Supporting Information

How the Balance between *CO and *H Intermediates in Dual Atom Catalysts Boosts Selectivity for Hydrocarbons

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Calculation details

The Gibbs free energy change (ΔG) was defined as [1]:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_{U} \quad (1)$$

where ΔE is the electronic energy difference directly obtained from DFT calculations, ΔE_{ZPE} is the change in zero-point energy, T is the temperature (298.15 k), and ΔS is the entropy change. $\Delta G_{U} = -neU$, where n is the number of transferred electrons and U is the electrode potential. ΔG_{pH} is the correction of the H^{+} free energy by the concentration; $\Delta G_{pH} = k_{B}T$ x In10 x pH, where k_{B} is the Boltzmann constant, and the value of pH was set to be zero foracidic conditions. Zero-point energies and total entropies of molecules were computed from the vibrational frequencies. The vibrational modes of the adsorbate were computed explicitly, while the catalyst sheet was fixed (assuming that the vibrations of the substrate were negligible).

The adsorption energies (E_{ads}) were calculated bythe following equation:

$$E_{ads} = E_{A-S} - E_{S} - E_{A} \quad (2)$$

where E_{A-S}, E_{S}, and E_{A} are the total energies of the adsorbate–substrate (A–S) complex, the substrate (S), and the absorbate (A), respectively.

Support Pictures

Figure S1.

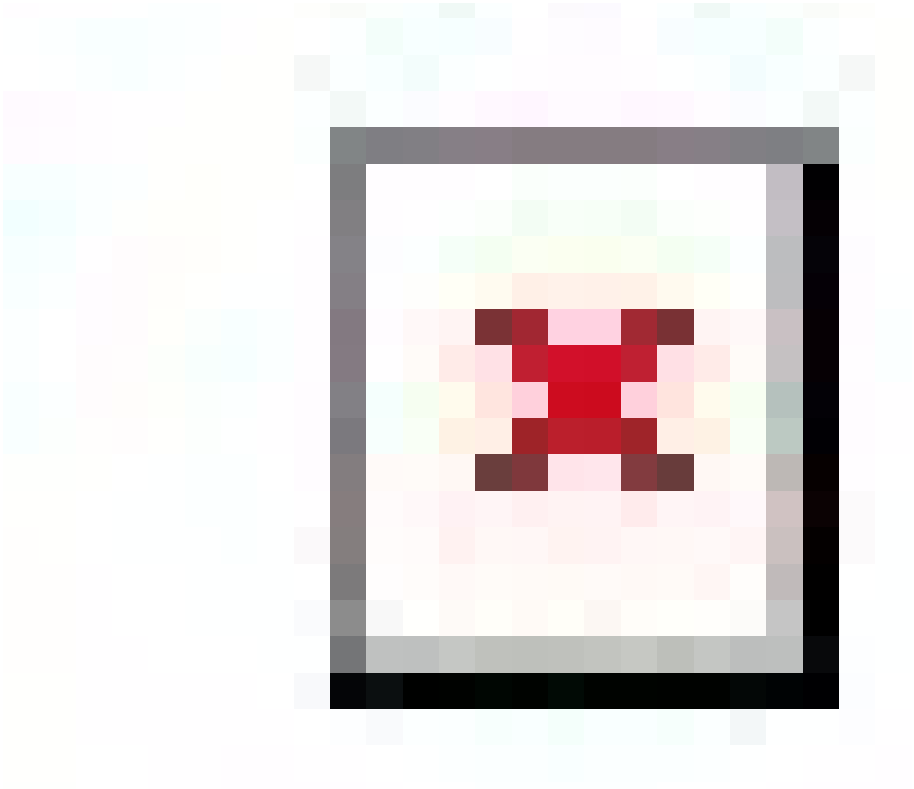

Figure S1. Initial optimized structures: (a) FeM_1-N_6C, (b) FeM_2-N_6C.

Figure S2.

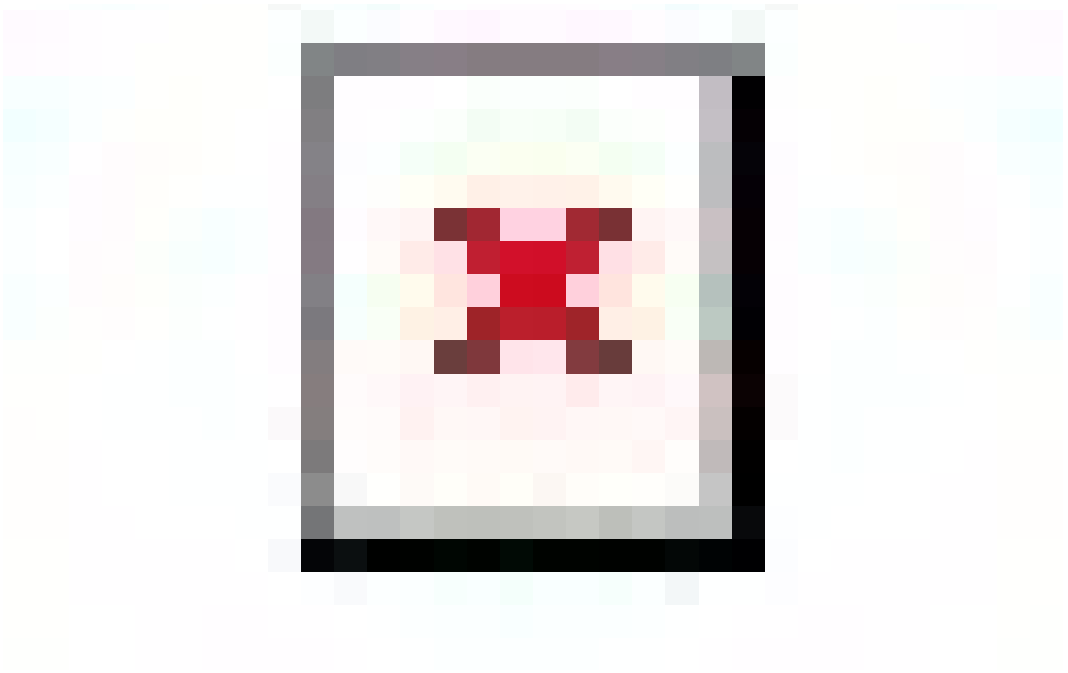

Figure S2. Charge density difference plots for the initial structure of FeM-N_6C: (a) FeM_1-N_6C, (b) FeM_2-N_6C. Yellow color represents an increase in electron density and green color represents a decrease in electron density.

