Supplementary Information

Theoretical Understanding and Prediction of Metal-doped CeO_2 Catalyst for Ammonia Dissociation

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Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y
U_{eff} (eV)	5.0	4.2	3.1	3.5	4.5	4.0	3.4	6.0	6.0	8.0	3.5
Ref	1	2	3	4	5	6	4	4	7	8	9
Element	Zr	Nb	Mo	Tc	Cd	La	Ce	Pr	Nd	Sm	W
U_{eff} (eV)	4.0	4.0	3.5	-	2.0	5.0	5.0	4.5	6.0	-	6.2
Ref	10	11	4		12	13	14	15	16		17

Table S1 U_{eff} (eV) value of transition metal elements.

Table S2 Distance between the doping metal and oxygen.

	Metal-oxygen distance (Å)						
	distance1	**distance 2**	**distance 3**	**distance 4**	**distance 5**	**distance 6**	**distance 7**
V	2.131	1.962	1.960	1.698	3.121	3.436	2.041
Cr	2.889	1.803	1.876	1.806	2.870	3.452	1.909
Mn	2.467	2.636	2.110	2.812	2.098	2.390	2.208
Fe	2.633	2.055	2.125	2.025	2.836	2.053	2.082
Co	1.780	3.680	3.357	3.666	1.774	1.757	1.868
Ni	1.805	1.848	1.805	3.662	3.385	3.690	1.887
Cu	1.839	3.705	3.324	3.684	1.837	1.841	1.878
Zn	1.997	3.501	2.010	3.517	1.995	3.191	1.955
Nb	2.580	1.942	2.424	1.941	2.602	1.950	2.005
Tc	2.646	1.790	2.745	1.787	2.694	1.757	1.903
W	2.428	1.837	2.399	1.837	2.869	1.825	1.924

Table S3 Relevant properties calculated by DFT for metal and metal-doped catalysts.

	E_{SMA}[a] (eV)	BG[b] (eV)	DBC[c] (eV)	VBM[d] (eV)	CBM[e] (eV)	WF[f] (eV)	E_{dope}[g] (eV)
V	-6.43	1.21	-0.27	-0.51	0.70	4.96	3.39
Cr	-5.91	1.80	0.14	-1.10	0.70	5.60	4.41
Mn	-6.82	0.56	-3.04	-1.25	-0.68	5.76	7.24
Fe	-5.45	0.93	-1.69	-1.16	-0.23	5.76	7.29
Co	-4.71	0.22	-2.38	-1.37	-1.15	5.94	8.29
Ni	-2.40	0.34	-3.16	-1.43	-1.09	6.17	9.03
Cu	-2.39	0.27	-3.84	-1.44	-1.17	6.22	10.48
Zn	-0.79	0.61	-6.97	-1.42	-0.81	5.94	8.98
Nb	-7.34	0.43	-4.14	0.33	0.76	4.35	0.96
Tc	-10.99	0.11	-3.64	0.43	0.54	4.49	5.76
W	-13.64	0.55	-3.20	0.22	0.77	4.39	2.64

A: the energy of single metal atom. *b*: band gap. *C*: d band center. *D*: valence band maximum. *E*: conduction band minimum. *F*: work function.

G: the energy of doping formation.

Table S4 Adsorption energies of NH_3-related species on metal-doped CeO_2.

	E_{NH3} (eV)	E_{NH2-H} (eV)	E_{NH-2H} (eV)	E_{N-3H} (eV)	E_H (eV)
V	-0.67	-1.26	-1.41	-1.42	-3.58
Cr	-0.54	-1.36	-1.44	-1.47	-4.23
Mn	-1.62	-1.81	-2.10	-1.98	-4.96
Fe	-0.40	-1.54	-0.70	0.14	-5.17
Co	-1.35	-1.47	-1.13	-1.49	-4.94
Ni	-1.62	-1.49	-1.76	-1.56	-5.22
Cu	-1.09	-1.09	-1.35	-1.66	-5.24
Zn	-1.38	-1.48	-1.91	-1.95	-5.09
Nb	-0.36	-0.90	-0.22	0.51	-3.91
Tc	0.23	0.15	-0.59	-2.48	-3.07
W	-0.05	-0.33	-0.29	0.29	-3.40

