Supporting information

Transition Metal-Doped Cobalt Phosphide for Efficient Hydrazine Oxidation: A Density Functional Theory Study

Zixin Zhou,[a] Min Zhou,[a] Xiaobin Liao,[a] Mengjun Zhou,*[a] Xiaolin Liu,*[b] Qian Liu,*[c] Yan Zhao*[b d]

[a]State Key Laboratory of Silicate Materials for Architectures, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, Hubei, P. R. China

[b]College of Materials Science and Engineering, Sichuan University, Chengdu 610065, P. R. China

[c]Hoffmann Institute of Advanced Materials, Shenzhen Polytechnic University, 7098 Liuxian Boulevard, Shenzhen, 518055 China

[d]The Institute of Technological Sciences, Wuhan University, Hubei, Wuhan 430072, P. R. China

*E-mail: zhoumj@whut.edu.cn (M. J. Zhou)
*E-mail: liuxiaolin@scu.edu.cn (X. L. Liu)
*E-mail: lq_mail@126.com (Q. Liu)
*E-mail: yanzhao@scu.edu.cn (Y. Zhao)

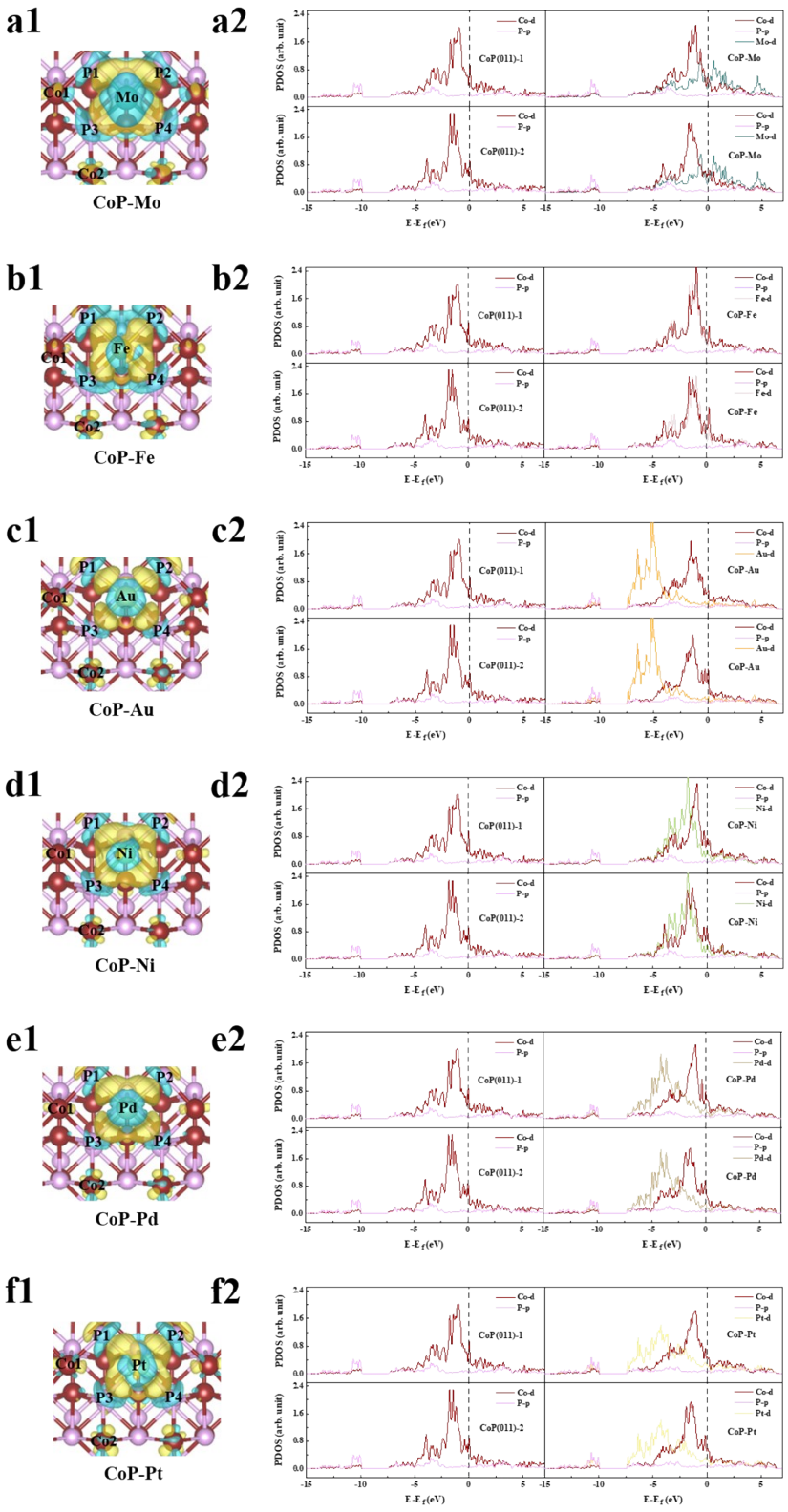


Figure. S1 Charge density difference (an isosurface of 0.003 e Å^{-3}) before and after Au, Ni, Mo, Fe, Pd and Pt doping in (a1), (b1), (c1), (d1), (e1) and (f1), respectively. (a2), (b2), (c2), (d2), (e2) and (f2) PDOS for orbitals for the adjacent atoms (as indicated in panels (a1), (b1), (c1), (d1), (e1) and (f1)).

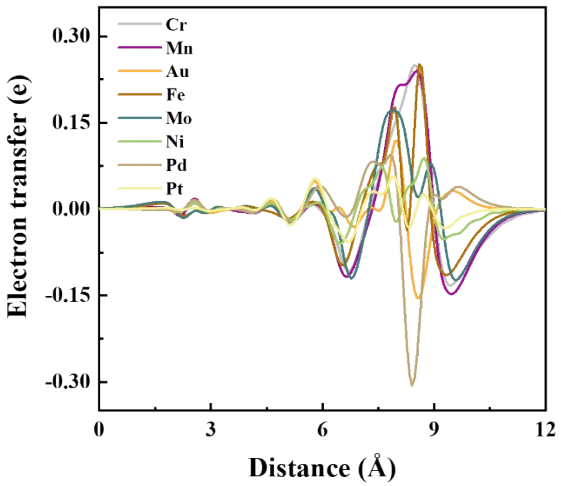


Figure. S2 Electronic charge transfer values of each doped substrate as a function of position.

