Rational Design of Single-Atom Catalysts for Enhanced Electrocatalytic Nitrogen Reduction Reaction

Sakshi Agarwal†, Ritesh Kumar†, Rakesh Arya†, and Abhishek K. Singh† *

† Materials Research Centre, Indian Institute of Science, Bangalore 560012, India

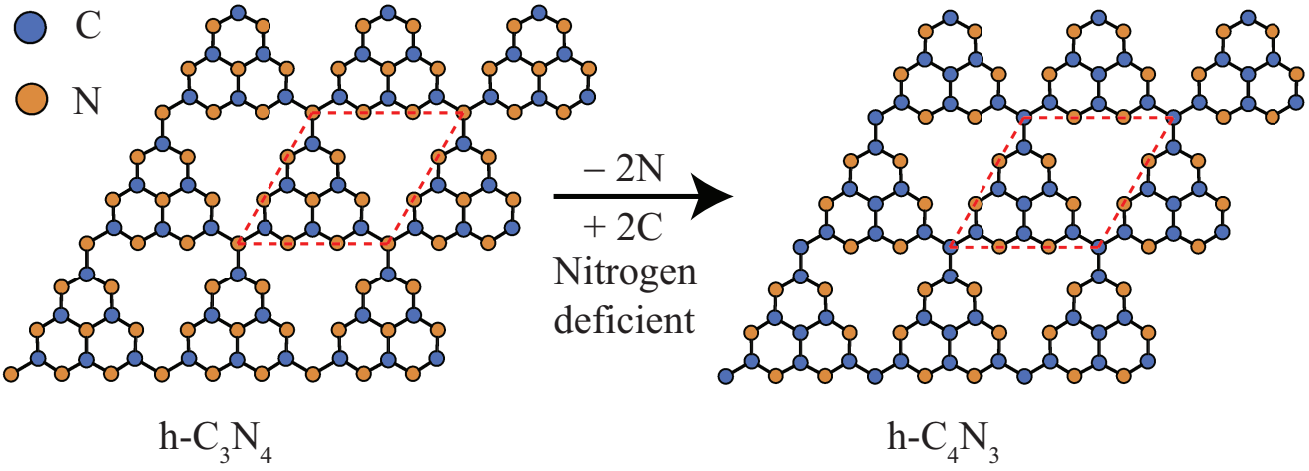

Figure S1: Structures of h-C_3N_4 and h-C_4N_3. With the substitution of 2N with 2C, the h-C_4N_3 is formed

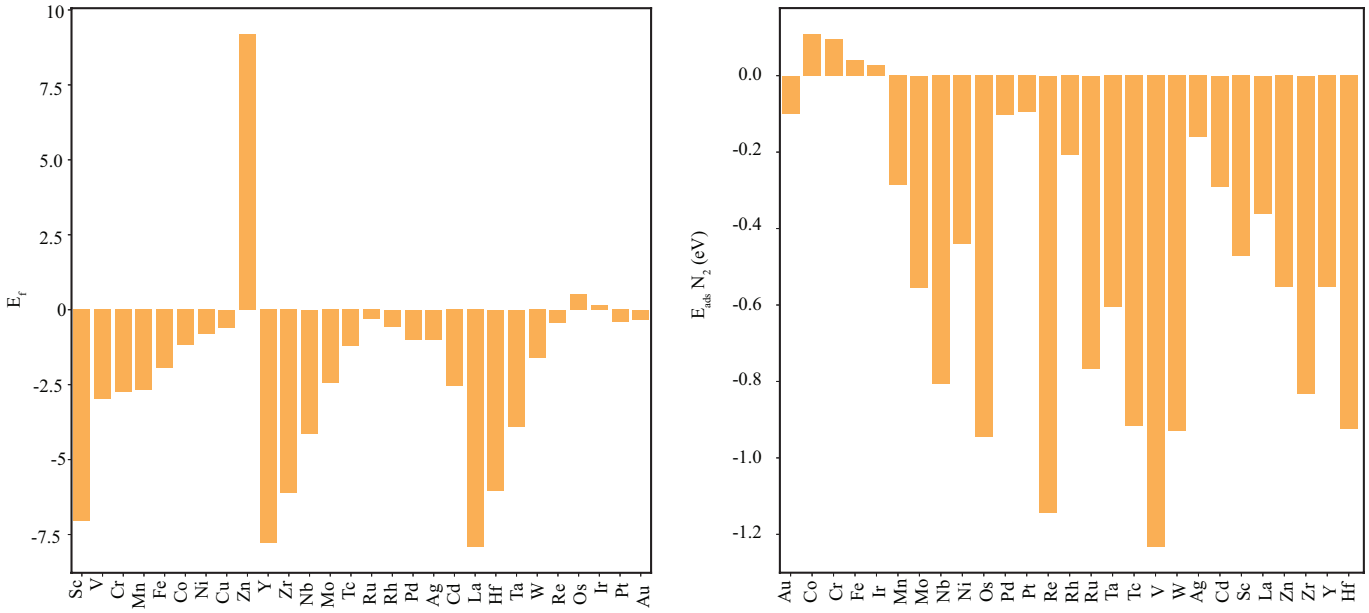

Figure S2: (a) The formation energies (ΔE_f) for all the SACs. (b) The adsorption energies ($\Delta E_{ads}^{N_2}$) for N_2 adsorption on all the SACs

