Supporting Information File

Understanding the activity of single atom catalysts for CO_2 reduction to C_2 products: A high throughput computational screening

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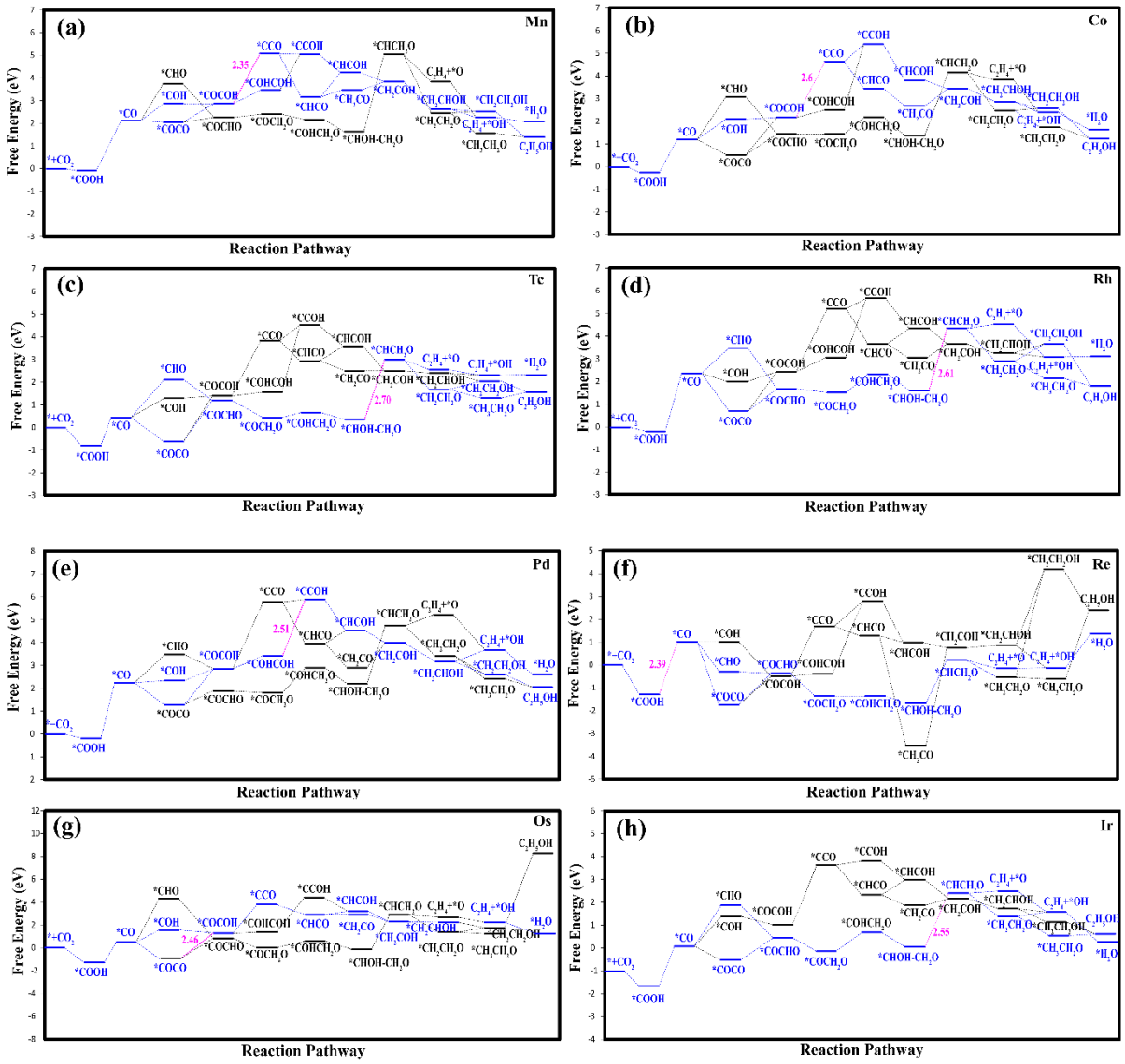
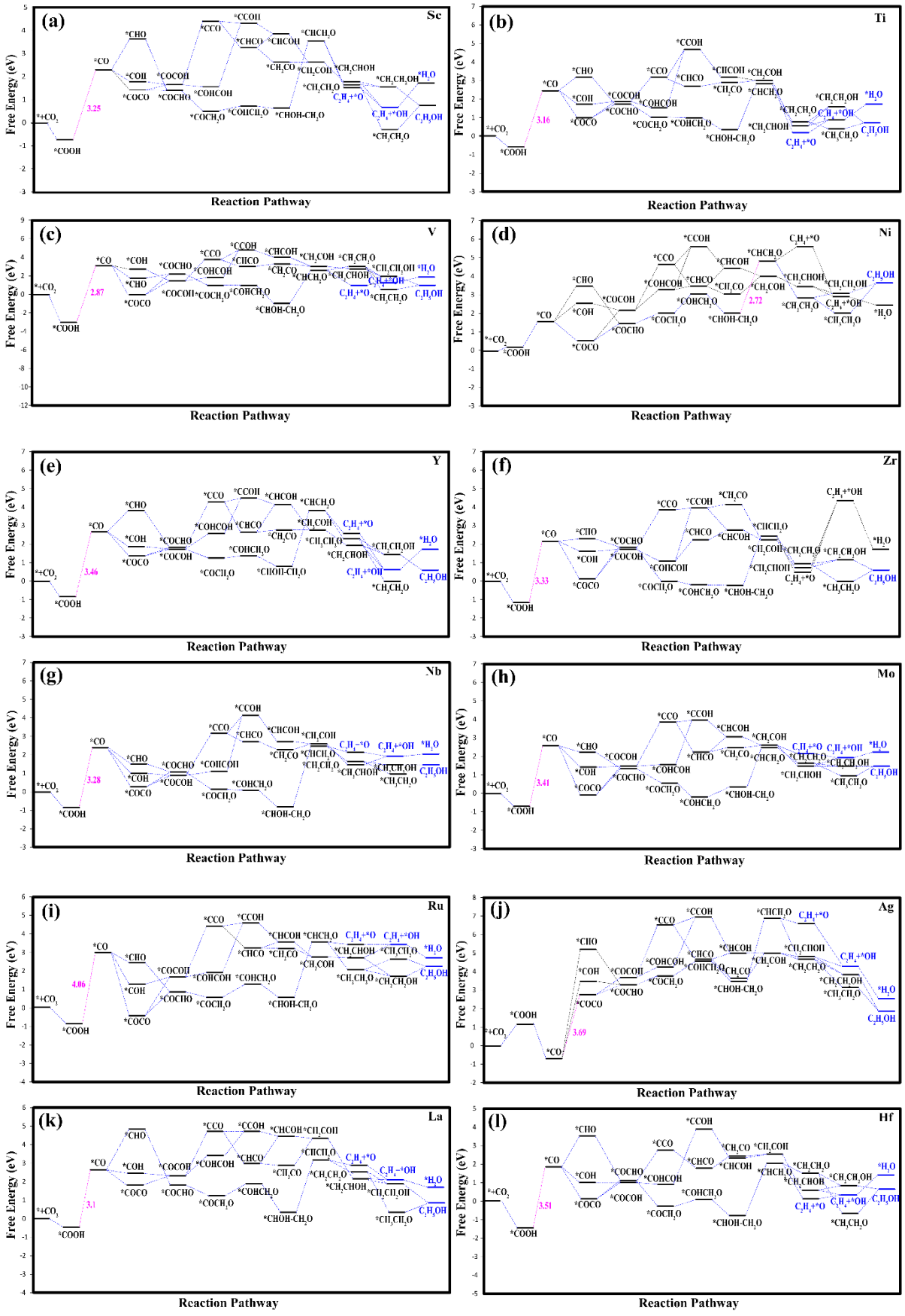


