Electronic Supplementary Material (ESI) for Nanoscale.

Computational screening of effective g-C_3N_4 based single atom electrocatalysts for the selective conversion of CO_2

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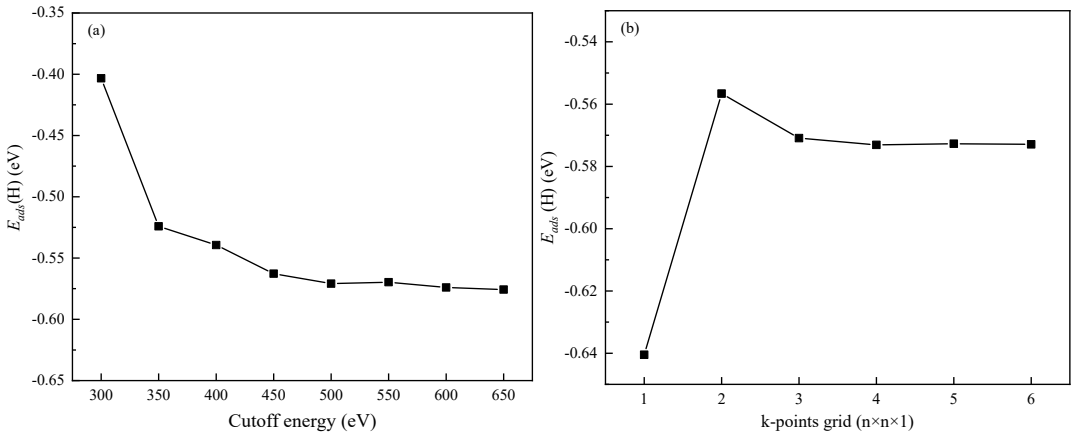
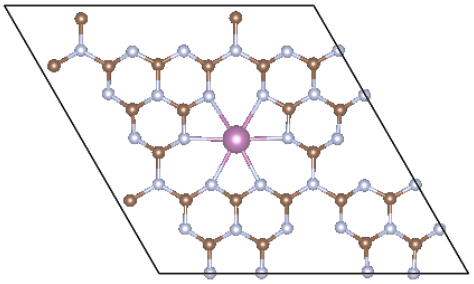
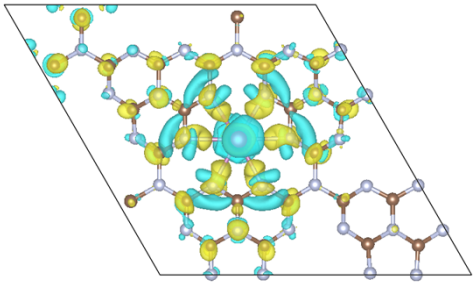