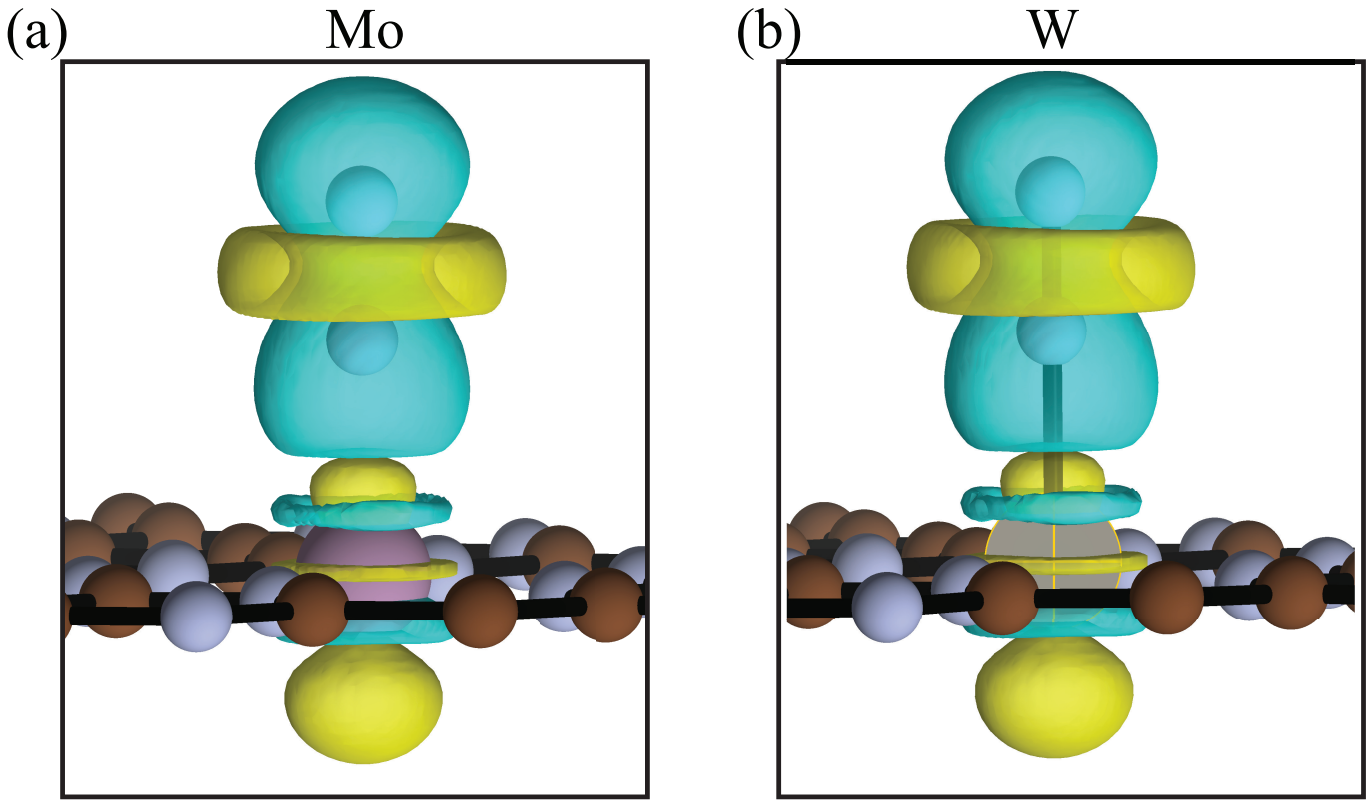

Figure S3: The charge density difference plots for N_2 adsorption on (a) Mo- and (b) W-SACs, where the yellow and cyan colors represent charge depletion and acccumulation, respectively. Isosurface value = 0.005 e/$\AA^3$