Figure S3.

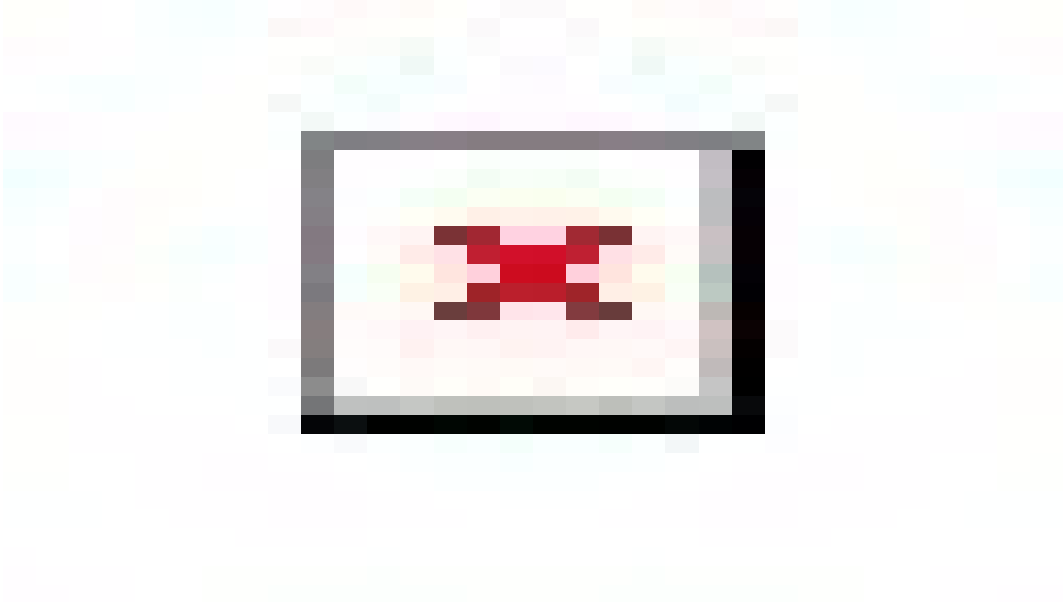

Figure S3. PDOS maps of each atom in the initial structure of FeM-N_6C: (a) FeTi-N_6C, (b) FeZr-N_6C, (c) FeHf-N_6C, (d) FeFe-N_6C, (e) FeCo-N_6C, (f) FeCu-N_6C. (The illustration in the bottom left corner is an enlarged view of the vicinity of the Fermi level)

Figure S4.

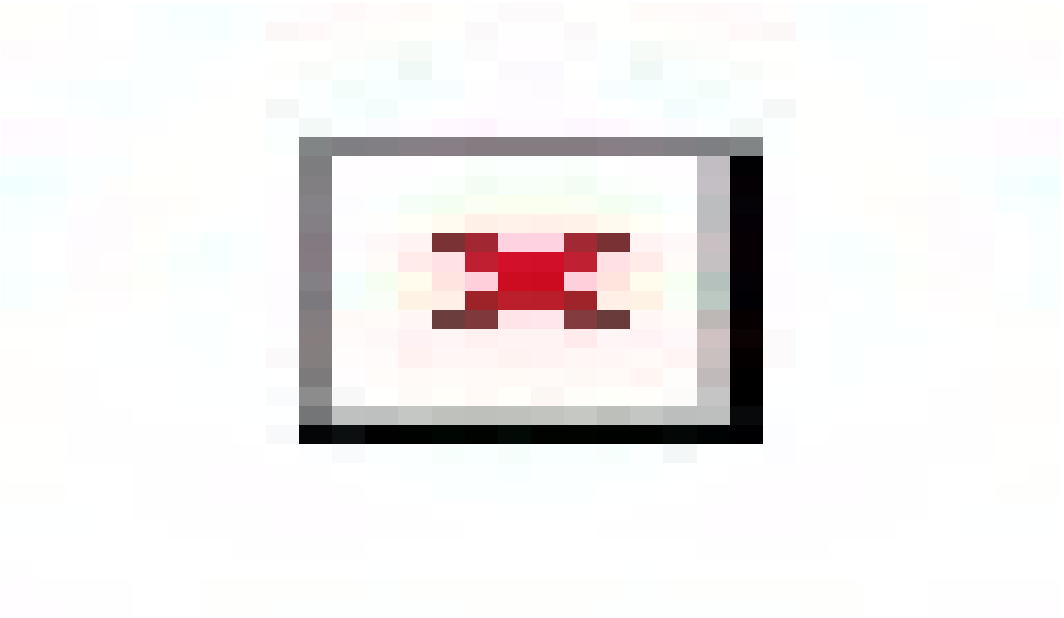

Figure S4. Calculated adsorption energies of *CO in FeM_2-N_6C catalysts: (a) FeV-N_6C, (b) FeMo-N_6C, (c) FeFe-N_6C, (d) FeCo-N_6C, (e) FeCu-N_6C.

Figure S5.