Fig. S1 *The reaction Pathways for CO_2 reduction to C_2H_4 and C_2H_5OH on (a) Mn@C_2N, (b) Co@C_2N, (c) Tc@C_2N, (d) Rh@C_2N, (e) Pd@C_2N, (f) Re@C_2N, (g) Os@C_2N and (h) Ir@C_2N catalysts. The most favourable pathways are highlighted in blue colour.*


(a)
Sc
(b)
Ti
(c)
V
(d)
Ni
(e)
Y
(f)
Zr
(g)
Nb
(h)
Mo
(i)
Ru
(j)
Ag
(k)
La
(l)
Hf
Free Energy (eV)
Reaction Pathway
3.25
3.16
2.87
2.72
3.46
3.33
3.28
3.41
4.06
3.69
3.1
3.51

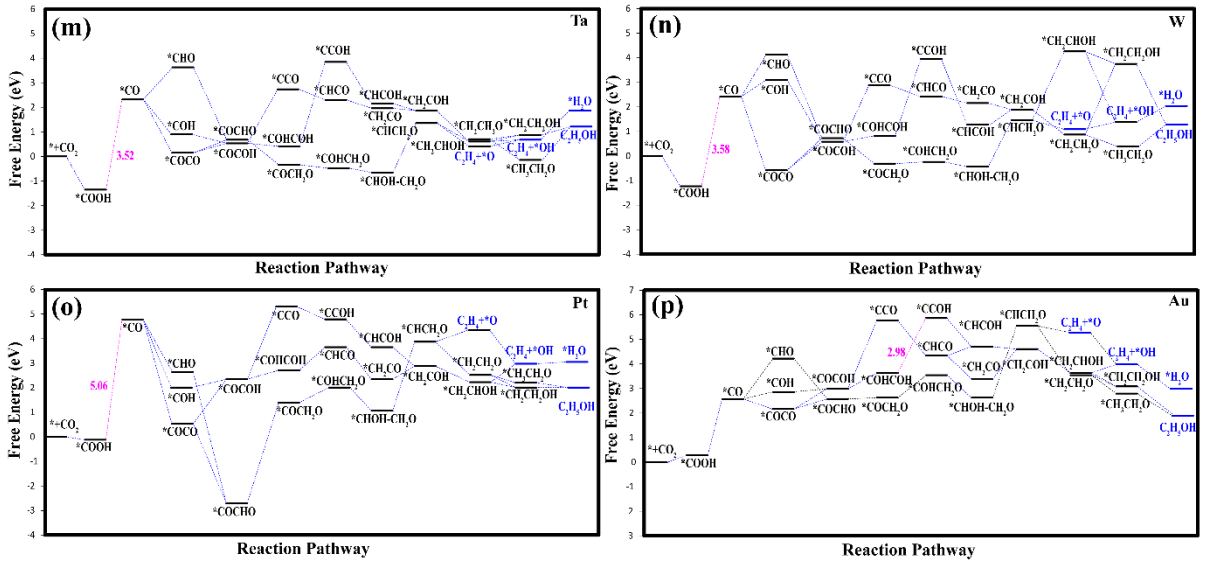


Fig. S2 *The reaction Pathways for CO_2 reduction to C_2H_4 and C_2H_5OH on (a) Sc@C_2N, (b) Ti@C_2N, (c) V@C_2N, (d) Ni@C_2N, (e) Y@C_2N, (f) Zr@C_2N, (g) Nb@C_2N (h) Mo@C_2N, (i) Ru@C_2N, (j) Ag@C_2N, (k) La@C_2N, (l) Hf@C_2N, (m) Ta@C_2N, (n) W@C_2N, (o) Pt@C_2N and (p) Au@C_2N catalysts.*

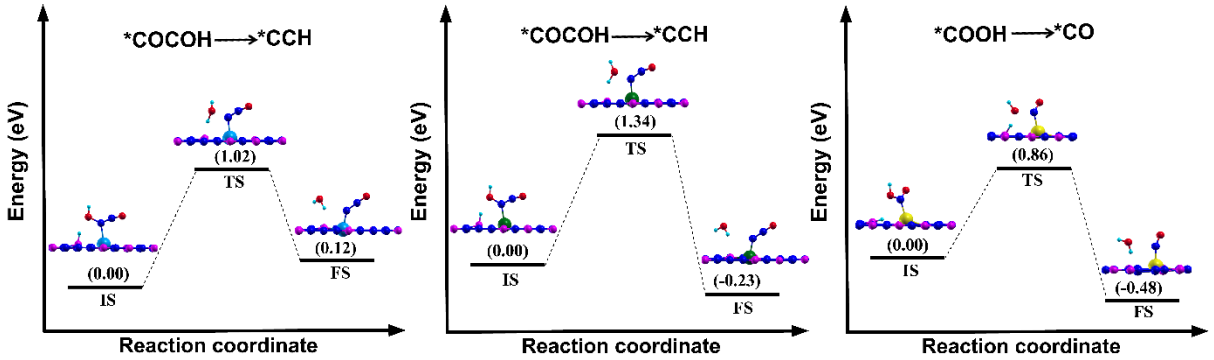


Fig. S3. *Energy barrier for hydrogenating *COCHO to *CCO (Cr@C_2N and Fe@C_2N) and *COOH to *CO (Cu@C_2N).*