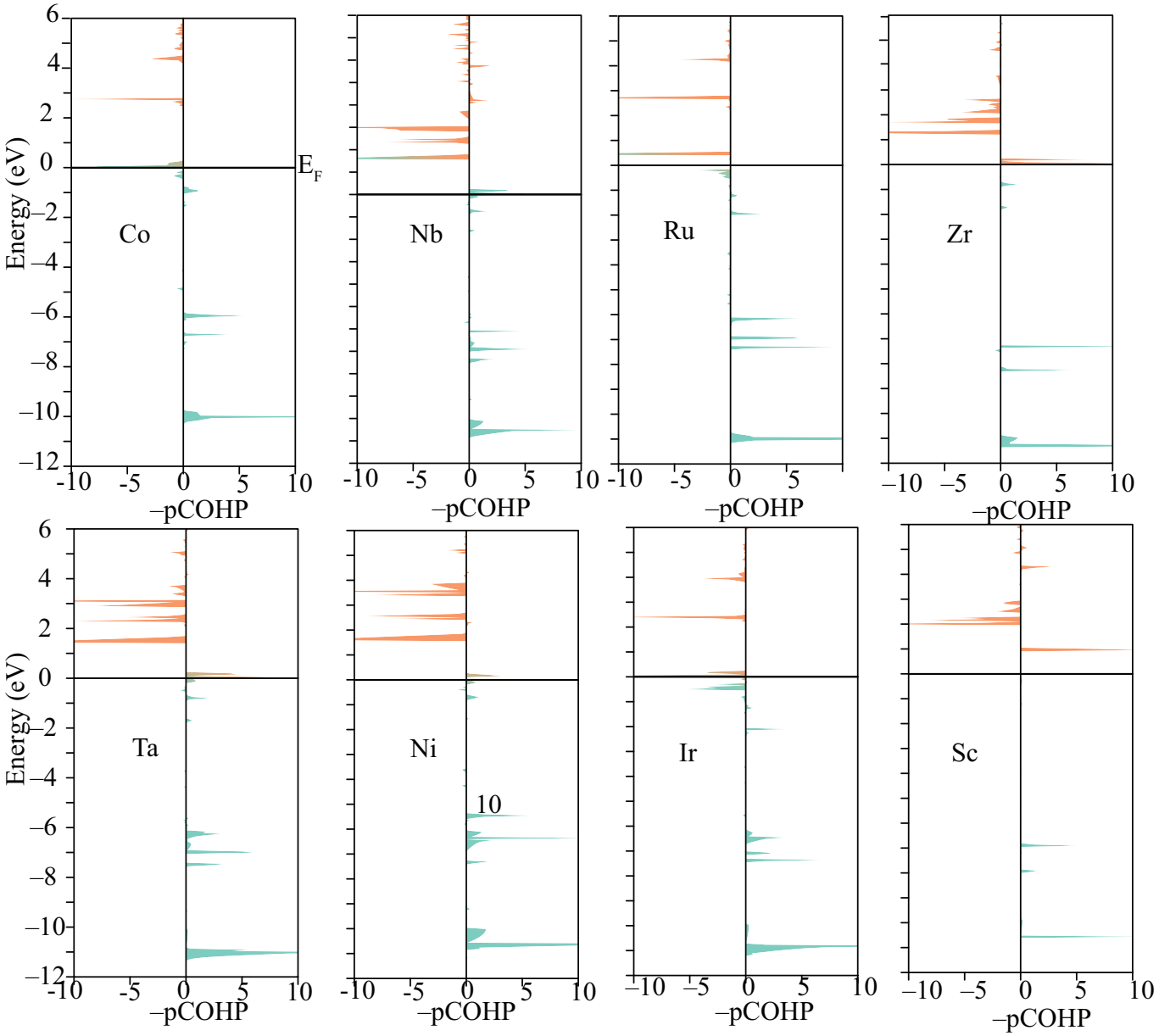

Figure S4: The –pCOHP plots for Co-, Nb-, Ru-, Zr-, Ta-, Ni-, Ir-, and Sc-SACs.

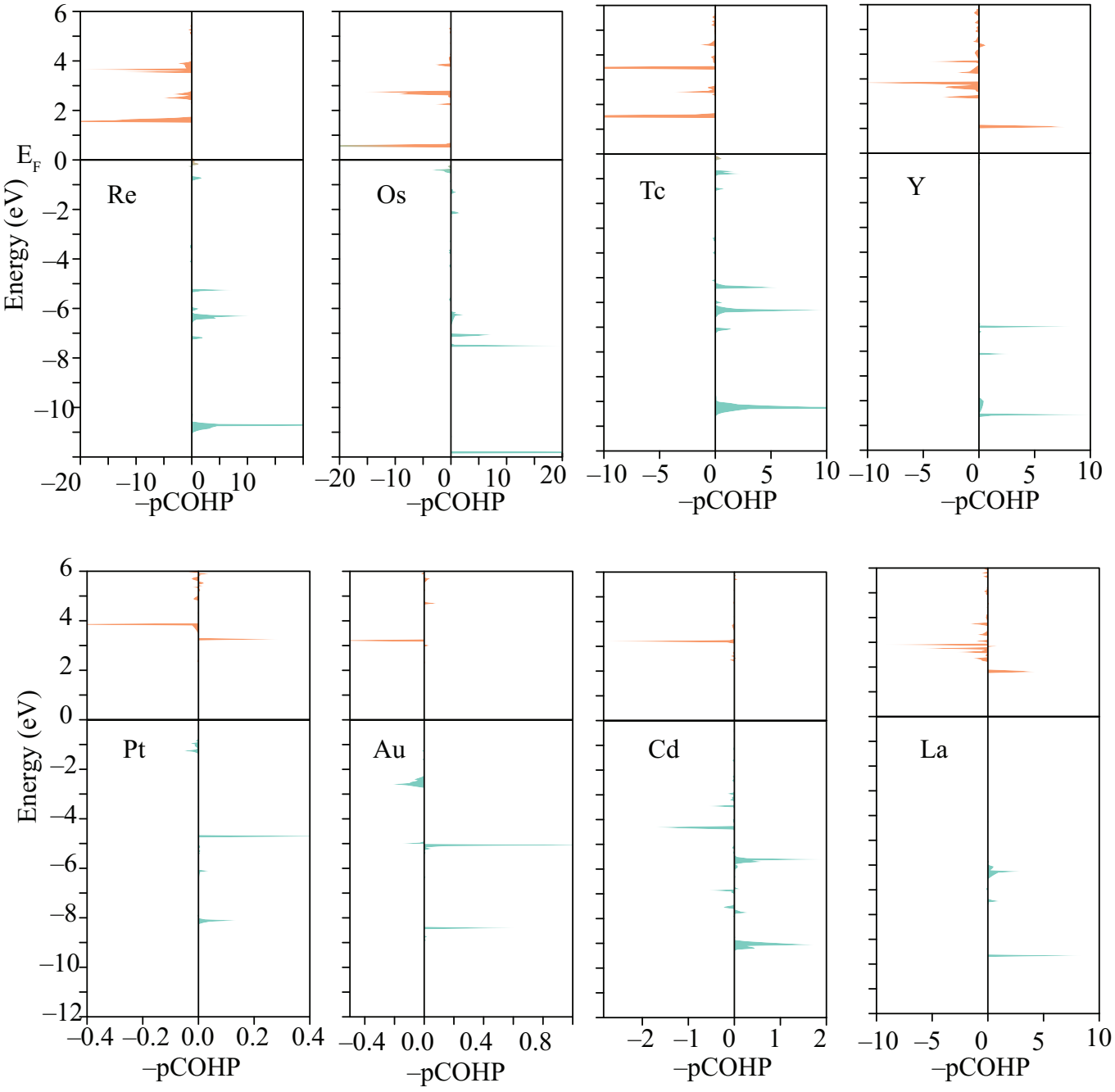

Figure S5: The –pCOHP plots for Re-, Os-, Tc-, Y-, Pt-, Au-, Cd-, and La-SACs.