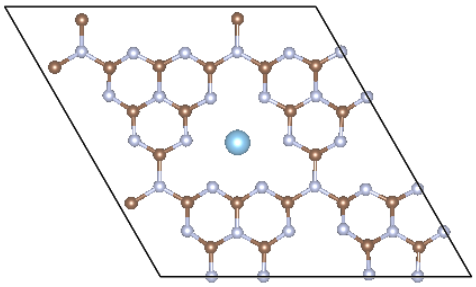
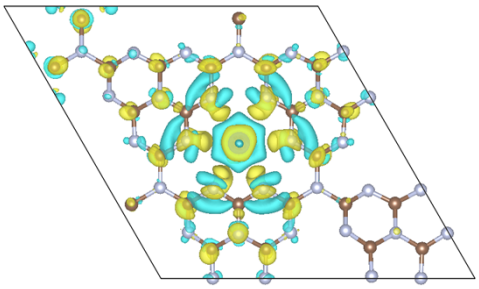
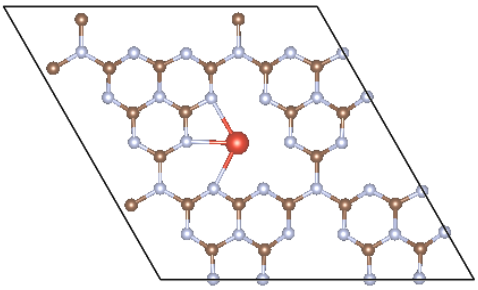
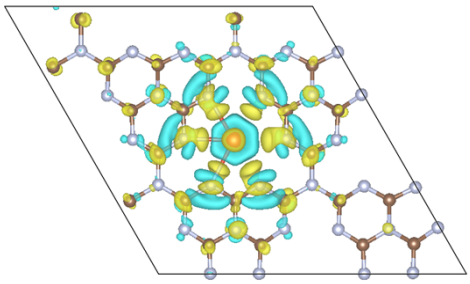
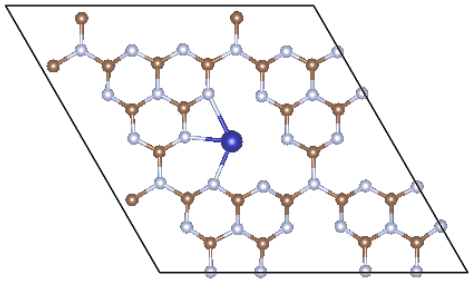
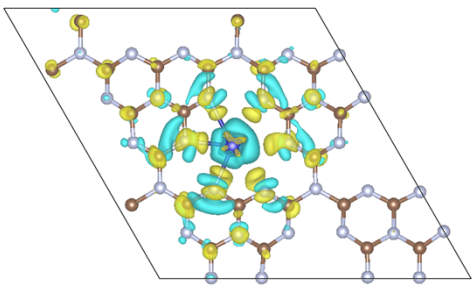
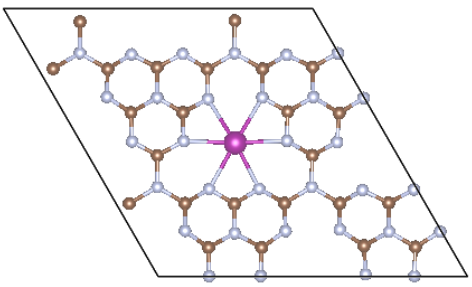
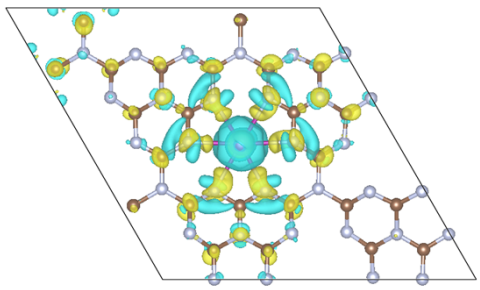
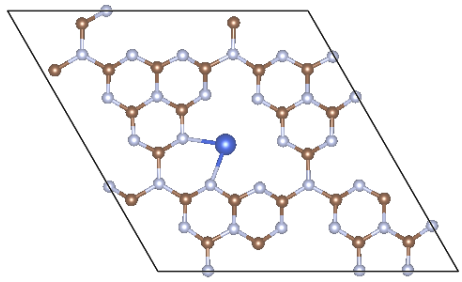