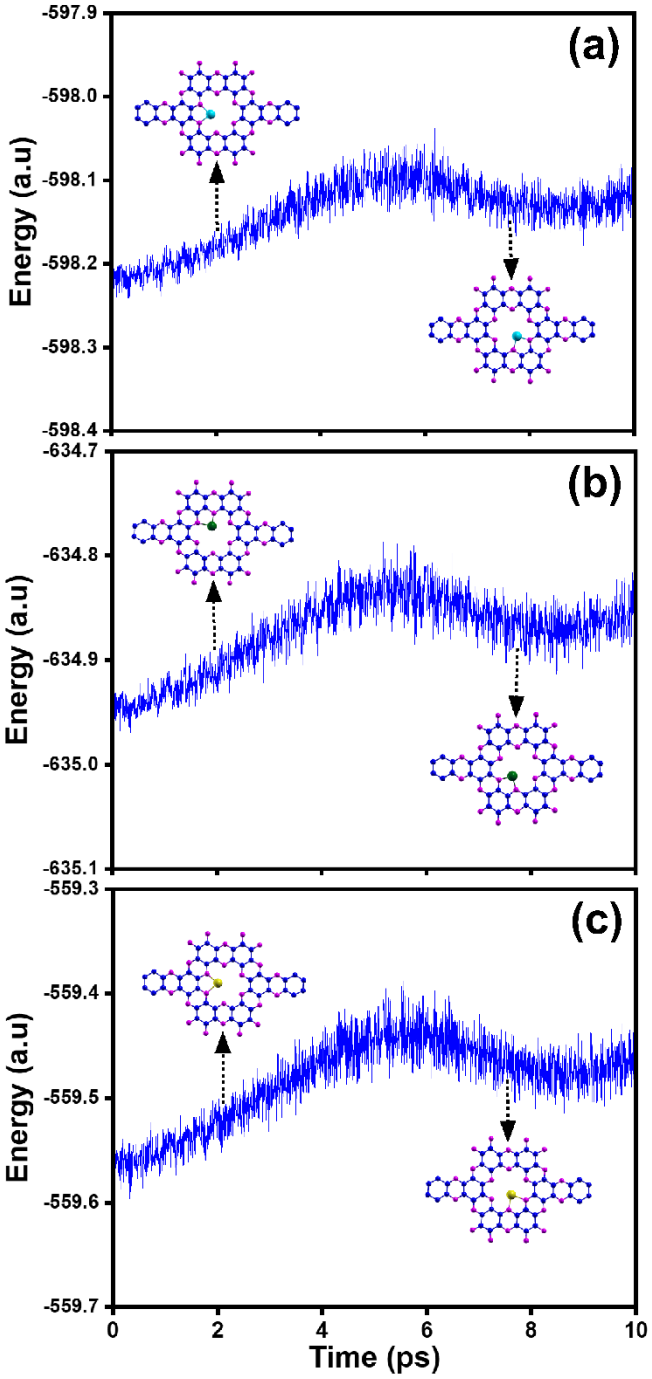


Fig. S4. *Variation of potential energy with respect to the AIMD simulation time for a period of 10 picoseconds obtained using of NVT ensemble and Nose-Hoover thermostat for (a) Cr@C_2N, (b) Fe@C_2N and (c) Cu@C_2N catalysts at 600 K.*