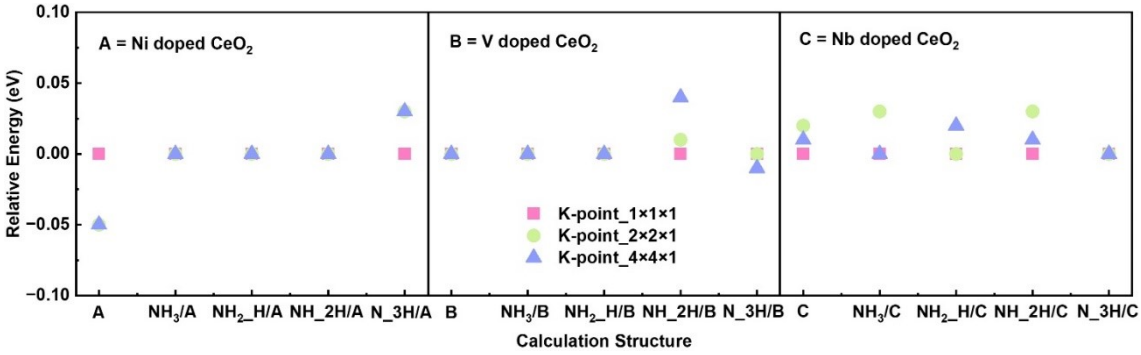

Figure. S1 Relative energies of Ni-doped, V-doped, and Nb-doped CeO_2 surfaces and the structures of adsorbed species (NH_3, NH_2_H, NH_2H and N_3H) on the corresponding surfaces at different k-point mesh density.

