Supplementary Information

Theoretical exploration of single-atom catalyst anchored on β_{12}-borophene for electrochemical nitrate reduction: catalyst screening and mechanistic insight

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The elementary steps of the NO_3RR process:

Common Steps:

$$* + NO_3^- \rightarrow *NO_3 + e^- \quad \text{(S1)}$$

Pathway 1:

$$*NO_3 + H^+ + e^- \rightarrow (*ONO + *OH) \quad \text{(S2)}$$

$$(*ONO + *OH) + H^+ + e^- \rightarrow *O_2N + H_2O \quad \text{(S3)}$$

$$*O_2N + H^+ + e^- \rightarrow *O_2NH \quad \text{(S4)}$$

$$*O_2NH + H^+ + e^- \rightarrow *O_2NH_2 \quad \text{(S5)}$$

$$*O_2NH_2 + H^+ + e^- \rightarrow 2*O + NH_3 \quad \text{(S6)}$$

$$2*O + H^+ + e^- \rightarrow *O + *OH \quad \text{(S7)}$$

$$*O + *OH + H^+ + e^- \rightarrow *O + H_2O \quad \text{(S8)}$$

$$*O + H^+ + e^- \rightarrow *OH \quad \text{(S9)}$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad \text{(S10)}$$

Pathway 2:

$$*NO_3 + H^+ + e^- \rightarrow (*ONO + *OH) \quad \text{(S2)}$$

$$(*ONO + *OH) + H^+ + e^- \rightarrow *O*NO + H_2O \quad \text{(S11)}$$

$$*O*NO + H^+ + e^- \rightarrow (*OH + *NO) \quad \text{(S12)}$$

$$(*OH + *NO) + H^+ + e^- \rightarrow *N*O + H_2O \quad \text{(S13)}$$

$$*N*O + H^+ + e^- \rightarrow *NH*O \quad \text{(S14)}$$

$$*NH*O + H^+ + e^- \rightarrow *NH_2*O \quad \text{(S15)}$$

$$*NH_2*O + H^+ + e^- \rightarrow (*NH_2 + *OH) \quad \text{(S16)}$$

$$(*NH_2 + *OH) + H^+ + e^- \rightarrow *OH + NH_3 \quad \text{(S17)}$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad \text{(S10)}$$

Pathway 3:

$$*NO_3 + H^+ + e^- \rightarrow (*ONO + *OH) \quad \text{(S2)}$$

$$(*ONO + *OH) + H^+ + e^- \rightarrow *O*NO + H_2O \quad \text{(S11)}$$

$$*O*NO + H^+ + e^- \rightarrow (*OH + *NO) \quad \text{(S12)}$$

$$(*OH + *NO) + H^+ + e^- \rightarrow *NO + H_2O \quad \text{(S18)}$$

$$*NO + H^+ + e^- \rightarrow *NHO \quad \text{(S19)}$$

$$*NHO + H^+ + e^- \rightarrow *NH_2*O \quad (S20)$$

$$*NH_2*O + H^+ + e^- \rightarrow *O + NH_3 \quad (S21)$$

$$*O + H^+ + e^- \rightarrow *OH \quad (S9)$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad (S10)$$

Pathway 4:

$$*NO_3 + H^+ + e^- \rightarrow (*ONO + *OH) \quad (S2)$$

$$(*ONO + *OH) + H^+ + e^- \rightarrow *O*NO + H_2O \quad (S11)$$

$$*O*NO + H^+ + e^- \rightarrow (*OH + *NO) \quad (S12)$$

$$(*OH + *NO) + H^+ + e^- \rightarrow *N*O + H_2O \quad (S13)$$

$$*N*O + H^+ + e^- \rightarrow *NH*O \quad (S14)$$

$$*NH*O + H^+ + e^- \rightarrow *NH_2*O \quad (S15)$$

$$*NH_2*O + H^+ + e^- \rightarrow *O + NH_3 \quad (S21)$$

$$*O + H^+ + e^- \rightarrow *OH \quad (S9)$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad (S10)$$

Pathway 5:

$$*NO_3 + H^+ + e^- \rightarrow (*ONO + *OH) \quad (S2)$$

$$(*ONO + *OH) + H^+ + e^- \rightarrow *O*NO + H_2O \quad (S11)$$

$$*O*NO + H^+ + e^- \rightarrow (*OH + *NO) \quad (S12)$$

$$(*OH + *NO) + H^+ + e^- \rightarrow *NO + H_2O \quad (S18)$$

$$*NO + H^+ + e^- \rightarrow *NOH \quad (S22)$$

$$*NOH + H^+ + e^- \rightarrow *NHOH \quad (S23)$$

$$*NHOH + H^+ + e^- \rightarrow *NH + H_2O \quad (S24)$$

$$*NH + H^+ + e^- \rightarrow *NH_2 \quad (S25)$$

$$*NH_2 + H^+ + e^- \rightarrow *NH_3 \quad (S26)$$

Pathway 6:

$$*NO_3 + H^+ + e^- \rightarrow (*ONO + *OH) \quad (S2)$$

$$(*ONO + *OH) + H^+ + e^- \rightarrow *O*NO + H_2O \quad (S11)$$

$$*O*NO + H^+ + e^- \rightarrow (*OH + *NO) \quad (S12)$$

$$(*OH + *NO) + H^+ + e^- \rightarrow *NO + H_2O \quad (S18)$$

$$*NO + H^+ + e^- \rightarrow *NOH \quad (S22)$$

$$*NOH + H^+ + e^- \rightarrow *N + H_2O \quad (S27)$$

$$*N + H^+ + e^- \rightarrow *NH \quad (S28)$$

$$*NH + H^+ + e^- \rightarrow *NH_2 \quad (S25)$$

$$*NH_2 + H^+ + e^- \rightarrow *NH_3 \quad (S26)$$

Pathway 7:

$$*NO_3 + H^+ + e^- \rightarrow (*ONO + *OH) \quad (S2)$$

$$(*ONO + *OH) + H^+ + e^- \rightarrow *O*NO + H_2O \quad (S11)$$

$$*O*NO + H^+ + e^- \rightarrow (*OH + *NO) \quad (S12)$$

$$(*OH + *NO) + H^+ + e^- \rightarrow *NO + H_2O \quad (S18)$$

$$*NO + H^+ + e^- \rightarrow *NH*O \quad (S27)$$

$$*NH*O + H^+ + e^- \rightarrow *NH_2*O \quad (S15)$$

$$*NH_2*O + H^+ + e^- \rightarrow (*NH_2 + *OH) \quad (S16)$$

$$(*NH_2 + *OH) + H^+ + e^- \rightarrow *OH + NH_3 \quad (S17)$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad (S10)$$

