SUPPORTING INFORMATION

Revealing the pH-Dependent Mechanism of Nitrate Electrochemical reduction to Ammonia on Single-Atom Catalysts

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PART I. Supplemental Notes

Supplemental Note 1

For the single atom adsorption on basal plane, its thermodynamic stability is judged based on the formation energy E_{form}. When metal atoms are adsorbed on the basal plane of MoS_2, the calculation formula is as follows:

$$E_{form} = E_{TM-MoS_2} - E_{TM} - E_{MoS_2}$$

For replacing Mo or S of the basal plane, the calculation formula is as follows:

$$E_{form} = E_{TM-MoS_2} + E_{TM} - E_{MoS_2} - E_{Mo/S}$$

When the metal atoms are loaded on the molybdenum disulfide edge surface, the formation energy is calculated as follows:

$$E_{form} = E_{TM-MoS_2} - E_{TM} - E_{MoS_2} - 8n * E_S$$

Among them, n refers to the coverage of S atoms, and the values are 12.5%, 25%, 37.5%, 50%. $E_{TM-MoS2}$, E_{TM}, E_{MoS2}, and E_S are the energies of TM-MoS_2, transition metal atom from bulk, MoS_2 slab, and S atom from bulk after considering the coverage of S atoms, respectively."

Supplemental Note 2

To avoid calculating the energy of charged NO_3^- directly, gaseous HNO_3 and H_2 is chosen as a reference instead[1]. The adsorption energy of NO_3^- (ΔG_{*NO3}) is described as

$$\Delta G_{*NO3} = G_{*NO3} - G_{*} - G_{HNO3(g)} + 1/2 G_{H2(g)}$$

where G_{*NO3}, G_{*}, $G_{HNO3(g)}$, and $G_{H2(g)}$ are the Gibbs free energy of NO_3^- adsorbed on substrates, as well as HNO_3 and H_2 molecules in the gas phase, respectively. The adsorption free energy of other intermediates on SACs were also calculated by taking gaseous HNO_3 and H_2 as a reference.