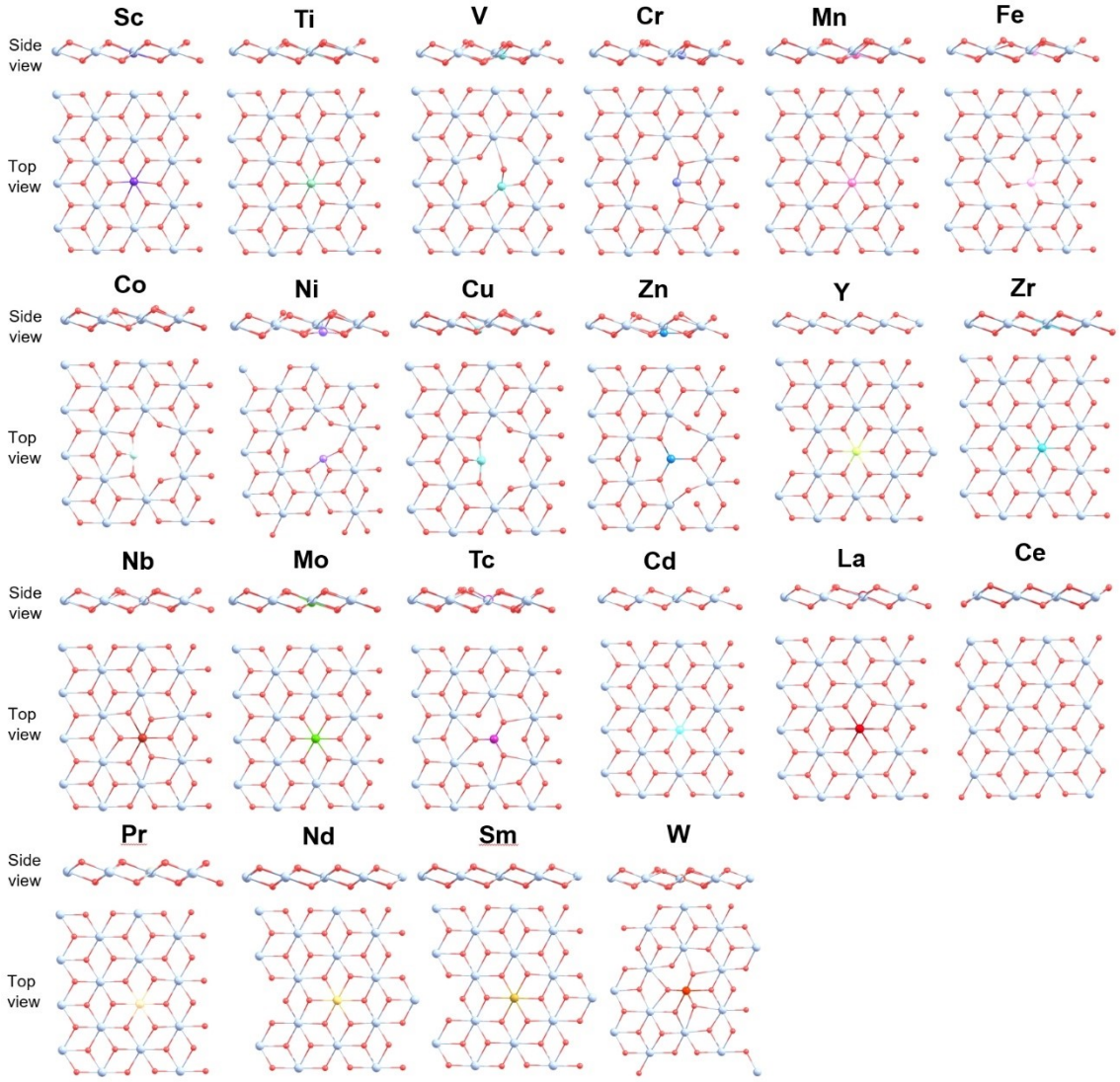

Figure. S2 Structural diagrams of pure CeO_2 and CeO_2 doped with different transition metals.