Pathway 8:

$$*NO_3 + H^+ + e^- \rightarrow *O_2NOH \quad (S28)$$

$$*O_2NOH + H^+ + e^- \rightarrow *NO_2 + H_2O \quad (S29)$$

$$*NO_2 + H^+ + e^- \rightarrow *NO_2H \quad (S30)$$

$$*NO_2H + H^+ + e^- \rightarrow *NO + H_2O \quad (S31)$$

$$*NO + H^+ + e^- \rightarrow *NHO \quad (S19)$$

$$*NHO + H^+ + e^- \rightarrow *NH_2*O \quad (S20)$$

$$*NH_2*O + H^+ + e^- \rightarrow *O + NH_3 \quad (S21)$$

$$*O + H^+ + e^- \rightarrow *OH \quad (S9)$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad (S10)$$

Pathway 9:

$$*NO_3 + H^+ + e^- \rightarrow *ONO_2H \quad (S32)$$

$$*ONO_2H + H^+ + e^- \rightarrow *O*NO + H_2O \quad (S33)$$

$$*O*NO + H^+ + e^- \rightarrow *NO_2H \quad (S34)$$

$$*NO_2H + H^+ + e^- \rightarrow *NO + H_2O \quad (S31)$$

$$*NO + H^+ + e^- \rightarrow *NHO \quad (S19)$$

$$*NHO + H^+ + e^- \rightarrow *NH_2*O \quad (S20)$$

$$*NH_2*O + H^+ + e^- \rightarrow *O + NH_3 \quad (S21)$$

$$*O + H^+ + e^- \rightarrow *OH \quad (S9)$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad (S10)$$

Pathway 10:

$$*NO_3 + H^+ + e^- \rightarrow (*ONO + *OH) \quad (S2)$$

$$(*ONO + *OH) + H^+ + e^- \rightarrow *O*NO + H_2O \quad (S11)$$

$$*O*NO + H^+ + e^- \rightarrow (*OH + *NO) \quad (S12)$$

$$(*OH + *NO) + H^+ + e^- \rightarrow *NO + H_2O \quad (S18)$$

$$*NO + H^+ + e^- \rightarrow *NH*O \quad (S27)$$

$$*NH*O + H^+ + e^- \rightarrow *NH_2*O \quad (S15)$$

$$*NH_2*O + H^+ + e^- \rightarrow *O + NH_3 \quad (S21)$$

$$*O + H^+ + e^- \rightarrow *OH \quad (S9)$$

$$*OH + H^+ + e^- \rightarrow * + H_2O \quad (S10)$$

Table S1. The formation energies (E_f), dissolution potentials (U_{diss}); the lattice parameters *a* and *b* of the fully relaxed $M@\beta_{12}$; the shortest ($d_{M\text{-}B(min)}$) and longest ($d_{M\text{-}B(max)}$) bond lengths of *M* – B bonds, respectively; and charges on *M* (Q_M)

Metal	E_f (eV)	U_{diss} (V)	*a* (Å)	*b* (Å)	$d_{M\text{-}B(min)}$ (Å)	$d_{M\text{-}B(max)}$ (Å)	Q_M (|e|)
Ti	-6.52	1.63	8.76	14.85	2.11	2.21	1.23
V	-5.65	1.65	8.76	14.86	2.00	2.09	1.03
Cr	-3.32	0.75	8.78	15.23	2.27	2.28	0.82
Mn	-3.81	0.72	8.78	15.14	2.14	2.17	0.74
Fe	-4.98	2.04	8.78	14.91	1.88	1.93	0.20
Co	-5.71	2.58	8.79	15.22	1.86	1.89	-0.22
Ni	-4.29	1.88	8.78	15.22	2.13	2,15	0.28
Cu	-3.34	2.01	8.79	15.23	2.16	2.17	0.33
Zr	-7.19	0.35	8.77	14.81	2.24	2.36	1.35
Nb	-6.70	1.13	8.77	14.81	2.14	2.24	1.15
Mo	-5.41	1.60	8.77	14.80	2.07	2.15	0.68
Ru	-5.78	3.35	8.77	15.20	2.28	2.22	0.18
Rh	-5.48	3.34	8.77	15.18	2.22	2.29	0.05
Pd	-3.70	2.80	8.78	15.20	2.35	2.38	0.11
Ag	-2.21	3.01	8.78	15.23	2.49	2.50	0.34
Hf	-9.95	0.94	8.77	14.82	2.21	2.32	1.36
Ta	-7.67	1.96	8.77	14.81	2.12	2.22	1.19
W	-7.32	2.54	8.77	14.83	2.06	2.15	0.71
Re	-6.17	2.36	8.77	14.92	2.04	2.10	0.08
Os	-5.89	1.58	8.77	15.22	2.15	2.19	-0.01
Ir	-6.13	3.20	8.76	15.20	2.20	2.26	-0.13
Pt	-4.90	3.63	8.78	15.20	2.29	2.35	-0.11
Au	-2.38	2.29	8.79	15.23	2.46	2.47	0.04

Table S2. The total energies ($E_{1\text{-O}}$, $E_{2\text{-O}}$) of two possible NO_3^- adsorption configurations on $M@\beta_{12}$; "–" represents convergence no achieved for the corresponding geometry optimization; the bonds lengths ($d_{O1\text{-M}}$, $d_{O2\text{-M}}$) of *M*-O bonds between metal atom and NO_3^-; charges on the metal atom (Q_M) and $*NO_3$ (Q_{NO3}); adsorption energies for $*NO_3$ (ΔG_{*NO3}) and *H on $M@\beta_{12}$, respectively

