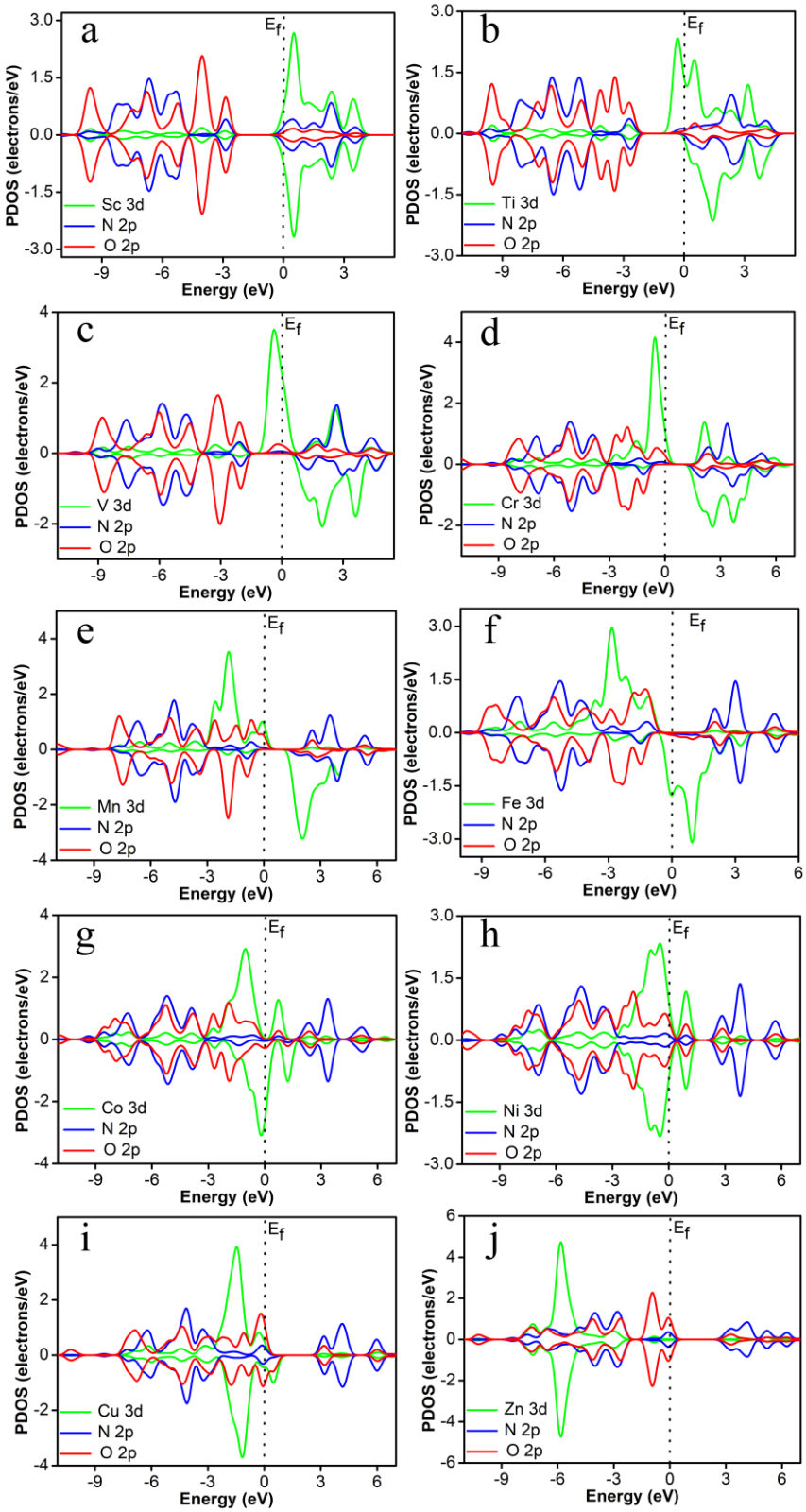


Figure S1. Projected partial density of states (PDOS) of TM-$N_2O_2C_x$, (a)Sc-$N_2O_2C_x$, (b)Ti-$N_2O_2C_x$, (c)V-$N_2O_2C_x$, (d)Cr-$N_2O_2C_x$, (e)Mn-$N_2O_2C_x$, (f)Fe-$N_2O_2C_x$, (g)Co-$N_2O_2C_x$, (h)Ni-$N_2O_2C_x$, (i)Cu-$N_2O_2C_x$, (j)Zn-$N_2O_2C_x$. The dotted line denotes the Fermi level. The green, red and blue lines represent the 3d orbital of the metal atoms, the 2p orbital of the oxygen atoms, and 2p orbital of the Nitrogen atoms, respectively.

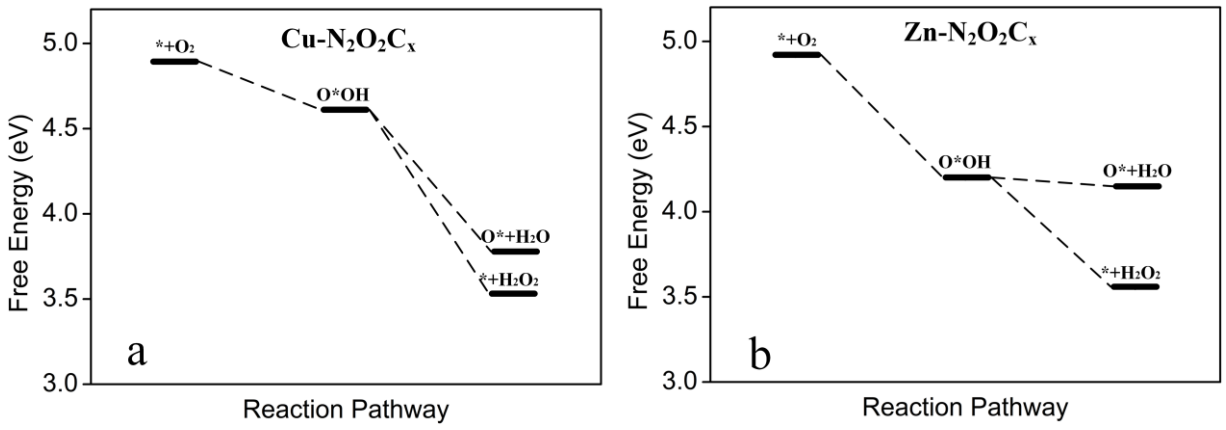


Figure S2. Free energy diagram of 2e⁻ ORR on Cu-$N_2O_2C_x$ (a) and Zn-$N_2O_2C_x$ (b) under 0 V.