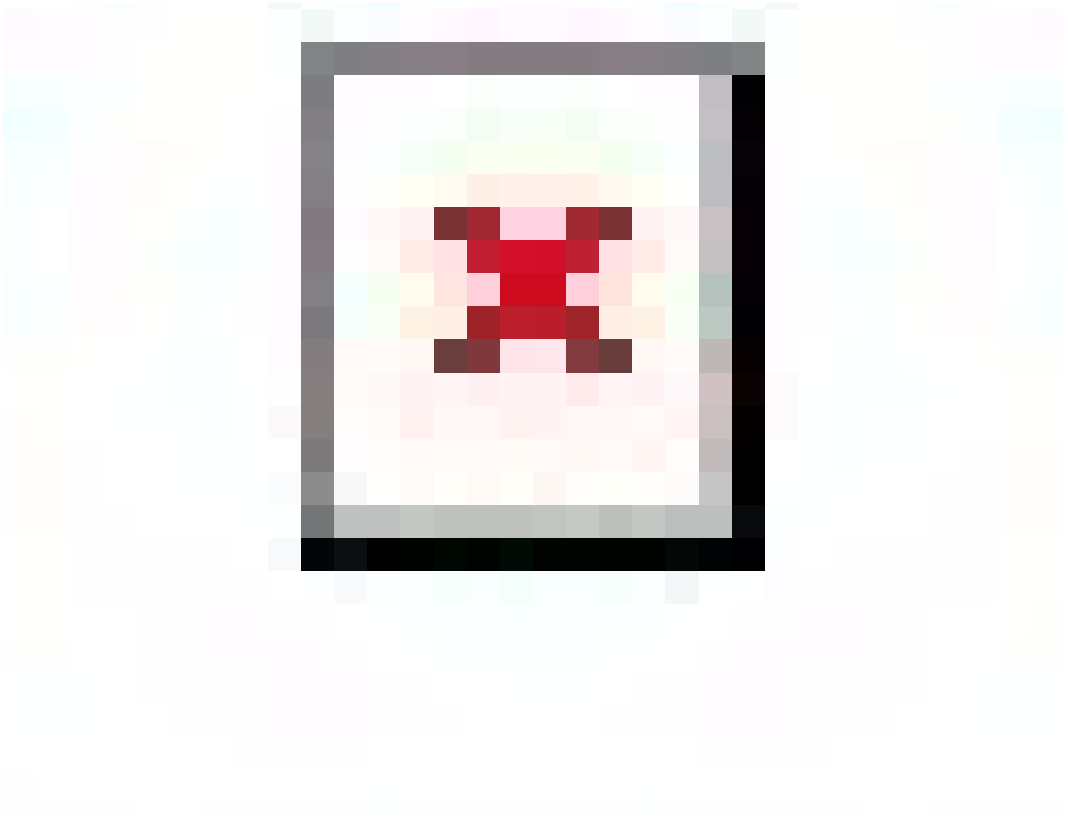

Figure S5. PDOS plots of each atom before and after adsorption of *CO intermediates on FeM_1-N_6C catalysts: (a) FeY-N_6C, (b) FeTi-N_6C, (c) FeZr-N_6C, (d) FeHf-N_6C.

Figure S6.

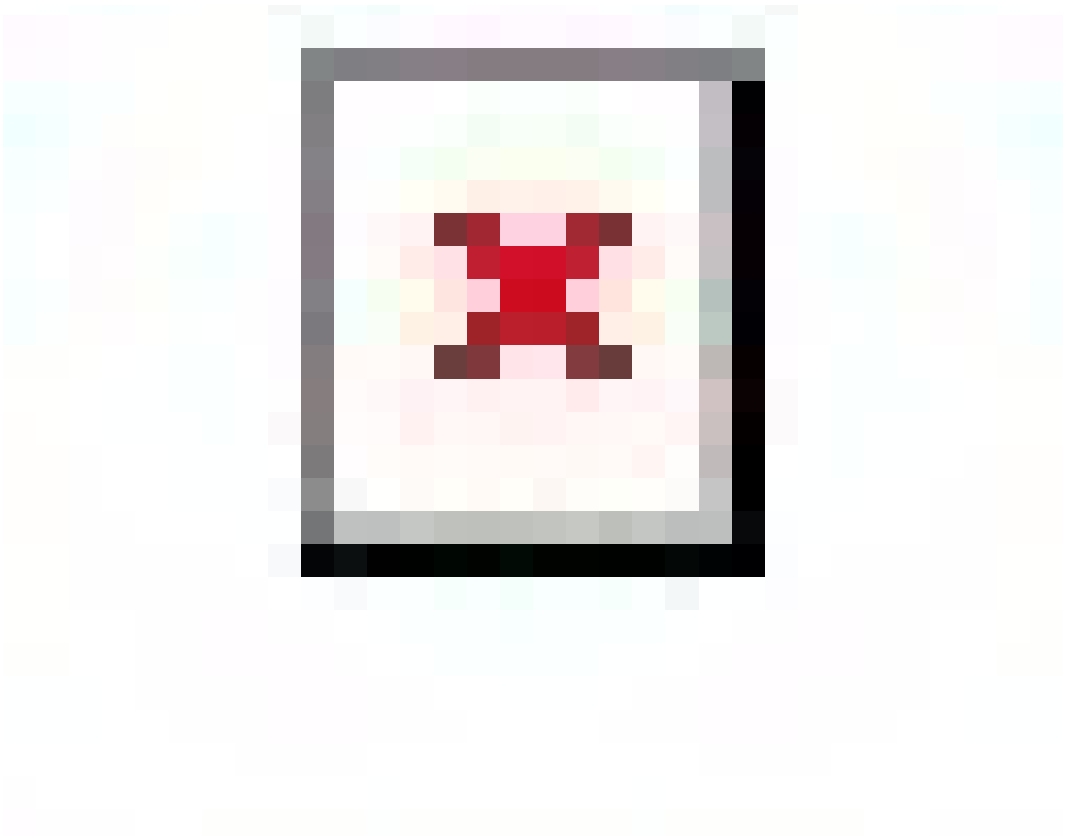

Figure S6. PDOS plots of each atom before and after adsorption of *CO intermediates on FeM_2-N_6C catalysts: (a) FeMo-N_6C, (b) FeFe-N_6C, (c) FeCo-N_6C, (d) FeCu-N_6C.

Figure S7.