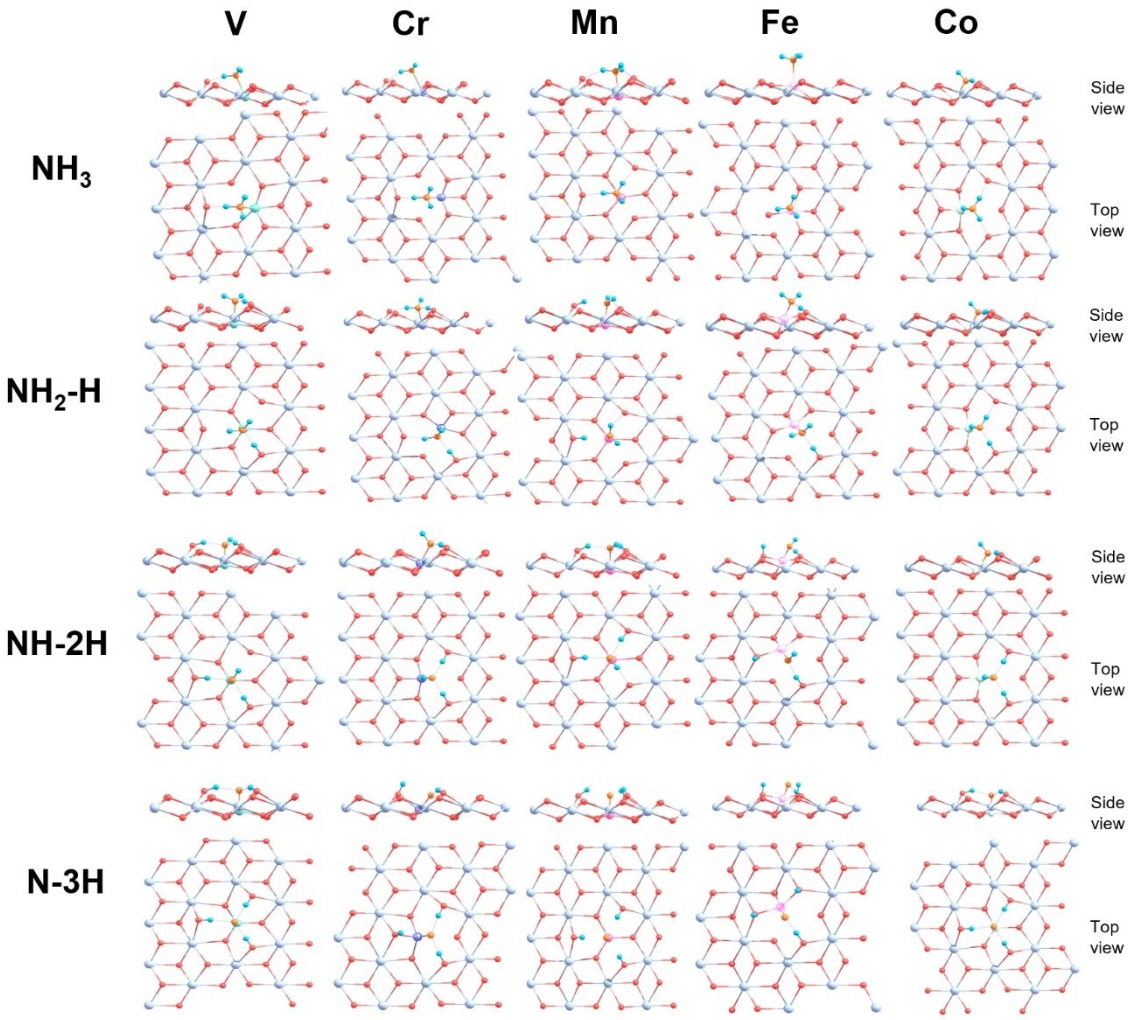

Figure. S3 Adsorption structures of NH_3, NH_2-H, NH-2H and N-3H on metal (V, Cr, Mn, Fe, and Co)-doped CeO_2.