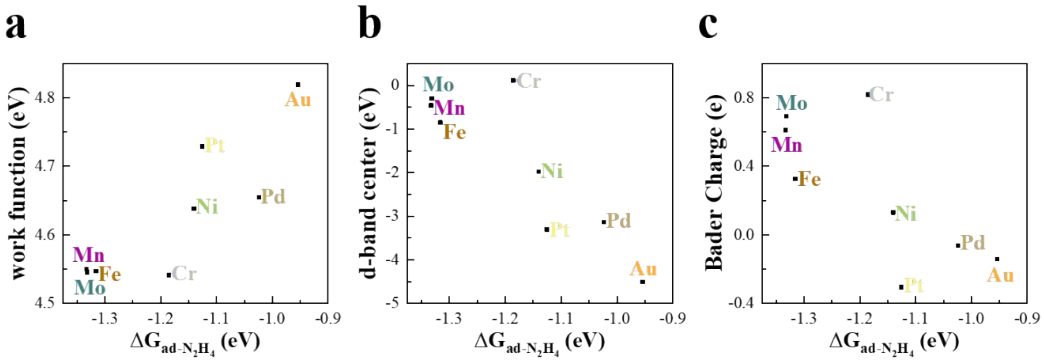
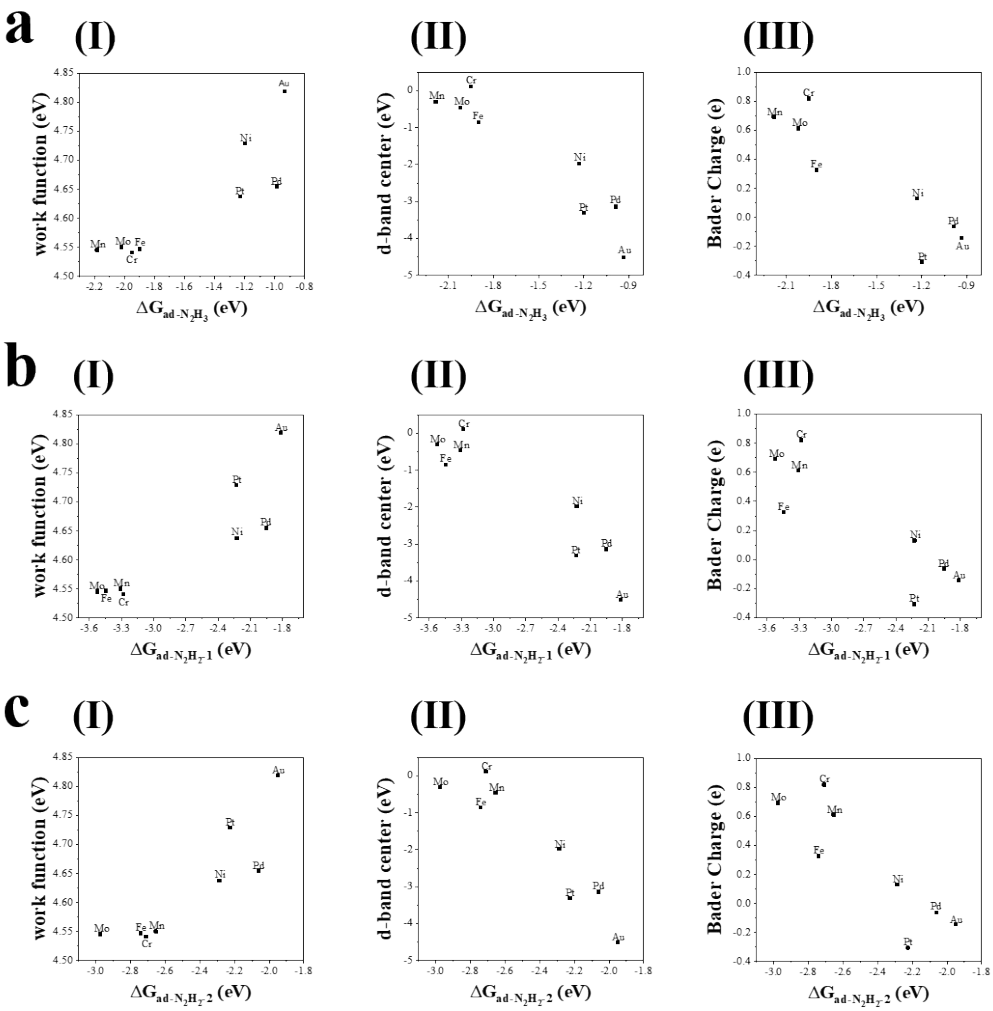


Figure. S3 Linear correlation of N_2H_4 between adsorption free energy and function, d-ban center and Bader charge.



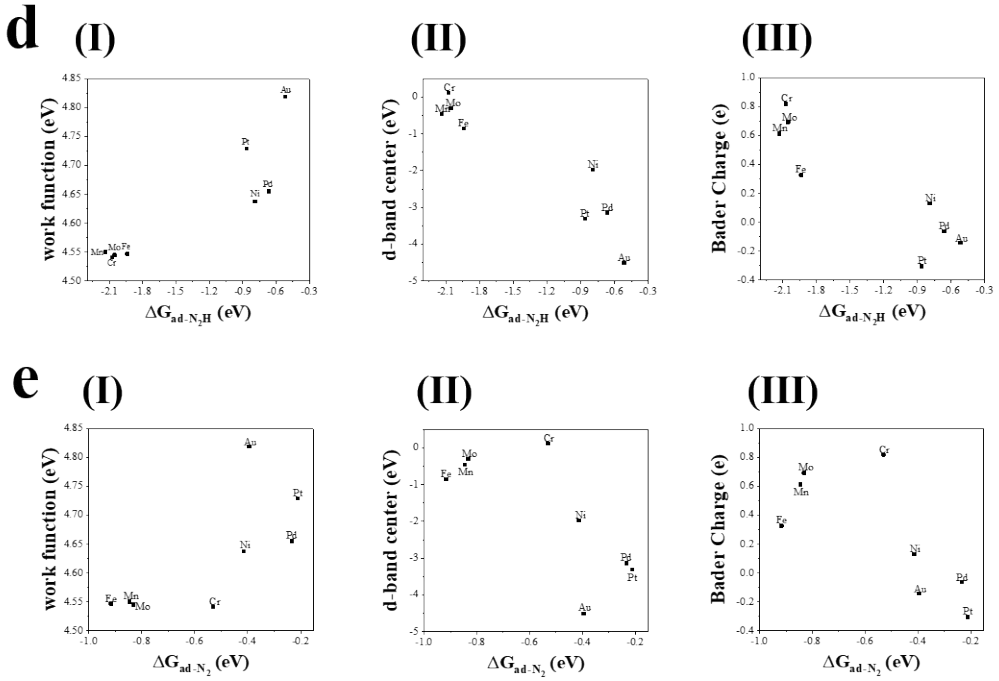


Figure. S4 Linear correlation (N_2H_3, N_2H_2-1, N_2H_2-2, N_2H, N_2) between adsorption free energy and function, d-band center and Bader charge.