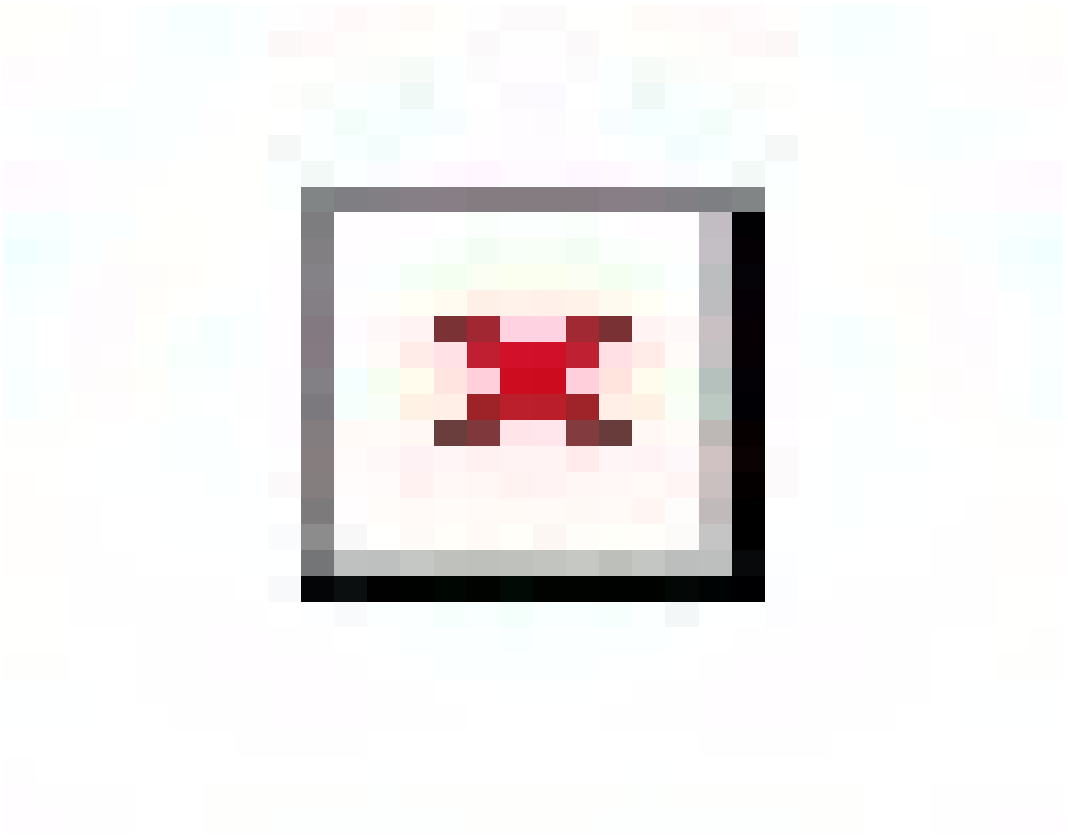

Figure S7. Adsorption energy calculations for *H intermediates: (a) FeY-N_6C, (b) FeTi-N_6C, (c) FeZr-N_6C, (d) FeHf-N_6C.

Figure S8.

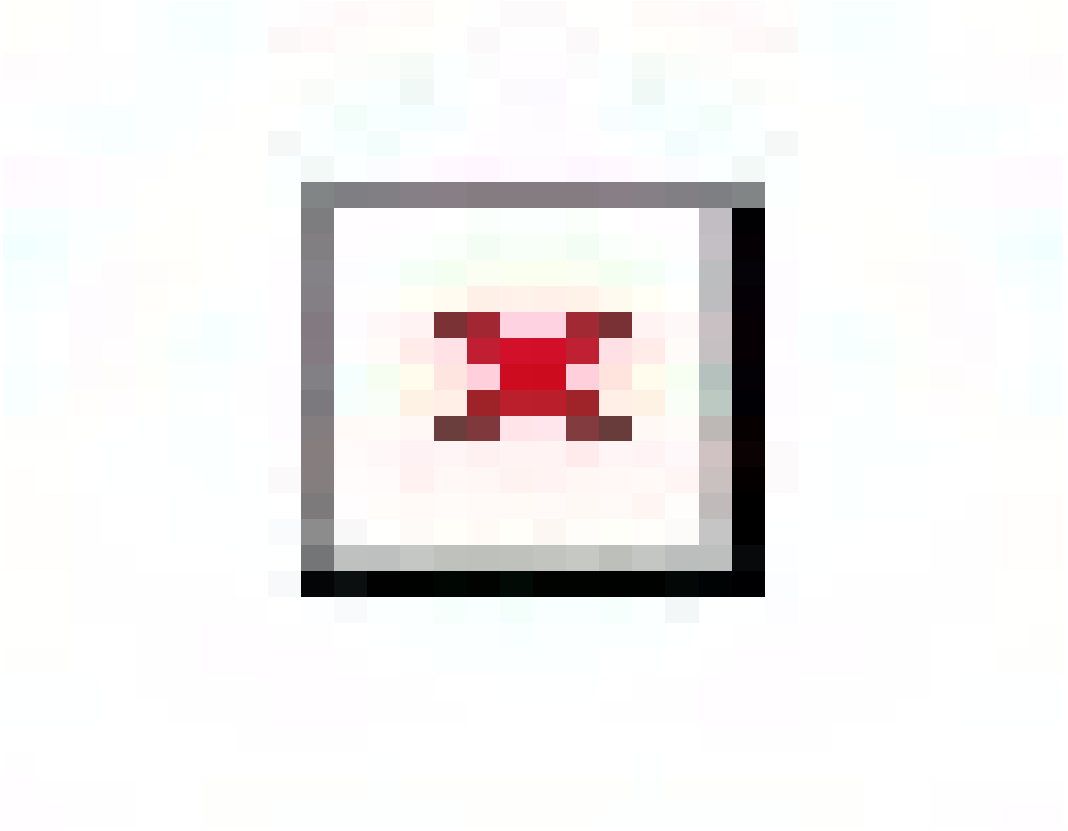

Figure S8. Adsorption energy calculations for *H intermediates: (a) FeMo-N_6C, (b) FeFe-N_6C, (c) FeCo-N_6C, (d) FeCu-N_6C.

Figure S9.

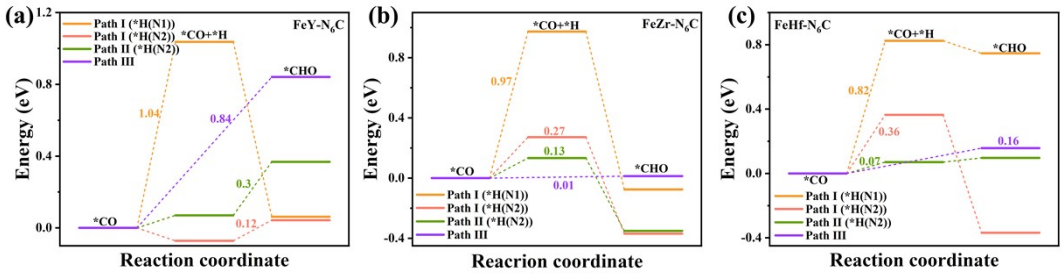

Figure S9. Free energy calculations for the *CO→*CHO reaction processes: (a) FeY-N_6C, (b) FeZr-N_6C, (c) FeHf-N_6C.