Elementary steps of NO_3RR

$$NO_3^- + H^+ + * \rightarrow NO_3H* \quad \text{R1}$$

$$NO_3H* + H^+ + e^- \rightarrow NO_2* + H_2O \quad \text{R2-1}$$

$$NO_3H* + H^+ + e^- \rightarrow NO_3H_2* \quad \text{R2-2}$$

$$NO_3H* + H^+ + e^- \rightarrow O_2N* + H_2O \quad \text{R2-3}$$

$$NO_2* + H^+ + e^- \rightarrow NO_2H* \quad \text{R3-1}$$

$$NO_3H_2* + H^+ + e^- \rightarrow O_2NH* + H_2O \quad \text{R3-2}$$

$$O_2N* + H^+ + e^- \rightarrow O_2NH* \quad \text{R3-3}$$

$$NO_2H* + H^+ + e^- \rightarrow NO* + H_2O \quad \text{R4-1}$$

$$NO_2H* + H^+ + e^- \rightarrow N*O* + H_2O \quad \text{R4-2}$$

$$O_2NH* + H^+ + e^- \rightarrow ON* + H_2O \quad \text{R4-3}$$

$$NO* + H^+ + e^- \rightarrow NOH* \quad \text{R5-1}$$

$$N*O* + H^+ + e^- \rightarrow N*OH* \quad \text{R5-2}$$

$$ON* + H^+ + e^- \rightarrow ONH* \quad \text{R5-3}$$

$$NOH* + H^+ + e^- \rightarrow N* + H_2O \quad \text{R6-1}$$

$$N*OH* + H^+ + e^- \rightarrow N* + H_2O \quad \text{R6-2}$$

$$ONH* + H^+ + e^- \rightarrow OHNH* \quad \text{R6-3}$$

$$N* + H^+ + e^- \rightarrow NH* \quad \text{R7-1}$$

$$OHNH* + H^+ + e^- \rightarrow NH* + H_2O \quad \text{R7-2}$$

$$NH* + H^+ + e^- \rightarrow NH_2* \quad \text{R8}$$

$$NH_2* + H^+ + e^- \rightarrow NH_3* \quad \text{R9}$$

$$NH_3* \rightarrow NH_3(g) + * \quad (PH=9.27\text{-}14) \quad \text{R10-1}$$

$$NH_3* + H^+ \rightarrow NH_4^+ + * \quad (PH=0\text{-}9.27) \quad \text{R10-2}$$

For each intermediate, the calculation of free energy is shown as follow.

$G(*)=E(*)+ZPE+T\Delta S$

For each elementary step, the Gibbs reaction free energy ΔG is the difference between the free energies of the reactants and products, and is expressed as follows. Since electron transfer is involved in the elementary reaction step and the reaction uses RHE

as the reference electrode, $G(H^+ + e^-) = 1/2G_{H2}$.

$\Delta G_1^0 = G(NO_3H^*) - G(NO_3^-) - G(H^+ + e^-)$

$\Delta G_{2\text{-}1}^0 = G(NO_2^*) + G(H_2O) - G(NO_3H^*) - G(H^+ + e^-)$

$\Delta G_{2\text{-}2}^0 = G(NO_3H_2^*) - G(NO_3H^*) - G(H^+ + e^-)$

$\Delta G_{2\text{-}3}^0 = G(O_2N^*) + G(H_2O) - G(NO_3H^*) - G(H^+ + e^-)$

$\Delta G_{3\text{-}1}^0 = G(NO_2H^*) - G(NO_2^*) - G(H^+ + e^-)$

$\Delta G_{3\text{-}2}^0 = G(O_2NH^*) + G(H_2O) - G(NO_3H_2^*) - G(H^+ + e^-)$

$\Delta G_{3\text{-}3}^0 = G(O_2NH^*) - G(O_2N^*) - G(H^+ + e^-)$

$\Delta G_{4\text{-}1}^0 = G(NO^*) + G(H_2O) - G(NO_2H^*) - G(H^+ + e^-)$

$\Delta G_{4\text{-}2}^0 = G(N^*O^*) + G(H_2O) - G(NO_2H^*) - G(H^+ + e^-)$

$\Delta G_{4\text{-}3}^0 = G(ON^*) + G(H_2O) - G(O_2NH^*) - G(H^+ + e^-)$

$\Delta G_{5\text{-}1}^0 = G(NOH^*) - G(NO^*) - G(H^+ + e^-)$

$\Delta G_{5\text{-}2}^0 = G(N^*OH^*) - G(N^*O^*) - G(H^+ + e^-)$

$\Delta G_{5\text{-}3}^0 = G(ONH^*) - G(ON^*) - G(H^+ + e^-)$

$\Delta G_{6\text{-}1}^0 = G(N^*) + G(H_2O) - G(NOH^*) - G(H^+ + e^-)$

$\Delta G_{6\text{-}2}^0 = G(N^*) + G(H_2O) - G(N^*OH^*) - G(H^+ + e^-)$

$\Delta G_{6\text{-}3}^0 = G(OHNH^*) - G(ONH^*) - G(H^+ + e^-)$

$\Delta G_{7\text{-}1}^0 = G(NH^*) - G(N^*) - G(H^+ + e^-)$

$\Delta G_{7\text{-}2}^0 = G(NH^*) + G(H_2O) - G(OHNH^*) - G(H^+ + e^-)$

$\Delta G_8^0 = G(NH_2^*) - G(NH^*) - G(H^+ + e^-)$

$\Delta G_9^0 = G(NH_3^*) - G(NH_2^*) - G(H^+ + e^-)$

$\Delta G_{10\text{-}1}^0 = G(^*) + G(NH_3) - G(NH_3^*)$

$\Delta G_{10\text{-}2}^0 = G(^*) + G(NH_4^+) - G(NH_3^*) - G(H^+)$

Correction of pH to Gibbs free energy[2], where k_B is the Boltzmann constant and T is the room temperature.