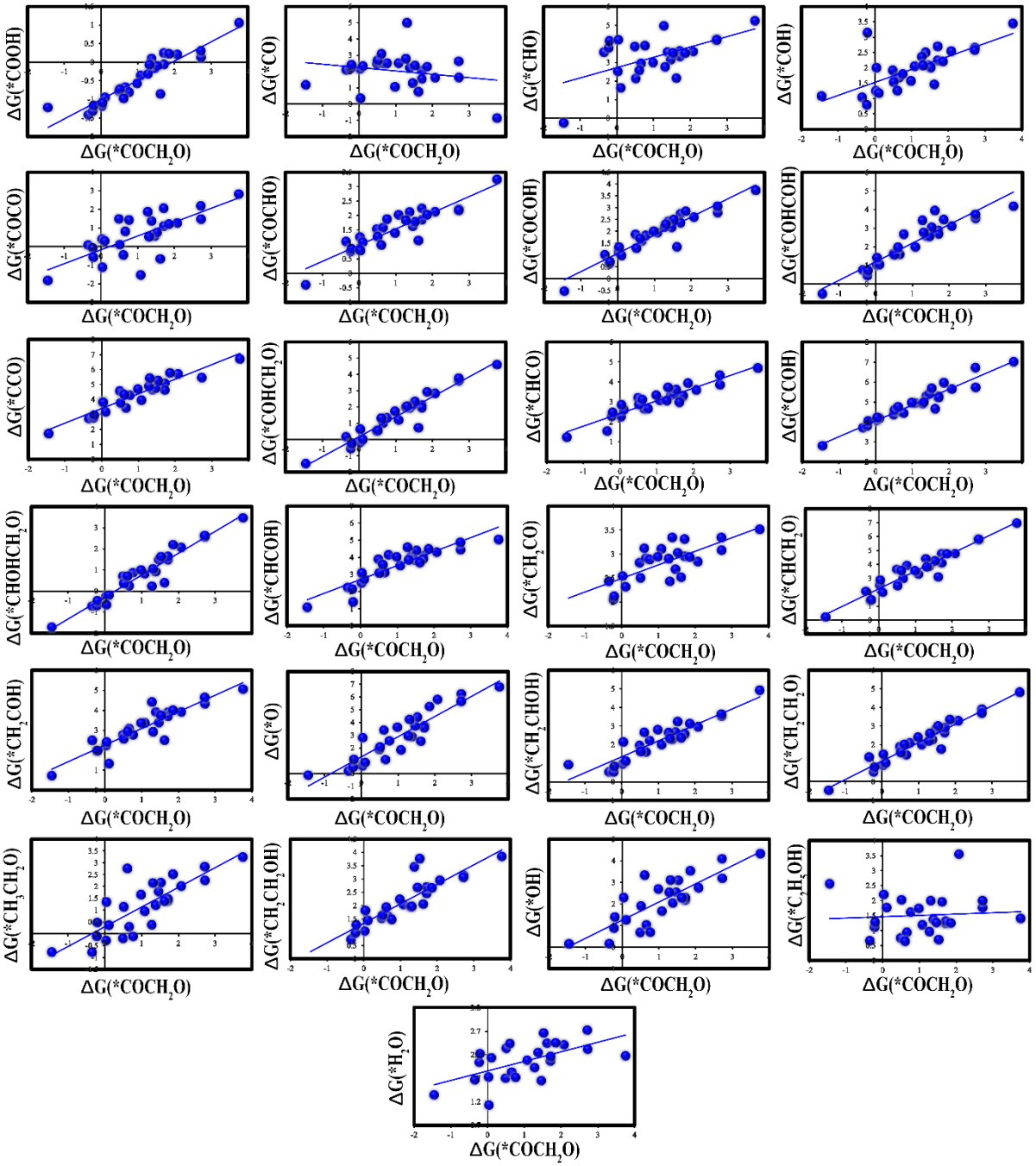


Fig. S5. *Correlation between adsorption free energies of CO_2RR intermediates versus ΔG(*COCH$_2$O).*