Metal	$E_{1\text{-O}}$ (eV)	$E_{2\text{-O}}$ (eV)	$d_{O1\text{-M}}$ (Å)	$d_{O2\text{-M}}$ (Å)	Q_M (|e|)	Q_{NO3} (|e|)	ΔG_{*NO3} (eV)	ΔG_{*H} (eV)
Ti	-317.12	-317.76	2.12	2.11	1.45	-0.63	-1.52	0.20
V	-317.83	-318.36	2.07	2.06	1.26	-0.60	-1.55	-0.01
Cr	–	-317.63	2.04	2.05	1.18	-0.63	-1.21	0.23
Mn	–	-317.12	2.03	2.03	1.08	-0.61	-0.61	-0.22
Fe	–	-315.82	1.97	1.97	0.68	-0.54	0.23	–
Co	–	-314.60	1.97	1.97	0.63	-0.55	0.36	–
Ni	-312.10	-313.07	1.97	1.98	0.60	-0.56	-0.43	-0.09
Cu	–	-310.98	2.05	2.05	0.66	-0.61	0.20	–
Zr	-317.74	-318.39	2.28	2.26	1.69	-0.67	-1.69	0.06
Nb	-318.81	-319.39	2.23	2.23	1.56	-0.68	-1.90	-0.42
Mo	-318.69	-319.32	2.17	2.17	1.10	-0.59	-1.74	-0.38
Ru	–	-316.52	2.12	2.12	0.54	-0.54	-0.97	0.01
Rh	-313.63	-314.61	2.13	2.14	0.41	-0.54	-0.37	0.20
Pd	-311.58	-312.55	2.19	2.19	0.39	-0.53	0.10	–
Ag	-309.58	-309.60	2.28	2.29	0.56	-0.59	0.46	–
Hf	-319.30	-319.95	2.24	2.22	1.74	-0.67	-2.05	-0.28
Ta	-320.81	-321.41	2.20	2.20	1.60	-0.65	-2.62	-0.91
W	-320.61	-321.16	2.15	2.15	1.24	-0.62	-2.15	-0.97
Re	–	-319.88	2.11	2.12	0.80	-0.59	-1.49	-0.84
Os	–	-317.93	2.10	2.10	0.52	-0.57	-1.59	-0.69
Ir	–	-315.70	2.10	2.13	0.35	-0.53	-0.83	-0.42
Pt	–	-313.23	2.17	2.17	0.28	-0.51	-0.29	-0.18
Au	–	-310.07	2.26	2.27	0.31	-0.54	0.29	–

Table S3. The adsorption energies for HNO_3, NO_2, and NO species with various adsorption configurations on $M@\beta_{12}$; "–" denotes that no such adsorption configuration can be formed

	HNO_3			NO_2			NO		
	$*O_2NOH$	*HNO+*OH	ONO_2H	$*O_2N$	*O*NO	$*NO_2$	*N*O	*NO	*ON
Ti	-1.55	-3.20	–	-2.05	-2.12	–	-2.04	-1.90	-1.39
V	-1.84	-2.87	–	-2.09	-2.33	–	-2.43	-2.40	-1.67
Cr	-2.36	-2.77	–	-2.85	-2.34	–	–	–	–
Mn	-1.23	-2.02	–	-2.07	-2.10	–	-1.98	-2.38	-0.57
Ni	-0.75	–	-0.78	-1.82	-2.04	–	–	-2.85	-1.26
Zr	-3.00	-3.91	–	-3.76	-3.79	–	-1.83	-1.95	-1.48
Nb	-2.17	-3.46	–	-3.49	-3.53	–	-2.43	-2.58	-1.97
Mo	-2.63	-3.40	–	-3.46	-3.52	–	-2.78	-2.96	-1.98
Ru	-1.60	-2.10	–	-2.55	-2.53	–	–	–	–
Rh	-0.58	-0.37	–	-1.58	–	-1.84	–	-2.57	-0.72
Hf	-3.36	-4.44	–	-3.47	-3.48	–	-2.09	-2.25	-1.76
Ta	-3.09	-4.24	–	-4.01	-4.08	–	-2.94	-3.02	-2.42
W	-3.17	-4.19	–	-3.62	-3.65	–	-3.01	-3.21	-2.04
Re	-2.92	-3.25	–	-3.16	-3.11	–	–	–	–
Os	-2.64	-3.13	–	-3.15	-3.16	–	-3.20	-4.41	-1.82
Ir	-1.50	-2.14	–	-2.23	-2.42	–	–	-3.55	-0.96

Table S4. Gibbs free energy change of each elementary step for all $M@\beta_{12}$ along their preferred reaction pathways

ΔG (eV)	Pathway1			Pathway2	Pathway3	Pathway4	Pathway5	
	Cr	Ru	Re	Ti	Mn	V	Mo	W
ΔG_1	-1.21	-0.97	-1.49	-1.52	-0.61	-1.55	-1.74	-2.15
ΔG_2	-1.18	-0.74	-1.37	-1.28	-1.02	-0.93	-1.26	-1.65
ΔG_3	-0.35	-0.76	-0.07	–	–	–	–	–
ΔG_4	-0.22	0.15	-0.35	–	–	–	–	–
ΔG_5	0.08	0.10	0.32	–	–	–	–	–
ΔG_6	-2.64	-1.66	-3.25	–	–	–	–	–
ΔG_7	-0.34	-0.77	-0.40	–	–	–	–	–
ΔG_8	-0.78	-1.59	-1.02	–	–	–	–	–
ΔG_9	0.03	0.02	0.45	–	0.23	-0.64	–	–
ΔG_{10}	1.08	0.70	1.64	1.46	0.33	1.73	–	–
ΔG_{11}	–	–	–	-0.08	-0.54	-0.60	-0.10	0.19
ΔG_{12}	–	–	–	-1.54	-1.51	-1.34	-1.53	-1.62
ΔG_{13}	–	–	–	0.99	–	0.63	–	–
ΔG_{14}	–	–	–	-0.76	–	-0.45	–	–
ΔG_{15}	–	–	–	-0.78	–	-0.99	–	–
ΔG_{16}	–	–	–	-1.85	–	–	–	–
ΔG_{17}	–	–	–	-0.15	–	–		–
ΔG_{18}	–	–	–	–	-0.04	–	0.56	0.65
ΔG_{19}	–	–	–	–	0.06	–	–	–
ΔG_{20}	–	–	–	–	-0.48	–	–	–
ΔG_{21}	–	–	–	–	-1.93	-1.36	–	–
ΔG_{22}	–	–	–	–	–	–	-0.10	-0.20
ΔG_{23}	–	–	–	–	–	–	-0.11	-0.08
ΔG_{24}	–	–	–	–	–	–	-2.11	-2.27
ΔG_{25}	–	–	–	–	–	–	-0.57	-0.40
ΔG_{26}	–	–	–	–	–	–	-0.53	0.69
ΔG_{27}	–	–	–	–	–	–	–	–
ΔG_{28}	–	–	–	–	–	–	–	–
ΔG_{29}	–	–	–	–	–	–	–	–
ΔG_{30}	–	–	–	–	–	–	–	–

ΔG_{31}	–	–	–	–	–	–	–	–
ΔG_{32}	–	–	–	–	–	–	–	–
ΔG_{33}	–	–	–	–	–	–	–	–
ΔG_{34}	–	–	–	–	–	–	–	–

Table S4 (Continued). Gibbs free energy change of each elementary step for all $M@\beta_{12}$ along their preferred reaction pathways