$$\Delta G_1 = \Delta G_1^0$$

$$\Delta G_2 = \Delta G_2^0 + k_B T \ln 10 \times pH$$

$$\Delta G_3 = \Delta G_3^0 + k_B T \ln 10 \times pH$$

$$\Delta G_4 = \Delta G_4^0 + k_B T \ln 10 \times pH$$

$$\Delta G_5=\Delta G_5^0+k_BTln10\times pH$$

$$\Delta G_6=\Delta G_6^0+k_BTln10\times pH$$

$$\Delta G_7=\Delta G_7^0+k_BTln10\times pH$$

$$\Delta G_8=\Delta G_8^0+k_BTln10\times pH$$

$$\Delta G_9=\Delta G_9^0+k_BTln10\times pH$$

$$\Delta G_{10}=\Delta G_{10}^0$$

Supplemental Note 3

HER is regarded as the most competitive reaction to NO_3RR[3]. If we assume: (1) the mass and electron transfer are not the rate determining factors for both HER and NO_3RR, (2) only HER and NO_3RR are competing reactions, and (3) the selectivity of NO_3RR in comparison to HER could be estimated by Boltzmann distribution, the Faradaic efficiency of NO_3RR can be expressed as:

$$f_{\text{NO3RR}} = \frac{1}{1+e^{\frac{-\delta G}{kBT}}} \times 100\%$$

where δG is Gibbs free energy difference between HER and NO_3RR potential determining step, k_B is the Boltzmann constant, and T is the room temperature.

Supplemental Note 4

We evaluated the thermodynamic and electrochemical stabilities of these 16 SA-MoS_2 monolayers by the formation energy E_f and dissolution potential U_{diss}, which are defined as[4]

$$E_f = E_{TM-MoS2} - E_{MoS2} - E_M$$

$$U_{diss} = U^{\circ}_{diss}(metal, bulk) - E_f/ne$$

where E_M is the total energy of metal atom in its most stable bulk structure, $E_{\text{TM-MoS2}}$ and E_{MoS2} are the total energies of SA-MoS_2 and substrate, $U^{\circ}_{diss}(metal, bulk)$ and n are the standard dissolution potential from bulk metal to solute and the number of electrons involved in the dissolution process, respectively. The values of E_f and U_{diss} are listed in **Table S28.**

Supplemental Note 5

In this section, we construct a chemical-potential-based thermodynamic model to explore how to improve the stability of SAs under realistic conditions. Its chemical potential μ_{NP} (R) can be expressed by the Gibbs−Thomson (G-T) relation, as shown in[5]

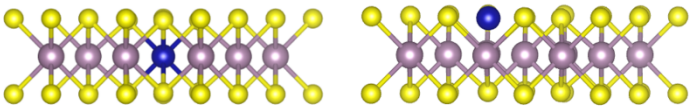
$$\mu_{Np}(R) = 2\,\Omega\gamma_{me}/R$$

$$\mu_{SA} \approx E_{SA/ox} - E_B - E_{ox}$$

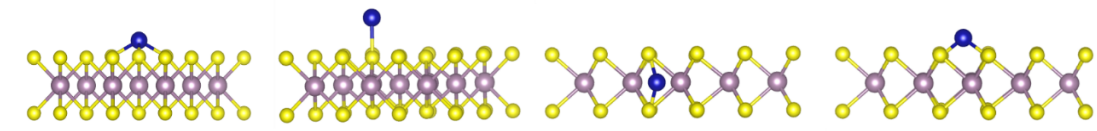
$$\Delta E^f{}_{SA}(R) = \mu SA - \mu Np(R)$$

where $E_{SA/ox}$ is the total energy of metal SA absorbed on an oxide surface, E_B the energy of bulk metal per atom, and E_{ox} the energy of the slab.

