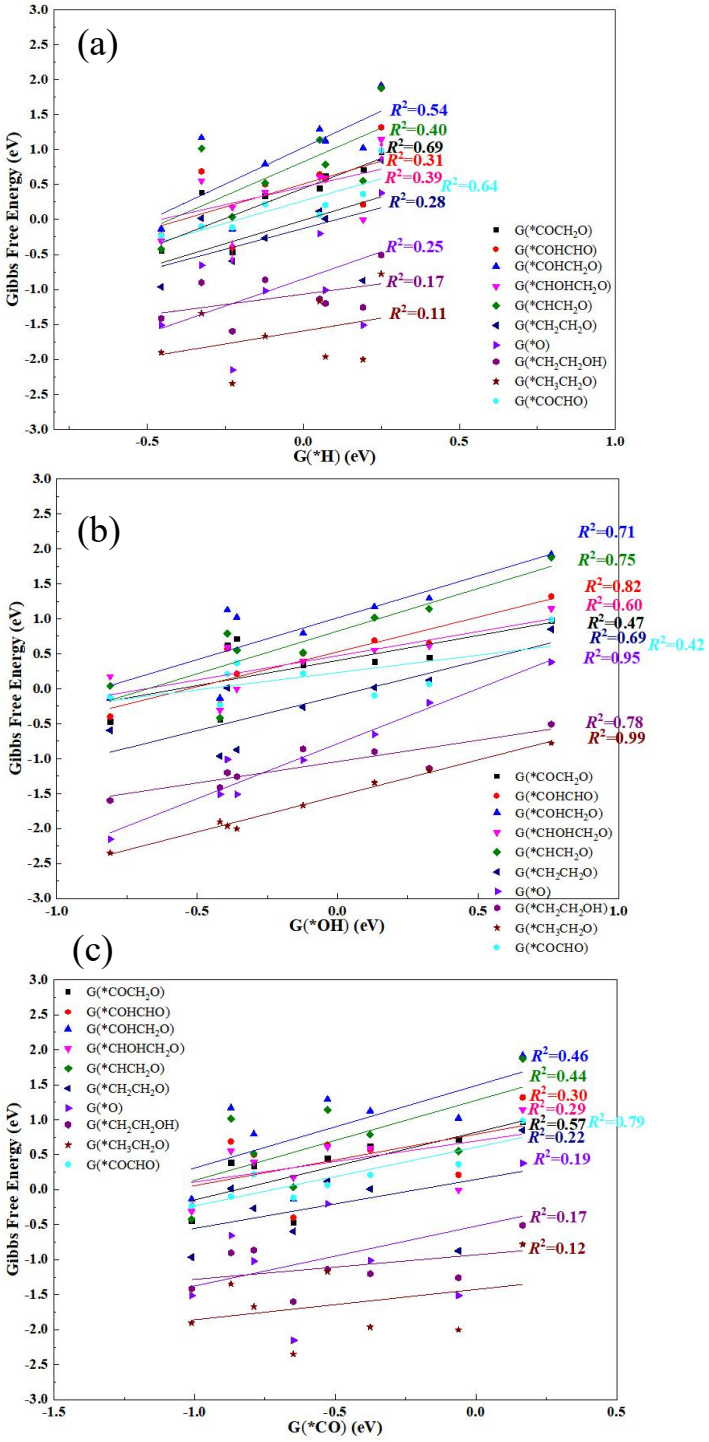

Figure S1 The adsorption free energy of *H, *OH and *CO against various C_2 related intermediates; (a) G(*H) versus every C_2 related intermediate; (b) G(*OH) versus every C_2 related intermediate. The linearity is marked with different color for different intermediates; (c) G(*CO) versus every C_2 related intermediate. The linearity is marked with different color for different intermediates

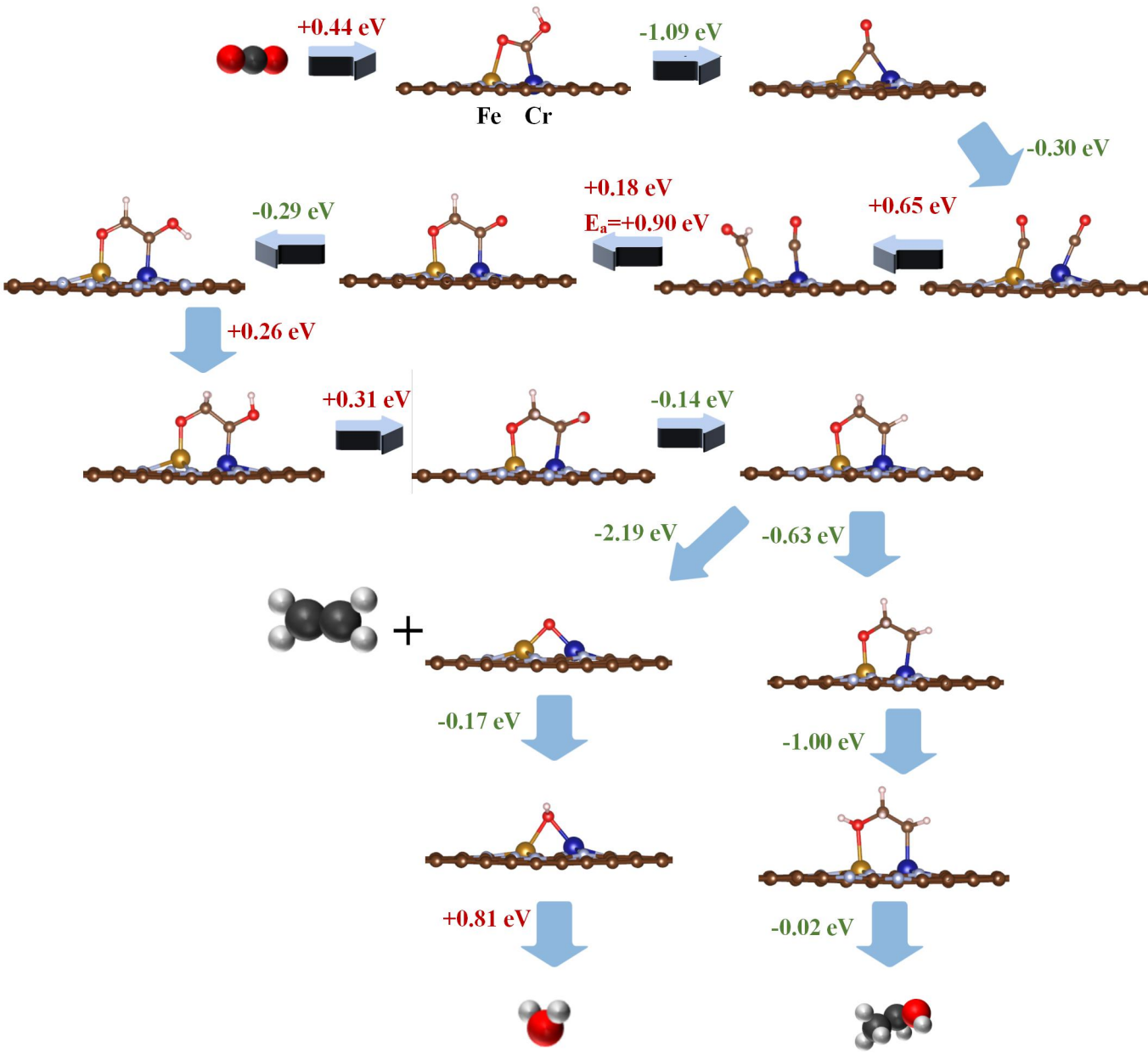

Figure S2 The pathway for CRR to C_2 products on Cr-Fe based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