ΔG (eV)	Pathway6		Pathway7		Pathway8	Pathway9	Pathway10	
	Os	Ir	Zr	Hf	Rh	Ni	Nb	Ta
ΔG_1	-1.59	-0.83	-1.69	-2.05	-0.37	-0.43	-1.90	-2.62
ΔG_2	-1.14	-0.91	-1.83	-2.01	–	–	-1.17	-1.22
ΔG_3	–	–	–	–	–	–	–	–
ΔG_4	–	–	–	–	–	–	–	–
ΔG_5	–	–	–	–	–	–	–	–
ΔG_6	–	–	–	–	–	–	–	–
ΔG_7	–	–	–	–	–	–	–	–
ΔG_8	–	–	–	–	–	–	–	–
ΔG_9	–	–	–		-0.94	-1.49	-0.83	-0.96
ΔG_{10}	–	–	1.63	2.06	-0.07	-0.03	1.99	2.59
ΔG_{11}	-0.31	-0.49	0.43	0.64	–	–	-0.23	0.01
ΔG_{12}	-1.94	-1.43	-1.72	-1.90	–		-1.47	-1.65
ΔG_{13}	–	–	–	–	–	–	–	–
ΔG_{14}	–	–	–		–	–	–	–
ΔG_{15}	–	–	-0.82	-0.71	–	–	-0.93	-0.94
ΔG_{16}	–	–	-2.23	-2.55	–	–	–	–
ΔG_{17}	–	–	0.23	0.43	–	–	–	–
ΔG_{18}	-0.60	-1.12	1.44	1.66	–		0.99	1.26
ΔG_{19}	–	–			0.56	0.78		
ΔG_{20}	–	–			-0.39	-0.47		
ΔG_{21}	–	–		–	-0.81	-0.17	-1.27	-1.27
ΔG_{22}	0.54	0.90	–	–	–	–	–	–
ΔG_{23}	–	–	–	–	–	–	–	–
ΔG_{24}	–	–	–	–	–	–	–	–
ΔG_{25}	0.25	-0.63	–	–	–	–	–	–
ΔG_{26}	0.28	-0.15	–	–	–	–	–	–
ΔG_{27}	-1.84	-1.69	-0.95	-1.10	–	–	-0.70	-0.70
ΔG_{28}	-0.34	-0.09	–	–	0.72	–	–	–
ΔG_{29}	–	–	–	–	-2.15	–	–	–
ΔG_{30}	–	–	–	–	-0.18	–	–	–

ΔG_{31}	–	–	–	–	-1.90	-1.98	–	–
ΔG_{32}	–	–	–	–	–	0.68	–	–
ΔG_{33}	–	–	–	–	–	-2.24	–	–
ΔG_{34}	–	–	–	–	–	-0.17	–	–

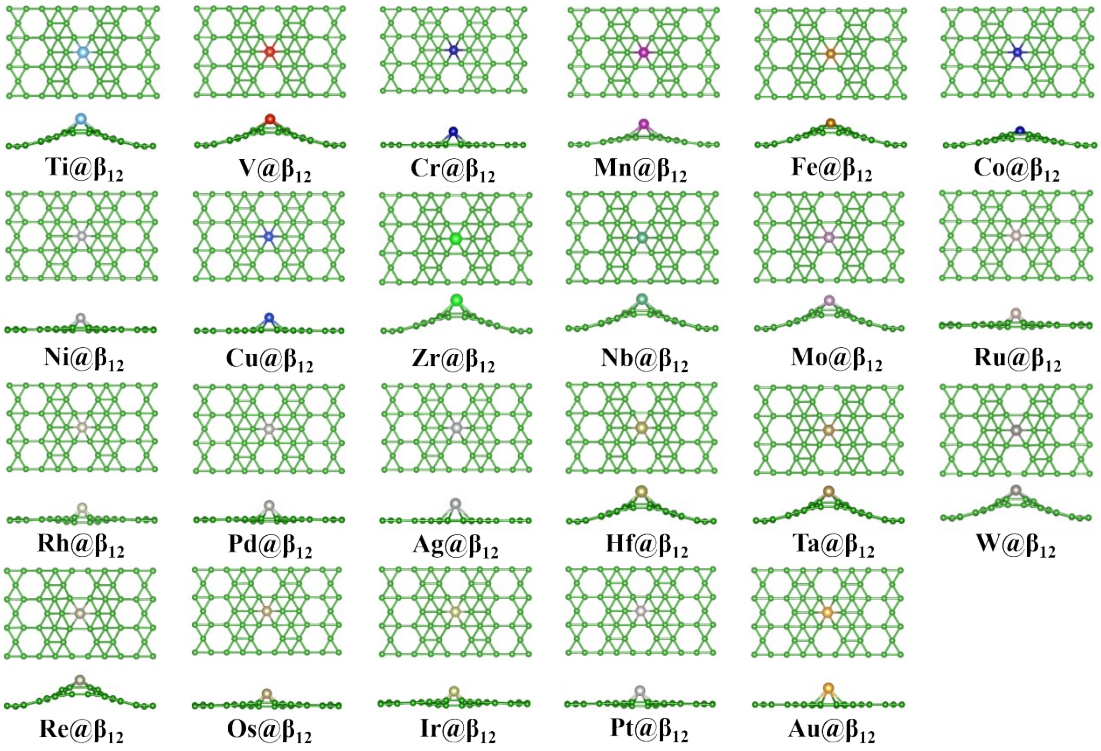


Figure S1. Optimized adsorption structures of $M@\beta_{12}$. The green balls represent B atoms, while other colors denote metal atoms as labeled.