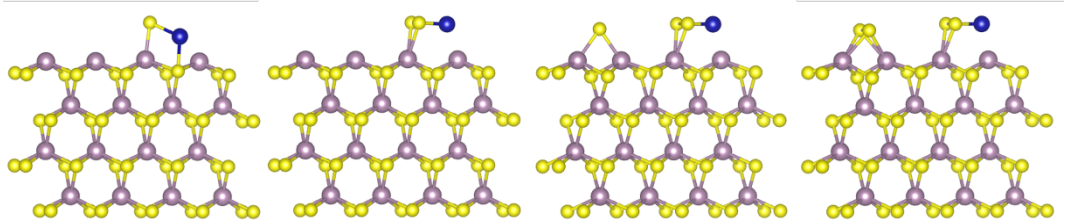
PART II. Supplemental Figures



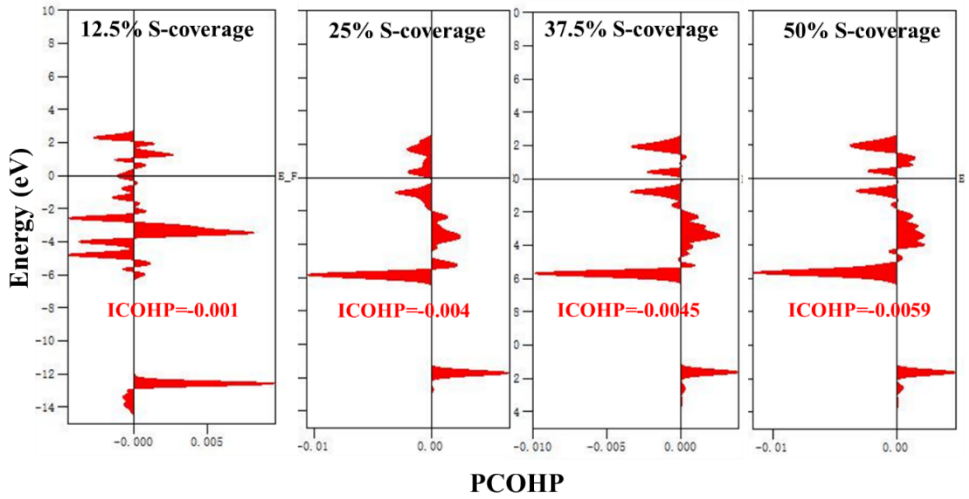
Supplementary Figure 1. Side view of the structures of TM (Fe, Co, Ni, Mn) replacing Mo and S atom of basal-MoS_2.



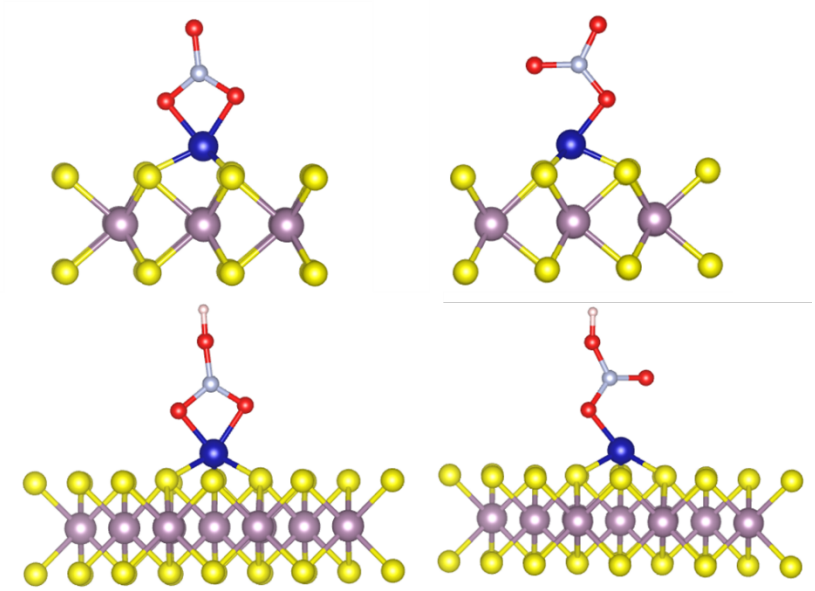
Supplementary Figure 2. Side view of the structures of TM (Fe, Co, Ni, Mn) adsorbed on different sites of basal-MoS_2.