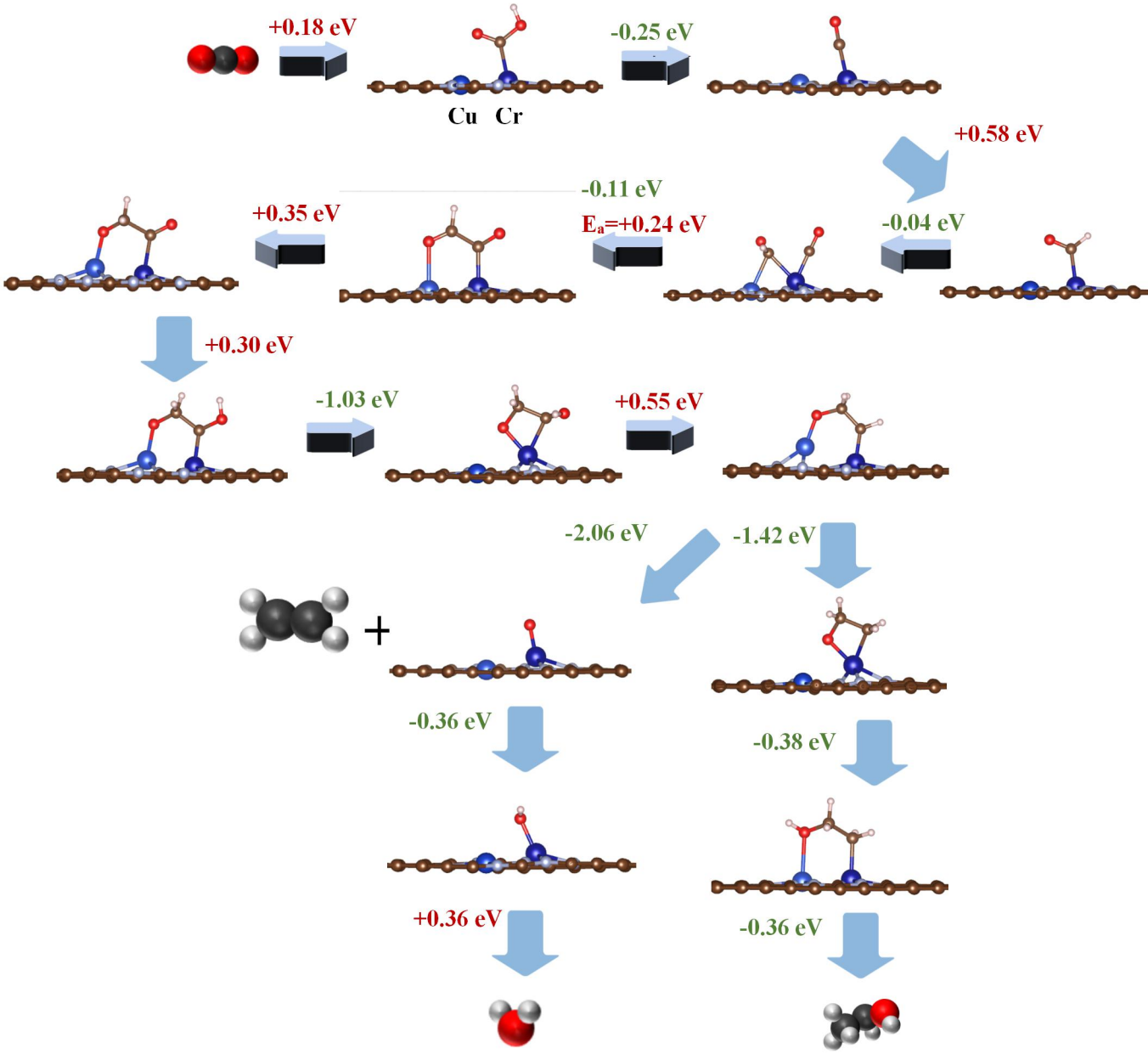

Figure S3 The pathway for CRR to C_2 products on Cr-Cu based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

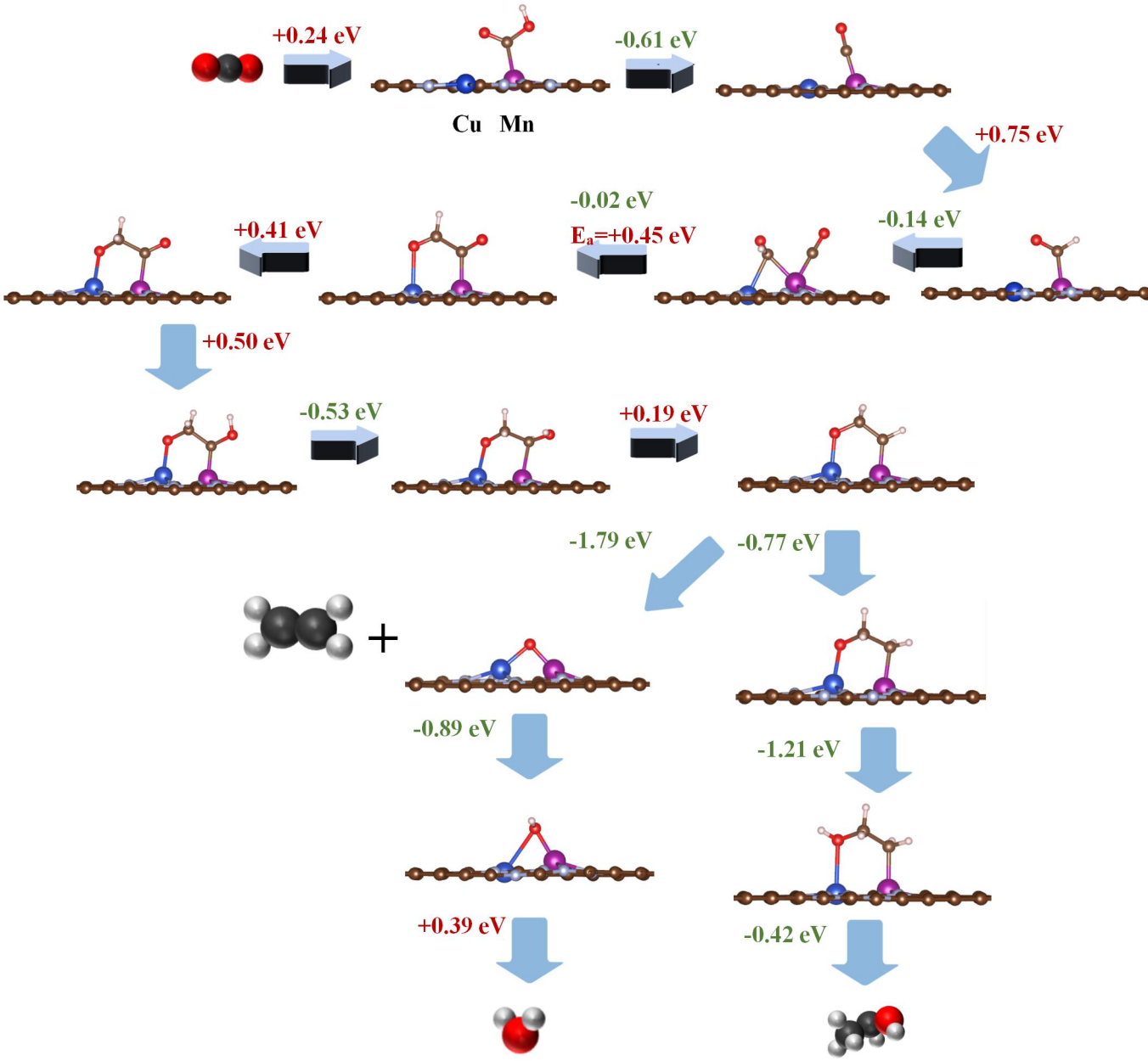

Figure S4 The pathway for CRR to C_2 products on Mn-Cu based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