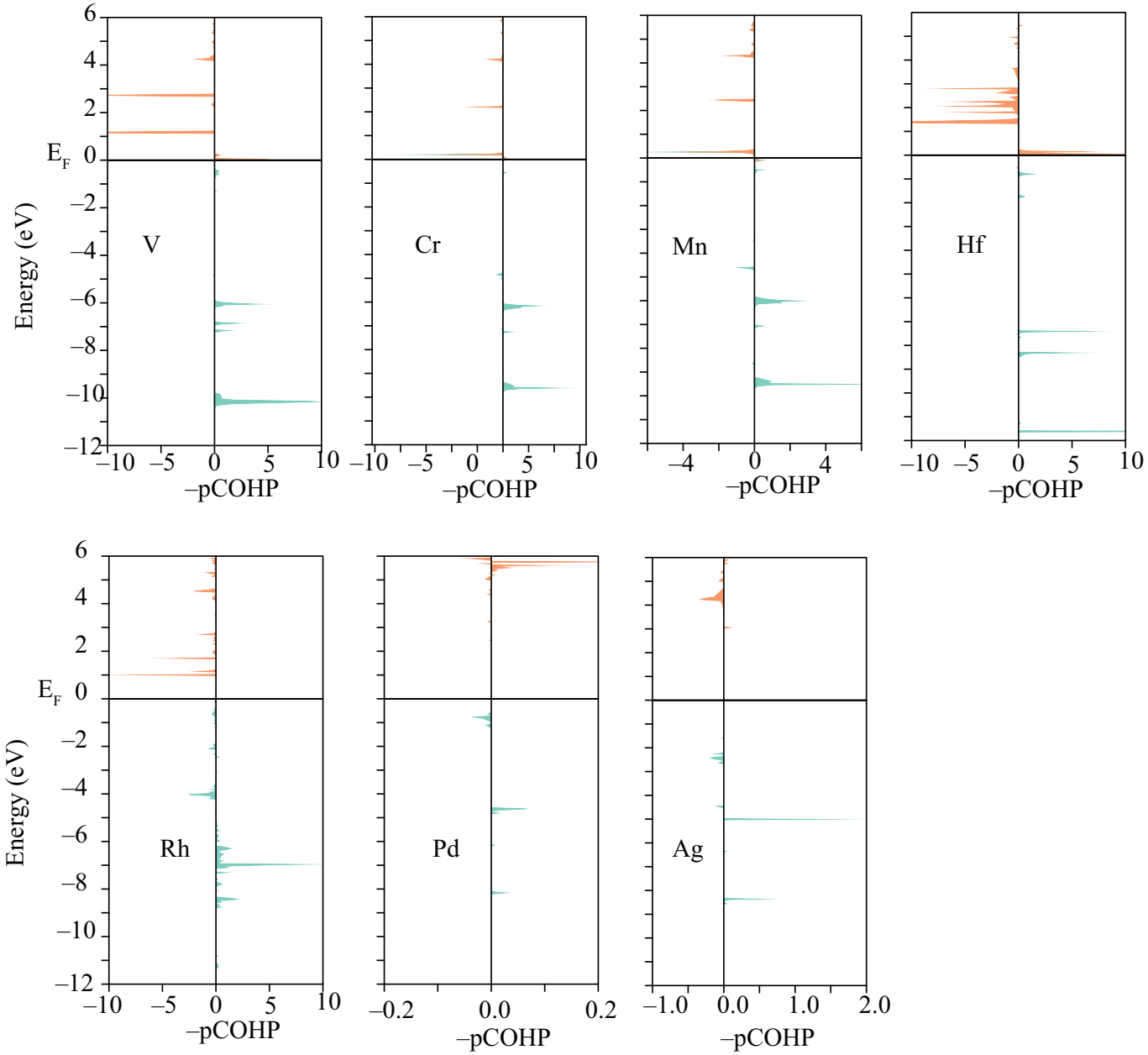

Figure S6: The –pCOHP plots for V-, Cr-, Mn-, Hf-, Rh-, Pd-, and Ag-SACs.