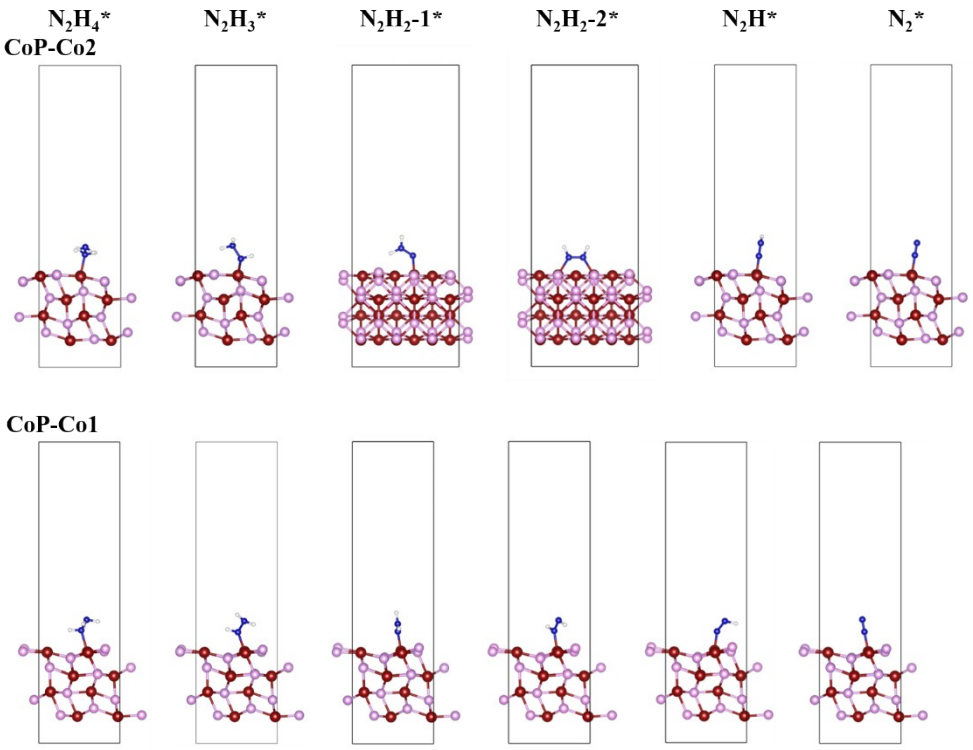
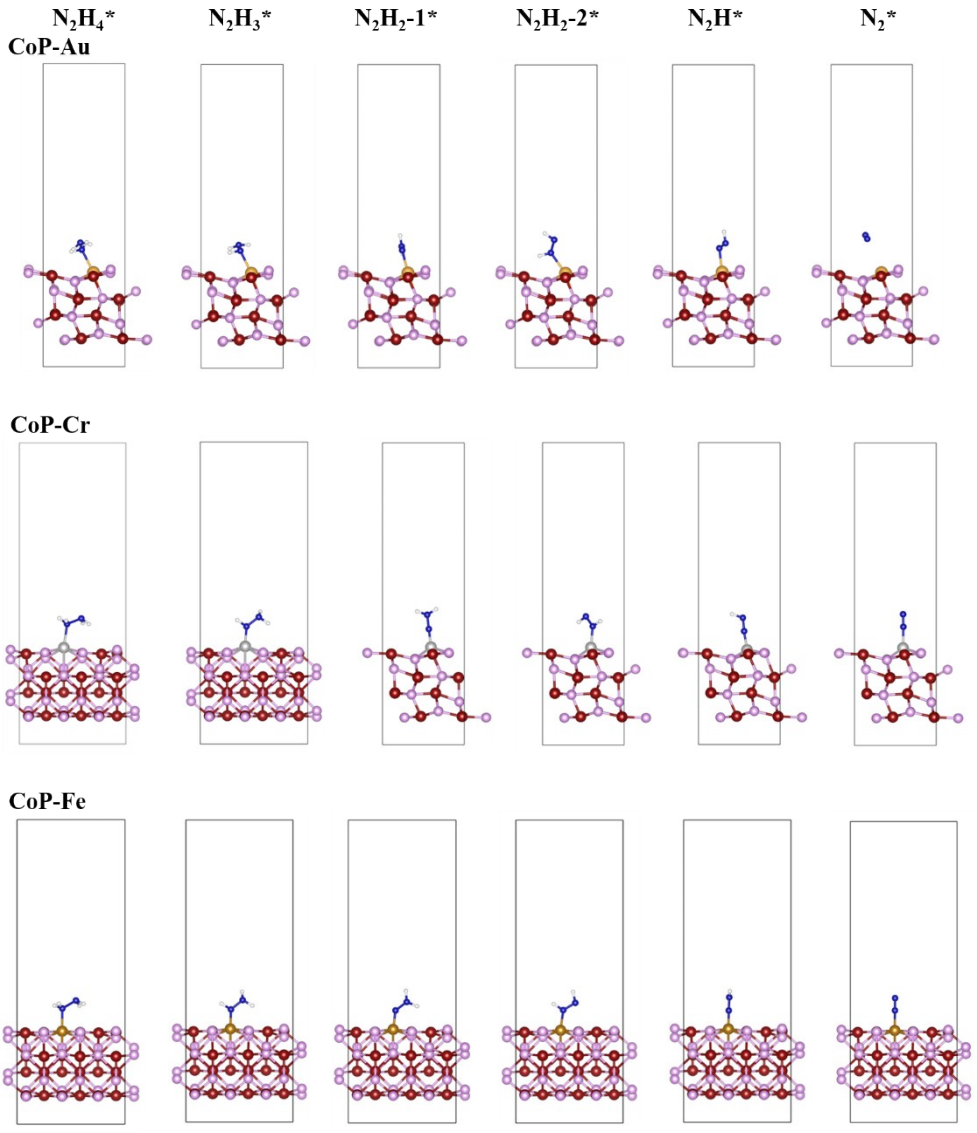
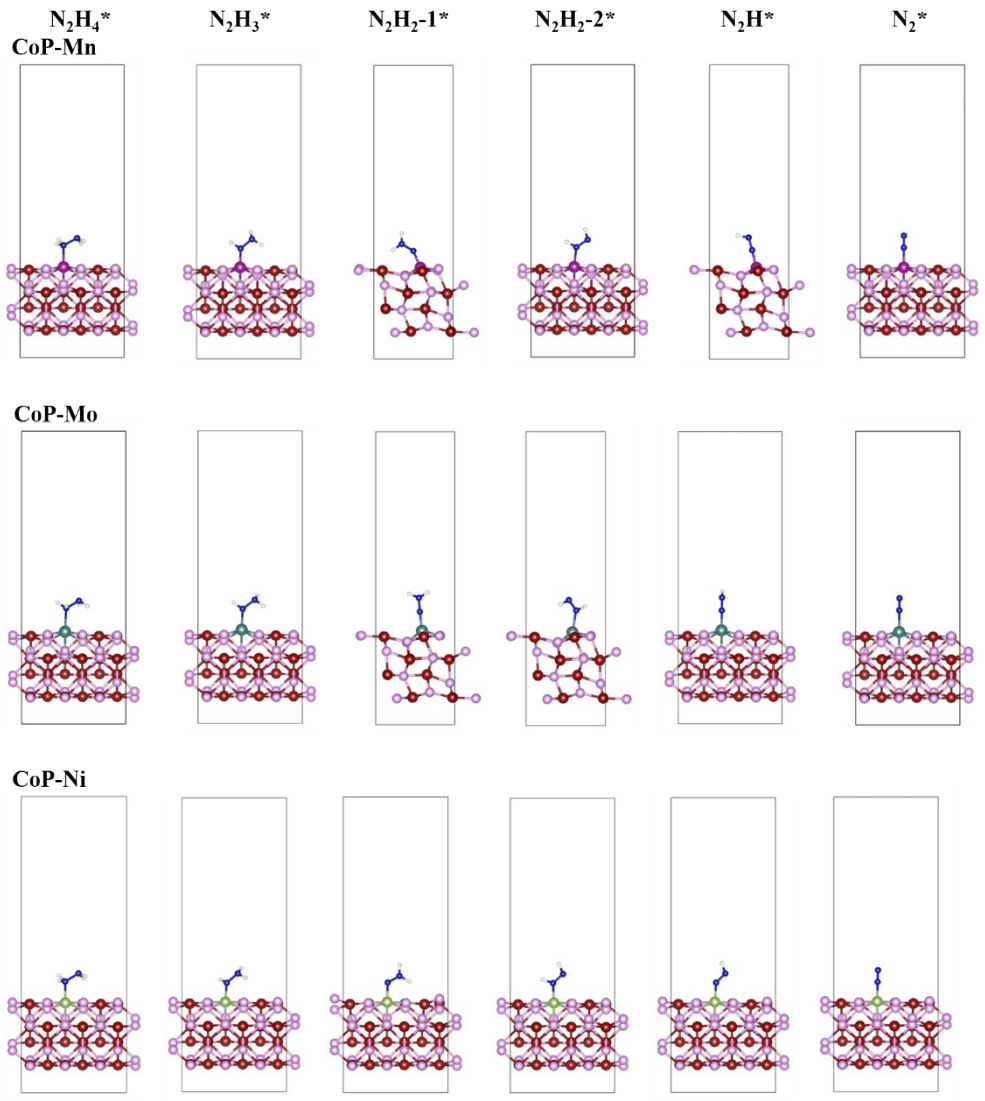


Figure. S5 The optimized structures for N_2H_4, N_2H_3, N_2H_2-1, N_2H_2-2, N_2 and N_2 adsorbed on CoP-Co1 and CoP-Co2,respectively.


N_2H_4*
N_2H_3*
N_2H_2-1*
N_2H_2-2*
N_2H*
N_2*
CoP-Au
CoP-Cr
CoP-Fe


N_2H_4*
N_2H_3*
N_2H_2-1*
N_2H_2-2*
N_2H*
N_2*
CoP-Mn
CoP-Mo
CoP-Ni

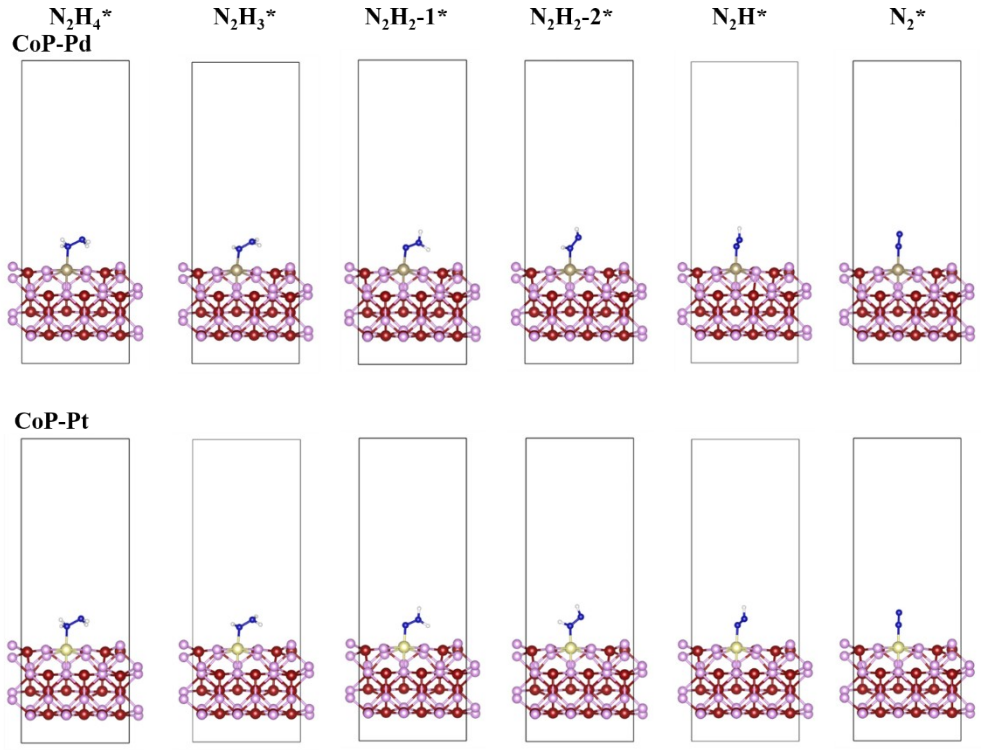


Figure. S6 The optimized structures for N_2H_4, N_2H_3, N_2H_2-1, N_2H_2-2, N_2 and N_2 adsorbed on doped CoP(Au, Cr, Fe, Mn, Mo, Ni, Pd, Pt), respectively.