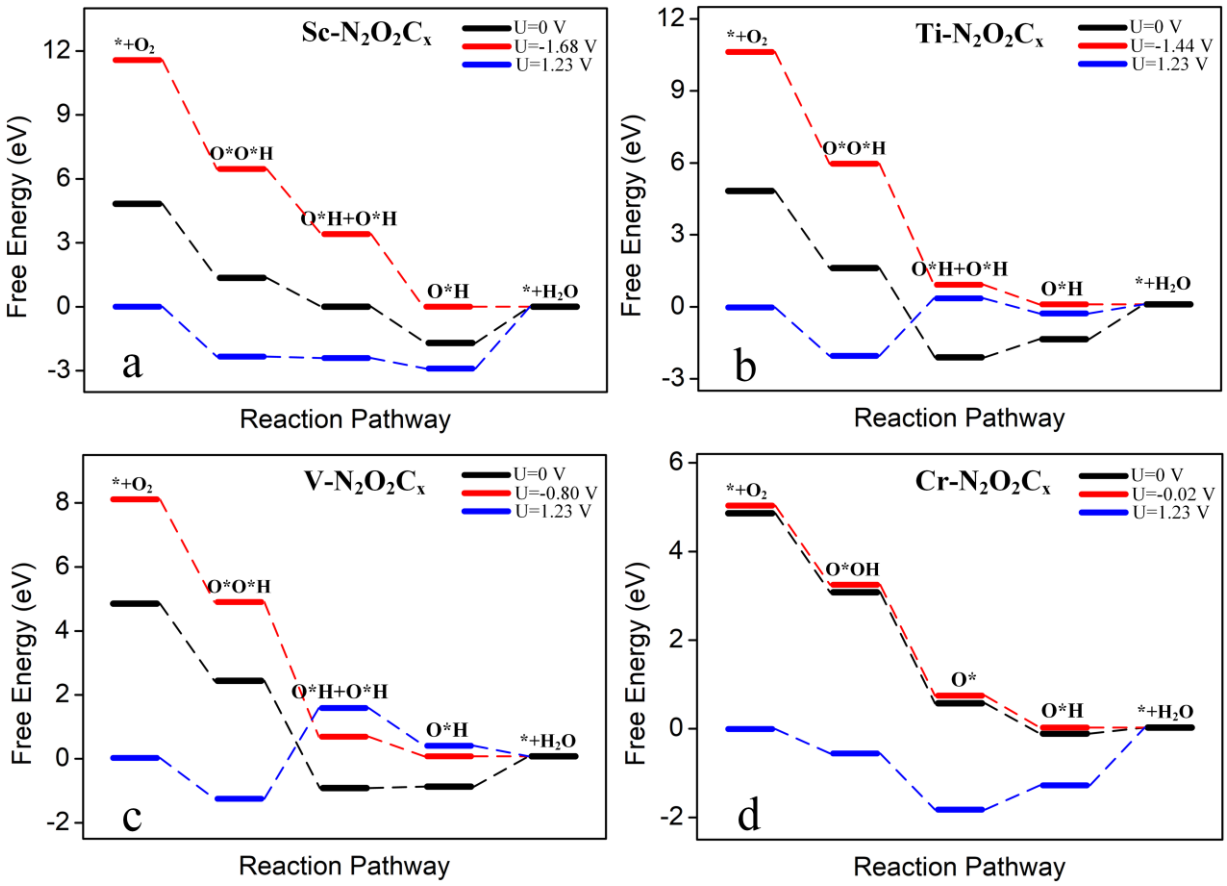
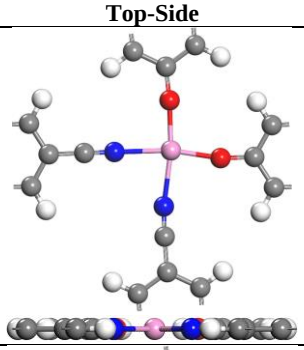
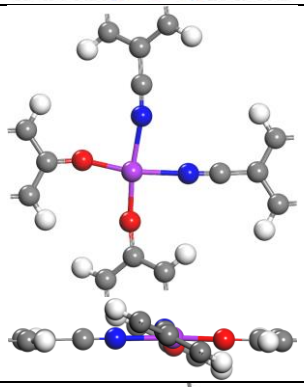
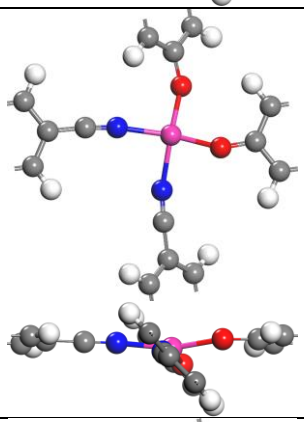
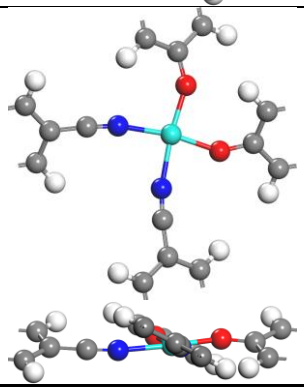