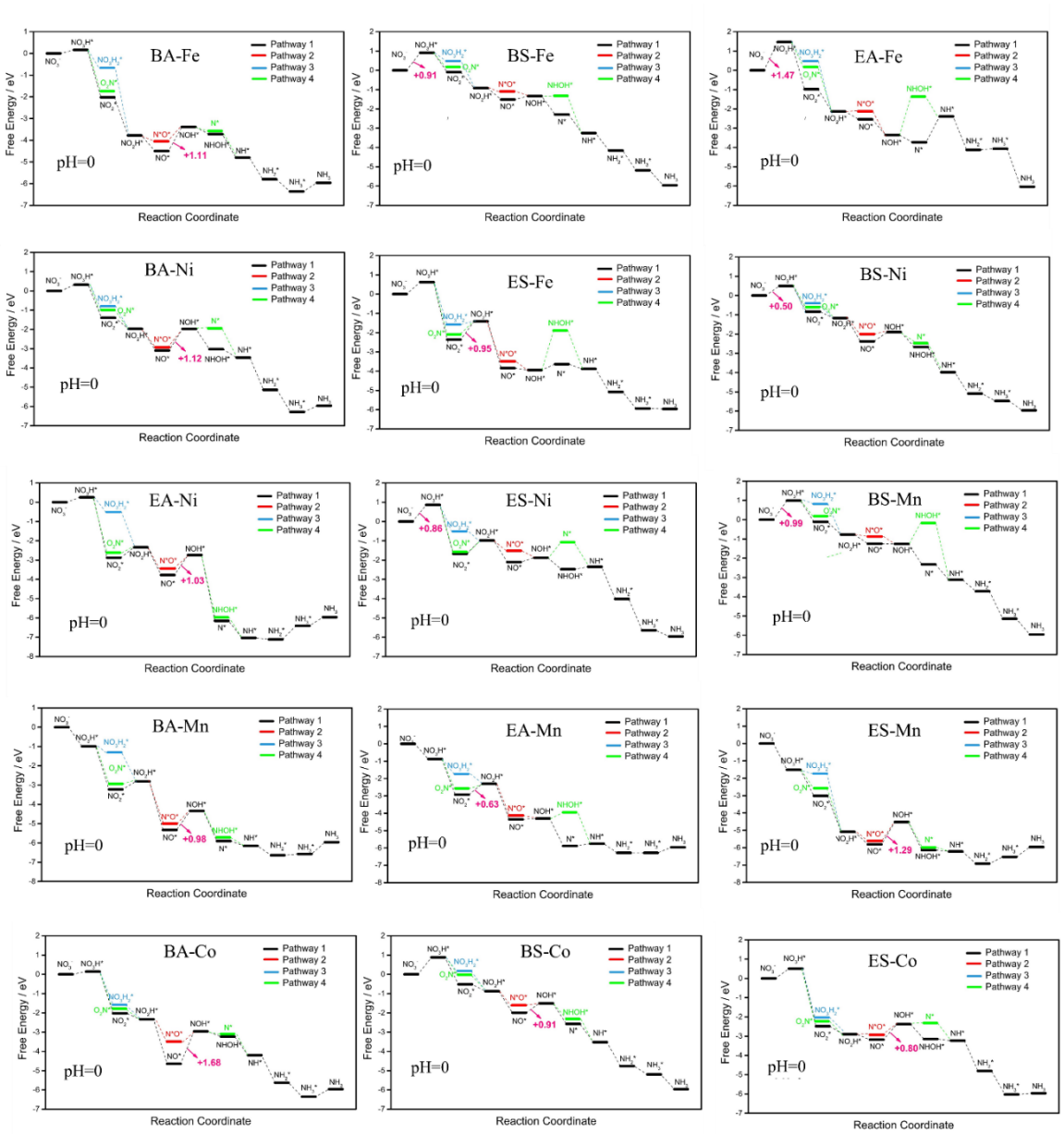
Supplementary Figure 3. Side view of the structures of TM (Fe, Co, Ni, Mn) embedded on different coverage of S atoms of edge-MoS_2.