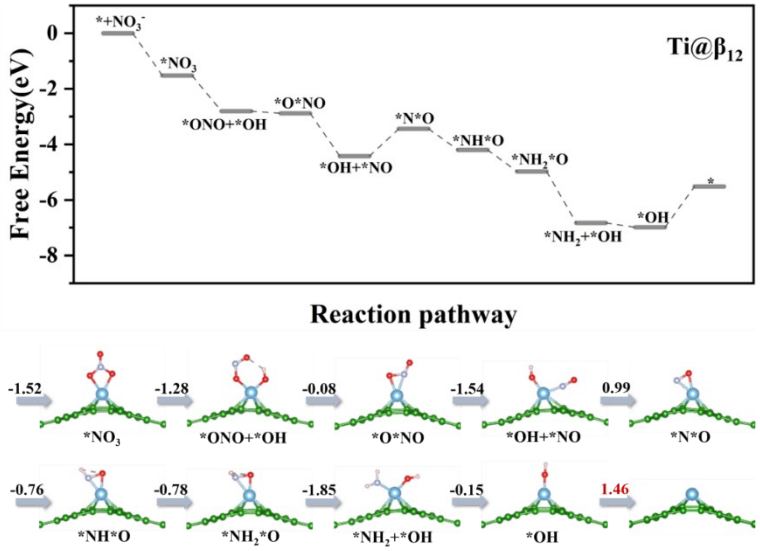


Figure S2-1

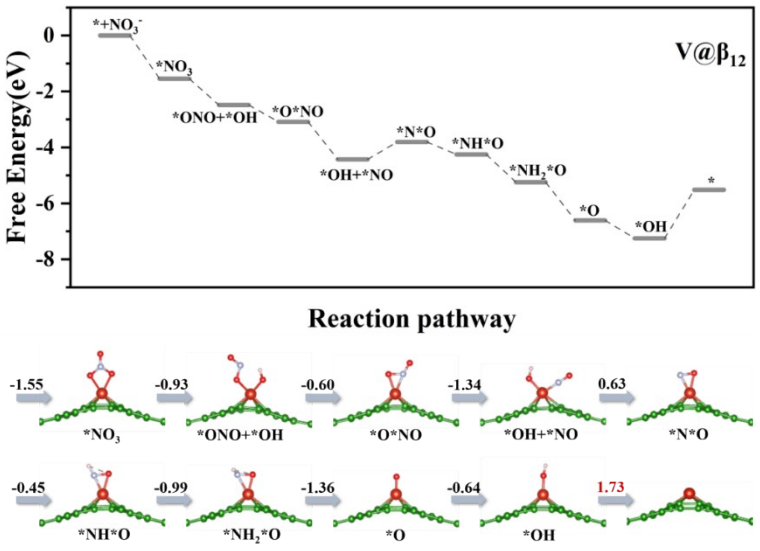


Figure S2-2

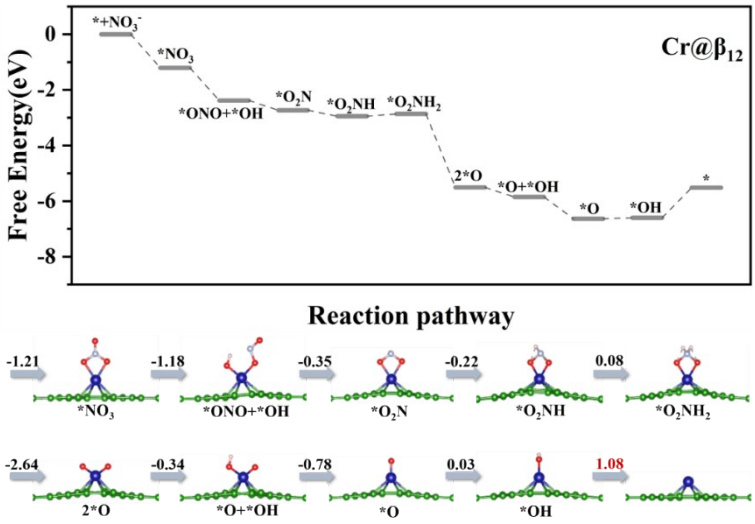


Figure S2-3

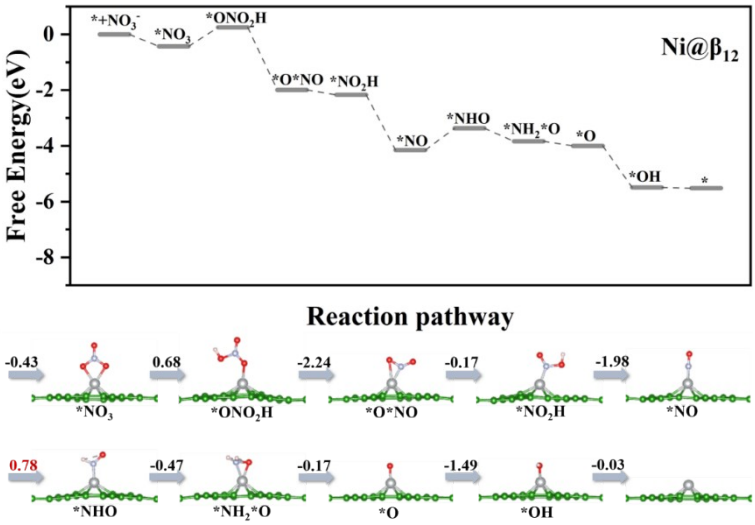
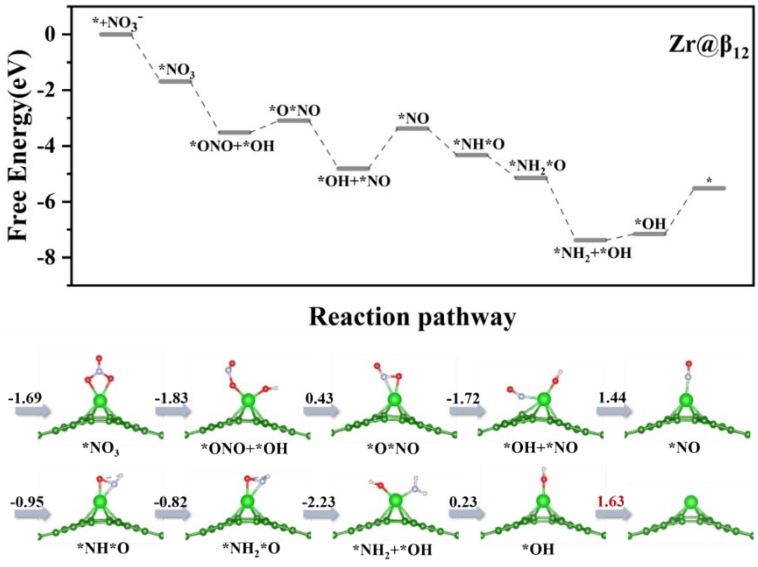


Figure S2-4



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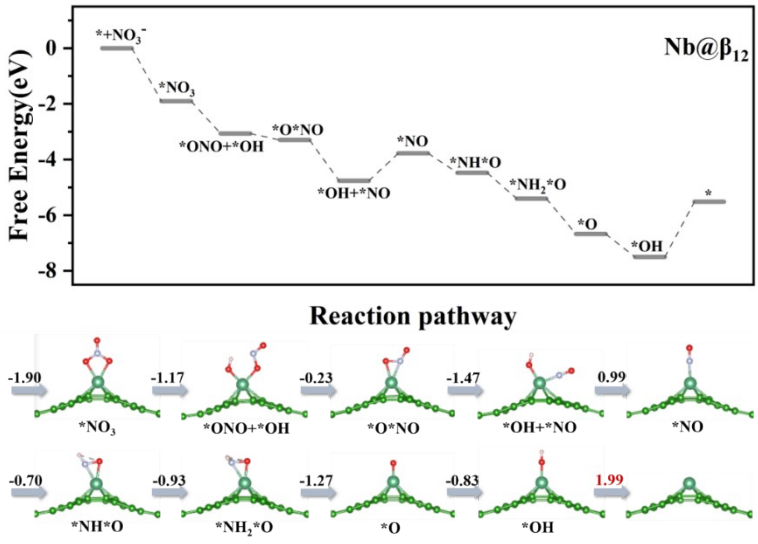