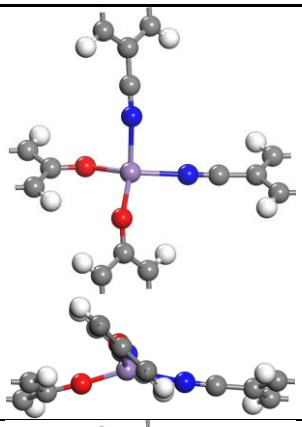
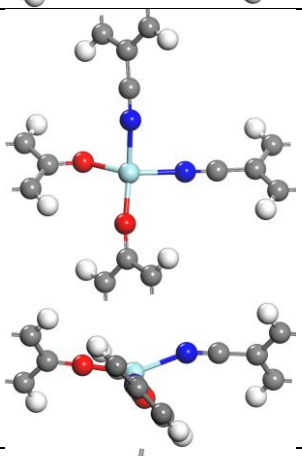
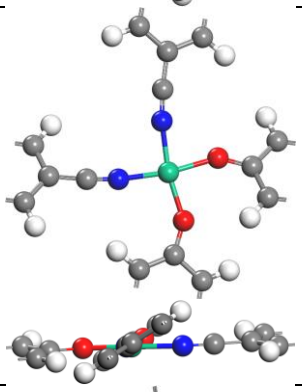
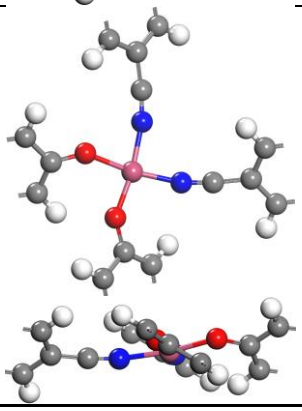