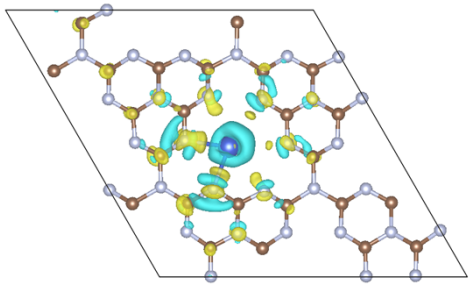
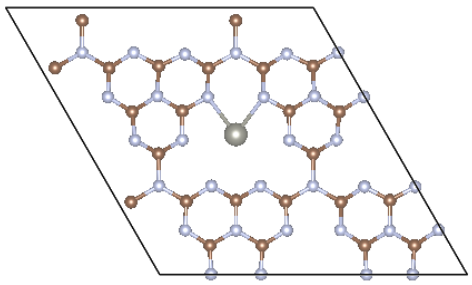
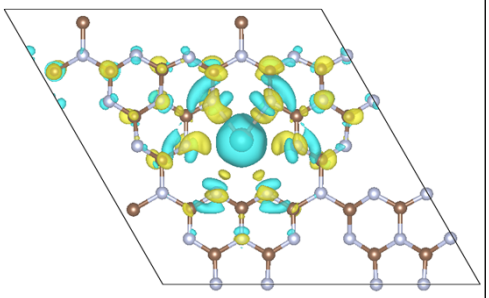
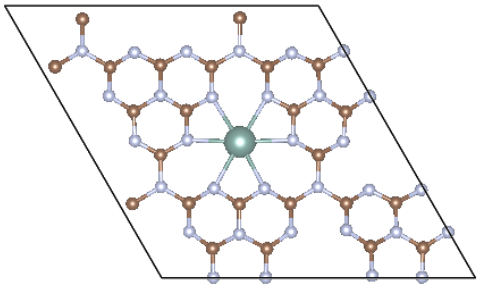
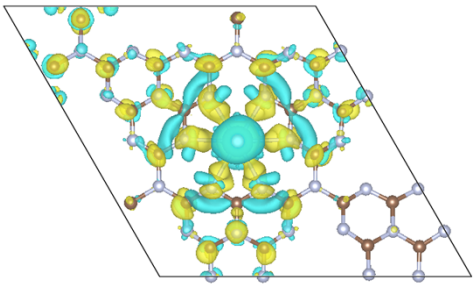
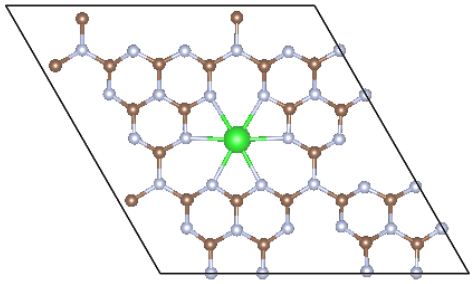
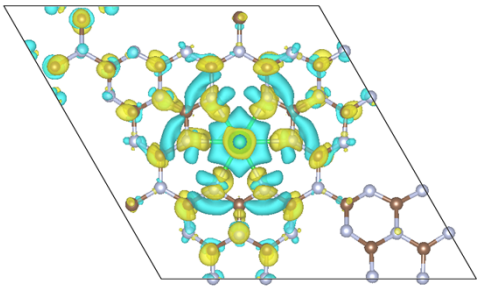
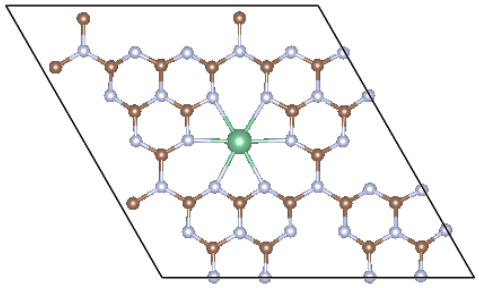
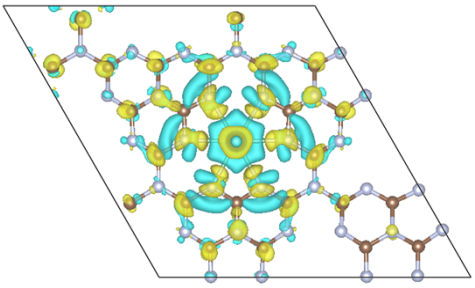