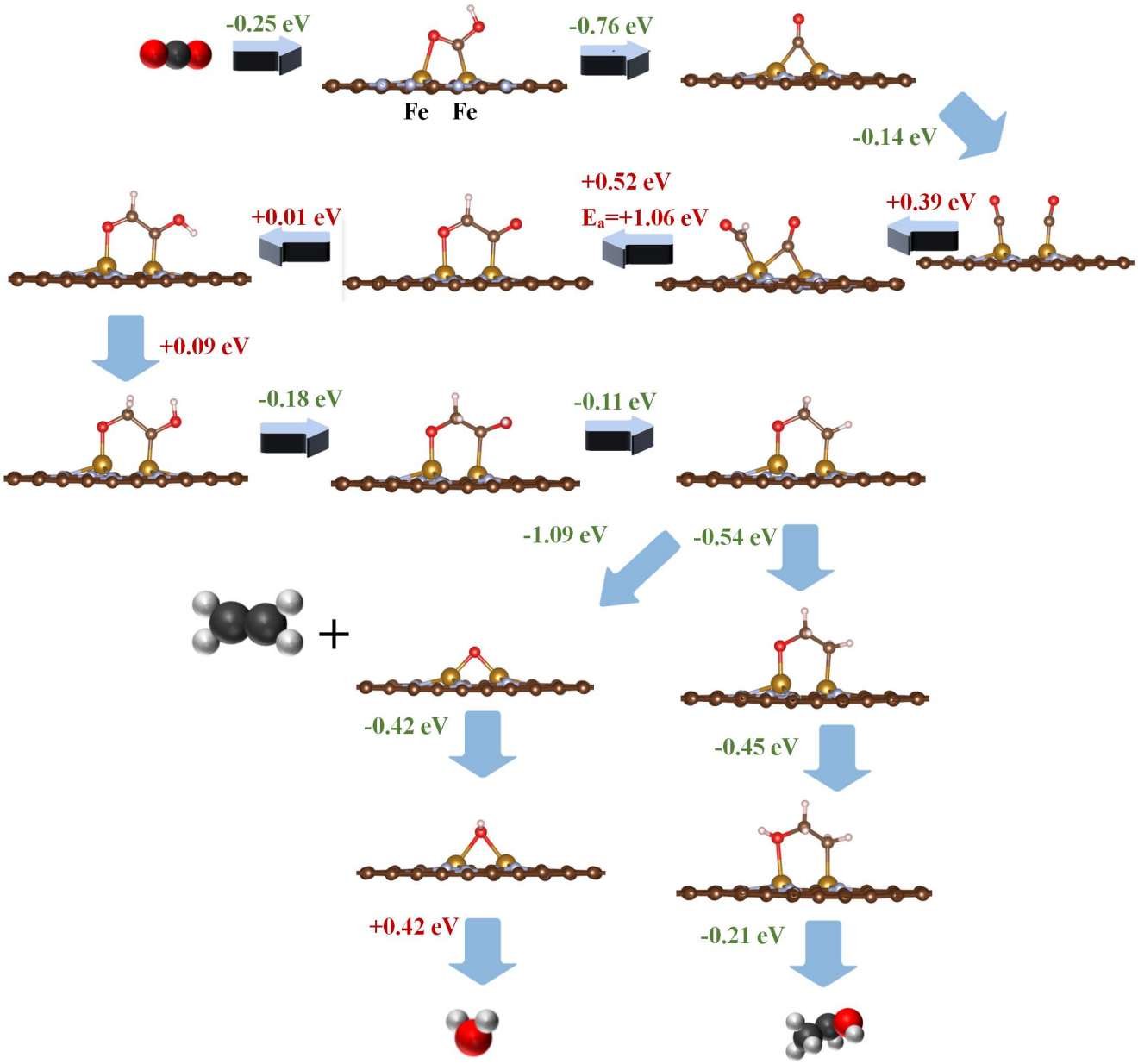

Figure S5 The pathway for CRR to C_2 products on Fe-Fe based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

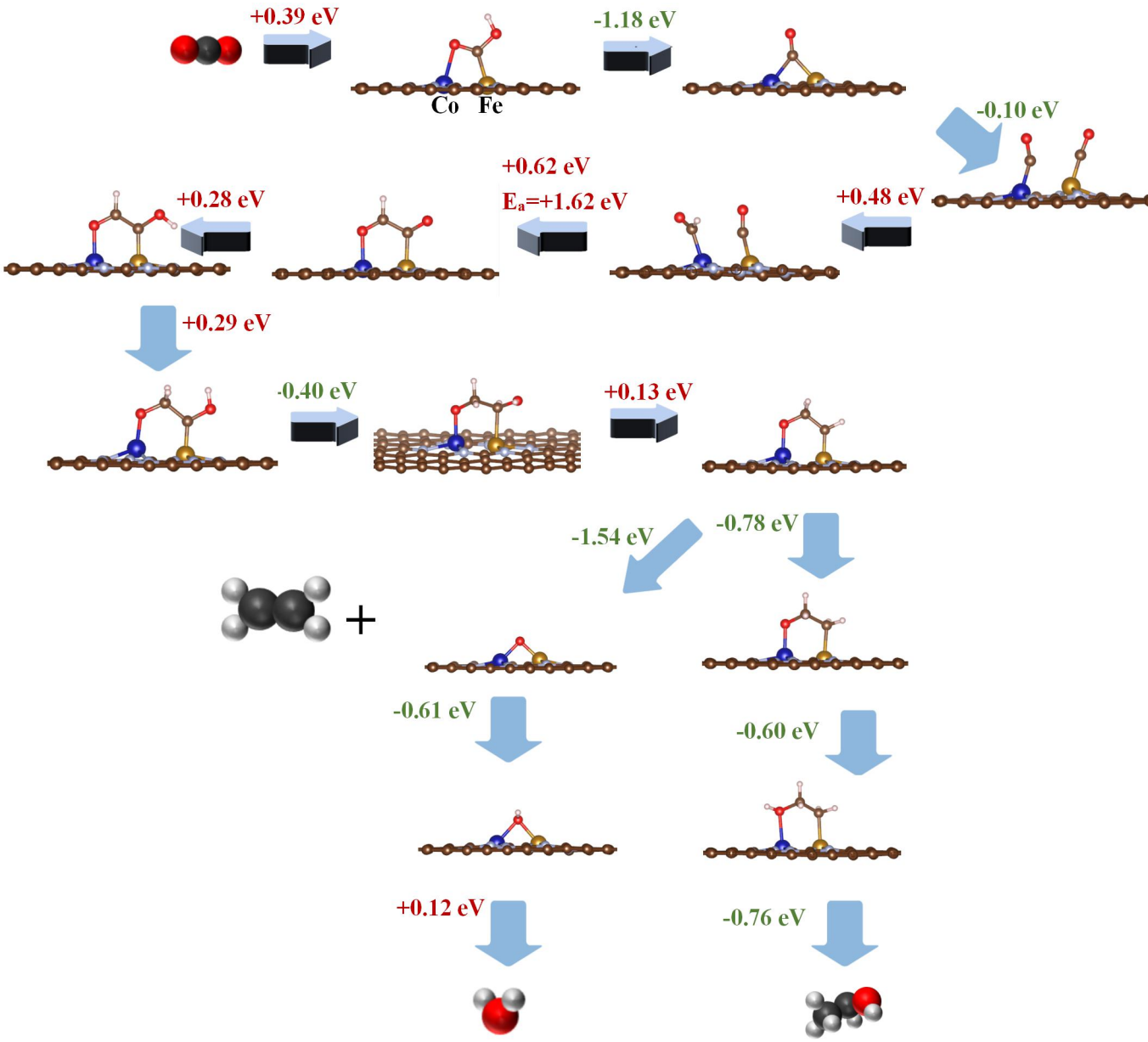

Figure S6 The pathway for CRR to C_2 products on Fe-Co based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