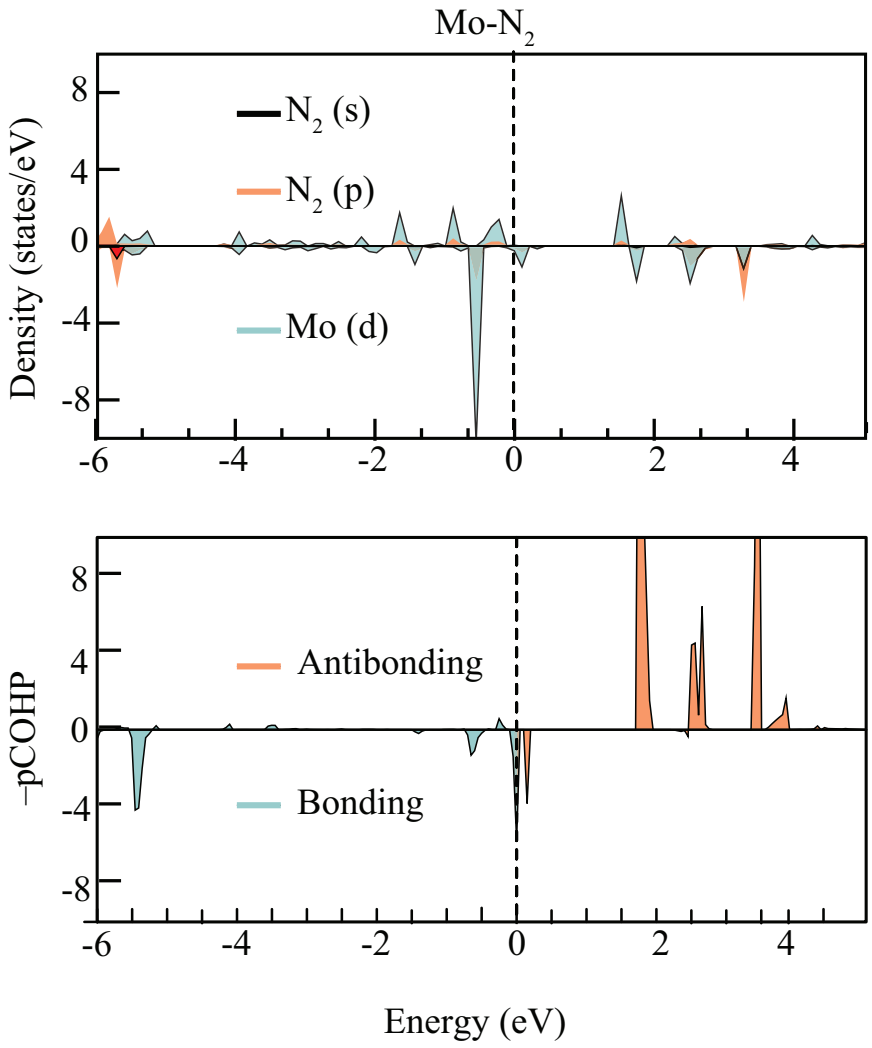

Figure S7: The pDOS for N_2 adsorption on Mo-SAC and the corresponding COHP.

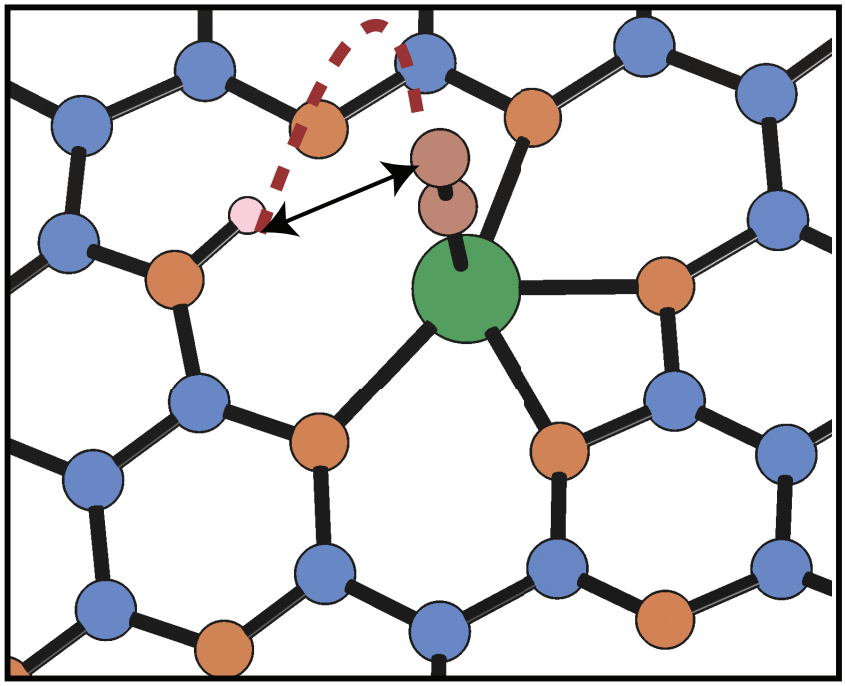

Figure S8: The co-adsorption of N_2 and H on the TM centers leads to the H intermediate preferring the support over the TMs. Blue, orange, green, pale red, and pink balls denote C, N, TM, adsorbed N_2, and H, respectively.