Figure S3. Free energy diagram of 4e⁻ ORR on Sc-$N_2O_2C_x$ (a), Ti-$N_2O_2C_x$ (b), V-$N_2O_2C_x$ (c) and Cr-$N_2O_2C_x$ (d) under different potentials. The black line, blue line and red line represent U=0 V, U=limting potential and U=1.23 V, respectively.

Table S1 The lattice constants, top and side views of optimized crystal structures of TM-$N_2O_2C_x$; Hirshfeld charges on metal atoms (Q_{TM}), nitrogen atoms (Q_N) and oxygen atoms (Q_O) of TM-$N_2O_2C_x$ SACs, and Hirshfeld spin of the metal atoms, and the length of TM-N bond (R_{M-N}) and TM-O (R_{M-O}).

TM-$N_2O_2C_x$	Top-Side	Lattice constant	Q / e	Spin	R / Å
Sc-$N_2O_2C_x$		a=10.89 Å b=10.88 Å c=20.00 Å	Q_{TM}=0.684 Q_N=-0.191 Q_O=-0.259	0.000	R_{M-N}=2.213 R_{M-O}=1.962
Ti-$N_2O_2C_x$		a=10.62 Å b=10.61 Å c=20.00 Å	Q_{TM}=0.371 Q_N=-0.166 Q_O=-0.226	1.446	R_{M-N}=2.120 R_{M-O}=1.893
V-$N_2O_2C_x$		a=10.53 Å b=10.53 Å c=20.00 Å	Q_{TM}=0.341 Q_N=-0.150 Q_O=-0.220	2.536	R_{M-N}=2.025 R_{M-O}=1.933
Cr-$N_2O_2C_x$		a=10.49 Å b=10.50 Å c=20.00 Å	Q_{TM}=0.495 Q_N=-0.173 Q_O=-0.262	3.569	R_{M-N}=2.029 R_{M-O}=1.941

Mn-$N_2O_2C_x$		a=10.59 Å b=10.59 Å c=20.00 Å	Q_{TM}=0.437 Q_N=-0.154 Q_O=-0.257	4.504	R_{M-N}=2.182 R_{M-O}=2.010
Fe-$N_2O_2C_x$		a=10.53 Å b=10.56 Å c=20.00 Å	Q_{TM}=0.345 Q_N=-0.149 Q_O=-0.241	3.478	R_{M-N}=2.079 R_{M-O}=1.907
Co-$N_2O_2C_x$		a=10.44 Å b=10.42 Å c=20.00 Å	Q_{TM}=0.165 Q_N=-0.109 Q_O=-0.201	0.816	R_{M-N}=1.876 R_{M-O}=1.888
Ni-$N_2O_2C_x$		a=10.21 Å b=10.15 Å c=20.00 Å	Q_{TM}=0.153 Q_N=-0.106 Q_O=-0.190	0.000	R_{M-N}=1.858 R_{M-O}=1.863