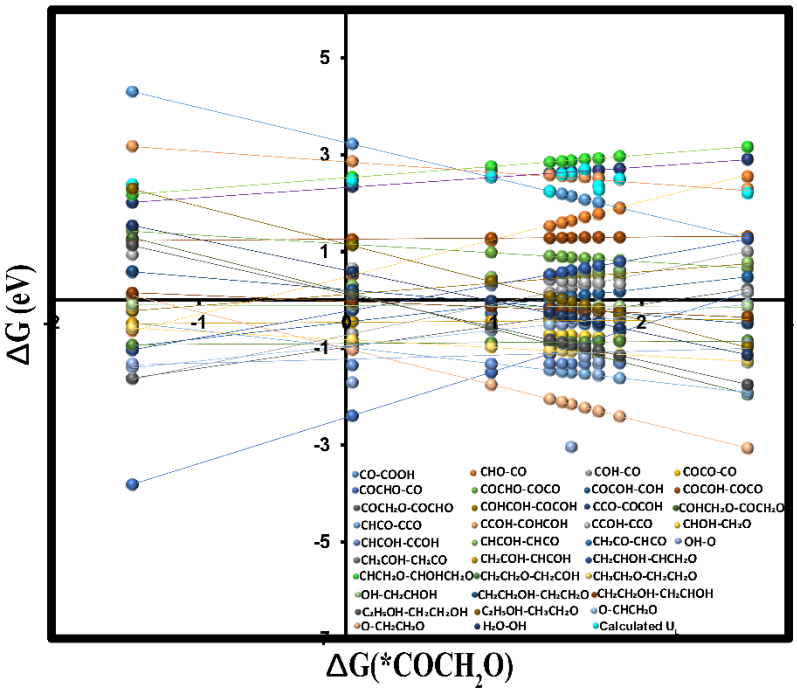


Fig. S6. *Free energy change for each reaction step, predicted based on linear correlation between adsorption free energy of intermediates and* $\Delta G_{(*COCH_2O)}$.

Table S1. *Adsorption free energies of* CO_2 *reduction intermediates on SACs supported on g-*C_2N *monolayer.*

Catalyst	*COOH	*CO	*CHO	*COH	*COCO	*COCHO	*COCOH
Sc	-0.78	2.47	3.86	1.91	1.48	1.52	1.87
Ti	-0.67	2.49	2.95	1.68	0.81	1.57	1.59
V	-0.36	2.51	0.01	2.05	-1.54	2.02	1.95
Cr	0.09	2.23	3.56	2.50	1.37	2.12	2.42
Mn	-0.06	2.04	3.62	2.70	2.06	2.25	2.74
Fe	0.25	1.54	3.32	2.24	1.09	1.85	2.36
Co	-0.16	1.27	3.14	2.08	0.56	1.62	2.16
Ni	0.21	1.61	3.58	2.54	1.26	2.13	2.60
Cu	0.13	1.62	4.24	2.65	1.47	2.21	2.79
Y	-0.81	2.51	3.90	1.79	1.43	1.87	1.82
Zr	-1.18	2.15	2.52	1.25	0.39	1.25	1.12
Nb	-0.95	2.33	1.62	1.17	0.30	1.08	0.98
Mo	-0.73	2.68	2.14	1.53	0.10	1.27	1.29
Tc	-0.86	0.75	2.15	1.46	-0.67	1.13	1.34
Ru	-0.98	3.08	2.58	1.25	-0.46	0.97	1.69
Rh	-0.10	2.37	3.50	2.01	0.76	1.78	2.50
Pd	0.22	2.29	3.49	2.21	1.20	2.03	2.85
Ag	1.06	-0.87	5.24	3.45	2.82	3.24	3.74
La	-0.32	2.78	4.96	2.36	1.86	1.83	2.18
Hf	-1.42	2.09	3.55	1.03	0.08	1.09	1.00
Ta	-1.31	2.21	3.78	0.79	-0.08	0.76	0.64
W	-1.16	2.42	4.16	3.14	-0.58	0.85	0.72
Re	-1.22	1.17	-0.25	1.07	-1.83	-0.40	-0.53
Os	-1.09	0.35	4.22	2.00	-1.12	0.78	1.33
Ir	-0.57	1.05	2.99	1.57	0.01	1.39	2.00
Pt	-0.07	4.99	2.76	2.08	0.53	0.01	2.30
Au	0.30	2.62	4.20	2.58	2.19	2.18	3.06