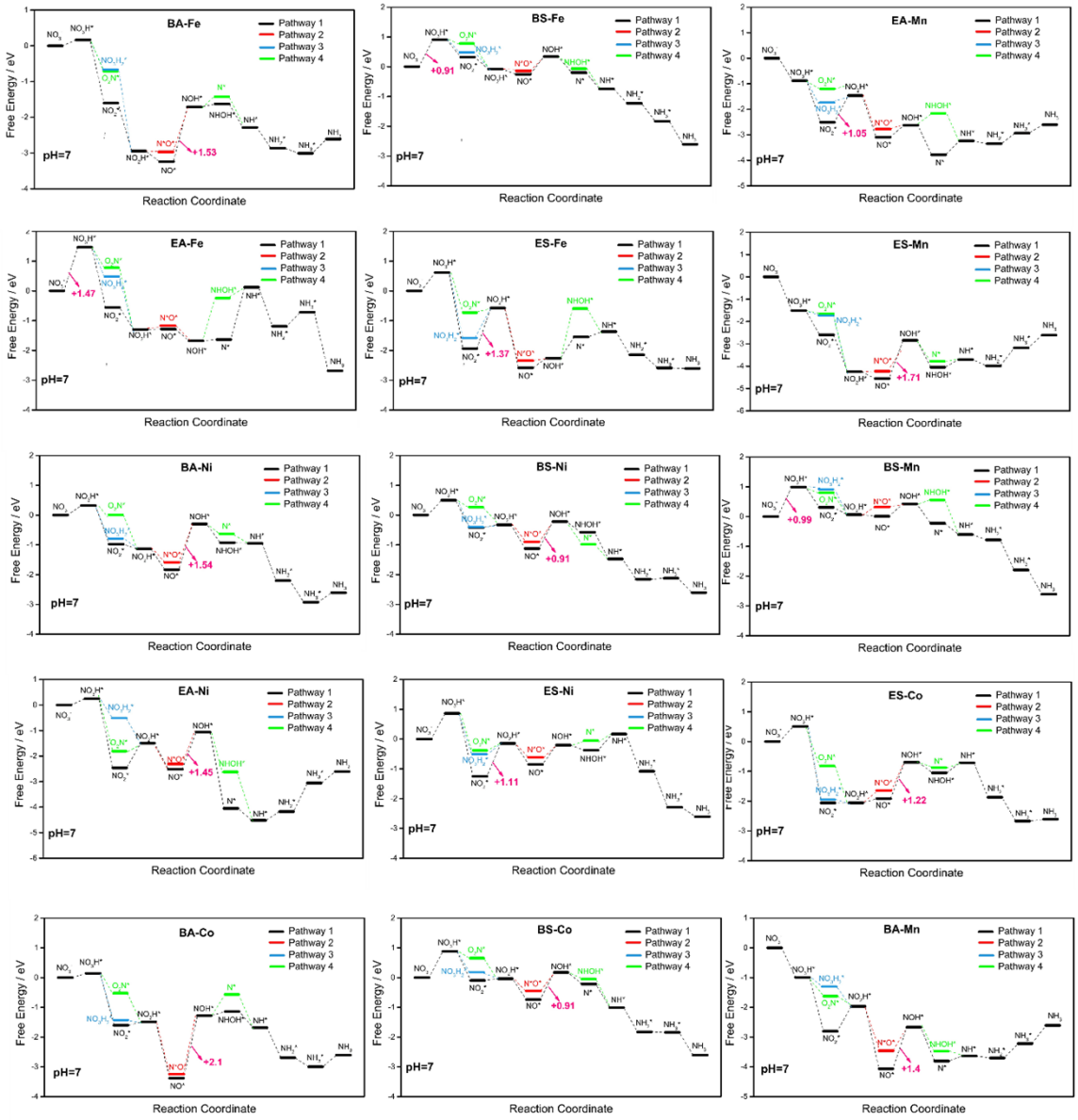
Supplementary Figure 4. The crystal orbital Hamilton populations (COHPs) of Co adsorbed on different coverage of S atoms of edge-MoS_2. The bonding contribution of Co-S in COHP are depicted by red.