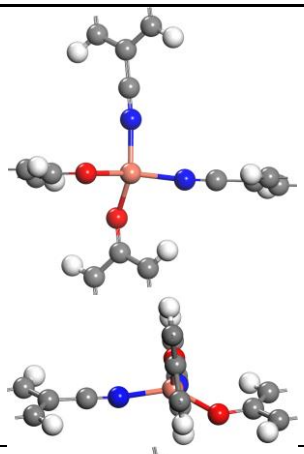
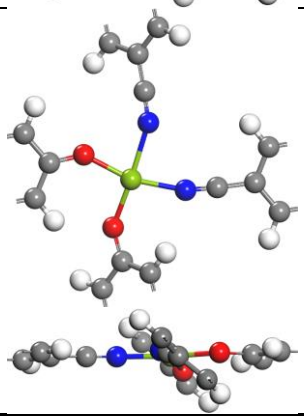
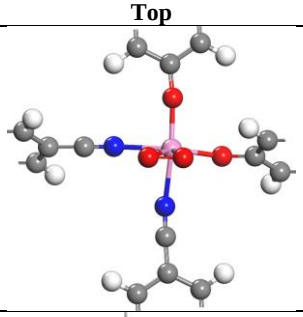
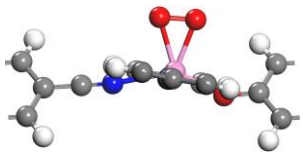
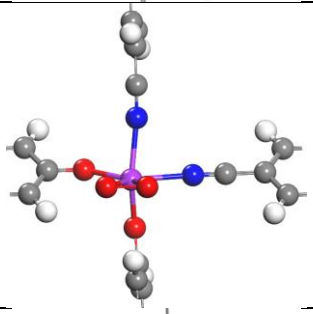
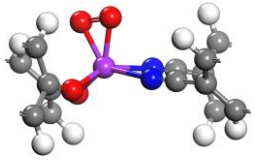
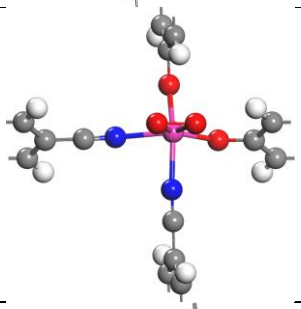
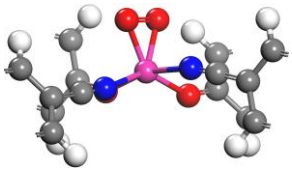
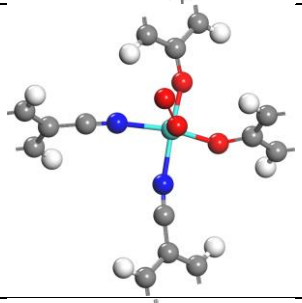
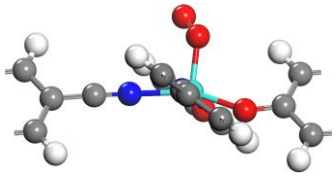
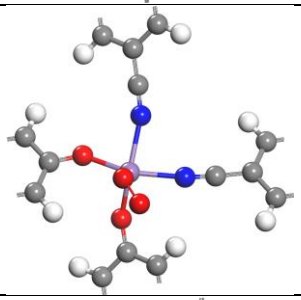
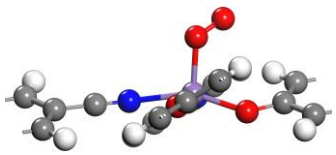
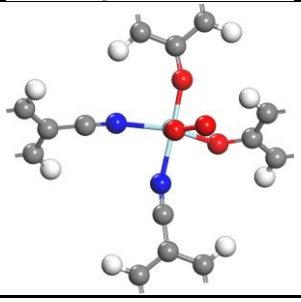
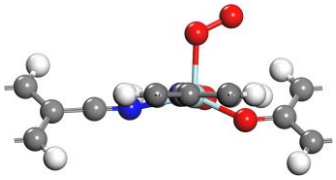
Cu-$N_2O_2C_x$		a=10.36 Å b=10.34 Å c=20.00 Å	Q_{TM}=0.410 Q_N=-0.169 Q_O=-0.255	0.416	R_{M-N}=2.005 R_{M-O}=1.981
Zn-$N_2O_2C_x$		a=10.41 Å b=10.45 Å c=20.00 Å	Q_{TM}=0.553 Q_N=-0.183 Q_O=-0.264	0.000	R_{M-N}=2.055 R_{M-O}=1.974