Figure S10.

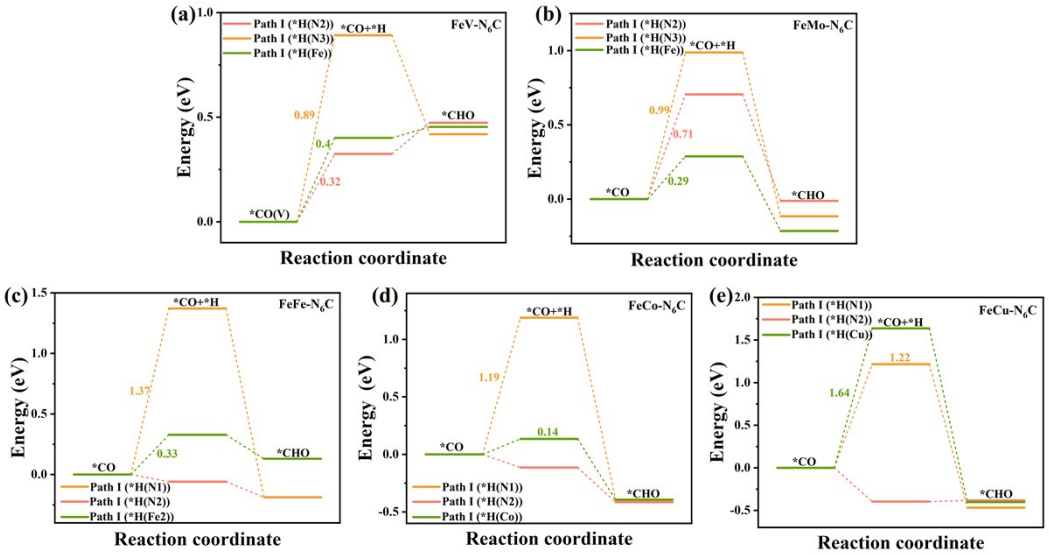

Figure S10. Free energy calculations for the *CO→*CHO reaction processes: (a) FeV-N_6C, (b) FeMo-N_6C, (c) FeFe-N_6C, (d) FeCo-N_6C, (c) FeCu-N_6C.

Figure S11.

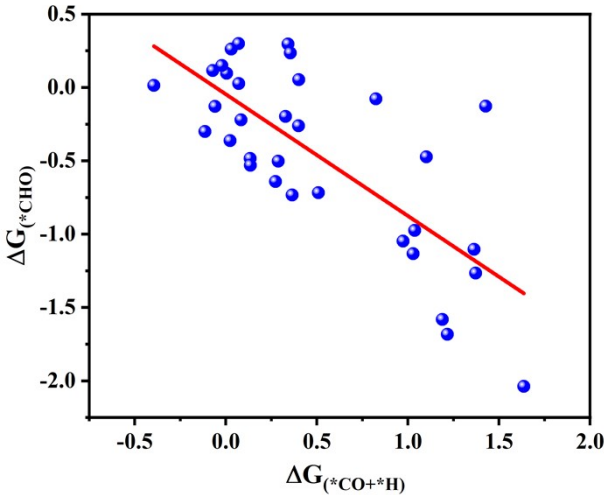

Figure S11. Relationship between $\Delta G_{(*CO+*H)}$ and $\Delta G_{(*CHO)}$.

Figure S12.

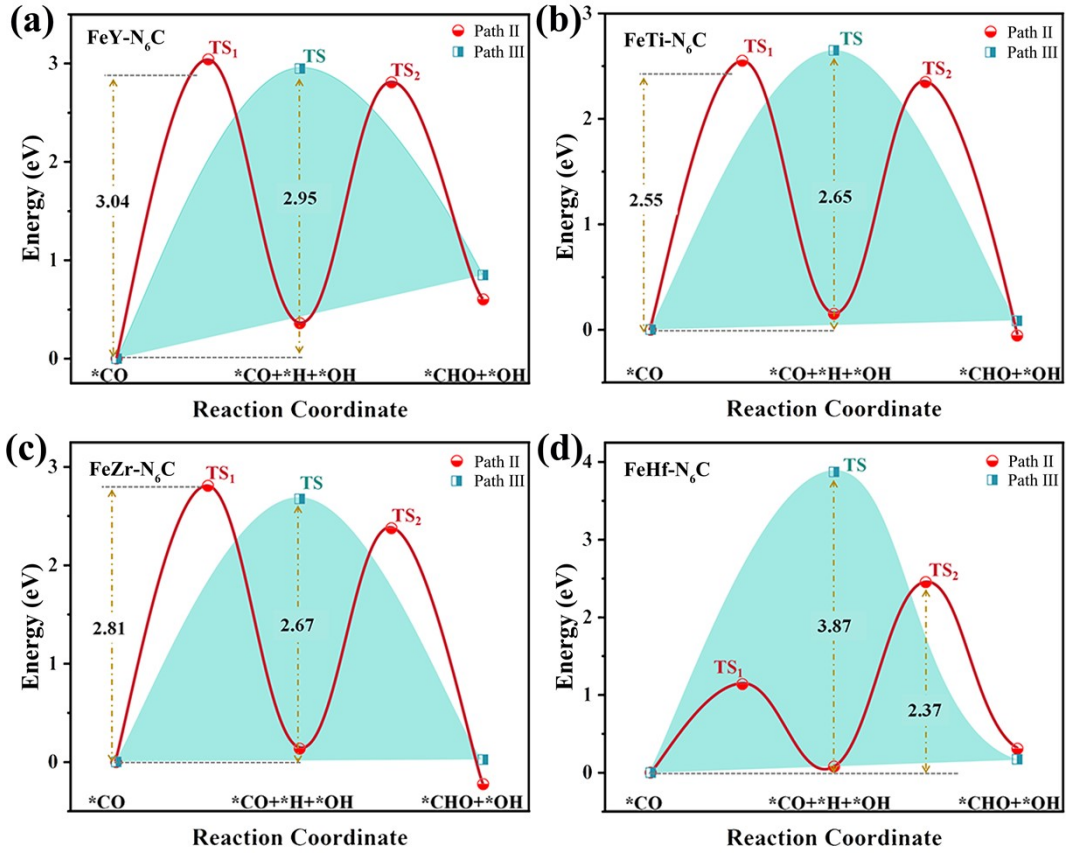

Figure S12. Transition state calculations. (a) FeY-N_6C, (b) FeTi-N_6C, (c) FeZr-N_6C, (d) FeHf-N_6C.