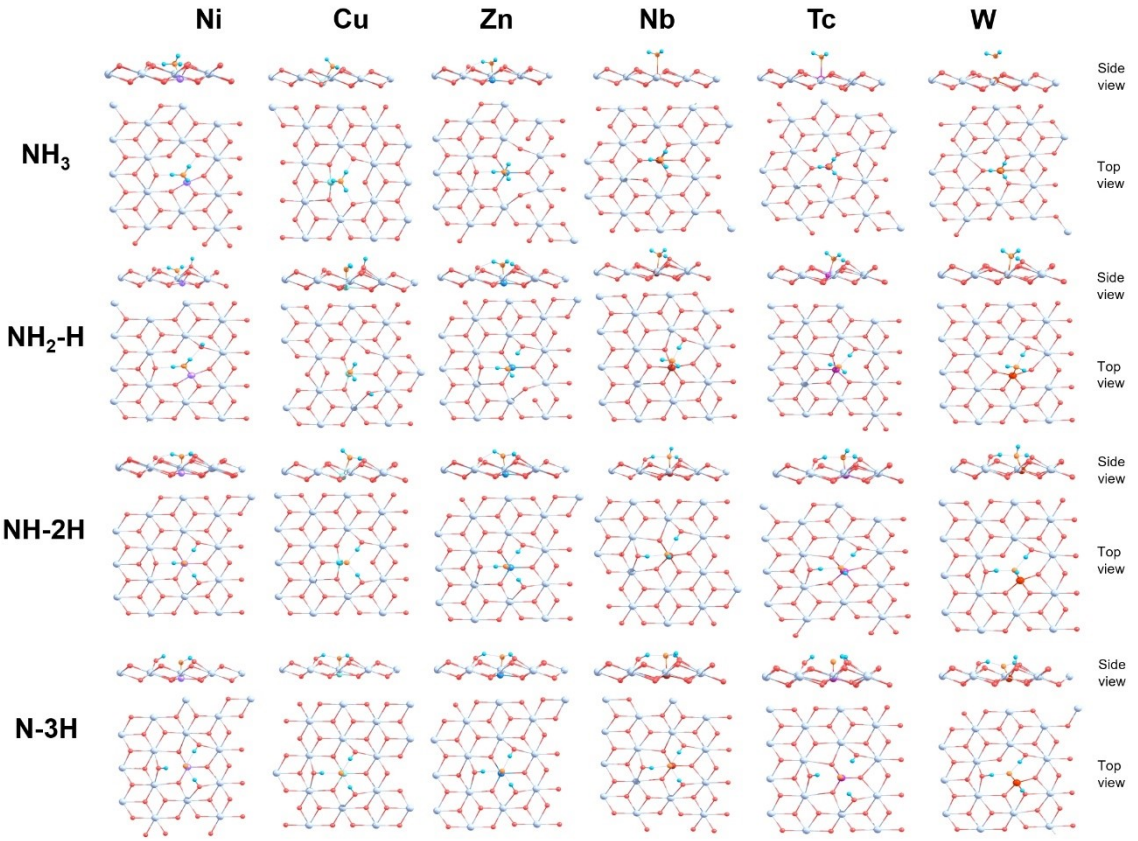

Figure. S4 Adsorption structures of NH_3, NH_2-H, NH-2H and N-3H on metal (Ni, Cu, Zn, Nb, Tc, and W)-doped CeO_2.

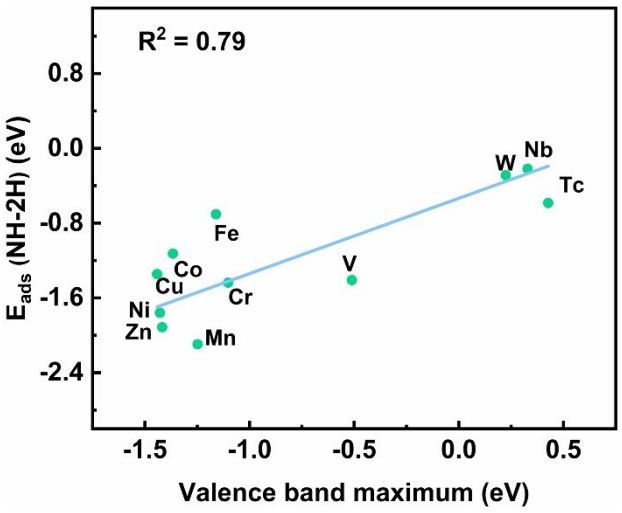

Figure. S5 Valence band maximum as function of the adsorption energies of NH_2-H species in NH_3 dissociation.

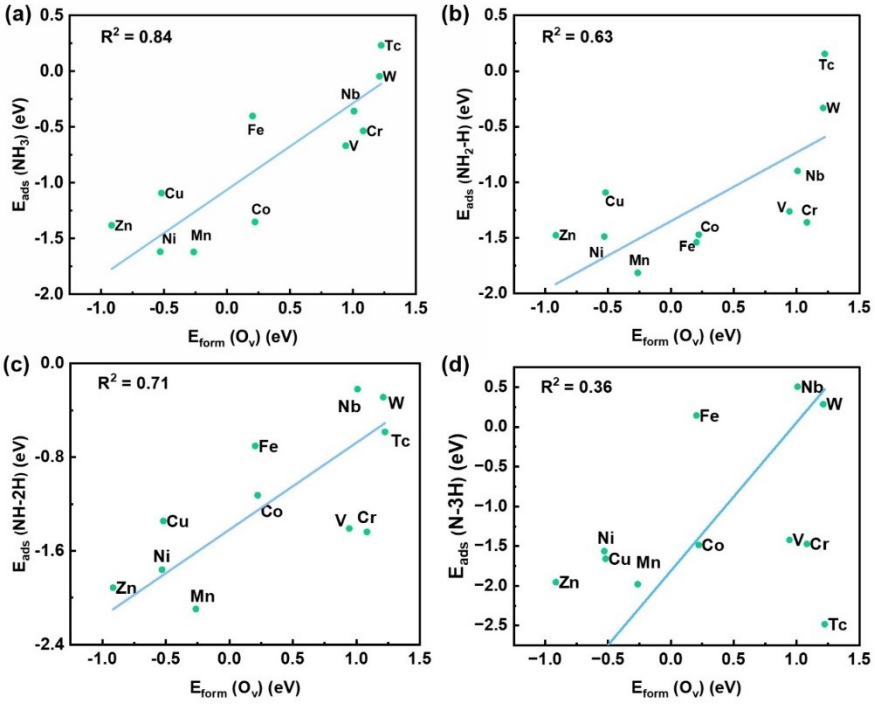

Figure. S6 Oxygen vacancy formation as function of the adsorption energies of (a) NH_3, (b) NH_2-H, (c) NH-2H, and (d) N-3H species in NH_3 dissociation.