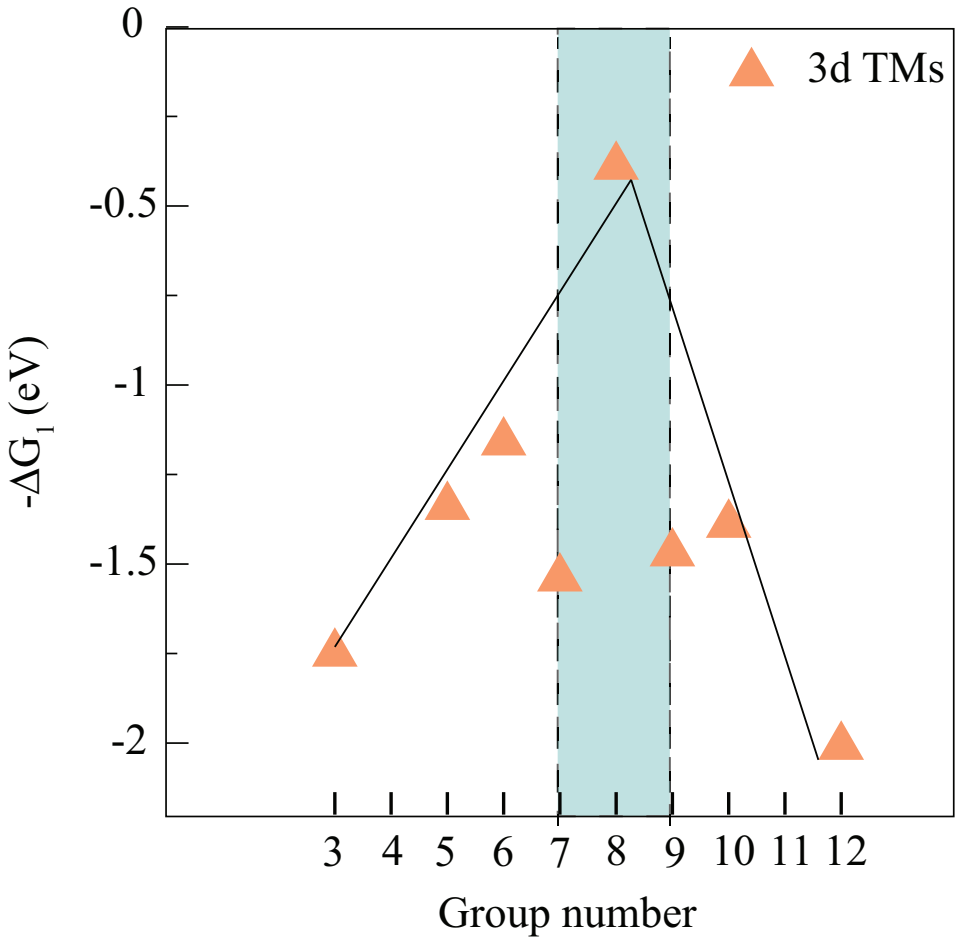

Figure S9: Variation of ΔG_1* as a function of group number for 3d metals

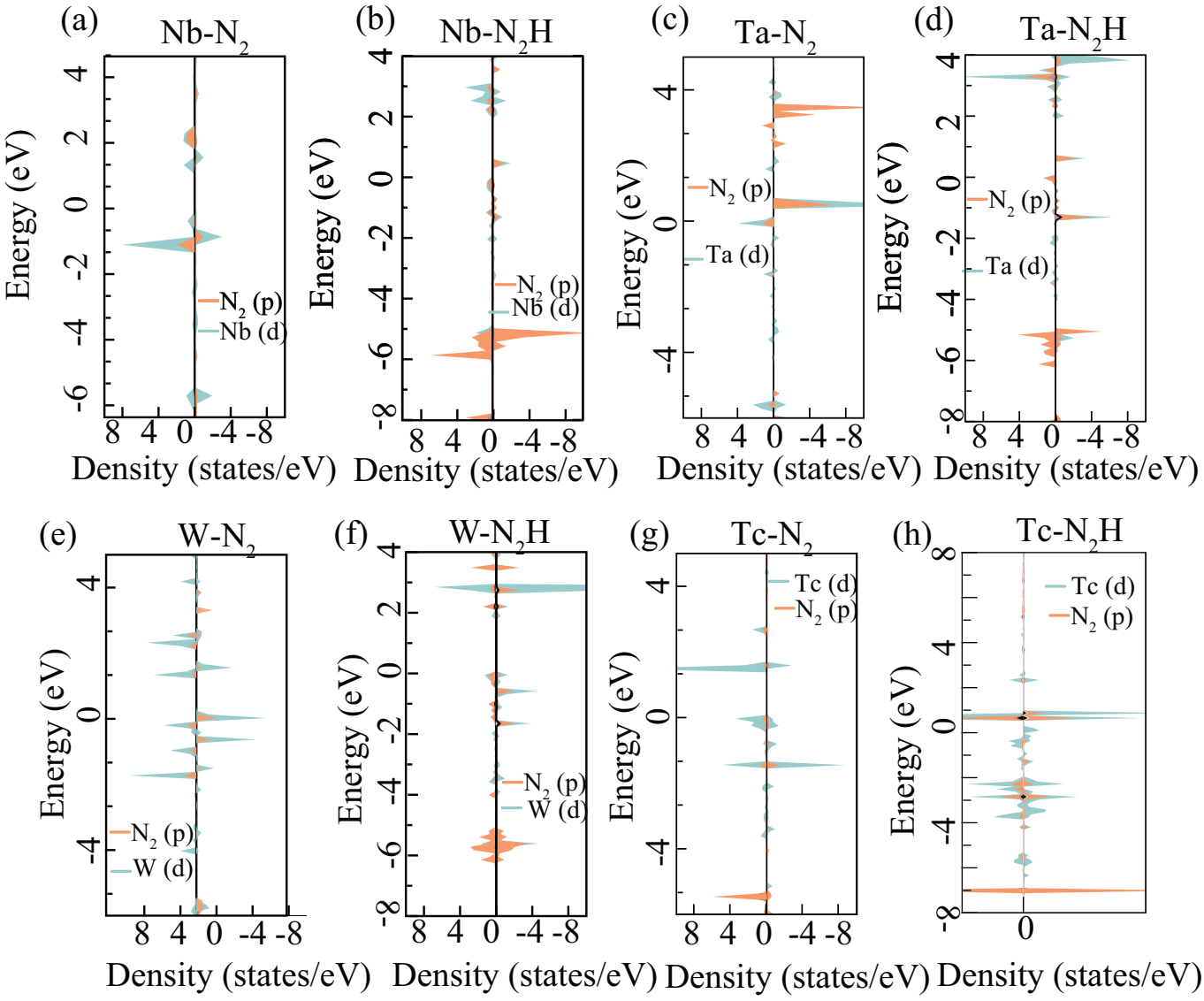

Figure S10: The pDOS for N_2* and N_2H* intermediates adsorbed on (a,b) Nb-, (c,d) Ta-, (e,f) W-, and (g,h) Tc-SACs.