Support Forms

Catalyst	Metal element	Atomic populations (Mulliken) charge (e)	Catalyst	Metal element	Atomic populations (Mulliken) charge (e)
FeSc-N_6C	Sc	1.81	FeV-N_6C	V	1.51
FeY-N_6C	Y	1.94	FeMo-N_6C	Mo	1.39
FeTi-N_6C	Ti	1.68	FeFe-N_6C	Fe	1.22
FeZr-N_6C	Zr	1.89	FeCo-N_6C	Co	1.22
FeHf-N_6C	Hf	1.8	FeCu-N_6C	Cu	1.3

Table S1. Atomic populations (Mulliken) charge of the M metal in FeM-N_6C.

Table S2. Orbital Populations of the d orbitals of the metal atoms of the initial structure of FeM-N_6C.

Catalyst	Atom	Orbital	Up	Down	Spin
Fe-N-C	Fe	d_{z^2}	0.949	0.136	0.813
		d_{zy}	0.981	0.057	0.924
		d_{zx}	0.948	0.858	0.091
		$d_{x^2-y^2}$	0.984	0.889	0.095
		d_{xy}	0.43	0.33	0.101

Catalyst	Ion	Orbital	Up	Down	Spin
FeSc-N_6C	Sc	d_{z^2}	0.093	0.093	-0.001
		d_{zy}	0.101	0.099	0.002
		d_{zx}	0.116	0.121	-0.005
		$d_{x^2-y^2}$	0.127	0.094	0.033
		d_{xy}	0.222	0.222	0
	Fe	d_{z^2}	0.941	0.05	0.891
		d_{zy}	0.925	0.804	0.121
		d_{zx}	0.948	0.833	0.115
		$d_{x^2-y^2}$	0.97	0.222	0.748
		d_{xy}	0.476	0.43	0.046

Catalyst	Ion	Orbital	Up	Down	Spin
FeY-N_6C	Y	d_{z^2}	0.089	0.09	-0.001
		d_{zy}	0.114	0.114	0
		d_{zx}	0.129	0.13	-0.001
		$d_{x^2-y^2}$	0.102	0.105	-0.003
		d_{xy}	0.174	0.175	0
	Fe	d_{z^2}	0.921	0.641	0.28
		d_{zy}	0.118	0.899	-0.781
		d_{zx}	0.944	0.35	0.594
		$d_{x^2-y^2}$	0.955	0.946	0.009
		d_{xy}	0.352	0.449	-0.097

Catalyst	Ion	Orbital	Up	Down	Spin
FeTi-N_6C	Ti	d_{z^2}	0.197	0.201	-0.004
		d_{zy}	0.152	0.176	-0.023
		d_{zx}	0.18	0.177	0.004
		$d_{x^2-y^2}$	0.306	0.349	-0.043
		d_{xy}	0.299	0.301	-0.002
	Fe	d_{z^2}	0.937	0.135	0.803
		d_{zy}	0.18	0.968	-0.788
		d_{zx}	0.918	0.857	0.061
		$d_{x^2-y^2}$	0.909	0.874	0.034
		d_{xy}	0.418	0.399	0.019

Catalyst	Ion	Orbital	Up	Down	Spin
FeZr-N_6C	Zr	d_{z^2}	0.192	0.202	-0.009
		d_{zy}	0.197	0.191	0.005
		d_{zx}	0.183	0.184	-0.001
		$d_{x^2-y^2}$	0.258	0.288	-0.03
		d_{xy}	0.271	0.271	0
	Fe	d_{z^2}	0.92	0.881	0.038
		d_{zy}	0.955	0.091	0.864
		d_{zx}	0.962	0.089	0.873
		$d_{x^2-y^2}$	0.938	0.907	0.031
		d_{xy}	0.488	0.342	0.147

Catalyst	Ion	Orbital	Up	Down	Spin
FeHf-N_6C	Hf	d_{z^2}	0.197	0.203	-0.006
		d_{zy}	0.189	0.184	0.004
		d_{zx}	0.185	0.186	-0.001
		$d_{x^2-y^2}$	0.23	0.251	-0.021
		d_{xy}	0.256	0.255	0
	Fe	d_{z^2}	0.921	0.905	0.016
		d_{zy}	0.943	0.091	0.852
		d_{zx}	0.964	0.067	0.897
		$d_{x^2-y^2}$	0.942	0.911	0.031
		d_{xy}	0.494	0.329	0.165

Catalyst	Ion	Orbital	Up	Down	Spin
FeV-N_6C	V	d_{z^2}	0.195	0.06	0.135
		d_{zy}	0.753	0.096	0.656
		d_{zx}	0.915	0.07	0.845
		$d_{x^2-y^2}$	0.418	0.279	0.139
		d_{xy}	0.368	0.293	0.075
	Fe	d_{z^2}	0.928	0.933	-0.005
		d_{zy}	0.972	0.07	0.902
		d_{zx}	0.969	0.074	0.895
		$d_{x^2-y^2}$	0.894	0.904	-0.011
		d_{xy}	0.468	0.359	0.109

Catalyst	Ion	Orbital	Up	Down	Spin
FeMo-N_6C	Mo	d_{z^2}	0.856	0.127	0.729
		d_{zy}	0.432	0.233	0.199
		d_{zx}	0.684	0.54	0.145
		$d_{x^2-y^2}$	0.498	0.452	0.046
		d_{xy}	0.395	0.369	0.025
	Fe	d_{z^2}	0.937	0.869	0.069
		d_{zy}	0.962	0.062	0.899
		d_{zx}	0.953	0.328	0.625
		$d_{x^2-y^2}$	0.883	0.816	0.068
		d_{xy}	0.465	0.346	0.118