Figure S1. The convergence of H adsorption energy with respective to the cut-off energy (a) and k-point grids (b) used in the calculations.

Sc-g-C_3N_4		
Ti-g-C_3N_4		
V-g-C_3N_4		
Cr-g-C_3N_4		
Mn-g-C_3N_4		

Cu-g-C_3N_4		
Zn-g-C_3N_4		
Y-g-C_3N_4		
Zr-g-C_3N_4		
Nb-g-C_3N_4		

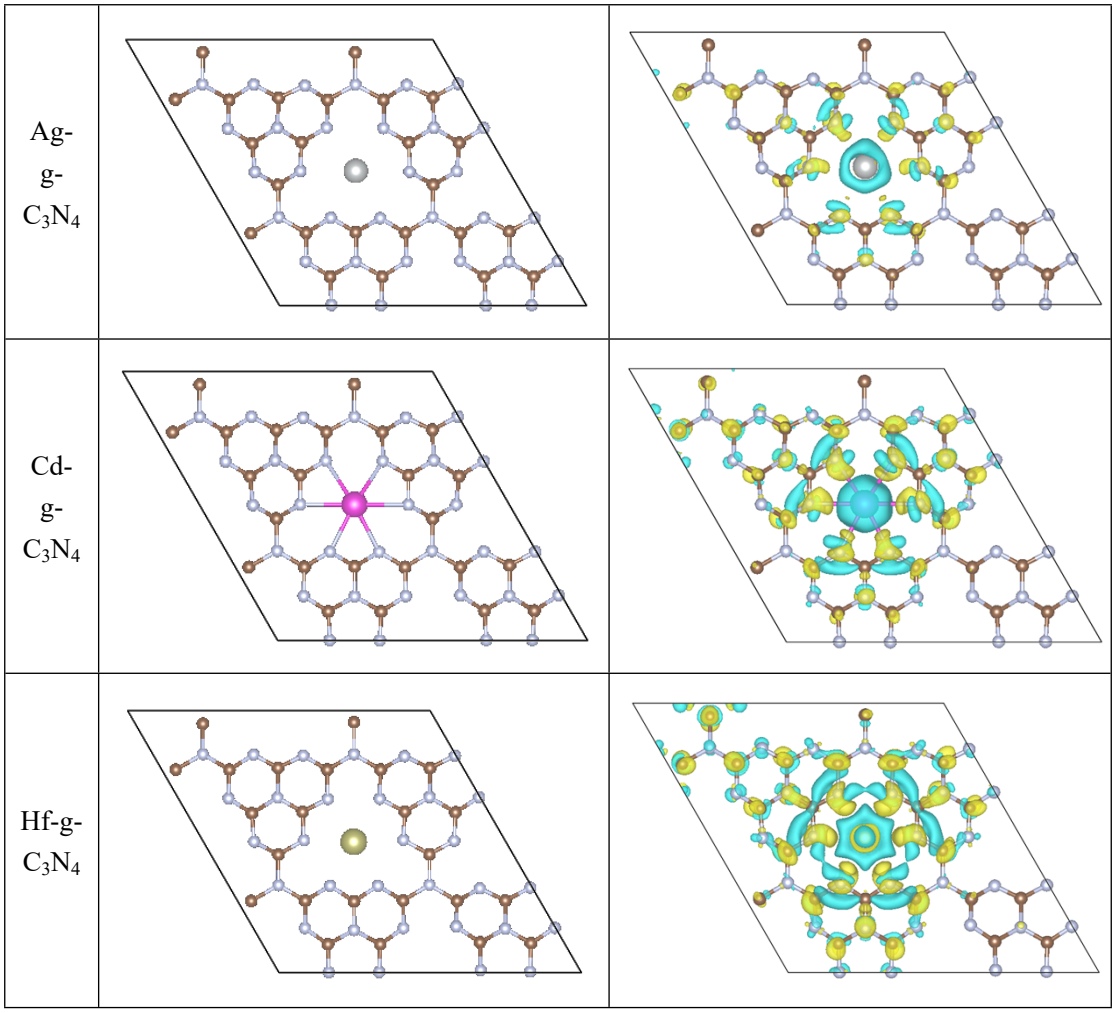
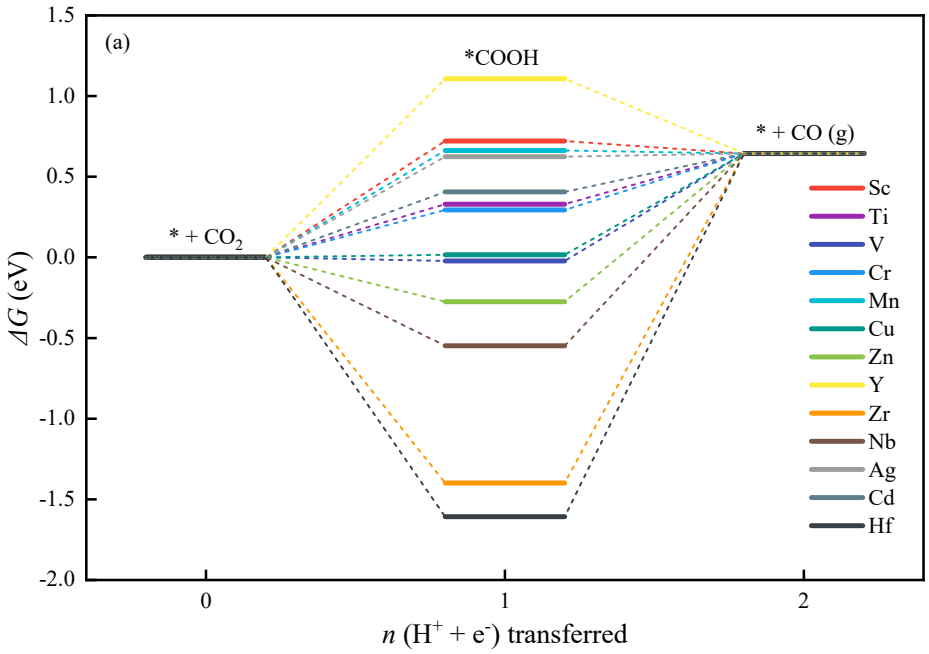
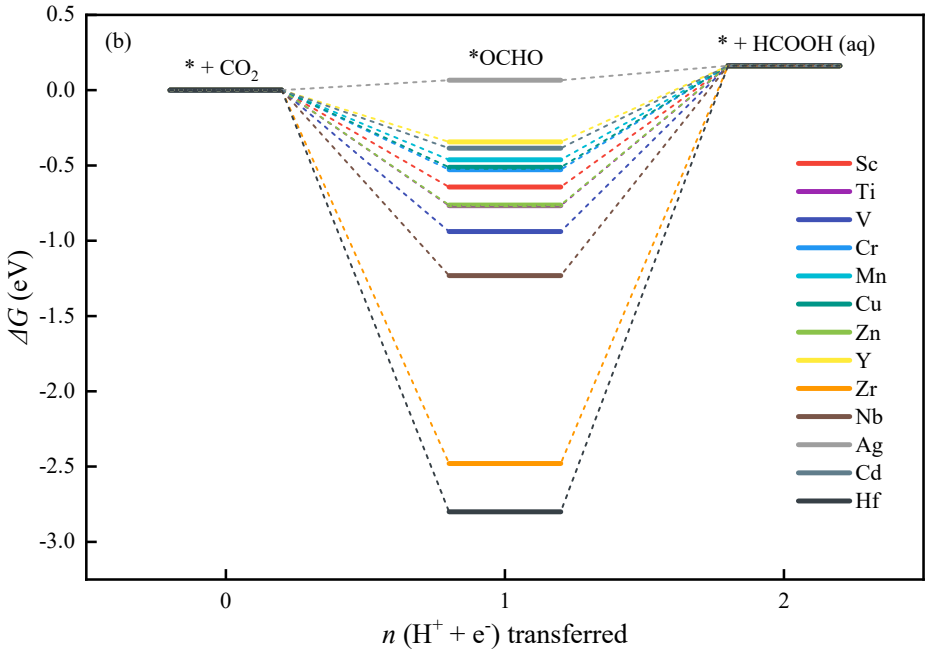