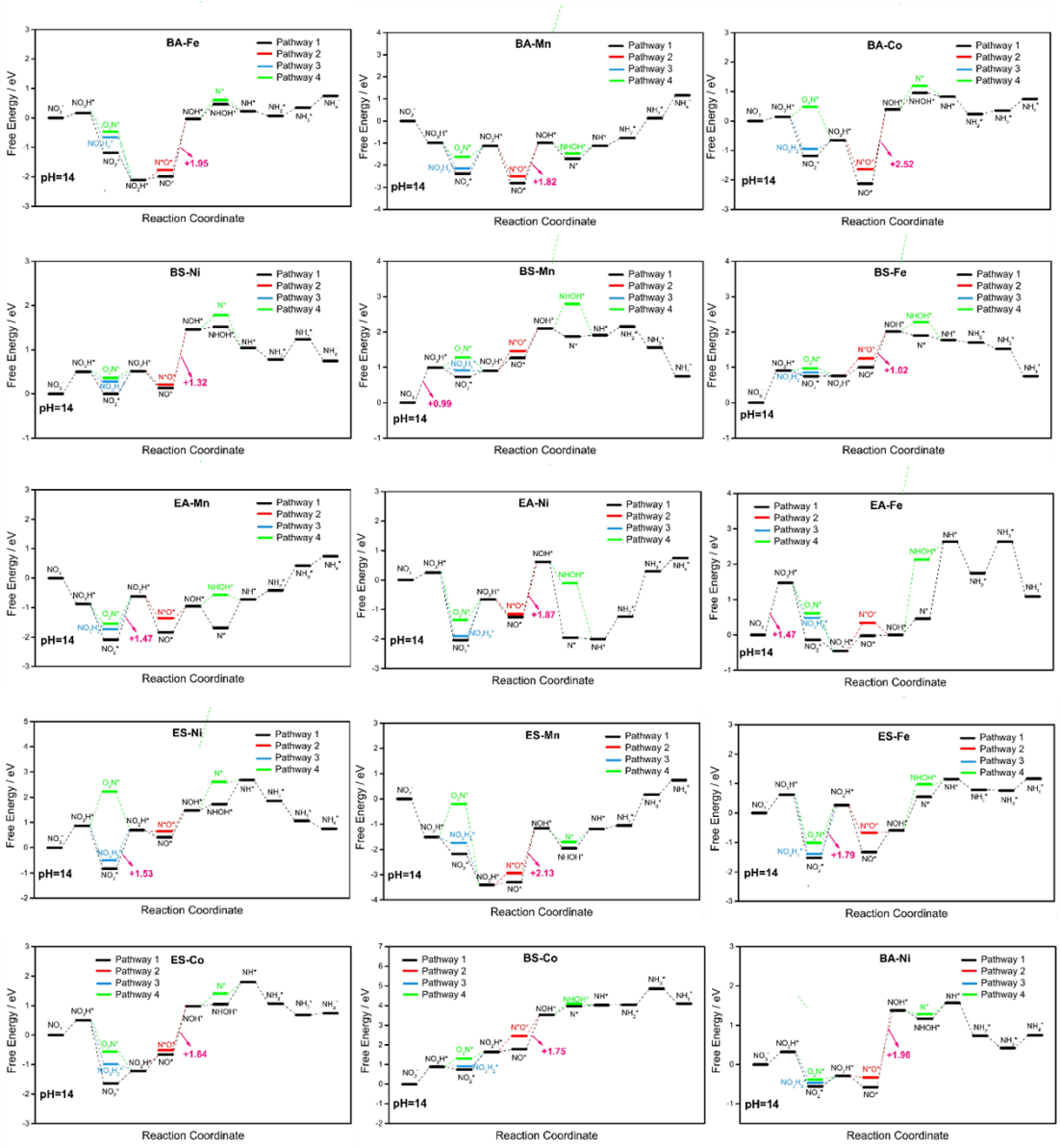
Supplementary Figure 5. Two configurations (1-O, 2-O) of NO_3 and NO_3H. The spheres with various colors represent Metal (blue), O (red), N (grey), and H (white).