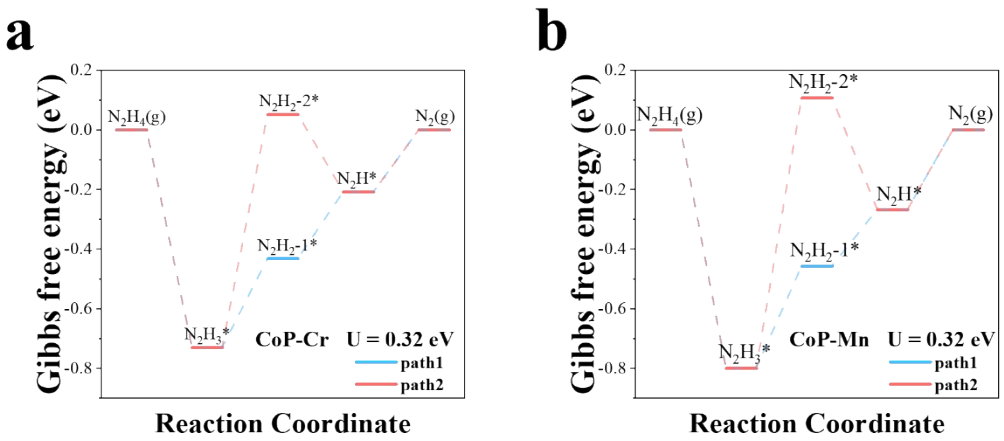


Figure. S7 Gibbs free energy diagram of HzOR on CoP-Cr (a) and CoP-Mn (b) at U = 0.32 V.

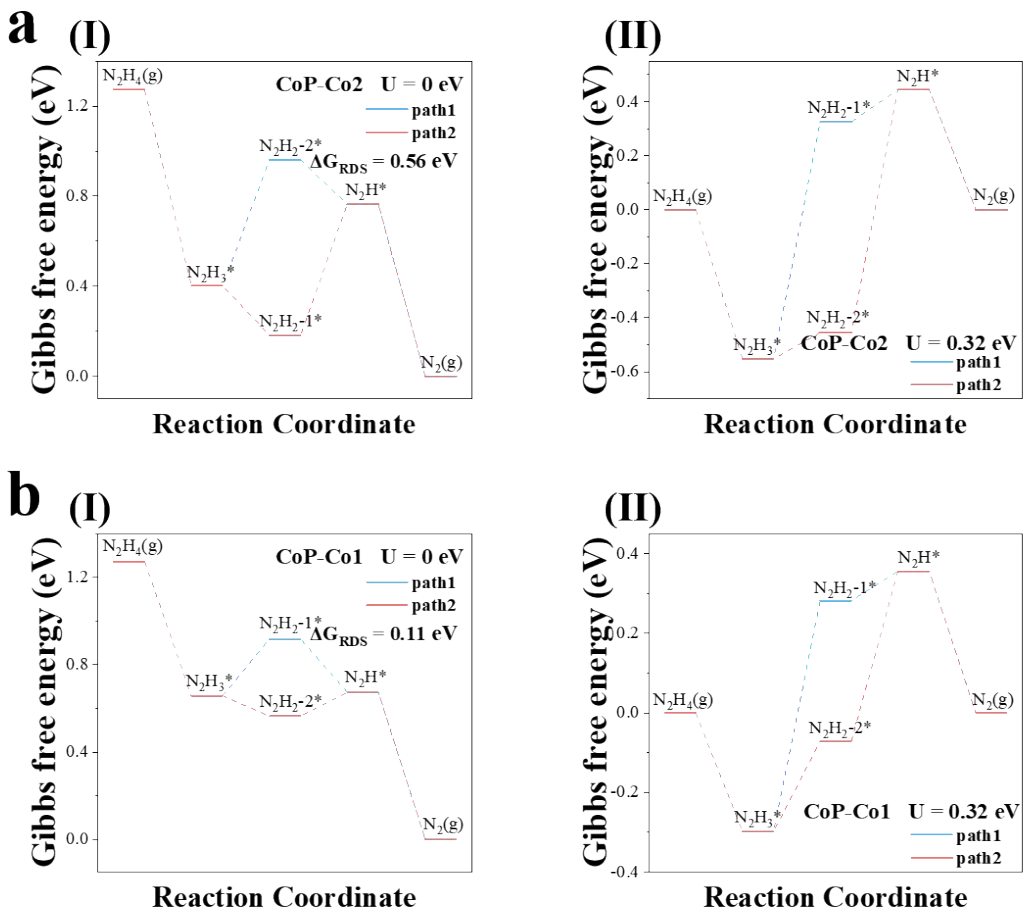
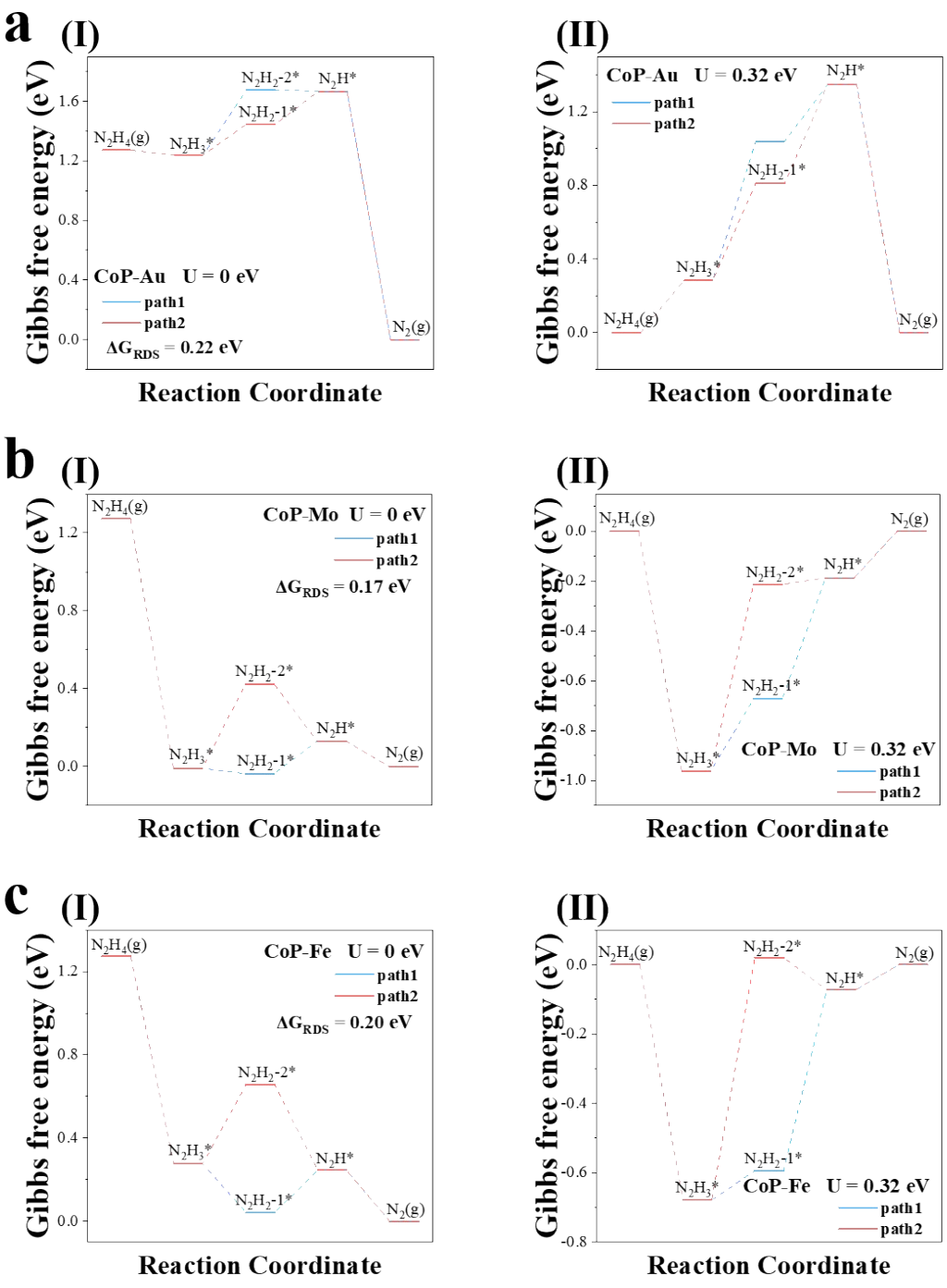