Catalyst	*$COCH_2O$	*COHCOH	*CCO	*$COHCH_2O$	*CHCO	*CCOH
Sc	0.49	1.62	4.56	0.52	3.20	4.36
Ti	0.66	1.59	3.44	1.01	2.65	4.53
V	1.08	1.97	3.96	1.19	3.08	4.95
Cr	1.38	2.56	4.65	1.93	3.31	5.30
Mn	1.71	2.88	5.08	2.12	3.26	5.28
Fe	1.71	2.68	4.63	1.94	3.32	5.23
Co	1.46	2.55	4.76	2.14	3.38	5.41
Ni	2.08	3.11	5.71	2.83	3.59	5.64
Cu	2.72	3.53	5.46	3.60	3.85	5.73
Y	0.76	2.67	4.28	1.33	2.66	4.44
Zr	0.03	1.02	3.82	-0.19	2.26	4.09
Nb	0.11	1.04	3.16	0.01	2.61	4.18
Mo	0.51	1.57	3.76	0.55	2.87	4.59
Tc	1.62	3.94	0.01	0.71	2.98	4.65
Ru	0.61	1.97	4.34	1.31	3.11	4.75
Rh	1.52	3.04	5.26	2.33	3.62	5.68
Pd	1.85	3.46	5.76	2.92	3.94	5.96
Ag	3.76	4.18	6.70	4.60	4.70	7.01
La	1.28	3.42	4.87	1.99	3.05	4.91
Hf	-0.35	0.75	2.71	0.17	1.54	3.70
Ta	-0.22	0.45	2.77	-0.57	2.27	3.81
W	-0.21	0.72	2.96	-0.25	2.48	4.05
Re	-1.45	-0.53	1.71	-1.49	1.23	2.81
Os	0.04	1.41	3.80	0.63	2.86	4.23
Ir	0.98	0.01	4.695	1.73	3.33	4.96
Pt	1.31	2.77	5.42	2.04	3.72	4.98
Au	2.72	3.74	0.01	3.77	4.34	6.72

Catalyst	*CHOH-CH_2O	*CHCOH	*CH_2CO	*$CHCH_2O$	*CH_2COH	*O
Sc	0.70	3.89	2.82	3.65	2.77	1.87
Ti	0.25	3.11	2.91	2.98	3.08	1.07
V	0.81	3.56	3.11	3.30	3.36	1.84
Cr	0.927	4.04	3.34	3.87	3.90	2.87
Mn	1.47	4.09	3.31	4.77	3.87	3.73
Fe	1.65	3.91	2.95	4.10	3.69	3.57
Co	1.47	3.85	2.68	4.17	3.38	3.73
Ni	2.06	4.30	2.84	4.78	3.91	5.79
Cu	2.55	4.45	3.08	5.77	4.32	6.23
Y	0.87	4.15	2.89	3.93	2.77	2.54
Zr	-0.26	2.51	2.54	2.52	2.23	0.58
Nb	-0.20	2.71	2.31	1.98	1.33	0.86
Mo	0.36	3.09	2.50	2.46	2.57	2.06
Tc	0.39	3.69	2.56	3.09	2.50	2.51
Ru	0.70	3.58	3.12	3.55	2.94	3.40
Rh	1.63	4.41	3.03	4.25	3.74	4.41
Pd	2.19	4.49	2.94	4.76	4.00	5.24
Ag	3.46	5.04	3.51	6.96	5.05	6.78
La	0.23	4.59	2.90	4.41	4.41	2.94
Hf	-0.72	2.23	2.43	2.07	2.48	0.18
Ta	-0.71	2.14	2.05	1.41	1.98	0.48
W	-0.46	1.39	2.12	1.46	1.97	1.09
Re	-1.71	1.08	0.01	0.22	0.72	-0.15
Os	-0.66	3.08	0.01	2.87	2.41	2.81
Ir	1.00	4.02	2.94	3.55	3.36	3.62
Pt	1.05	3.85	2.43	3.81	2.92	4.22
Au	2.63	4.88	3.35	5.82	4.65	5.64