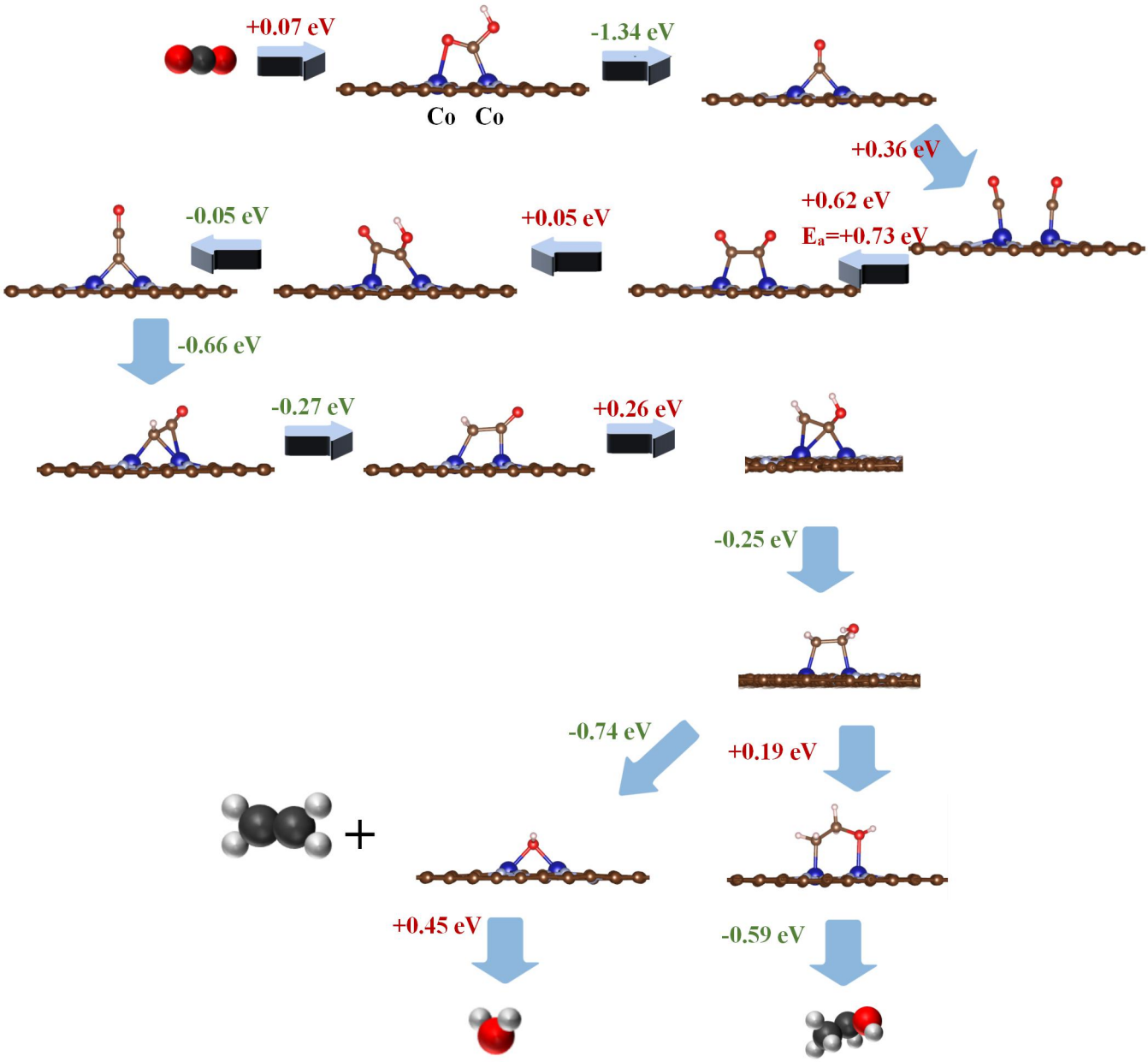

Figure S7 The pathway for CRR to C_2 products on Co-Co based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

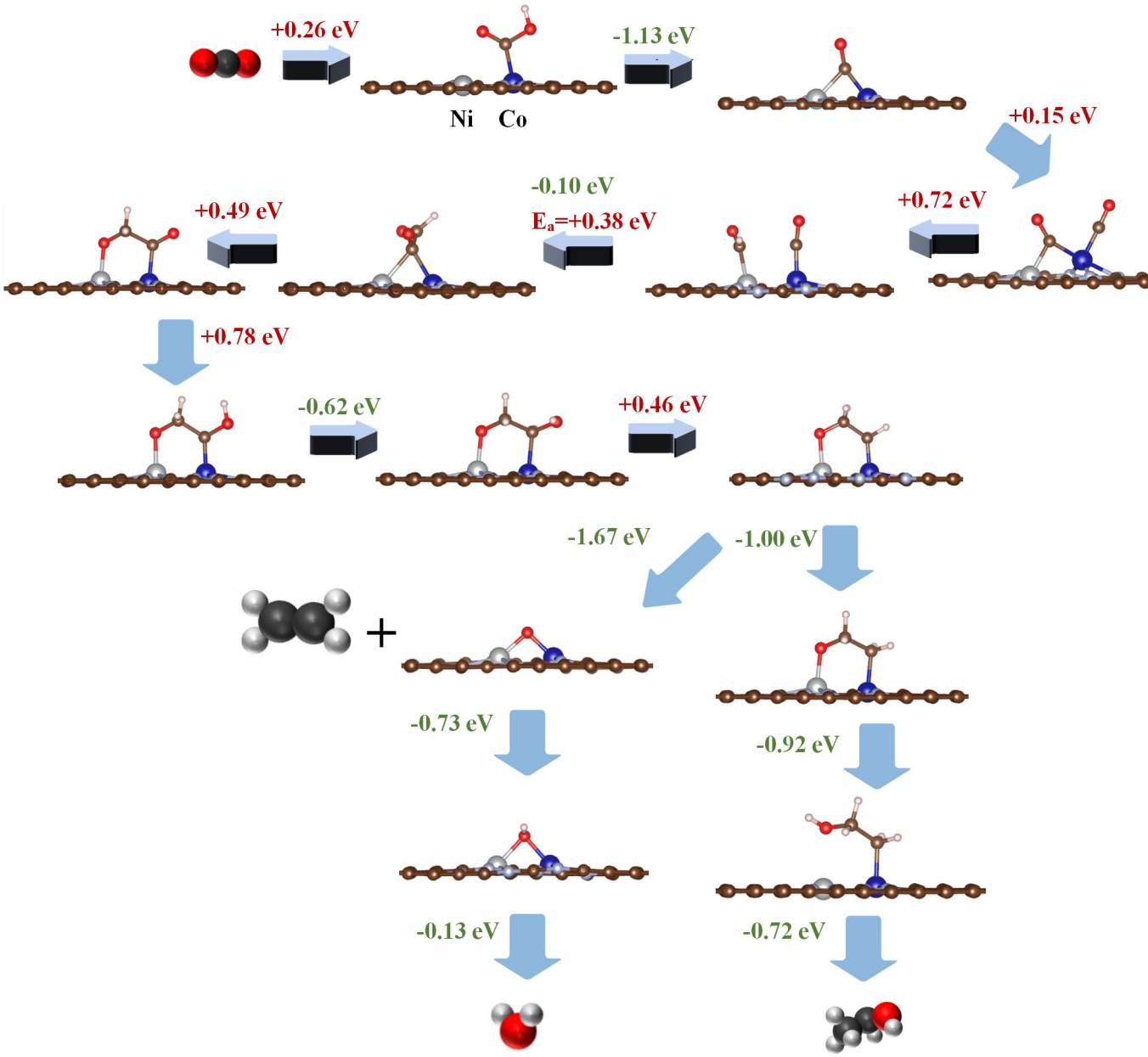

Figure S8 The pathway for CRR to C_2 products on Co-Ni based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

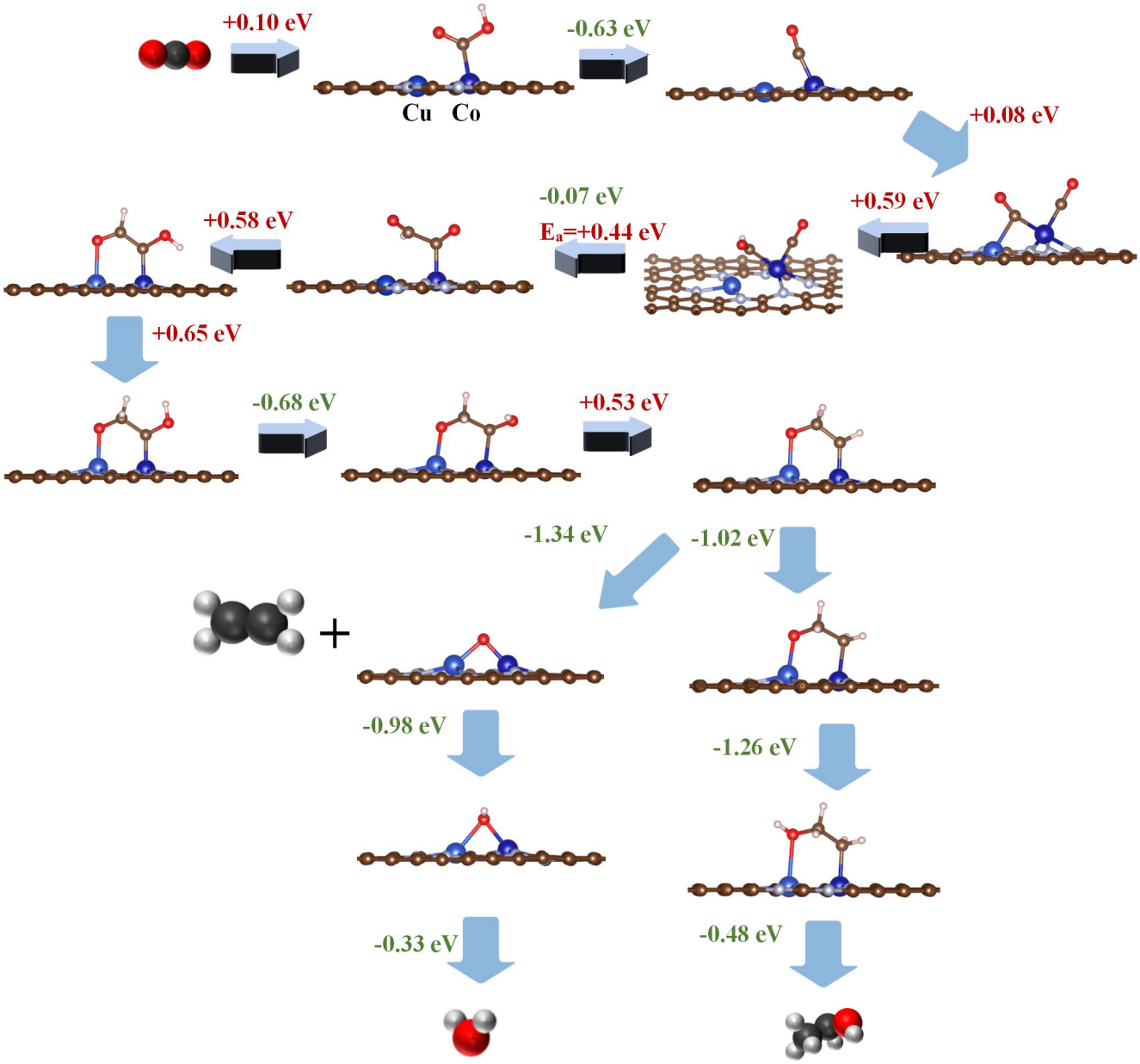

Figure S9 The pathway for CRR to C_2 products on Co-Cu based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