Figure. S8 Gibbs free energy diagram of HzOR on CoP-Co2 (a) and CoP-Co1 (b). (I) at U = 0 V and (II) at U = 0.32 V.


a
(I)
Gibbs free energy (eV)
Reaction Coordinate
CoP-Au U = 0 eV
path1
path2
ΔG_RDS = 0.22 eV
N2H4(g)
N2H3*
N2H2-2*
N2H2-1*
N2H*
N2(g)
(II)
CoP-Au U = 0.32 eV
path1
path2
b
(I)
CoP-Mo U = 0 eV
path1
path2
ΔG_RDS = 0.17 eV
(II)
CoP-Mo U = 0.32 eV
path1
path2
c
(I)
CoP-Fe U = 0 eV
path1
path2
ΔG_RDS = 0.20 eV
(II)
CoP-Fe U = 0.32 eV
path1
path2

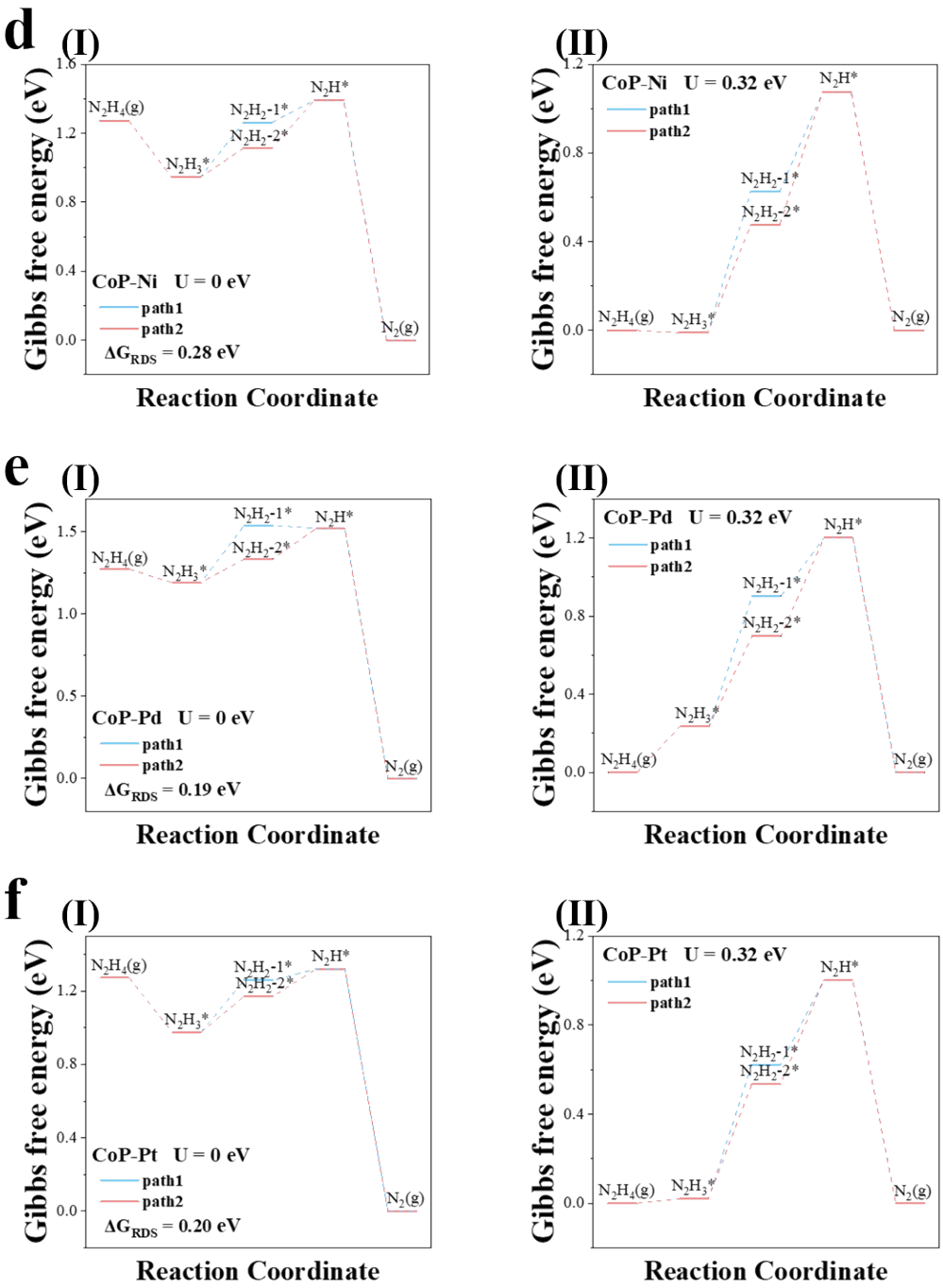


Figure. S9 Gibbs free energy diagram of HzOR on doped CoP (Au, Mo, Fe, Ni, Pd, Pt). (I) at U = 0 V and (II) at U = 0.32 V.

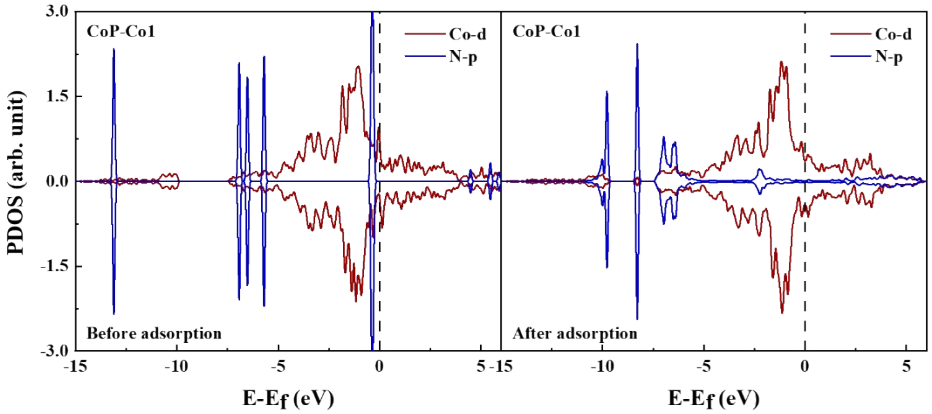


Figure. S10 After N_2H_4 adsorbed, PDOS on CoP-Co1.

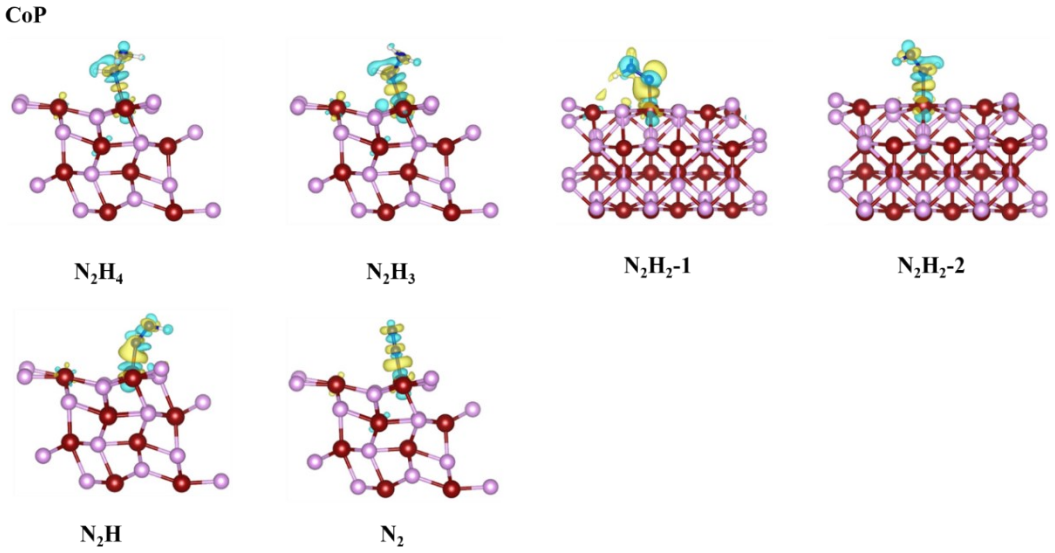


Figure. S11 Charge density difference plots of all intermediates adsorbed on CoP-Co1.