Catalyst	*CH_2CHOH	*CH_2CH_2O	*CH_3CH_2O	*CH_2CH_2OH	*OH	*C_2H_5OH	*H_2O
Sc	1.96	1.88	-0.20	1.52	0.68	0.75	1.70
Ti	1.61	1.44	0.29	1.61	1.03	0.94	1.83
V	1.99	1.99	0.95	2.04	1.67	1.19	2.08
Cr	2.29	2.27	1.21	3.45	2.04	1.37	2.24
Mn	2.55	2.64	1.39	2.46	2.18	1.24	2.06
Fe	2.59	2.92	1.47	2.69	2.29	1.31	2.16
Co	2.66	2.81	1.79	2.68	2.55	1.26	1.65
Ni	2.95	3.28	2.02	2.95	2.75	3.55	2.41
Cu	3.53	3.90	2.25	3.13	3.19	1.77	2.32
Y	2.21	2.09	-0.11	1.48	0.69	1.61	1.71
Zr	0.96	0.88	-0.28	1.04	0.01	2.20	1.73
Nb	1.11	1.01	0.36	1.45	1.26	1.76	2.13
Mo	1.63	1.57	1.14	1.64	1.91	2.02	2.34
Tc	2.35	1.76	1.38	2.05	2.27	1.95	2.44
Ru	2.65	2.01	2.76	1.94	3.33	0.64	2.43
Rh	3.22	3.00	2.16	3.76	3.10	0.70	2.66
Pd	3.13	3.35	2.51	2.67	3.53	1.25	2.46
Ag	4.9	4.81	3.24	3.84	4.32	1.41	2.18
La	2.64	2.19	0.38	1.96	2.54	0.96	1.93
Hf	0.53	1.32	-0.7	0.73	0.16	0.66	1.67
Ta	0.52	0.52	-0.10	0.97	0.87	1.11	2.04
W	0.83	0.79	0.47	1.28	1.40	1.28	2.22
Re	0.92	-0.46	-0.77	0.01	0.15	2.56	1.34
Os	2.14	1.48	1.35	1.81	2.30	0.01	1.13
Ir	2.80	2.40	1.65	2.24	2.69	1.74	0.01
Pt	2.33	260	2.15	1.97	3.10	2.00	0.01
Au	3.65	3.69	2.84	3.07	4.09	1.99	2.72

***Table S2**. The linear correlation y = a*x + b between adsorption free energy of intermediate species and that of *$COCH_2O$. R^2 represents the mean square error.*

Species	**a**	**b**	**R^2**
*COOH	0.52	1.00	0.84
*CO	-0.21	2.25	0.05
*CHO	0.55	2.72	0.32
*COH	0.42	1.52	0.50
*COCO	0.74	-0.18	0.52
*COCHO	0.56	0.97	0.81
*COCOH	0.77	1.07	0.89
*COHCOH	1.00	1.19	0.87
*CCO	0.98	3.40	0.87
*$COHCH_2O$	1.23	0.16	0.92
*CHCO	0.63	2.42	0.86
*CCOH	0.79	4.06	0.92
*$CHOH\text{-}CH_2O$	1.03	-0.28	0.92
*CHCOH	0.81	2.71	0.79
*CH_2CO	0.28	2.49	0.54
*$CHCH_2O$	1.27	2.25	0.91
*CH_2COH	0.83	2.26	0.82
*O	1.58	1.31	0.83
*CH_2CHOH	0.85	1.36	0.84
*CH_2CH_2O	0.99	1.12	0.92
*CH_3CH_2O	0.83	0.30	0.65
*CH_2CH_2OH	0.73	1.33	0.75
*OH	0.84	1.24	0.67
*C_2H_5OH	0.04	1.46	0.01
*H_2O	0.20	1.85	0.35

***Table S3**. Comparison between limiting potential values [in Volts (V)] for Cr, Mn, Fe, Co, Cu, Tc, Rh, Pd, Re, Os and Ir based catalysts predicted using linear correlation between adsorption free energies of different intermediates vs adsorption free energy of *$COCH_2O$ and limiting potentials computed using the free energy pathways.*

System	U_L (Predicted)	U_L(Calculated)
Cr	-2.85	-2.23
Mn	-2.93	-2.35
Fe	-2.93	-2.27
Co	-2.87	-2.60
Cu	-3.17	-1.50
Tc	**-2.91**	**-2.70**
Rh	-2.88	-2.61
Pd	-2.96	-2.51
Re	-4.30	-2.39
Os	-3.22	-2.46
Ir	**-2.76**	**-2.55**

*The predicted and calculated limiting potential is given by the following equation

$$U_L = \frac{-\Delta G_{Max.}}{e}$$