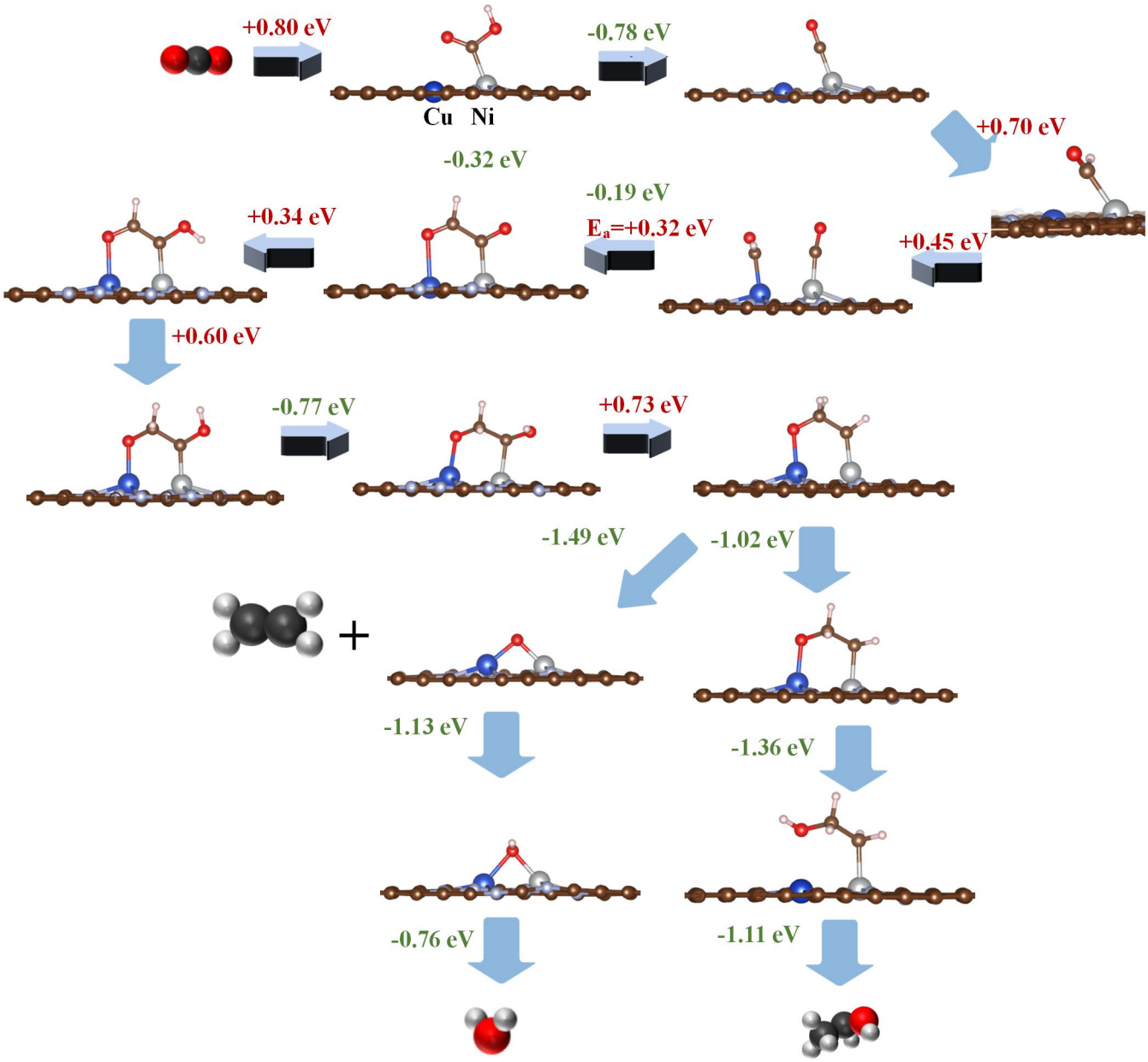

Figure S10 The pathway for CRR to C_2 products on Ni-Cu based DAC with the minimum limiting potential. The calculated free energies are all at U= 0 V versus RHE. (The red atoms are O, the brown atoms are C, the white atoms are H and the silver atoms in DAC are N)

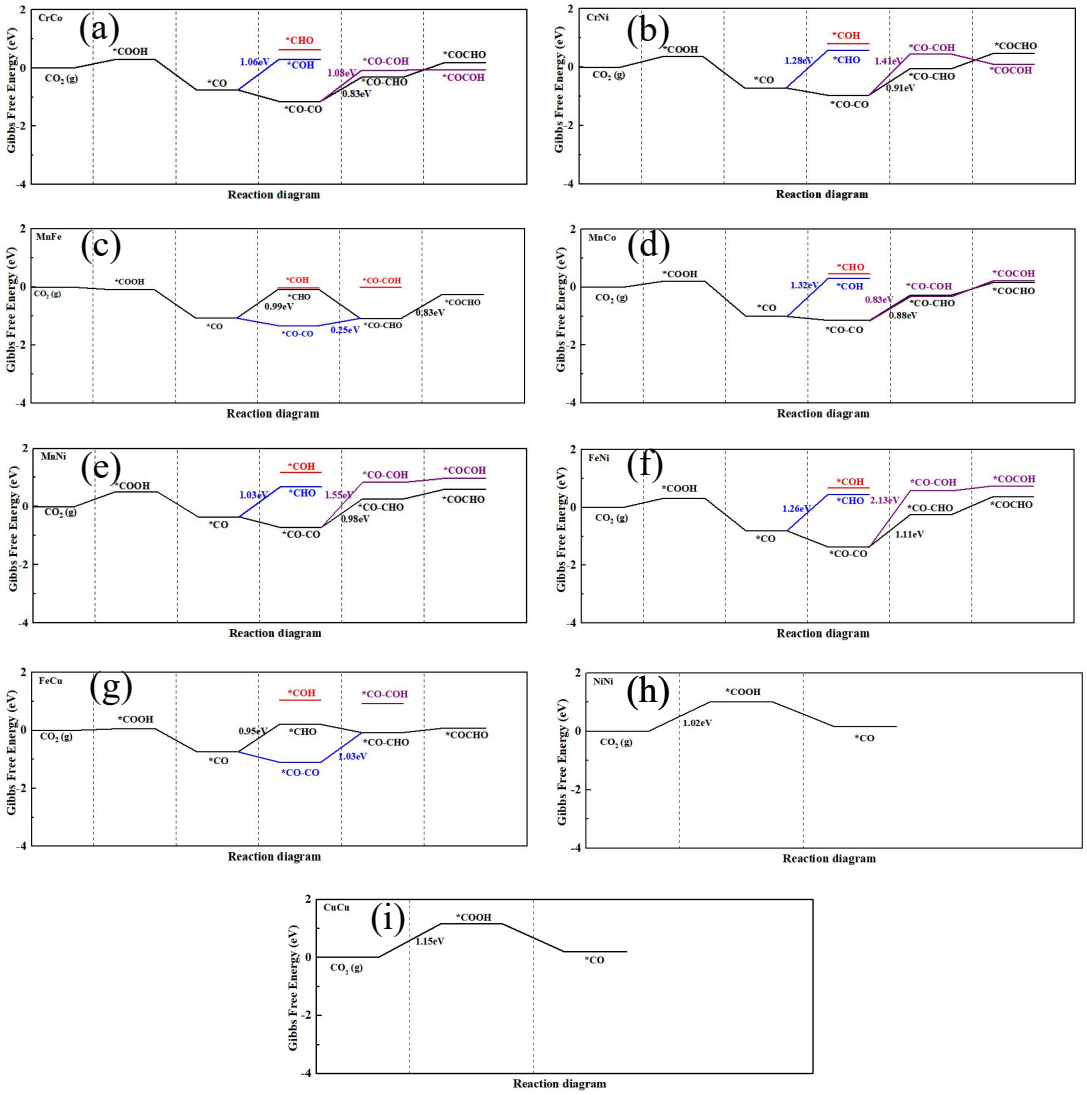

Figure S11 The reaction diagrams of CRR on other DACs. The value larger than +0.8 eV means that the corresponding reaction is difficult to happen.