Figure S2-6

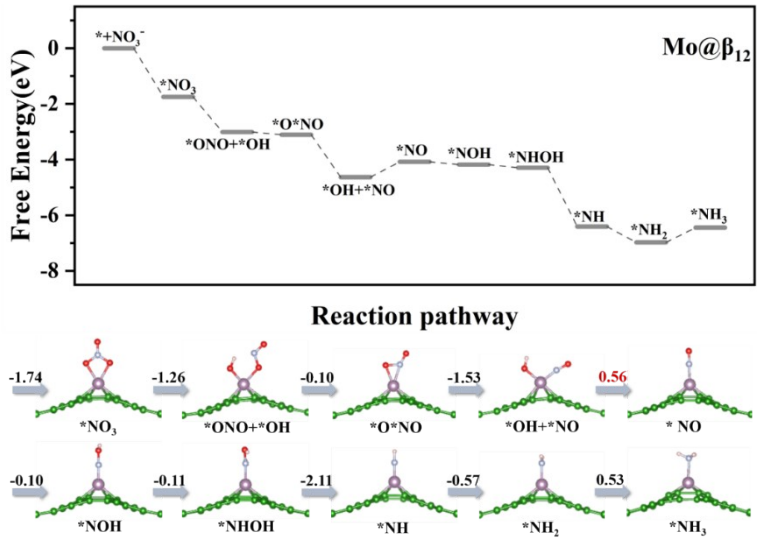

Figure S2-7

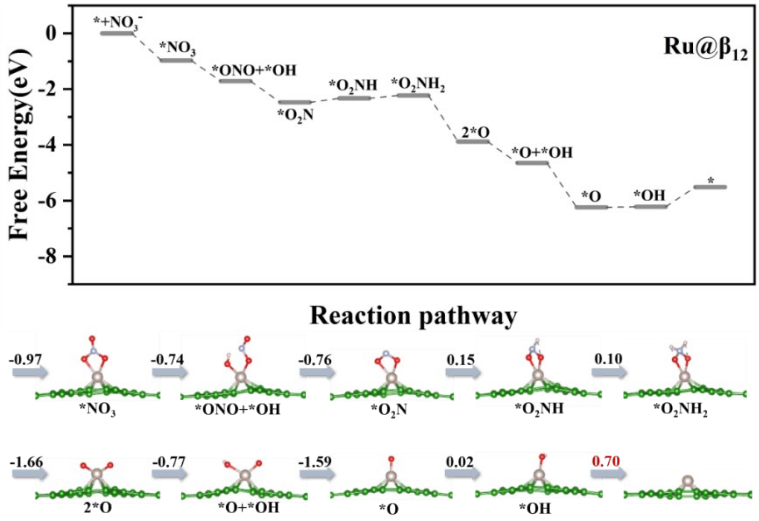

Figure S2-8

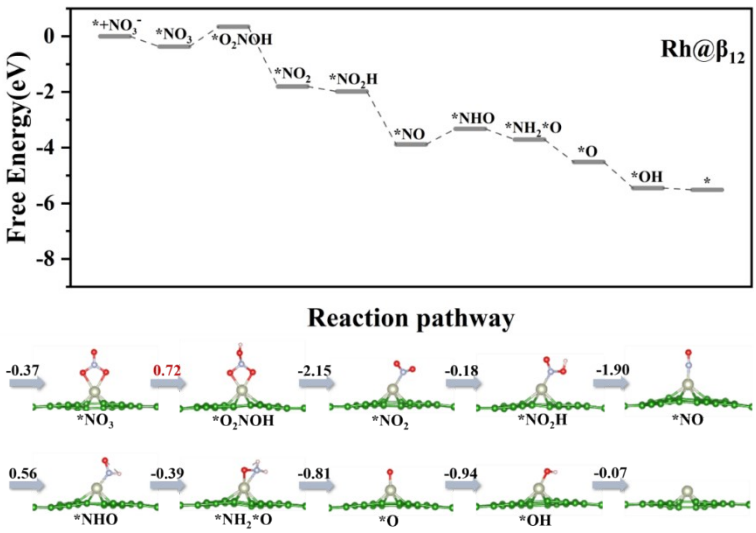

Figure S2-9

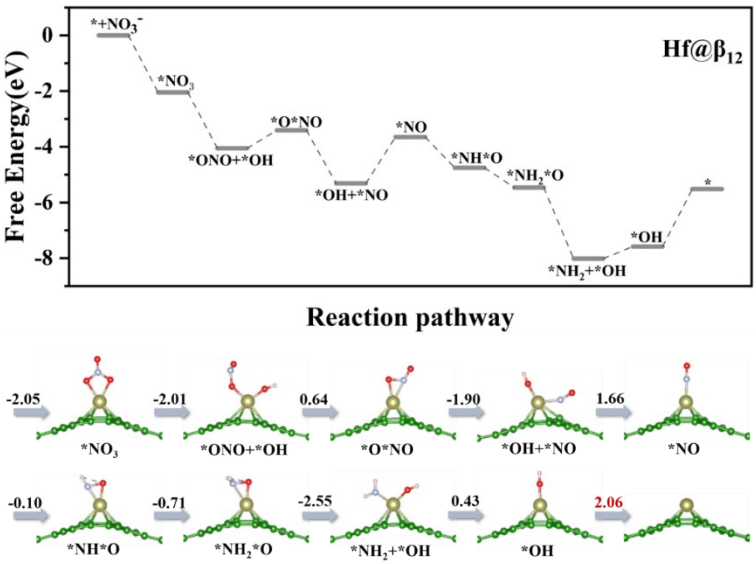

Figure S2-10

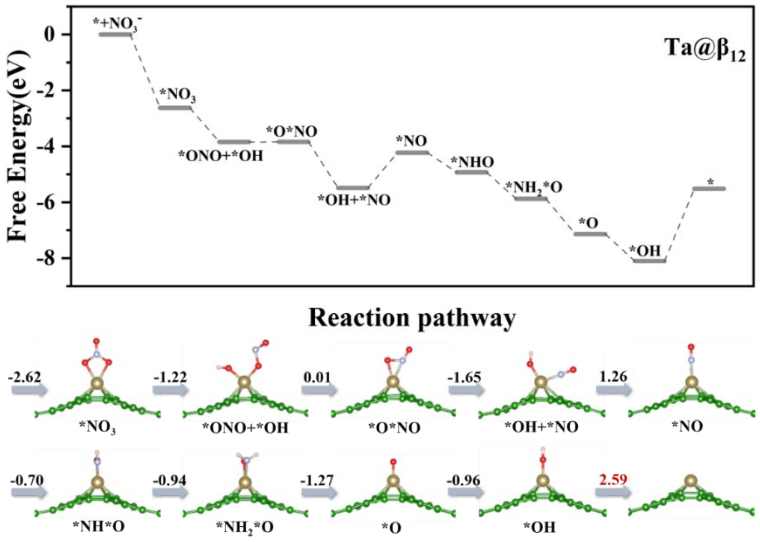

Figure S2-11

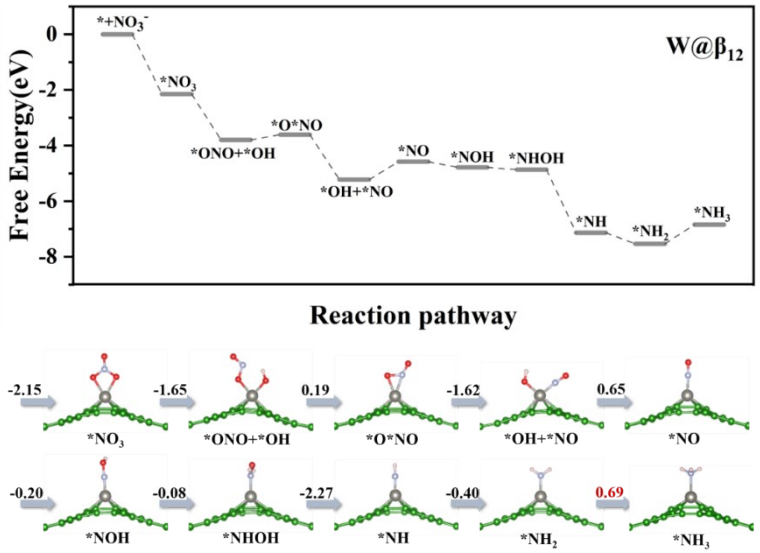

Figure S2-12

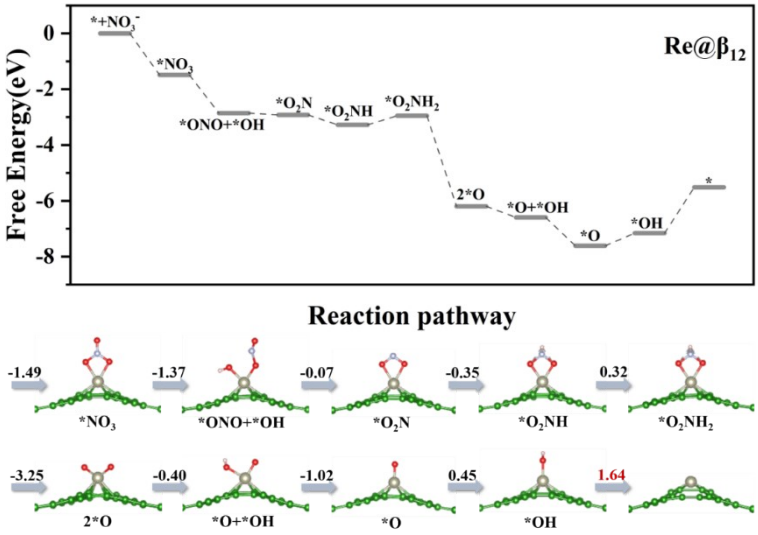