Figure S2. Stable configurations of TM-g-C_3N_4 (TM= Sc, Ti, V, Cr, Mn, Cu, Zn, Y, Zr, Nb, Ag, Cd and Hf) and charge density difference between TM atom and g-C_3N_4 (isosurface value is set to be 0.003 e/Å^3, the yellow and cyan indicate the electron accumulation and electron depletion respectively).


(a)
*COOH
* + CO (g)
* + CO2
Sc
Ti
V
Cr
Mn
Cu
Zn
Y
Zr
Nb
Ag
Cd
Hf
ΔG (eV)
n (H+ + e-) transferred


(b)
* + CO2
*OCHO
* + HCOOH (aq)
Sc
Ti
V
Cr
Mn
Cu
Zn
Y
Zr
Nb
Ag
Cd
Hf
ΔG (eV)
n (H+ + e-) transferred

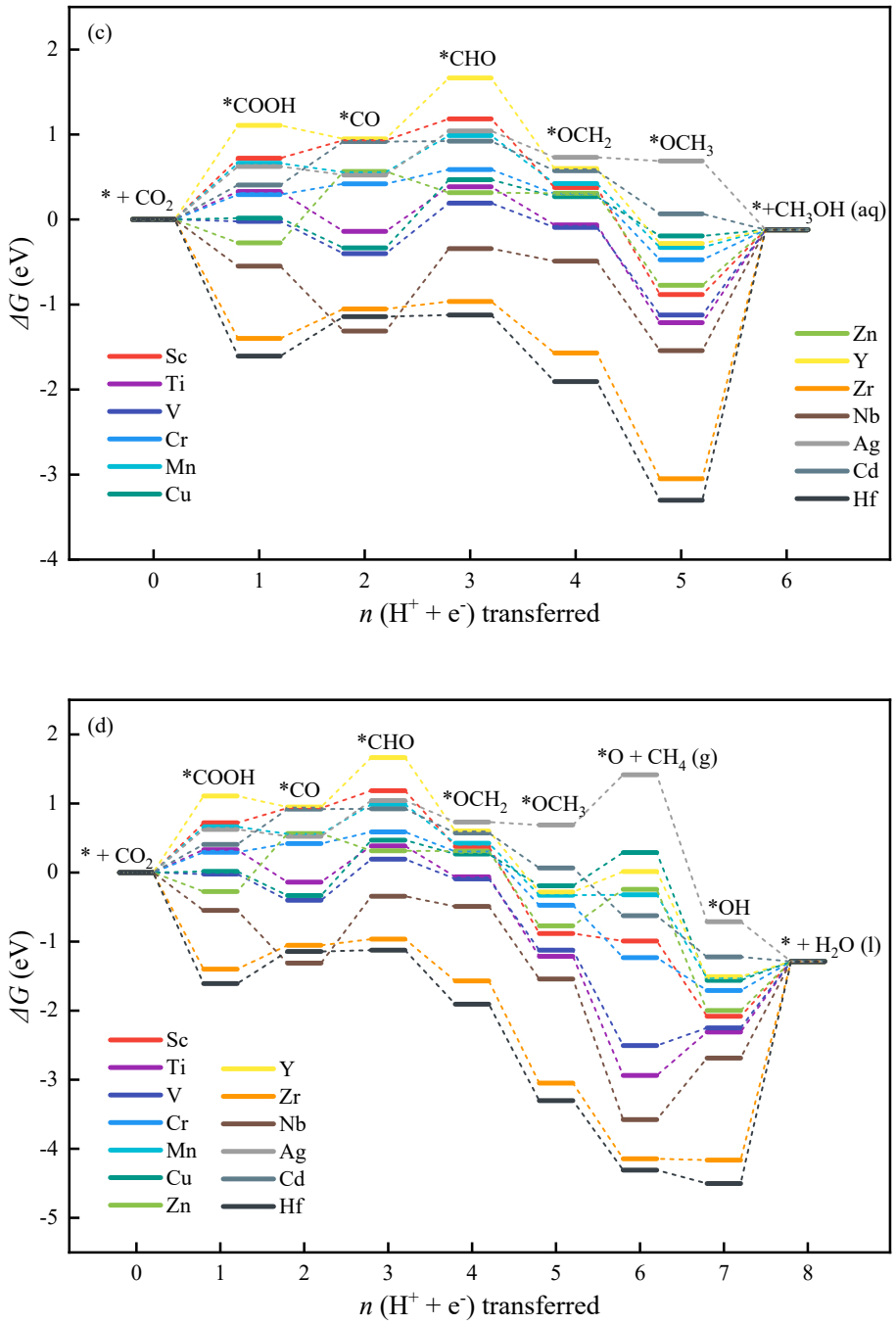


Figure S3. Gibbs free energy diagram for CO (a), HCOOH (b), CH_3OH (c) and CH_4 (d) along the most favourable pathway

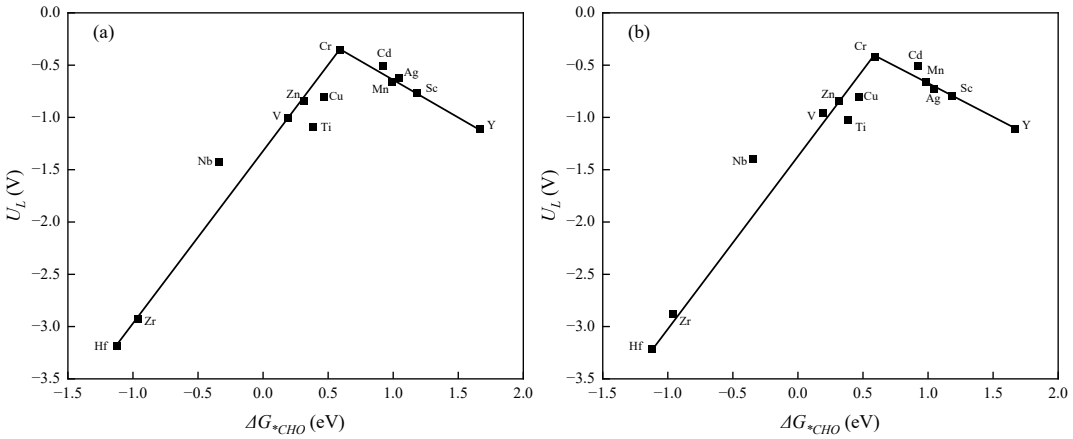


Figure S4. Volcano plots of U_L for CH_3OH (a) and CH_4 (b) as a function of ΔG_{*CHO}

Table S1. Binding energies (E_{bind}) and cohesive energies (E_{coh}) (in eV) of TM atoms on g-C_3N_4, as well as the crystal phase of TMs in their most stable bulk structures.