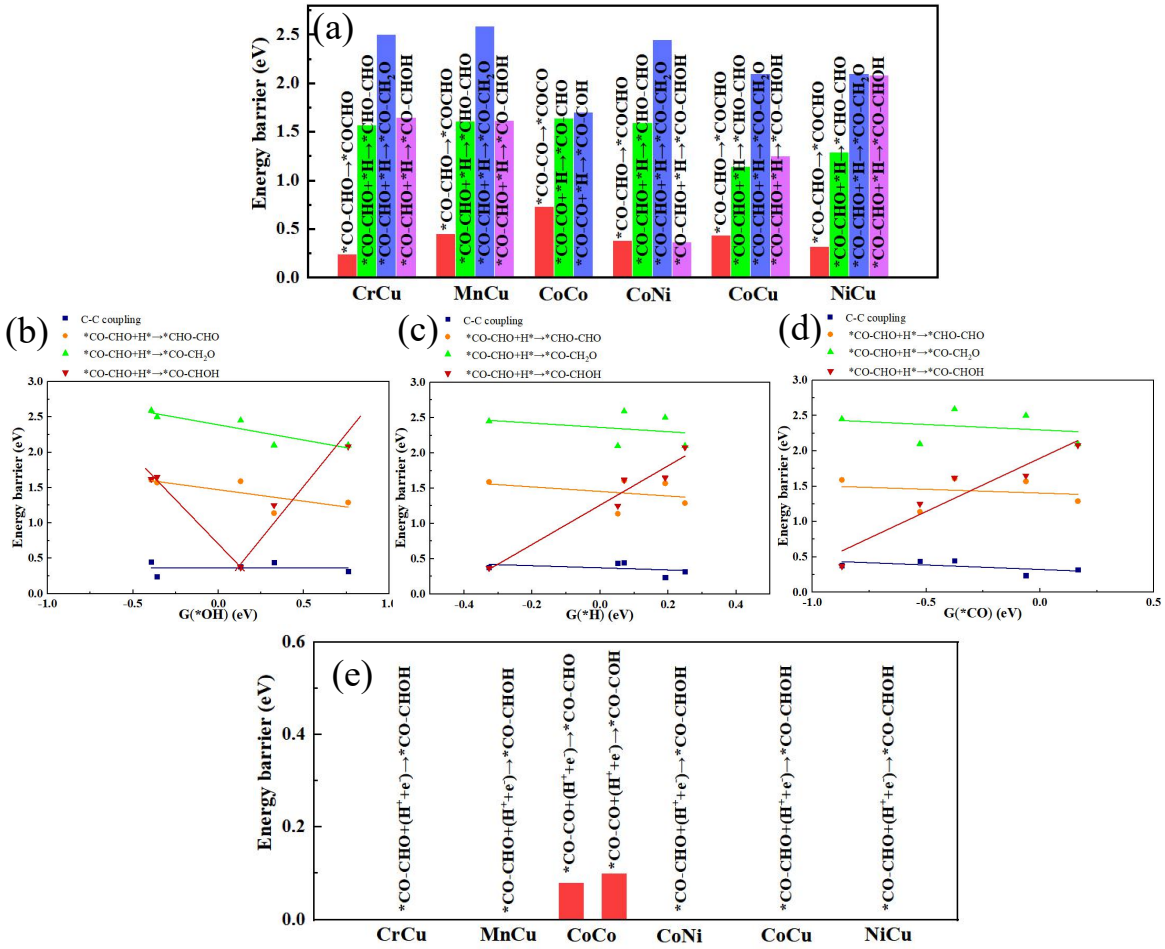

Figure S12 Comparison of energy barriers between the coupling process and protonation process on DACs, and the relationship with the descriptors: (a) comparison between the energy barriers of different reactions (LH mechanism); (b) relationship between the energy barriers and G(*OH); (c) relationship between the energy barriers and G(*H); (d) relationship between the energy barriers and G(*CO); (e) energy barriers of protonation process via ER mechanism at applied potential.

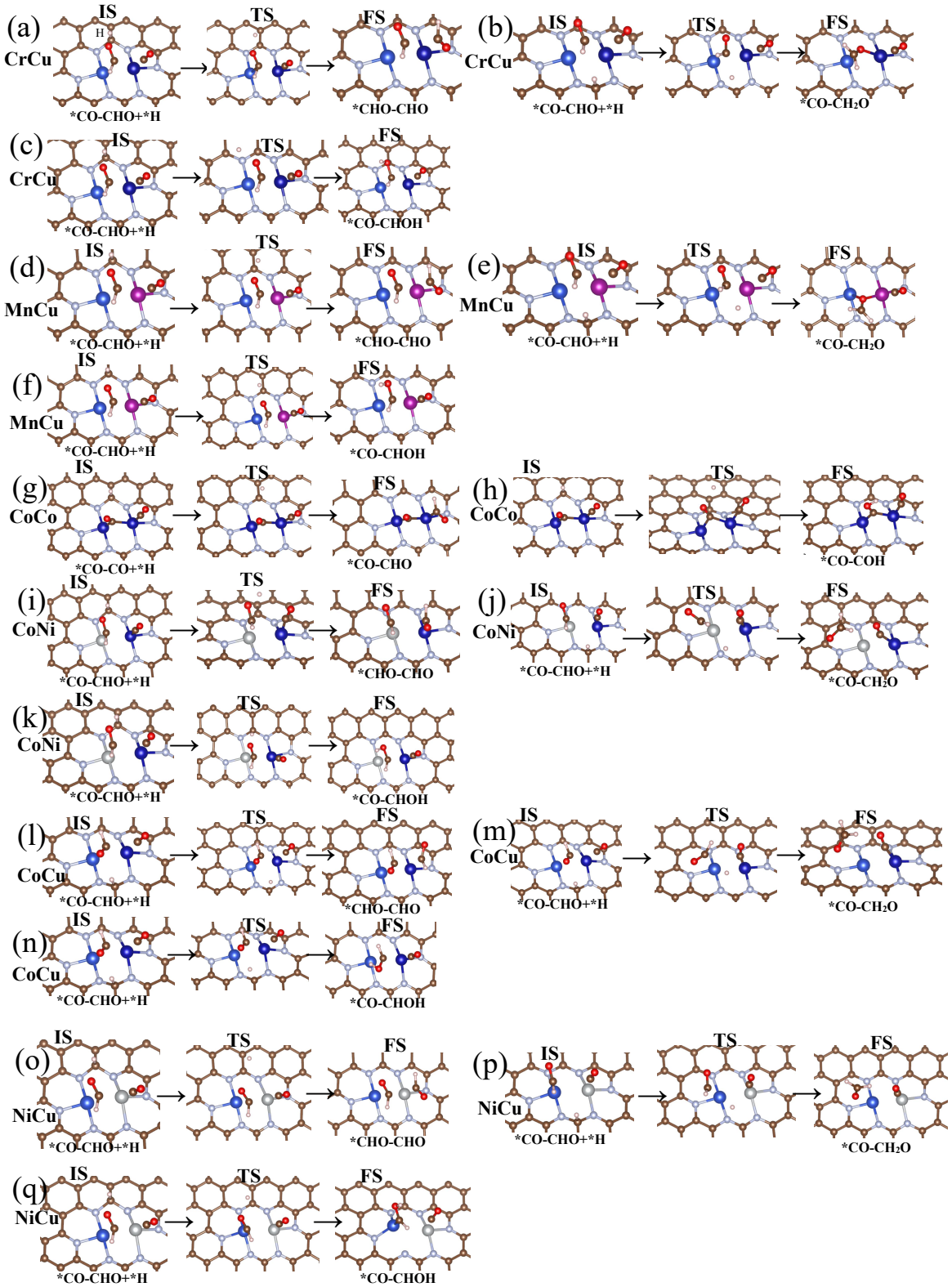

Figure S13 Configurations of protonation process of *CO-CHO or *CO-CO on DACs (LH mechanism).