Figure S2-13

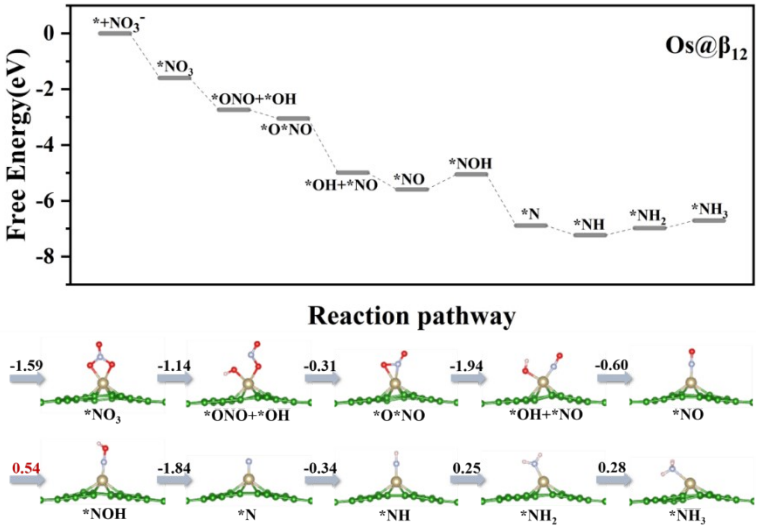

Figure S2-14

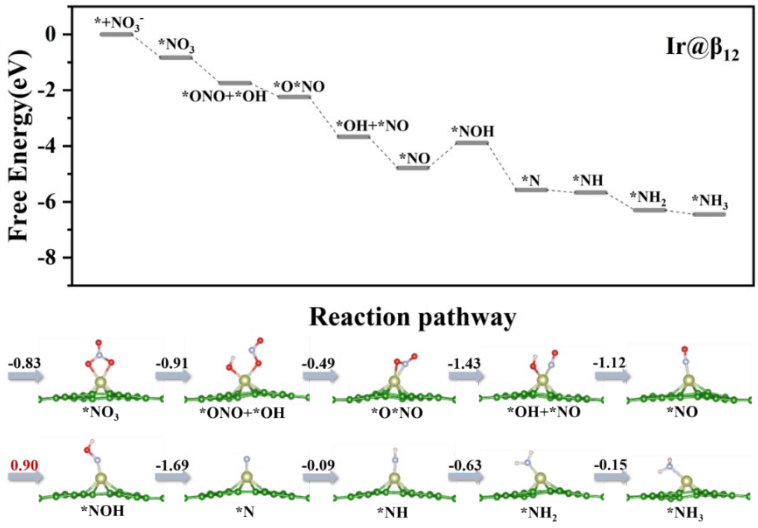

Figure S2-15

Figure S2. Free energy diagrams and the adsorption configurations of reaction intermediates on *M*@β$_{12}$ (excluding Mn@β$_{12}$). The green, red, pale blue and white balls represent B, O, N and H atoms respectively, while other colors denote metal atoms as labeled.