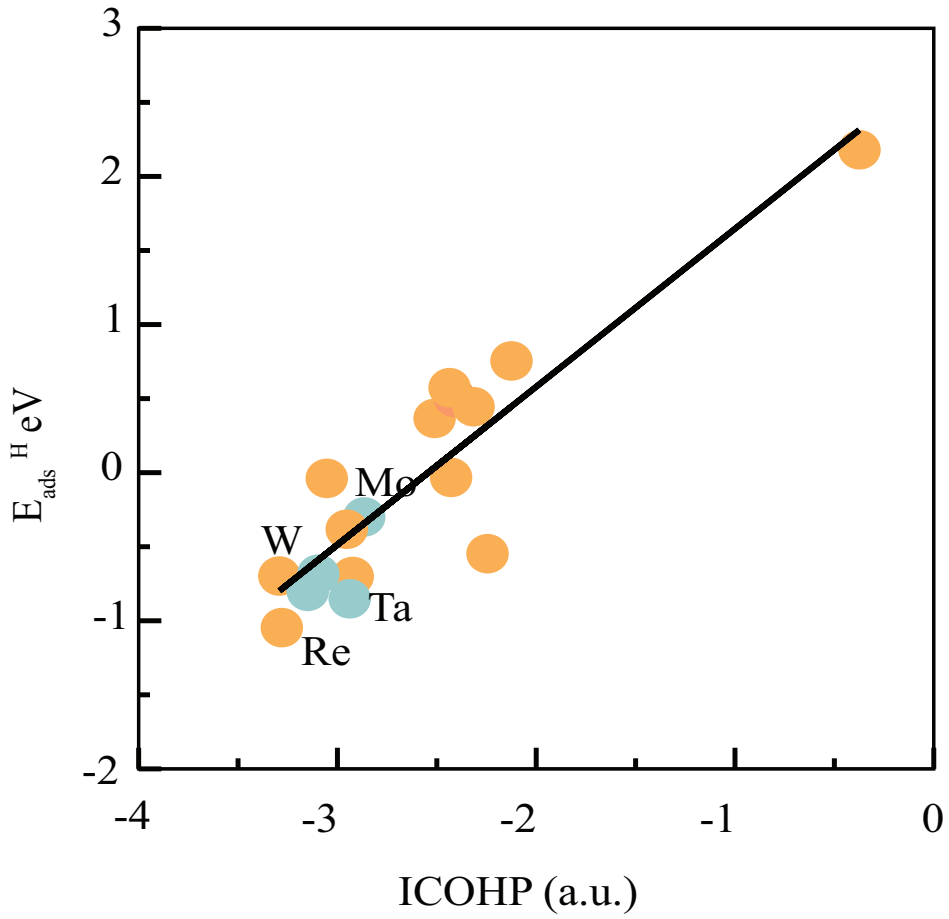

Figure S11: A linear trend between the ICOHP values for H* adsorbed on SAC and the corresponding ΔE_{ads}^{H} values.

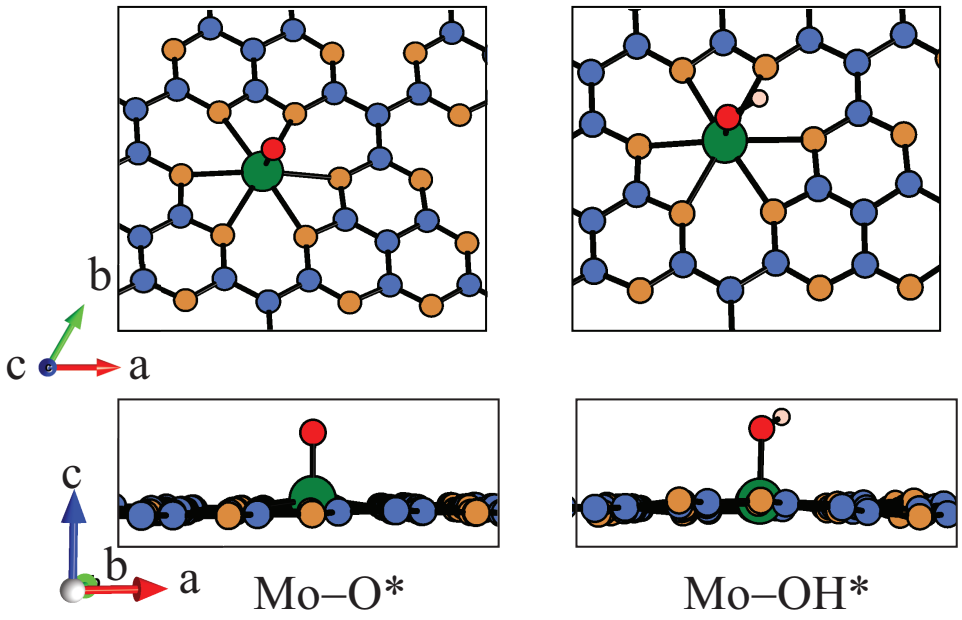

Figure S12: Optimized structure for Mo-O* and Mo-OH* in top and side view.

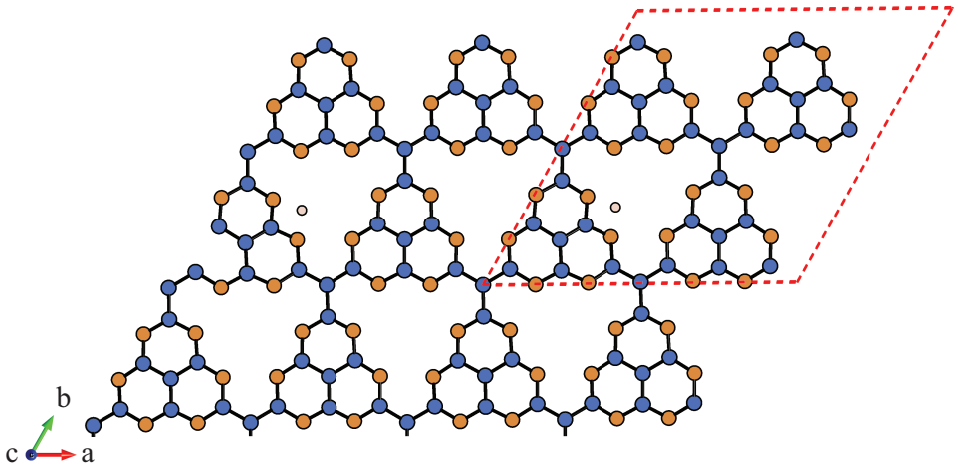

Figure S13: Optimized structure for H-C_4N_3.