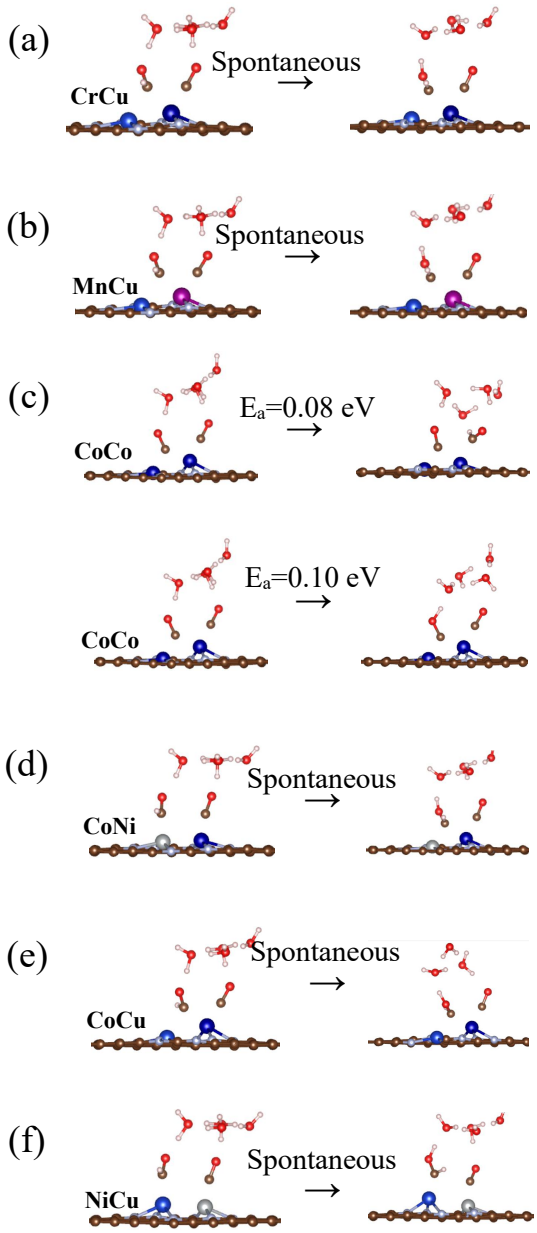

Figure S14 Protonation process of *CO-CHO or *CO-CO on DACs (ER mechanism) at applied potential: (a)*CO-CHO+(H^++e^-)→*CO-CHOH on Cr-Cu; (b)*CO-CHO+(H^++e^-)→*CO-CHOH on Mn-Cu; (c)*CO-CO+(H^++e^-)→*CO-CHO on Co-Co; *CO-CO+(H^++e^-)→*CO-COH on Co-Co; (d)*CO-CHO+(H^++e^-)→*CO-CHOH on Co-Ni; (e)*CO-CHO+(H^++e^-)→*CO-CHOH on Co-Cu; (f)*CO-CHO+(H^++e^-)→*CO-CHOH on Ni-Cu;

Table S1. Average binding energies (eV) of metal atoms for TM_2N_6-graphene system and average cohesive energy in bulk metals for doped two metal atoms

TM atoms	Average binding energy (eV)	Average cohesive energy (bulk metal) (eV)	Difference value between binding energy and cohesive energy (bulk metal) (eV)	Magnetic moment (μ_B)
CrCr	-4.66	-4.10	-0.56	7.99
CrMn	-4.59	-3.51	-1.08	8.15
CrFe	-5.14	-4.19	-0.95	6.23
CrCo	-5.67	-4.25	-1.42	1.50
CrNi	-5.45	-4.27	-1.18	2.70
CrCu	-4.72	-3.80	-0.92	3.53
MnMn	-4.58	-2.92	-1.66	7.06
MnFe	-5.25	-3.60	-1.65	5.57
MnCo	-5.62	-3.66	-1.96	2.51
MnNi	-5.58	-3.68	-1.90	3.40
MnCu	-4.58	-3.21	-1.37	3.51
FeFe	-5.93	-4.28	-1.65	4.16
FeCo	-6.26	-4.34	-1.92	3.20
FeNi	-5.96	-4.36	-1.6	2.92
FeCu	-5.06	-3.89	-1.17	2.16
CoCo	-6.32	-4.39	-1.93	2.42
CoNi	-6.15	-4.42	-1.73	1.03
CoCu	-5.31	-3.94	-1.37	0.66
NiNi	-6.06	-4.44	-1.62	0.00
NiCu	-5.11	-3.97	-1.14	0.21
CuCu	-4.22	-3.49	-0.73	0.80

Table S2. The values of thermal correction containing the zero-point energy, the enthalpic correction, and the entropy correction of the relevant molecules, and the adsorbed species. The temperature is set as 298 K.

Species	Zero-point energy (eV)	Enthalpic correction at 298K (eV)	Entropy at 298K (eV)	Correction for liquid phase (eV)	Solvent correction (eV)
CO_2 (g)	0.31	0.13	0.66	/	/
H_2O (l)	0.57	0.1	0.58	–0.09	/
H_2 (g)	0.27	0.09	0.40	/	/
C_2H_5OH (l)	2.11	0.20	0.83	–0.07	/
C_2H_4 (g)	1.36	0.13	0.71	/	/
*H	0.17	0.03	0.02	/	/
*OH	0.37	0.05	0.08	/	–0.20
*COOH	0.6	0.08	0.22	/	–0.10
*CO	0.19	0.05	0.18	/	/
*CHO	0.51	0.08	0.08	/	/
*COH	0.57	0.06	0.09	/	–0.10
*CO-CO	0.41	0.13	0.29	/	/
*COCO	0.42	0.11	0.24	/	/
*CO-CHO	0.70	0.11	0.30	/	/
*COCHO	0.72	0.10	0.29	/	/
*CO-COH	0.74	0.13	0.24	/	–0.10
*COCOH	0.72	0.11	0.28	/	–0.10
*$COCH_2O$	1.05	0.12	0.23	/	/
*COHCHO	1.03	0.13	0.26	/	–0.10
*$COHCH_2O$	1.33	0.13	0.26	/	–0.10
*$CHOHCH_2O$	1.66	0.15	0.26	/	–0.10
*$CHCH_2O$	1.15	0.11	0.22	/	/
*CH_2CH_2O	1.55	0.12	0.18	/	/
*CH_2CH_2OH	1.86	0.12	0.26	/	–0.10
*CH_3CH_2O	1.89	0.12	0.24	/	/
*COHCOH	1.00	0.13	0.31	/	–0.10
*CCO	0.34	0.08	0.18	/	/
*CHCO	0.63	0.09	0.19	/	/
*CCOH	0.63	0.10	0.21	/	–0.10
*CH_2CO	0.92	0.10	0.13	/	/
*CHCOH	0.89	0.12	0.20	/	–0.10
*CH_2COH	1.24	0.13	0.17	/	–0.10
*CH_2CHOH	1.55	0.13	0.22	/	–0.10

Table S3. Values of G(*H), G(*OH) on various of DACs and magnetic moments, the DACs of which G(*H) or G(*OH) lower than -0.9 eV are excluded

TM atoms	G(*H) (eV)	Magnetic moment (μ_B)	G(*OH) (eV)	Magnetic moment (μ_B)
CrCr	-0.83	7.10	-1.79 (<-0.9 eV)	6.90
CrMn	-1.05 (<-0.9 eV)	0.34	-1.43 (<-0.9 eV)	6.23
CrFe	-0.23	1.48	-0.81	0.29
CrCo	-0.34	2.84	-0.86	2.72
CrNi	-0.32	3.57	-0.55	1.96
CrCu	0.19	2.89	-0.36	2.96
MnMn	-0.71	5.88	-1.13 (<-0.9 eV)	6.11
MnFe	-0.52	4.63	-0.80	4.48
MnCo	-0.50	3.41	-0.54	3.18
MnNi	0.07	2.97	0.00	2.45
MnCu	0.07	3.31	-0.39	3.50
FeFe	-0.46	3.24	-0.42	3.29
FeCo	-0.12	2.61	-0.12	1.25
FeNi	-0.19	1.68	-0.10	1.13
FeCu	0.09	1.56	-0.18	2.24
CoCo	-0.47	1.05	-0.45	0.00
CoNi	-0.33	0.00	0.13	0.59
CoCu	0.05	0.00	0.33	1.23
NiNi	-0.01	0.00	0.86	0.21
NiCu	0.25	0.50	0.76	0.69
CuCu	0.59	0.00	0.79	1.18