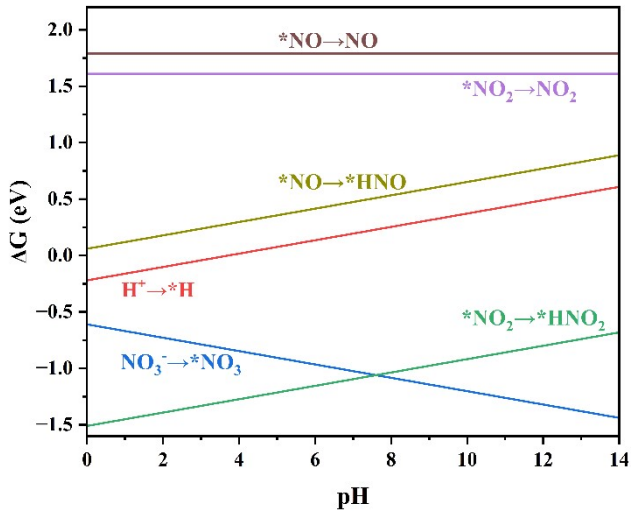

Figure S3 illustrates the Gibbs free energies for the reaction steps NO_3^-→ *NO_3 (blue line), H^+ → *H (red line), *NO → *HNO (olive gold line), *NO → NO (brown line), *NO_2 → *HNO_2 (green line), and *NO_2 → NO_2 (purple line)as a function of pH.

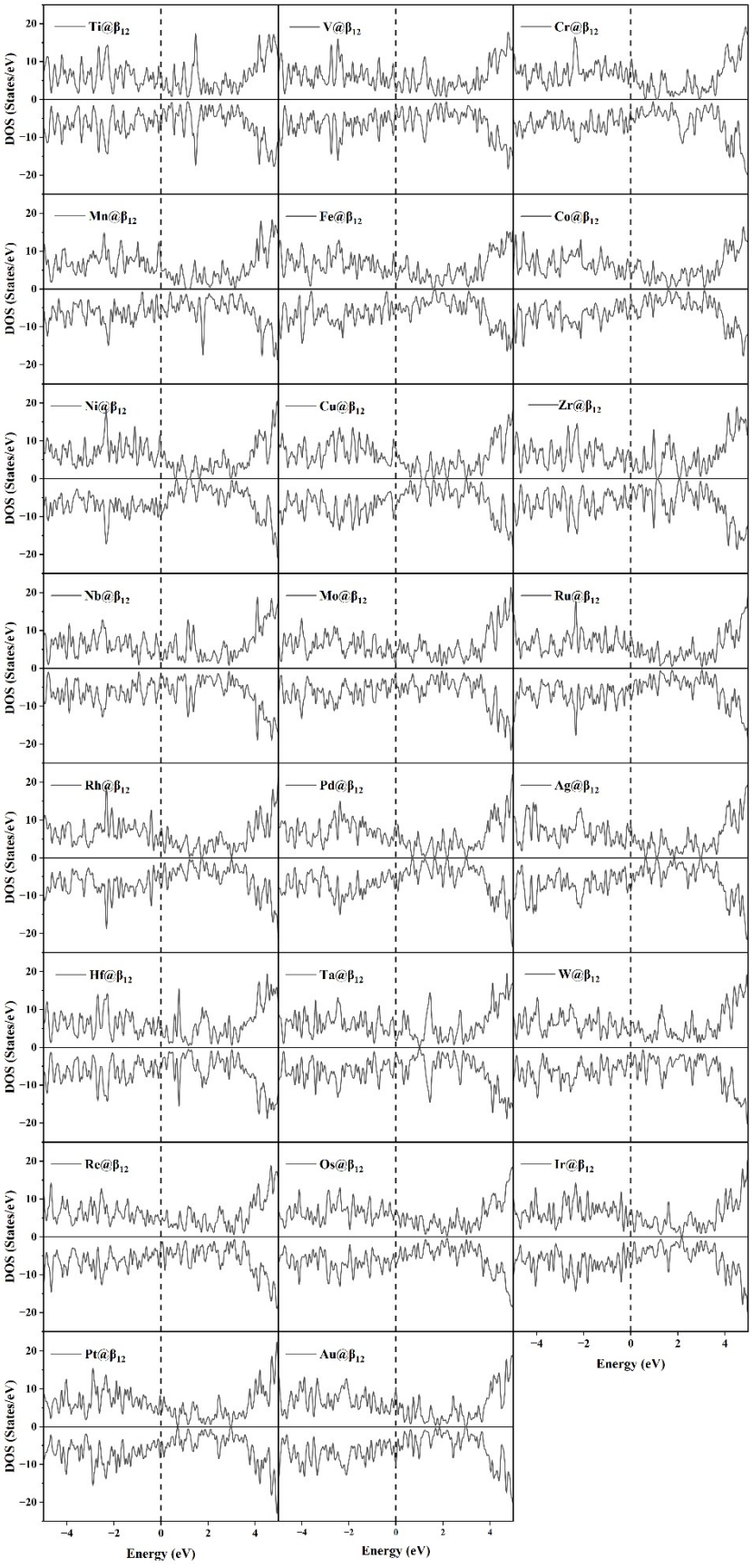

Figure S4. The total DOSs of the $M@\beta_{12}$.

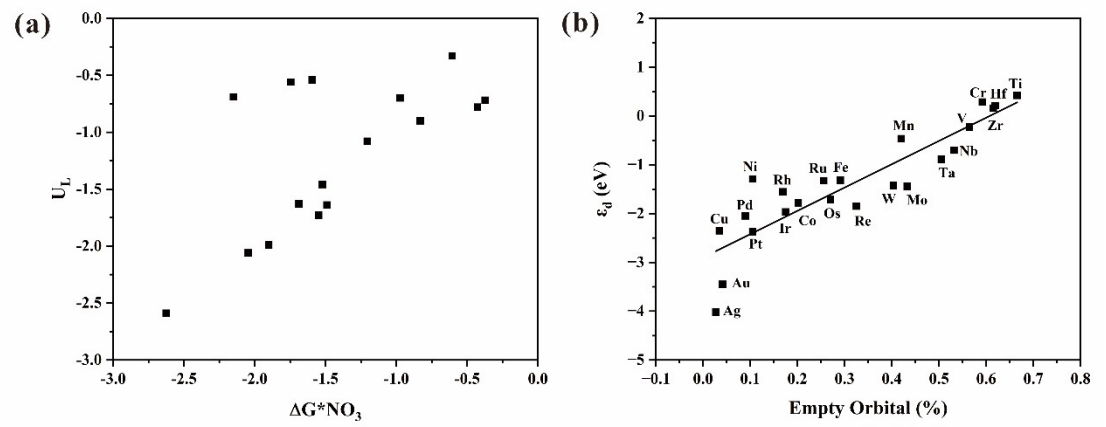

Figure S5. The relationship between U_L and ΔG_{*NO3} (a), and the scaling relationship between the d-band center ε_d and the empty orbitals (b).