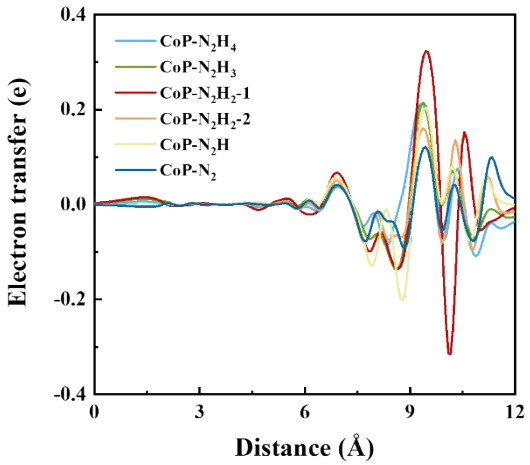


Figure. S12 Electronic charge transfer values of CoP with adsorbed intermediate molecules as a function of position.

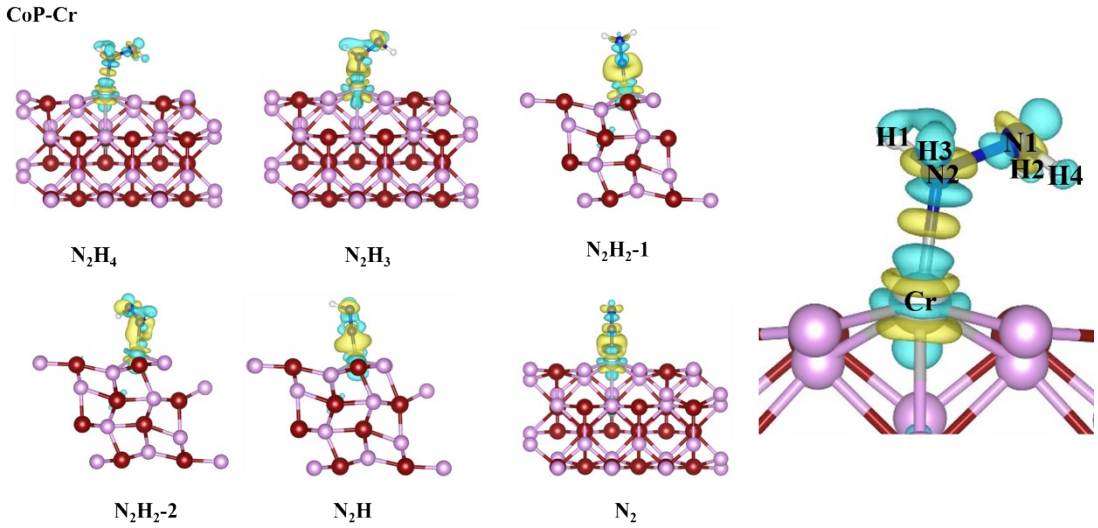


Figure. S13 Charge density difference plots of all intermediates adsorbed on CoP-Cr.

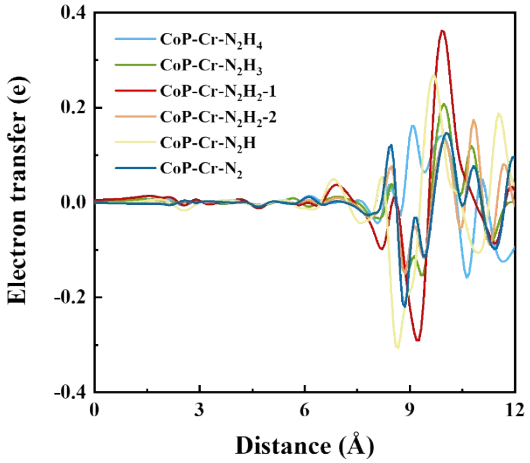


Figure. S14 Electronic charge transfer values of CoP-Cr with adsorbed intermediate molecules as a function of position.

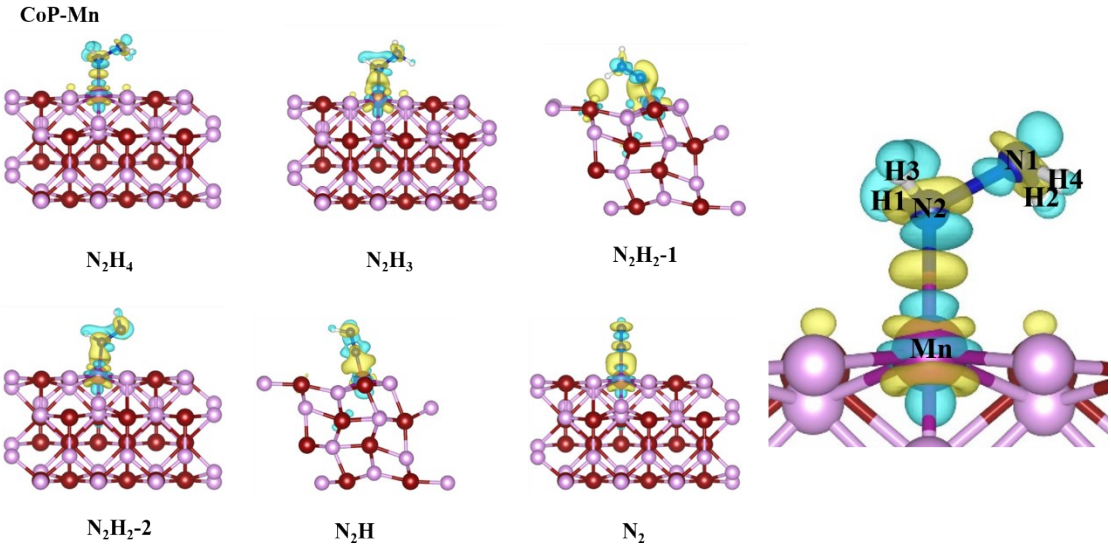


Figure. S15 Charge density difference plots of all intermediates adsorbed on CoP-Mn.

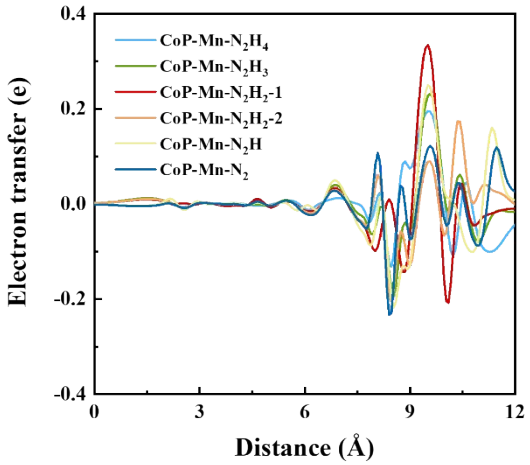


Figure. S16 Electronic charge transfer values of CoP-Mn with adsorbed intermediate molecules as a function of position.