Table S2 Computed formation energy (E_f) of TM-$N_2O_2C_x$, dissolution potential (U_{diss}) and number of transferred electrons (n) during the dissolution of metals. For comparison, the standard dissolution potential (**$U°_{diss}$**) of metal atoms are also listed.

TM-$N_2O_2C_x$	**E_f / eV**	**$U°_{diss}$ / V**	**n / e**	**U_{diss} / V**
Sc-$N_2O_2C_x$	-6.46	-2.08	3	0.07
Ti-$N_2O_2C_x$	-4.40	-1.63	2	0.57
V-$N_2O_2C_x$	-3.33	-1.18	2	0.48
Cr-$N_2O_2C_x$	-3.24	-0.91	2	0.71
Mn-$N_2O_2C_x$	-2.72	-1.19	2	0.17
Fe-$N_2O_2C_x$	-2.18	-0.45	2	0.64
Co-$N_2O_2C_x$	-1.72	-0.28	2	0.58
Ni-$N_2O_2C_x$	-2.24	-0.26	2	0.86
Cu-$N_2O_2C_x$	-1.51	0.34	2	1.09
Zn-$N_2O_2C_x$	-3.62	-0.76	2	1.05

Table S3. The top and side views of the most stable adsorption state of O_2 on TM-$N_2O_2C_x$, as well as the corresponding adsorption energy ($E_{ads\text{-}O2}$).

TM-$N_2O_2C_x$-O_2	Top	Side	$E_{ads\text{-}O2}$ / eV
Sc-$N_2O_2C_x$-O_2			-2.85
Ti-$N_2O_2C_x$-O_2			-4.22
V-$N_2O_2C_x$-O_2			-3.03
Cr-$N_2O_2C_x$-O_2			-1.33
Mn-$N_2O_2C_x$-O_2			-0.87
Fe-$N_2O_2C_x$-O_2			-0.77

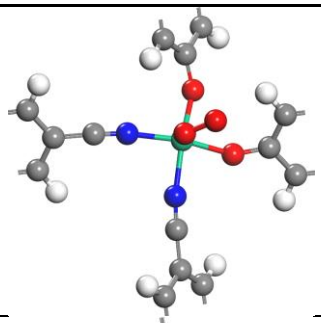
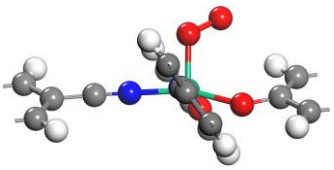
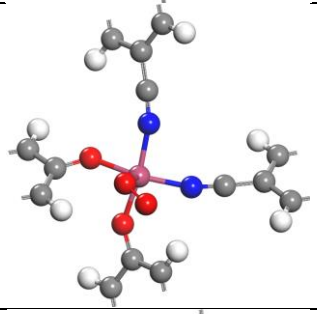
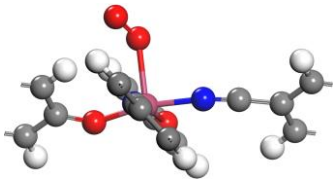
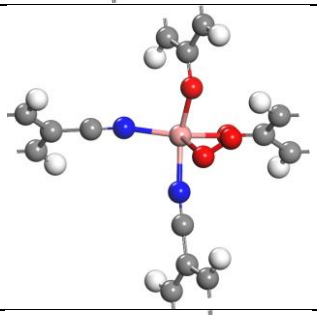
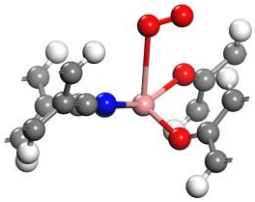
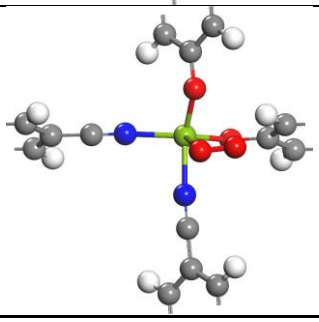
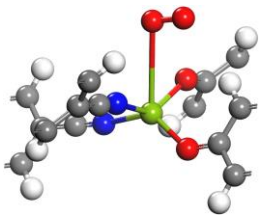
Co-$N_2O_2C_x$-O_2			-0.83
Ni-$N_2O_2C_x$-O_2			-0.42
Cu-$N_2O_2C_x$-O_2			-0.39
Zn-$N_2O_2C_x$-O_2			-0.57