TM	E_{bind}	E_{coh}	$E_{bind} - E_{coh}$	Crystal phase
Sc	-8.214	-4.512	-3.702	hexagonal
Ti	-7.866	-5.911	-1.955	hexagonal
V	-6.552	-5.947	-0.605	cubic
Cr	-4.816	-4.462	-0.354	cubic
Mn	-4.960	-4.158	-0.803	cubic
Fe	-4.478	-5.256	0.778	cubic
Co	-5.236	-5.858	0.622	hexagonal
Ni	-5.152	-5.327	0.175	cubic
Cu	-4.027	-3.986	-0.041	cubic
Zn	-1.859	-1.434	-0.425	hexagonal
Y	-8.984	-4.558	-4.426	hexagonal
Zr	-9.319	-6.690	-2.630	hexagonal
Nb	-8.155	-7.590	-0.565	cubic
Mo	-5.588	-6.921	1.333	cubic
Tc	-5.618	-7.647	2.029	hexagonal
Ru	-6.664	-8.577	1.913	hexagonal
Rh	-5.555	-6.572	1.018	cubic
Pd	-3.610	-4.297	0.687	cubic
Ag	-3.294	-2.983	-0.312	cubic
Cd	-1.803	-1.049	-0.754	hexagonal
Hf	-9.109	-6.818	-2.290	hexagonal
Ta	-8.759	-8.908	0.149	cubic
W	-5.621	-8.988	3.367	cubic
Re	-4.851	-8.381	3.531	hexagonal
Os	-5.543	-8.945	3.402	hexagonal
Ir	-5.959	-8.333	2.374	cubic
Pt	-4.321	-6.315	1.994	cubic
Au	-2.677	-3.670	0.993	cubic

Table S2. Bader charge transfer (|***e***|) from TM to g-C_3N_4 and magnetic moments of TMs

TM	Bader charge transfer |*e*|	Magnetic Moment (μB)
Sc	2.239	0.011
Ti	1.957	1.181
V	1.398	2.520
Cr	1.405	3.591
Mn	1.553	4.556
Cu	0.767	0.010
Zn	1.298	0.000
Y	2.431	0.004
Zr	1.873	0.719
Nb	1.563	1.679
Ag	0.664	0.006
Cd	1.351	-0.010
Hf	1.891	0.649

Table S3. Corresponding thermodynamic energy corrections (in eV) for molecules

Molecules*	**ZPE**	**-TS**	$\int C_p dT$
H_2 (g)	0.268	-0.403	0.090
CO (g)	0.132	-0.611	0.090
CO_2 (g)	0.307	-0.662	0.098
H_2O (l)	0.568	-0.670	0.103
HCOOH (aq)	0.887	-1.048	0.113
CH_3OH (aq)	1.342	-0.865	0.130
CH_4 (g)	1.185	-0.576	0.104

*: The gaseous species, CO_2, CO, CH_4 and H_2, were calculated at 101325 Pa, while H_2O, HCOOH and CH_3OH were treated with pressure correction at a fugacity of 3534 Pa, 2 Pa and 6080 Pa.

Table S4. Free energy corrections (in eV) for intermediates

Intermediate	TM	ZPE	-TS	$\int C_p dT$
***COOH**	Sc	0.612	-0.115	0.065
	Ti	0.608	-0.217	0.110
	V	0.608	-0.160	0.086
	Cr	0.603	-0.138	0.068
	Mn	0.610	-0.212	0.108
	Cu	0.621	-0.202	0.103
	Zn	0.633	-0.194	0.098
	Y	0.614	-0.174	0.088
	Zr	0.636	-0.190	0.097
	Nb	0.605	-0.228	0.111
	Ag	0.616	-0.147	0.082
	Cd	0.615	-0.231	0.111
	Hf	0.634	-0.126	0.074

Intermediate	TM	ZPE	-TS	$\int C_p dT$
***OCHO**	Sc	0.603	-0.176	0.087
	Ti	0.603	-0.158	0.083
	V	0.624	-0.183	0.096
	Cr	0.620	-0.199	0.100
	Mn	0.609	-0.223	0.107
	Cu	0.615	-0.152	0.079
	Zn	0.613	-0.170	0.083
	Y	0.606	-0.114	0.062
	Zr	0.607	-0.158	0.082
	Nb	0.611	-0.148	0.079
	Ag	0.606	-0.162	0.083
	Cd	0.613	-0.216	0.107
	Hf	0.610	-0.157	0.082