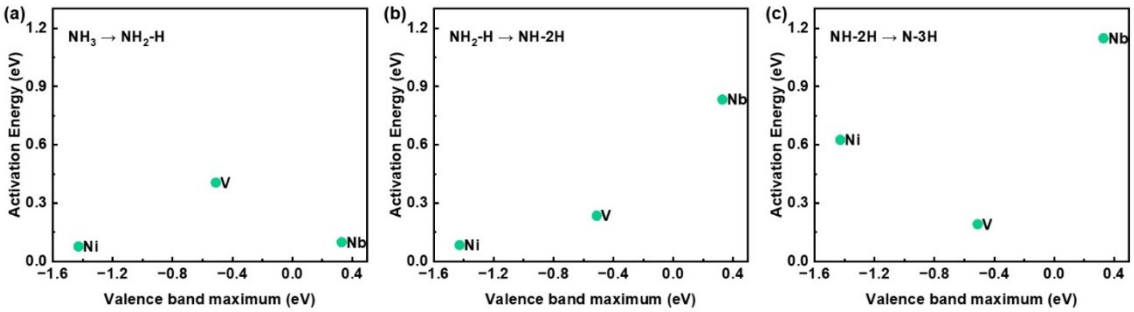

Figure. S7 Valence band maximum as function of the activation energies for the transition states of (a) NH_3→NH_2-H, (b) NH_2-H→NH-2H, and (c) NH-2H→N-3H in NH_3 dissociation.

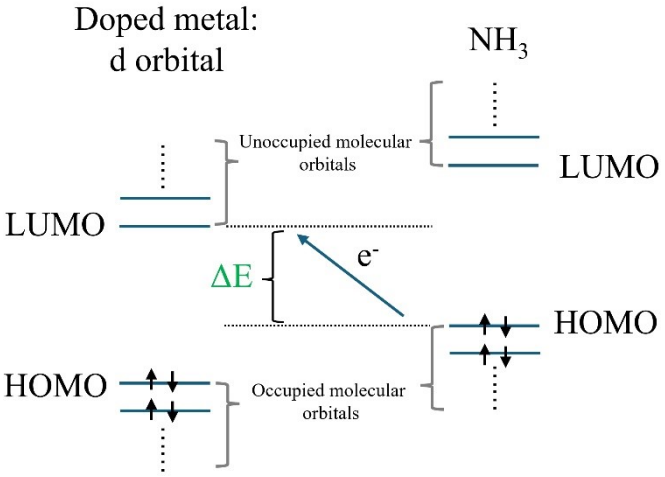

Figure. S8 Schematic diagram of the interaction between HOMO and LUMO.

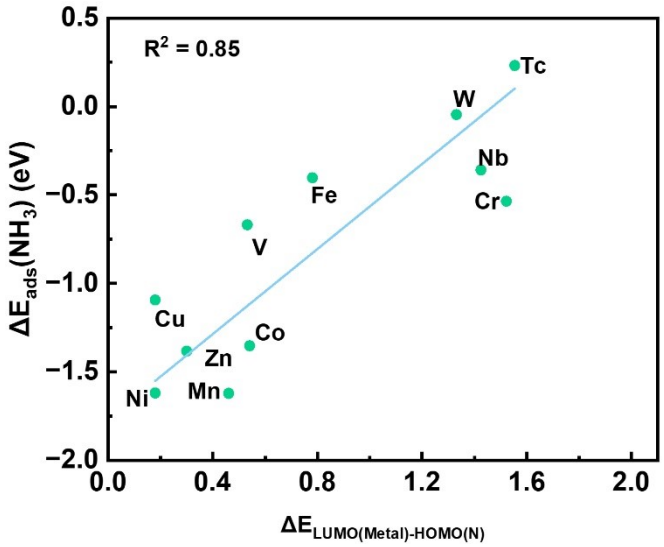

Figure. S9 The Linear relationship between NH_3 adsorption energy and $\Delta E_{LUMO(Metal)-HOMO(N)}$ (the difference between the LUMO energy of doped metal d orbital and the HOMO energy of N p orbital in NH_3).