Catalyst	Ion	Atom	Orbital	Up	Down	Spin
FeFe-N_6C	Fe	2	d_{z^2}	0.931	0.047	0.884
			d_{zy}	0.933	0.929	0.005
			d_{zx}	0.942	0.875	0.067
			$d_{x^2-y^2}$	0.737	0.477	0.26
			d_{xy}	0.443	0.372	0.071
	Fe	1	d_{z^2}	0.935	0.938	-0.002
			d_{zy}	0.974	0.108	0.866
			d_{zx}	0.971	0.149	0.822
			$d_{x^2-y^2}$	0.805	0.82	-0.016
			d_{xy}	0.488	0.384	0.104

Catalyst	Ion	Orbital	Up	Down	Spin
FeCo-N_6C	Co	d_{z^2}	0.964	0.114	0.85
		d_{zy}	0.97	0.92	0.05
		d_{zx}	0.968	0.931	0.037
		$d_{x^2-y^2}$	0.99	0.834	0.156
		d_{xy}	0.471	0.406	0.065
	Fe	d_{z^2}	0.95	0.895	0.056
		d_{zy}	0.976	0.109	0.866
		d_{zx}	0.968	0.139	0.829
		$d_{x^2-y^2}$	0.99	0.562	0.428
		d_{xy}	0.485	0.403	0.082

Catalyst	Ion	Orbital	Up	Down	Spin
FeCu-N_6C	Cu	d_{z^2}	0.984	0.985	0
		d_{zy}	0.993	0.984	0.009
		d_{zx}	0.987	0.984	0.004
		$d_{x^2-y^2}$	0.996	0.971	0.025
		d_{xy}	0.993	0.591	0.402
	Fe	d_{z^2}	0.949	0.92	0.029
		d_{zy}	0.971	0.114	0.857
		d_{zx}	0.97	0.107	0.862
		$d_{x^2-y^2}$	0.989	0.54	0.449
		d_{xy}	0.518	0.388	0.13

Table S3. Orbital Populations of metal active sites after adsorption of *CO by FeM-N_6C.

Catalyst	Ion	Orbital	Up	Down	Spin
Fe-N-C *CO(Fe)	Fe	d_{z^2}	0.421	0.421	0
		d_{zy}	0.847	0.847	0
		d_{zx}	0.817	0.817	0
		$d_{x^2-y^2}$	0.975	0.975	0
		d_{xy}	0.344	0.344	0

Catalyst	Ion	Orbital	Up	Down	Spin
FeSc-N_6C *CO(Fe)	Fe	d_{z^2}	0.52	0.518	0.001
		d_{zy}	0.824	0.823	0.001
		d_{zx}	0.726	0.713	0.013
		$d_{x^2-y^2}$	0.93	0.928	0.002
		d_{xy}	0.399	0.399	0

Catalyst	Ion	Orbital	Up	Down	Spin
FeY-N_6C *CO(Fe)	Fe	d_{z^2}	0.639	0.454	0.185
		d_{zy}	0.842	0.837	0.005
		d_{zx}	0.864	0.667	0.197
		$d_{x^2-y^2}$	0.764	0.908	-0.145
		d_{xy}	0.419	0.39	0.029

Catalyst	Ion	Orbital	Up	Down	Spin
FeTi-N_6C *CO(Fe)	Fe	d_{z^2}	0.532	0.532	0
		d_{zy}	0.823	0.823	0
		d_{zx}	0.735	0.735	0
		$d_{x^2-y^2}$	0.891	0.891	0
		d_{xy}	0.417	0.417	0

Catalyst	Ion	Orbital	Up	Down	Spin
FeZr-N_6C *CO(Fe)	Fe	d_{z^2}	0.52	0.52	0
		d_{zy}	0.835	0.835	0
		d_{zx}	0.741	0.741	0
		$d_{x^2-y^2}$	0.9	0.9	0
		d_{xy}	0.407	0.407	0

Catalyst	Ion	Orbital	Up	Down	Spin
FeHf-N_6C *CO(Fe)	Fe	d_{z^2}	0.518	0.518	0
		d_{zy}	0.828	0.828	0
		d_{zx}	0.741	0.741	0
		$d_{x^2-y^2}$	0.908	0.908	0
		d_{xy}	0.405	0.405	0

Catalyst	Ion	Orbital	Up	Down	Spin
FeV-N_6C *CO(V)	V	d_{z^2}	0.259	0.22	0.04
		d_{zy}	0.646	0.122	0.524
		d_{zx}	0.574	0.53	0.044
		$d_{x^2-y^2}$	0.348	0.322	0.026
		d_{xy}	0.336	0.304	0.032

Catalyst	Ion	Orbital	Up	Down	Spin
FeMo-N_6C *CO(Mo)	Mo	d_{z^2}	0.461	0.472	-0.011
		d_{zy}	0.549	0.593	-0.044
		d_{zx}	0.537	0.532	0.006
		$d_{x^2-y^2}$	0.426	0.473	-0.047
		d_{xy}	0.372	0.375	-0.002

Catalyst	Ion	Orbital	Up	Down	Spin
FeFe-N_6C *CO(Fe)	Fe	d_{z^2}	0.603	0.456	0.147
		d_{zy}	0.859	0.831	0.028
		d_{zx}	0.835	0.685	0.15
		$d_{x^2-y^2}$	0.825	0.847	-0.022
		d_{xy}	0.399	0.399	0.001

Catalyst	Ion	Orbital	Up	Down	Spin
FeCo-N_6C *CO(Fe)	Fe	d_{z^2}	0.82	0.248	0.572
		d_{zy}	0.895	0.853	0.042
		d_{zx}	0.881	0.781	0.1
		$d_{x^2-y^2}$	0.97	0.387	0.583
		d_{xy}	0.438	0.392	0.046

Catalyst	Ion	Orbital	Up	Down	Spin
FeCu-N_6C *CO(Fe)	Fe	d_{z^2}	0.891	0.384	0.507
		d_{zy}	0.871	0.822	0.049
		d_{zx}	0.897	0.543	0.354
		$d_{x^2-y^2}$	0.979	0.392	0.587
		d_{xy}	0.459	0.386	0.073

Table S4 Hubbard U value test

Fe(FeCo-N_6C) without aqueous solvent layer	
Hubbard U (eV)	Energy (eV)
2	-11481.4085
2.5	-11481.4091
3	-11481.1429
3.5	-11480.9033