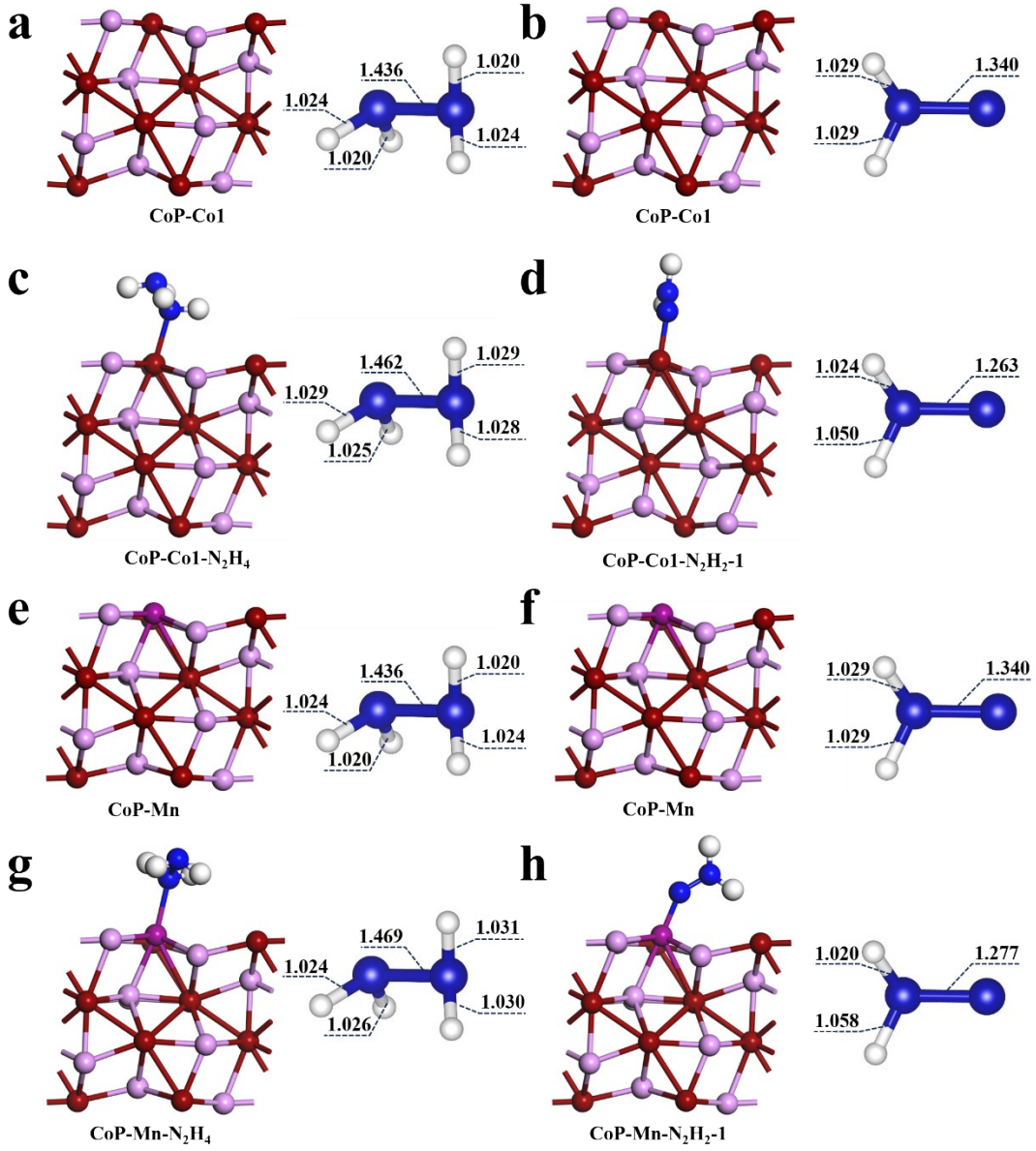


Figure. S17 The bond length values (Å) of CoP-Co1 and CoP-Mn before (a, b, e, f) and after (c, d, g, h) adsorbing intermediate molecules N_2H_4 and N_2H_2-1.

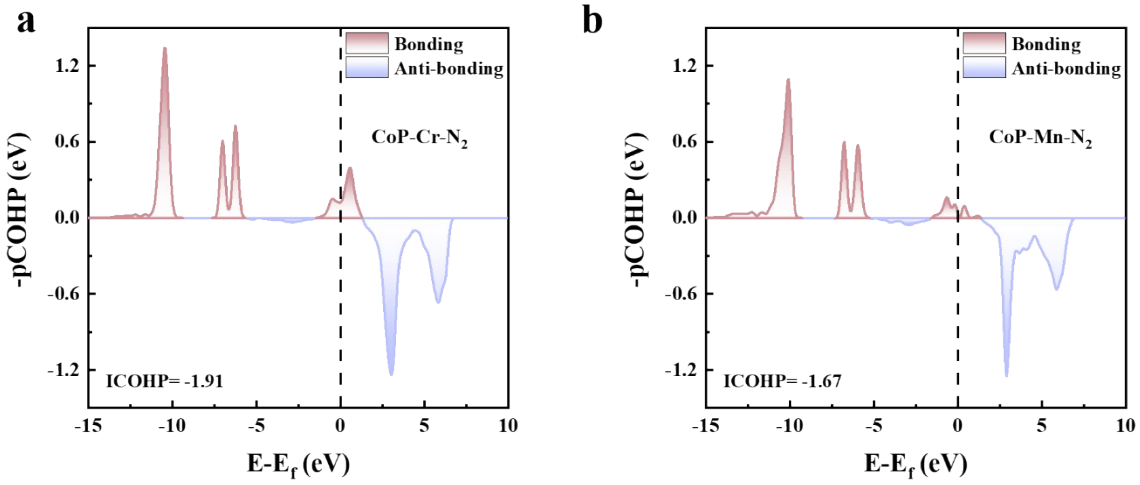


Figure. S18 −PCOHP of N_2 adsorbed on CoP-Cr (a) and CoP-Mn (b)

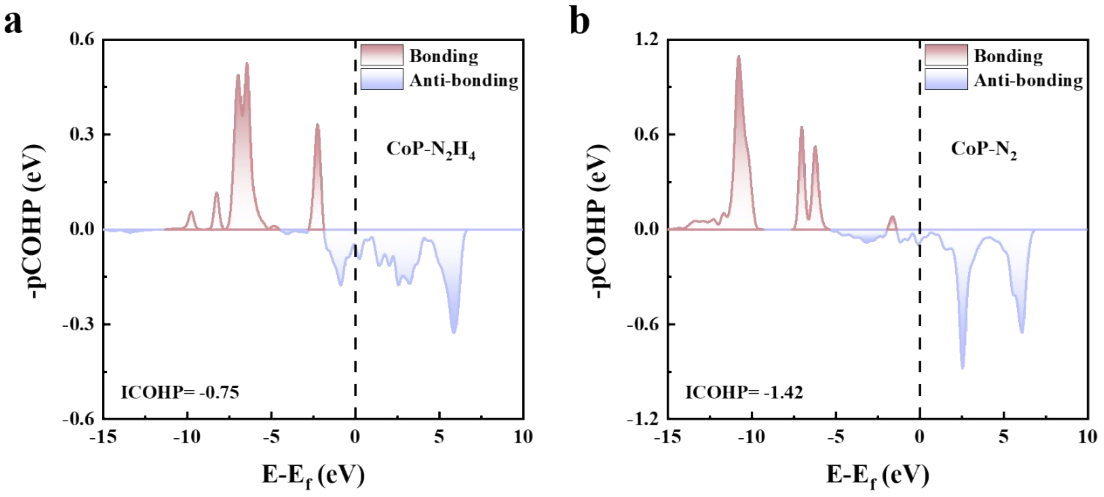


Figure. S19 −PCOHP of N_2H_4 (a) and N_2 (b) adsorbed on CoP, respectively.

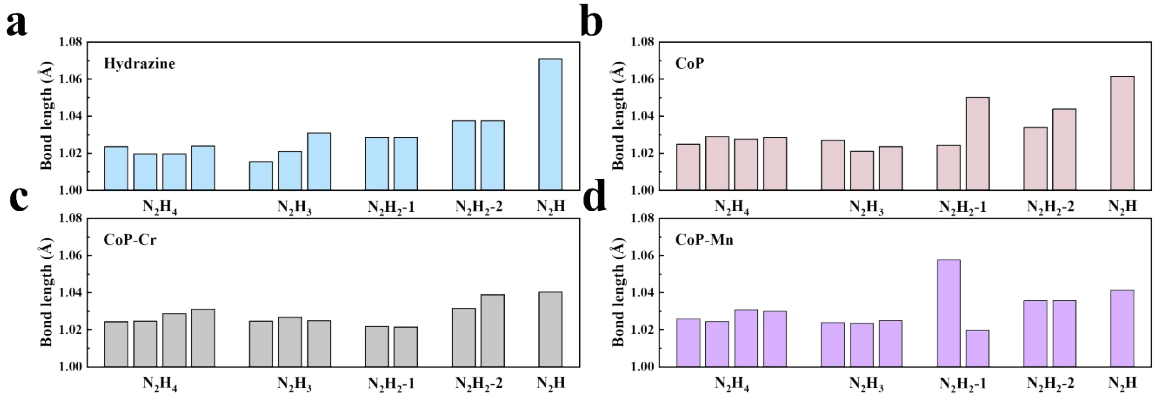


Figure. S20 Statistical comparison charts of N–H bond lengths in free intermediates and after adsorption on CoP, CoP-Cr, and CoP-Mn.