Intermediate	TM	ZPE	-TS	$\int C_p dT$
***CO**	Sc	0.199	-0.115	0.067
	Ti	0.185	-0.106	0.053
	V	0.210	-0.115	0.061
	Cr	0.204	-0.115	0.064
	Mn	0.174	-0.119	0.060
	Cu	0.223	-0.103	0.059
	Zn	0.167	-0.141	0.067
	Y	0.170	-0.131	0.063
	Zr	0.184	-0.096	0.051
	Nb	0.202	-0.135	0.065
	Ag	0.190	-0.153	0.079
	Cd	0.186	-0.160	0.082
	Hf	0.188	-0.088	0.049

Intermediate	TM	ZPE	-TS	$\int C_p dT$
***CHO**	Sc	0.469	-0.131	0.072
	Ti	0.476	-0.117	0.067
	V	0.446	-0.168	0.083
	Cr	0.437	-0.182	0.087
	Mn	0.457	-0.134	0.075
	Cu	0.440	-0.123	0.063
	Zn	0.466	-0.106	0.057
	Y	0.448	-0.127	0.062
	Zr	0.467	-0.139	0.073
	Nb	0.441	-0.109	0.060
	Ag	0.435	-0.183	0.087
	Cd	0.446	-0.142	0.066
	Hf	0.466	-0.133	0.072

Intermediate	TM	ZPE	-TS	$\int C_p dT$
***OCH_2**	Sc	0.711	-0.173	0.087
	Ti	0.741	-0.199	0.099
	V	0.753	-0.190	0.096
	Cr	0.721	-0.144	0.070
	Mn	0.724	-0.136	0.068
	Cu	0.771	-0.191	0.094
	Zn	0.749	-0.203	0.100
	Y	0.730	-0.196	0.098
	Zr	0.719	-0.161	0.084
	Nb	0.710	-0.163	0.085
	Ag	0.726	-0.247	0.105
	Cd	0.738	-0.181	0.087
	Hf	0.718	-0.229	0.110

Intermediate	TM	ZPE	-TS	$\int C_p dT$
***OCH_3**	Sc	1.087	-0.188	0.086
	Ti	1.093	-0.159	0.078
	V	1.079	-0.185	0.086
	Cr	1.065	-0.199	0.091
	Mn	1.059	-0.204	0.092
	Cu	1.059	-0.141	0.066
	Zn	1.081	-0.233	0.106
	Y	1.080	-0.128	0.064
	Zr	1.094	-0.171	0.083
	Nb	1.084	-0.163	0.081
	Ag	1.070	-0.192	0.098
	Cd	1.070	-0.166	0.082
	Hf	1.100	-0.111	0.058

Intermediate	TM	ZPE	-TS	$\int C_p dT$
***O**	Sc	0.081	-0.045	0.028
	Ti	0.082	-0.055	0.031
	V	0.079	-0.066	0.034
	Cr	0.062	-0.096	0.043
	Mn	0.052	-0.053	0.023
	Cu	0.038	-0.005	0.004
	Zn	0.051	-0.096	0.044
	Y	0.063	-0.070	0.037
	Zr	0.078	-0.053	0.031
	Nb	0.082	-0.052	0.030
	Ag	0.041	-0.104	0.047
	Cd	0.099	-0.026	0.018
	Hf	0.084	-0.051	0.030

Intermediate	TM	ZPE	-TS	$\int C_p dT$
***OH**	Sc	0.309	-0.109	0.056
	Ti	0.342	-0.107	0.056
	V	0.340	-0.113	0.058
	Cr	0.343	-0.101	0.056
	Mn	0.328	-0.126	0.065
	Cu	0.338	-0.130	0.063
	Zn	0.343	-0.066	0.037
	Y	0.326	-0.126	0.067
	Zr	0.334	-0.101	0.058
	Nb	0.332	-0.122	0.062
	Ag	0.337	-0.118	0.061
	Cd	0.332	-0.138	0.066
	Hf	0.332	-0.116	0.064

Table S5. Bader charge transfer (|*e*|) of TM metals with different intermediates

	TM-g-C_3N_4	***OCHO**	***COOH**	***CO**	***CHO**	***OCH_2**	***OCH_3**	***O**	***OH**
Cr	1.405	1.437	1.405	1.379	1.415	1.442	1.468	1.646	1.440
Cd	1.351	1.288	1.071	1.301	1.008	1.320	1.254	1.335	1.242
Nb	1.563	2.167	1.993	1.925	1.948	2.273	2.316	2.551	2.294
Zr	1.873	2.691	2.491	2.299	2.416	2.578	2.623	2.474	2.621
Hf	1.891	2.711	2.526	2.409	2.461	2.611	2.622	2.417	2.599