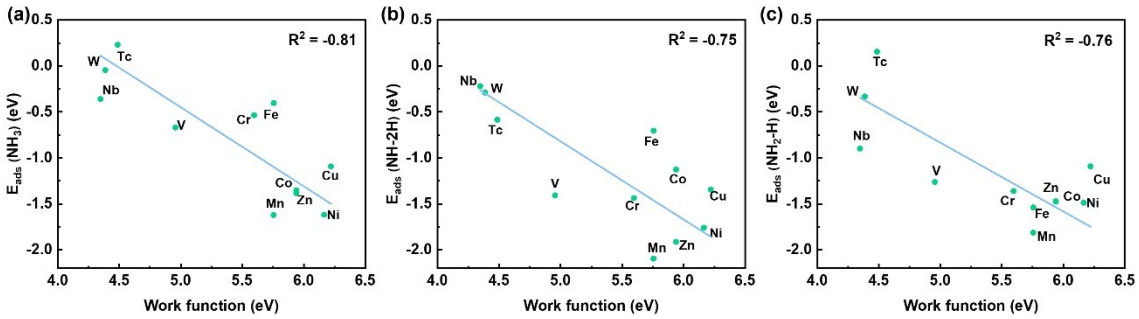

Figure. S10 Work function as function of the adsorption energies of (a) NH_3, (b) NH_2-H, and (c) NH-2H species in NH_3 dissociation.

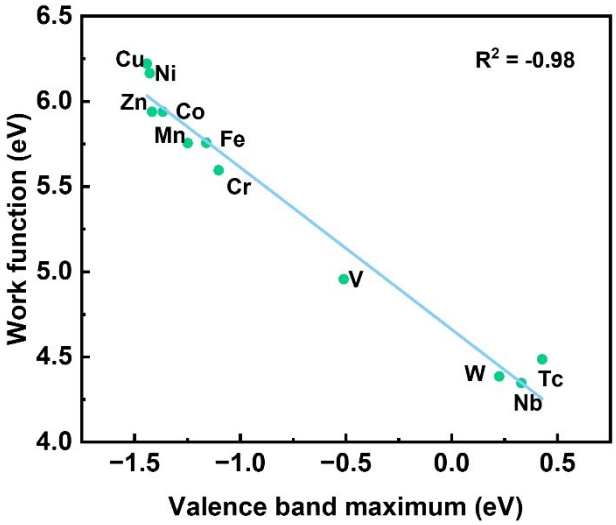

Figure. S11 Valence band maximum as function of the work function.

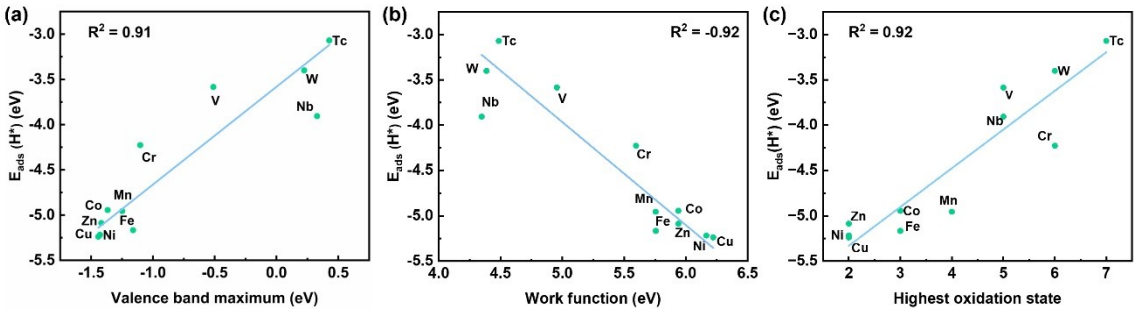

Figure. S12 (a) Valence band maximum, (b) work function, and (c) highest oxidation state as function of the adsorption energies of H.

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