Table S5 Calculation data for $E_{ads\ (*CO)}$

Catalyst	E_* (eV)	$E_{*CO(Fe)}$ (eV)	$E_{*CO(M)}$ (eV)
H_2	-31.1850392		
CO	-594.083018		
Fe-N_4C	-15203.2525	-15800.9361	
FeSc-N_6C	-16372.9073	-16967.7628	
FeY-N_6C	-16172.6574	-16767.3274	
FeTi-N_6C	-16692.6075	-17287.4291	
FeZr-N_6C	-16392.3184	-16987.4195	
FeHf-N_6C	-22968.094	-23563.3161	
FeV-N_6C	-17049.3603	-17644.2186	-17644.2753
FeMo-N_6C	-17031.7814	-17626.7259	-17627.4129
FeFe-N_6C	-15959.8801	-16554.7662	-16554.5161
FeCo-N_6C	-16791.0328	-16791.5984	-16791.2373
FeCu-N_6C	-16777.4508	-17372.2989	-17371.1829

Table S6 Calculation data for $E_{ads\ (*H)}$

Catalyst	E_{*} (eV)	$E_{*H(Fe)}$ (eV)	$E_{*H(M)}$ (eV)	$E_{*H(N1)}$ (eV)	$E_{*H(N2)}$ (eV)	$E_{*H(N2)}$ ($*H_2O \rightarrow *H(N2)+*OH$)
FeSc-N_6C	-16372.9073	-16388.1061		-16386.9852	-16388.5737	-16372.9254
FeY-N_6C	-16172.6574	-16187.79		-16187.01	-16188.33	-16172.5036
FeTi-N_6C	-16692.6075	-16708.1944		-16707.3504	-16707.8465	-16692.6077
FeZr-N_6C	-16392.3184	-16407.857		-16407.006	-16407.626	-16392.905
FeHf-N_6C	-22968.094	-22983.4976		-22982.6955	-22968.5167	-22968.5167
FeV-N_6C	-17049.3603	-17064.6079	-17064.7239	-17064.3497	-17064.7488	
FeMo-N_6C	-17031.7814	-17047.2806	-17048.0224	-17046.6895	-17047.0891	
FeFe-N_6C	-15959.8801	-15975.4126	-15975.3516	-15974.7435	-15975.626	
FeCo-N_6C	-16196.9809	-16212.3093	-16212.2815	-16211.7863	-16212.5583	
FeCu-N_6C	-16777.4508	-16792.8657	-16791.9672	-16792.3306	-16793.8899	

Table S7 Calculation data for E_{*CO+*H} and E_{*CHO}

Catalyst	Path	E_{*CO} (eV)	E_{*CO+*H} (eV)	E_{*CHO} (eV)
FeSc-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-16967.7628	-16982.3269	-16983.4605
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-16967.7628	-16983.332	-16983.6956
	CO+H_2O(Sc)=*CO+*H(N2)+*OH(Sc)=*CHO+*OH(Sc)	-16967.7628	-16967.7335	-16967.4723
	CO+H_2O(Sc)=*CHO+*OH(Sc)	-16967.7628		-16966.8806
FeY-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-16767.3274	-16781.8907	-16782.8657
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-16767.3274	-16782.9996	-16782.8842
	CO+H_2O(Y)=*CO+*H(N2)+*OH(Y)=*CHO+*OH(Y)	-16767.3274	-16767.2575	-16766.9592
	CO+H_2O(Y)=*CHO+*OH(Y)	-16767.3274		-16766.4864
FeTi-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-17287.4291	-17302.0918	-17302.22
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-17287.4291	-17302.5976	-17302.8599
	CO+H_2O(Ti)=*CO+*H(N2)+*OH(Ti)=*CHO+*OH(Ti)	-17287.4291	-17287.2903	-17287.5108
	CO+H_2O(Ti)=*CHO+*OH(Ti)	-17287.4291		-17287.4764
FeZr-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-16987.4195	-17002.0384	-17003.0869
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-16987.4195	-17002.7397	-17003.3808
	CO+H_2O(Zr)=*CO+*H(N2)+*OH(Zr)=*CHO+*OH(Zr)	-16987.4195	-16987.286	-16987.77
	CO+H_2O(Zr)=*CHO+*OH(Zr)	-16987.4195		-16987.4062
FeHf-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-16987.4195	-17002.0384	-17003.0869
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-16987.4195	-17002.7397	-23579.2775
	CO+H_2O(Hf)=*CO+*H(N2)+*OH(Hf)=*CHO+*OH(Hf)	-16987.4195	-23563.2453	-23563.2196
	CO+H_2O(Hf)=*CHO+*OH(Hf)	-16987.4195		-23563.1589
FeV-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-17644.2753	-17658.9761	-17659.449
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-17644.2753	-17659.5432	-17659.3942
	*CO+H^++e^-=*CO+*H(Fe)=*CHO	-17644.2753	-17659.4668	-17659.414
FeMo-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-17627.4129	-17642.0176	-17643.1212
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-17627.4129	-17642.2998	-17643.0177
	*CO+H^++e^-=*CO+*H(Mo)=*CHO	-17627.4129	-17642.7174	-17643.2203
FeFe-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-16554.7662	-16568.9874	-16570.2532
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-16554.7662	-16570.4175	-16570.547
	*CO+H^++e^-=*CO+*H(Fe2)=*CHO	-16554.7662	-16570.031	-16570.2281
FeCo-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-16791.5984	-16806.002	-16807.5837
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-16791.5984	-16807.3053	-16807.6062
	*CO+H^++e^-=*CO+*H(Co)=*CHO	-16791.5984	-16807.0559	-16807.5862
FeCu-N_6C	*CO+H^++e^-=*CO+*H(N1)=*CHO	-17372.2989	-17386.6752	-17388.3584
	*CO+H^++e^-=*CO+*H(N2)=*CHO	-17372.2989	-17388.287	-17388.2737
	*CO+H^++e^-=*CO+*H(Cu)=*CHO	-17372.2989	-17386.2548	-17388.2934

Notes and references:

1 Y. L. Wang, Y. Tian, Z. L. Lang, W. Guan and L. K. Yan, J. Mater. Chem. A, 2018, **6**, 21056–21063.