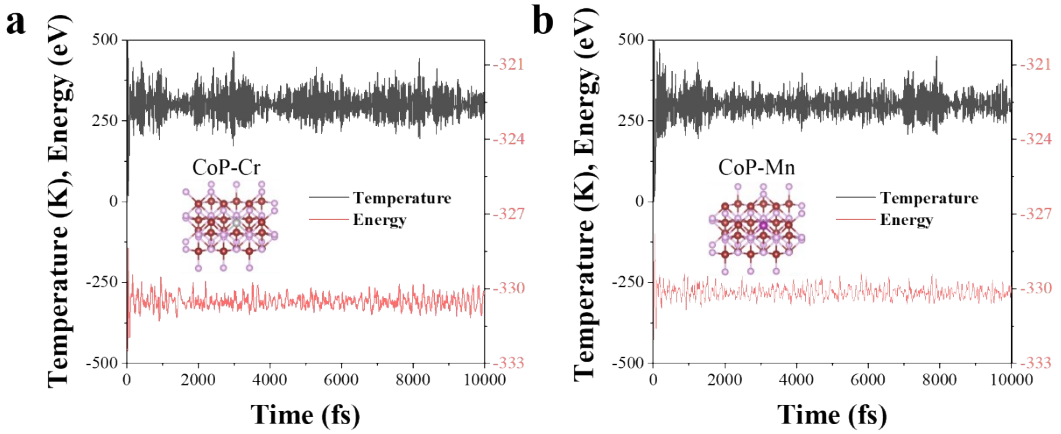


Figure. S21 The variations of temperature and energy versus the AIMD simulation time for 10 ps of CoP-Cr (a) and CoP-Mn (b) under 300K.

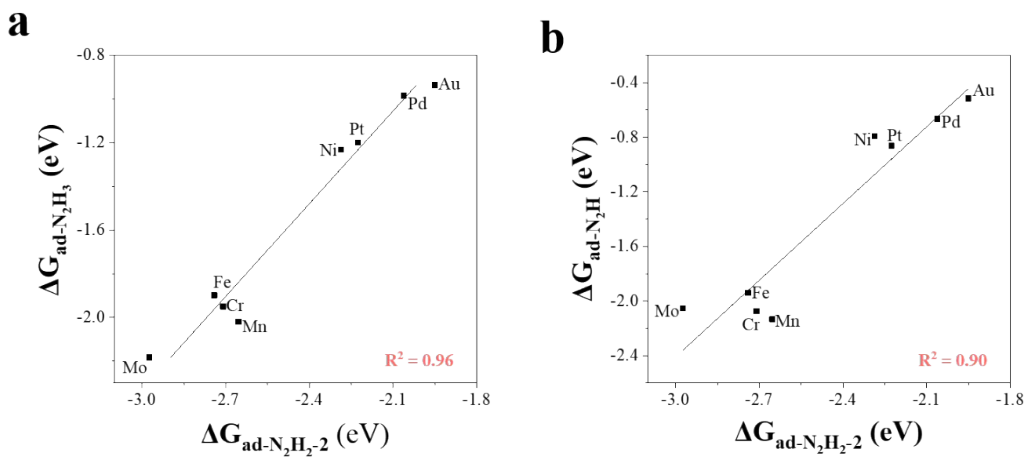


Figure. S22 The scaling relationship of the adsorption free energies for CoP-M in Path2.

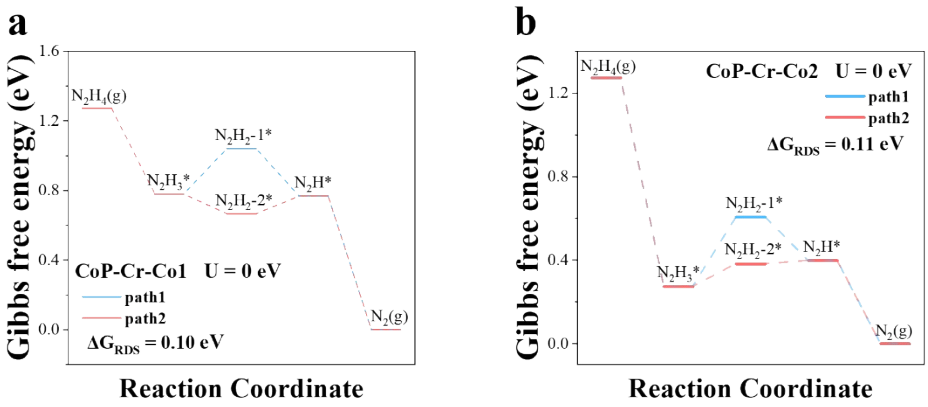


Figure. S23 Gibbs free energy diagram of HzOR on Co1 (a) and Co2 (b) of CoP-Cr at U = 0 V.

Table S1. The cohesive energies and formation energies of ten M-CoP structures, in units of eV.

Catalyst	Formation Energy	Cohesive Energy
CoP-Ag	0.12	-22.15
CoP-Au	-0.22	-22.48
CoP-Cr	-0.80	-23.06
CoP-Fe	-0.98	-23.24
CoP-Mn	-1.07	-23.33
CoP-Mo	-0.71	-22.97
CoP-Ni	-1.30	-23.56
CoP-Pd	-1.10	-23.37
CoP-Pt	-1.06	-23.32
CoP-W	0.13	-22.14

Table S2. The molecules' adsorption energy of CoP/M-CoP structures, in units of eV.

Catalyst	$\Delta G_{ad\text{-}N2H4}$	$\Delta G_{ad\text{-}N2H3}$	$\Delta G_{ad\text{-}N2H2\text{-}1}$	$\Delta G_{ad\text{-}N2H2\text{-}2}$	$\Delta G_{ad\text{-}N2H}$	$\Delta G_{ad\text{-}N2}$
CoP-Co1	−1.29	−1.52	−2.57	−2.83	−1.51	−0.77
CoP-Au	−0.95	−0.94	−1.81	−1.95	−0.52	−0.39
CoP-Cr	−1.19	−1.95	−3.28	−2.71	−2.07	−0.53
CoP-Fe	−1.32	−1.90	−3.45	−2.74	−1.94	−0.92
CoP-Mn	−1.33	−2.02	−3.31	−2.65	−2.13	−0.85
CoP-Mo	−1.33	−2.18	−3.52	−2.97	−2.05	−0.83
CoP-Ni	−1.14	−1.23	−2.23	−2.29	−0.79	−0.41
CoP-Pd	−1.02	−0.98	−1.95	−2.06	−0.66	−0.23
CoP-Pt	−1.13	−1.20	−2.23	−2.23	−0.86	−0.21

Table S3. The Gibbs free energy of CoP/M-CoP structures, in units of eV.

Catalyst		ΔG1	ΔG2	ΔG3	ΔG4
CoP-Co2	Path1	-0.87	0.56	-0.20	-0.76
	Path2	-0.87	-0.22	0.58	-0.76
CoP-Co1	Path1	-0.62	0.26	-0.24	-0.67
	Path2	-0.62	-0.09	0.11	-0.67
CoP-Au	Path1	-0.03	0.44	-0.01	-1.67
	Path2	-0.03	0.21	0.22	-1.67
CoP-Cr	Path1	-1.05	-0.02	-0.09	-0.11
	Path2	-1.05	0.46	-0.58	-0.11
CoP-Fe	Path1	-1.00	-0.23	0.20	-0.25
	Path2	-1.00	0.38	-0.41	-0.25
CoP-Mn	Path1	-1.12	0.02	-0.13	-0.05
	Path2	-1.12	0.59	-0.69	-0.05
CoP-Mo	Path1	-1.28	-0.03	0.17	-0.13
	Path2	-1.28	0.43	-0.29	-0.13
CoP-Ni	Path1	-0.33	0.32	0.13	-1.39
	Path2	-0.33	0.17	0.28	-1.39
CoP-Pd	Path1	-0.08	0.35	-0.02	-1.52
	Path2	-0.08	0.14	0.19	-1.52
CoP-Pt	Path1	-0.30	0.28	0.06	-1.32
	Path2	-0.30	0.20	0.15	-1.32