Table S4. Values of G(*COOH), G(*CO) on various of DACs and magnetic moments

TM atoms	G(*COOH) (eV)	Magnetic moment (μ_B)	G(*CO) (eV)	Magnetic moment (μ_B)
CrFe	0.44	0.98	-0.65	0.54
CrCo	0.29	0.55	-0.75	2.00
CrNi	0.36	3.48	-0.71	2.64
CrCu	0.19	2.60	-0.06	2.17
MnFe	-0.09	4.57	-1.07	4.75
MnCo	0.21	3.32	-1.01	1.66
MnNi	0.52	2.32	-0.35	2.50
MnCu	0.24	2.36	-0.38	2.08
FeFe	-0.25	3.21	-1.01	1.37
FeCo	0.39	2.73	-0.79	2.32
FeNi	0.32	1.55	-0.81	1.40
FeCu	0.05	0.24	-0.74	0.47
CoCo	0.07	1.52	-1.27	0.00
CoNi	0.26	0.00	-0.87	0.00
CoCu	0.10	0.00	-0.53	0.00
NiNi	1.02	0.00	0.17	0.00
NiCu	0.80	0.50	0.03	1.08
CuCu	1.15	0.66	0.19	0.04

Table S5. Values of G(*CHO), G(*COH) on various of DACs and magnetic moments

TM atoms	G(*CHO) (eV)	Magnetic moment (μ_B)	G(*COH) (eV)	Magnetic moment (μ_B)
CrFe	0.74	0.72	0.56	1.54
CrCo	0.64	0.02	0.31	2.67
CrNi	0.57	1.59	0.81	2.03
CrCu	0.52	2.47	1.31	1.13
MnFe	-0.08	4.64	-0.03	2.56
MnCo	0.46	3.11	0.31	2.12
MnNi	0.68	2.11	1.17	1.35
MnCu	0.37	2.12	1.22	1.43
FeFe	-0.07	3.20	0.28	2.08
FeCo	0.59	2.63	0.50	0.80
FeNi	0.46	1.51	0.68	0.00
FeCu	0.21	0.49	1.05	0.00
CoCo	0.18	1.47	0.03	0.00
CoNi	0.29	0.00	0.99	0.20
CoCu	0.15	0.00	1.49	0.00
NiNi	0.50	0.00	2.11	1.63
NiCu	0.72	0.49	2.14	0.00
CuCu	1.26	0.00	2.42	0.00

Table S6. Values of G(*CO-CO), G(*CO-CHO) and G(*CO-COH) on various of DACs and magnetic moments

TM atoms	G(*CO-CO) (eV)	Magnetic moment (μ_B)	G(*CO-CHO) (eV)	Magnetic moment (μ_B)	G(*CO-COH) (eV)	Magnetic moment (μ_B)
CrFe	-0.94	1.56	-0.30	0.31	0.11	0.11
CrCo	-1.15	1.81	-0.31	1.50	-0.07	1.08
CrNi	-0.96	1.49	-0.05	1.53	0.45	1.25
CrCu	-0.57	1.09	0.48	1.70	0.80	0.25
MnFe	-1.33	1.82	-1.08	2.67	-0.01	1.27
MnCo	-1.15	1.14	-0.27	1.45	-0.32	0.00
MnNi	-0.72	0.00	0.26	1.31	0.83	0.00
MnCu	-0.85	0.00	0.23	0.88	0.73	0.00
FeFe	-1.15	0.72	-0.75	1.58	0.32	1.16
FeCo	-0.89	0.00	-0.41	0.42	0.64	0.48
FeNi	-1.36	0.00	-0.25	0.00	0.58	0.00
FeCu	-1.10	0.24	-0.07	0.00	0.93	0.73
CoCo	-0.92	0.06	-0.93	0.00	-0.06	0.00
CoNi	-0.72	0.95	0.00	0.00	0.66	0.35
CoCu	-0.45	0.47	0.14	0.95	1.75	0.23
NiNi	0.70	1.70	0.91	0.64	1.39 (*COCOH)	0.00
NiCu	0.26	0.99	1.17	1.05	1.81 (*COCOH)	1.70
CuCu	0.14	0.00	1.21	0.00	1.49 (*COCOH)	0.69

Table S7. Values of G(*COCO), G(*COCHO) and G(*COCOH) on various of DACs and magnetic moments

TM atoms	G(*COCO) (eV)	Magnetic moment (μ_B)	G(*COCHO) (eV)	Magnetic moment (μ_B)	G(*COCOH) (eV)	Magnetic moment (μ_B)
CrFe	-0.12	0.00	-0.11	0.76	0.19	0.00
CrCo	1.02	0.34	0.19	0.35	-0.05	0.98
CrNi	0.94	0.96	0.47	1.14	0.11	1.82
CrCu	0.98	1.83	0.37	2.29	0.66	2.54
MnFe	-0.37	0.73	-0.25	4.44	0.07	0.68
MnCo	-0.11	2.51	0.16	2.82	0.22	1.84
MnNi	0.59	2.10	0.60	2.03	0.97	2.62
MnCu	1.03	2.11	0.21	2.01	0.60	3.12
FeFe	-0.26	2.28	-0.23	2.83	-0.11	1.88
FeCo	0.05	1.75	0.22	2.44	0.27	1.11
FeNi	-1.36 (*CO-CO)	0.00	0.36	1.46	0.75	0.00
FeCu	0.03	0.00	0.08	0.37	0.58	1.95
CoCo	-0.29	0.00	0.01	1.26	-0.24	0.00
CoNi	0.12	0.00	-0.10	0.00	0.97	0.00
CoCu	0.50	0.27	0.07	0.00	1.15	0.00
NiNi	1.17	0.44	0.47	0.00	1.39	0.00
NiCu	1.46	0.00	0.98	0.00	1.81	1.70
CuCu	0.66	0.00	1.20	0.39	1.86	0.69

Table S8. Values of G(*$COCH_2O$), G(*COHCHO), G(*$COHCH_2O$), G(*$CHOHCH_2O$), G(*$CHCH_2O$), G(*CH_2CH_2O), G(*CH_2CH_2OH), G(*CH_2CH_2OH) and G(*O) on various of DACs and magnetic moments

TM atoms	G(*$COCH_2O$) (eV)	Magnetic moment (μ_B)	G(*$OHCHO$) (eV)	Magnetic moment (μ_B)	G(*$OHCH_2O$) (eV)	Magnetic moment (μ_B)	G(*$HOHCH_2O$) (eV)	Magnetic moment (μ_B)	G(*HCH_2O) (eV)	Magnetic moment (μ_B)	G(*H_2CH_2O) (eV)	Magnetic moment (μ_B)	G(*H_2CH_2OH) (eV)	Magnetic moment (μ_B)	G(*H_3CH_2O) (eV)	Magnetic moment (μ_B)	G(*O) (eV)	Magnetic moment (μ_B)
CrFe	-0.47	0.84	-0.40	0.79	-0.14	1.58	0.17	0.00	0.04	0.00	-0.60	0.00	-1.60	0.54	-2.35	0.32	-2.15	0.69
CrCu	0.72	2.99	0.21	1.77	1.02	1.89	0.00	1.93	0.55	2.45	-0.87	2.01	-1.26	2.65	-2.00	2.69	-1.51	1.68
MnCu	0.62	2.21	0.57	1.67	1.12	1.62	0.59	2.52	0.79	1.49	0.01	2.49	-1.20	2.93	-1.96	3.47	-1.01	2.74
FeFe	-0.44	3.63	-0.22	2.44	-0.14	3.45	-0.31	4.07	-0.42	3.48	-0.96	4.06	-1.41	3.32	-1.90	5.01	-1.51	3.30
FeCo	0.34	3.16	0.50	2.46	0.80	2.45	0.39	3.13	0.52	2.63	-0.27	3.20	-0.86	3.26	-1.67	1.36	-1.02	0.60
CoNi	0.39	0.81	0.69	1.51	1.17	0.64	0.55	0.86	1.01	0.64	0.02	1.00	-0.90	0.00	-1.35	0.83	-0.65	0.94
CoCu	0.45	0.00	0.65	1.05	1.29	0.00	0.61	0.00	1.14	0.00	0.12	0.00	-1.14	0.00	-1.17	1.02	-0.20	2.00
NiCu	0.97	0.00	1.32	2.50	1.92	1.72	1.14	1.08	1.87	1.70	0.85	0.00	-0.51	0.64	-0.78	0.59	0.38	1.09

Table S9. Values of adsorbed species on Co-Co and magnetic moments

	Adsorbed species (eV)	Magnetic moment (μ_B)
G(*COHCOH)	0.78	0.00
G(*CCO)	-0.30	0.73
G(*CHCO)	-0.96	0.00
G(*CCOH)	0.46	1.08
G(*CH_2CO)	-1.23	0.00
G(*CHCOH)	0.02	0.00
G(*CH_2COH)	-0.97	0.00
G(*CH_2CHOH)	-1.22	0.00
G(*CH_2CH_2OH)	-1.03	1.88
G(*O)	-1.31	1.07