Table S1: Total energy of the system (SAC+N_2), total energy of SAC without adsorbate, nitrogen Adsorption energies, ZPE -TΔS, and free energies of all the TM based SACs. The reference molecule used for the calculations is N_2 (g)

Transition metal	Total Energy (E_{SAC+ad})	Total Energy (E_{SAC})	ΔE_{N_2} (eV)	ZPE -TΔS (eV)	ΔG_{N_2}
Sc	-503.16	-486.08	-0.47	0.09	0.02
V	-502.45	-484.61	-1.23	-0.27	-1.11
Cr	-501.82	-485.083	-0.13	0.09	0.35
Mn	-501.43	-484.54	-0.28	0.10	0.21
Fe	-498.77	-482.63	0.45	0.04	0.89
Co	-498.11	-480.76	-0.74	0.10	-0.23
Ni	-496.27	-479.23	-0.44	0.07	0.03
Zn	-493.16	-476.19	-0.36	0.02	0.05
La	-502.71	-485.55	-0.55	0.05	-0.10
Zr	-504.81	-487.37	-0.83	0.10	-0.32
Nb	-504.47	-487.06	-0.80	0.01	-0.38
Mo	-503.15	-485.99	-0.55	0.05	-0.10
Tc	-501.80	-484.28	-0.91	0.07	-0.43
Ru	-499.66	-482.28	-0.76	0.04	-0.31
Rh	-497.43	-480.61	2.06	0.11	2.57
Pd	-495.58	-478.87	-0.10	0.07	0.37
Ag	-493.29	-476.52	-0.16	-0.04	0.19
Cd	-493.05	-476.15	-0.29	-0.03	0.07
Y	-503.98	-486.94	-0.43	0.06	0.02
Hf	-506.216	-488.68	-0.92	-0.04	-0.48
Ta	-505.67	-488.46	-0.60	0.02	-0.17
W	-504.86	-487.32	-0.92	0.05	-0.47
Re	-503.31	-485.56	-1.14	0.08	-0.65
Os	-500.96	-483.41	-0.94	0.07	-0.47
Ir	-498.00	-481.42	0.02	0.04	0.47
Pt	-495.88	-479.17	-0.09	-0.03	0.27
Au	-493.00	-476.30	-0.09	0.04	0.34

Table S2: Total energy of the system (SAC+N_2H), N_2H Adsorption energies, ZPE -TΔS, and free energies of all the TM based SACs. The reference molecule used for the calculations is N_2 + H $_2$ (g)

Transition metal	Total energy (E_{SAC+ad})	ΔE_{N_2H} (eV)	ZPE -TΔS (eV)	ΔG_{N_2H}	ΔG_1
Sc	-505.03	1.03	0.30	1.77	1.75
V	-505.14	0.54	0.26	0.23	1.34
Cr	-504.35	0.71	0.30	1.52	1.16
Mn	-503.44	1.08	0.33	1.81	1.59
Fe	-502.05	0.55	0.31	1.32	0.42
Co	-500.27	0.47	0.31	1.24	1.47
Ni	-498.55	0.66	0.29	1.43	1.39
Zn	-494.83	1.35	0.27	2.07	2.01
La	-504.34	1.19	0.32	1.96	2.06
Zr	-507.37	-0.01	0.30	0.76	1.07
Nb	-507.44	-0.39	0.31	0.37	0.76
Mo	-506.74	-0.75	0.33	0.05	0.15
Tc	-504.56	-0.28	0.26	0.44	0.88
Ru	-502.16	0.11	0.32	0.88	1.20
Rh	-500.07	0.52	0.34	1.26	0.96
Pd	-497.41	1.44	0.29	2.19	1.82
Cd	-494.62	1.51	0.25	2.23	2.16
Y	-505.84	1.09	0.29	1.86	1.83
Hf	-508.90	-0.23	0.23	0.46	0.94
Ta	-509.23	-0.78	0.31	0.00	0.17
W	-508.56	-1.24	0.34	-0.43	0.03
Re	-506.46	-0.90	0.28	-0.16	0.49
Os	-503.41	0.00	0.30	0.76	0.88
Ir	-501.24	0.16	0.31	0.93	0.45
Pt	-497.86	1.30	0.30	2.06	2.45
Au	-494.59	1.69	0.30	2.48	2.14

Table S3: Total energies of the system (SAC+adsorbates), adsorption energies, ZPE -TΔS, and free energies of various intermediates for Mo-, W-, and Ta- based SACs. The reference molecule used for the calculations is N_2 (g) + H_2 (g)

Transition metal	Total energy (E_{SAC+ad})	ΔE_{ads} (eV)	ZPE -TΔS (eV)	ΔG	intermediate
Mo	-510.37	-1.00	0.66	0.19	N_2H_2*
Mo	-495.32	-1.02	-0.02	-0.84	N*
Mo	-498.58	-0.90	0.23	-0.40	NH*
Mo	-502.63	-1.57	0.55	-0.69	NH_2*
Mo	-506.66	-1.12	0.90	-0.53	NH_3*
Mo	-509.56	-0.20	0.53	0.86	NHNH*
Mo	-513.97	-1.22	0.53	0.86	$NHNH_2$*
Mo	-517.56	-1.43	1.31	0.53	NH_2NH_2*
W	-512.58	-1.88	0.65	-0.70	N_2H_2*
W	-496.83	-1.20	0.03	-0.97	N*
W	-501.01	-2.00	0.27	-1.45	NH*
W	-504.42	-2.02	0.55	-1.14	NH_2*
W	-508.11	-1.24	0.90	-0.65	NH_3*
W	-511.20	-0.50	0.62	0.64	NHNH*
W	-515.83	-1.75	0.62	0.64	$NHNH_2$
W	-519.03	-1.54	1.29	0.38	NH_2NH_2*
Ta	-513.76	-1.92	0.6	-0.79	N_2H_2*
Ta	-496.83	-0.06	0.03	0.16	N*
Ta	-502.52	-2.38	0.29	-1.82	NH*
Ta	-506.29	-2.76	0.55	-1.86	NH_2*
Ta	-509.30	-1.29	0.80	-0.79	NH_3*
Ta	-512.44	-0.60	0.55	0.47	NHNH*
Ta	-516.30	-1.08	0.55	0.47	$NHNH_2$*
Ta	-520.17	-1.57	1.30	0.38	NH_2NH_2*

Table S4: Total energies, ZPE, and TΔS of the reference molecule.

Reference molecule	Total energy (E_{ref})	ZPE (eV)	TΔS (eV)
H_2	-6.76	0.27	0.41
N_2	-16.60	0.15	0.55
NH_3	-19.54	0.91	0.60