Table S4. The calculated free energy corrections (Gc) for adsorbates: zero point energy (E_{ZPE}) and entropy correction (TS). The temperature of the reaction is 298.15k.

Sc-$N_2O_2C_x$	**E_{ZPE} (kcal/mol)**	**TS (eV)**	**G_c (kcal/mol)**
O*O*H	10.492	-0.089	12.567
O*	2.206	-0.015	2.557
O*H+O*H	15.081	-0.104	17.471
O*H	9.334	-0.018	9.748

Ti-$N_2O_2C_x$	E_{ZPE} (kcal/mol)	TS (eV)	G_c (kcal/mol)
O*O*H	10.476	-0.082	12.367
O*	2.289	-0.012	2.555
O*H+O*H	15.760	-0.080	17.616
O*H	9.407	-0.017	9.788

V-$N_2O_2C_x$	E_{ZPE} (kcal/mol)	TS (eV)	G_c (kcal/mol)
O*O*H	10.603	-0.082	12.498
O*	2.266	-0.013	2.555
O*H+O*H	16.018	-0.074	17.717
O*H	9.301	-0.014	9.600

Cr-$N_2O_2C_x$	E_{ZPE} (kcal/mol)	TS (eV)	G_c (kcal/mol)
O*OH	10.205	-0.098	12.454
O*	2.273	-0.013	2.567
O*H	9.403	-0.013	9.713

Mn-$N_2O_2C_x$	E_{ZPE} (kcal/mol)	TS (eV)	G_c (kcal/mol)
O*OH	10.452	-0.090	12.538
O*	2.263	-0.013	2.559
O*H	9.403	-0.013	9.713

Fe-$N_2O_2C_x$	E_{ZPE} (kcal/mol)	TS (eV)	G_c (kcal/mol)
O*OH	9.920	-0.112	12.510
O*	2.200	-0.012	2.481
O*H	9.322	-0.015	9.676

Co-$N_2O_2C_x$	E_{ZPE} (kcal/mol)	TS (eV)	G_c (kcal/mol)
O*OH	9.819	-0.125	12.454
O*	2.244	-0.013	2.549
O*H	9.341	-0.014	9.670

Ni-$N_2O_2C_x$	E_{ZPE} (kcal/mol)	TS (eV)	G_c (kcal/mol)

O*OH	9.555	-0.094	11.733
O*	2.323	-0.012	2.599
O*H	9.509	-0.013	9.804

Cu-$N_2O_2C_x$	**E_{ZPE} (kcal/mol)**	**TS (eV)**	**G_c (kcal/mol)**
O*OH	9.868	-0.121	12.649
O*	2.323	-0.012	2.599
O*H	9.348	-0.014	9.676
Zn-$N_2O_2C_x$	**E_{ZPE} (kcal/mol)**	**TS (eV)**	**G_c (kcal/mol)**
O*OH	9.575	-0.099	11.867
O*	2.198	-0.016	2.556
O*H	9.414	-0.015	9.757