Supplementary Figure 6. Free energy diagrams of NO_3RR via the four pathways on SA-MoS_2 at pH=0, respectively.



Supplementary Figure 7. Free energy diagrams of NO_3RR via the four pathways on SA-MoS_2 at pH=7, respectively.



Supplementary Figure 8. Free energy diagrams of NO_3RR via the four pathways on SA-MoS_2 at pH=14, respectively.

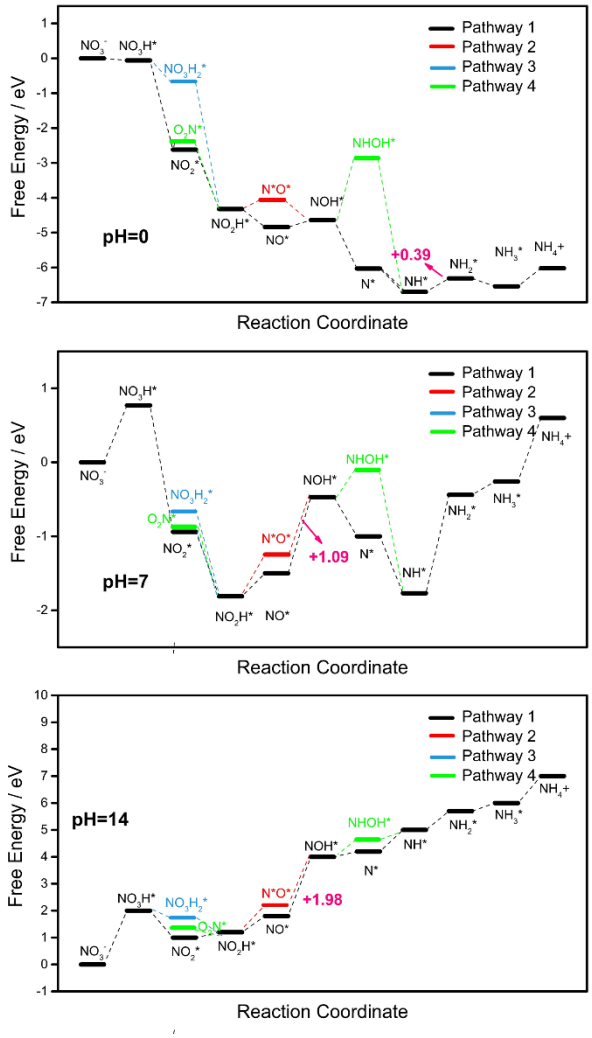
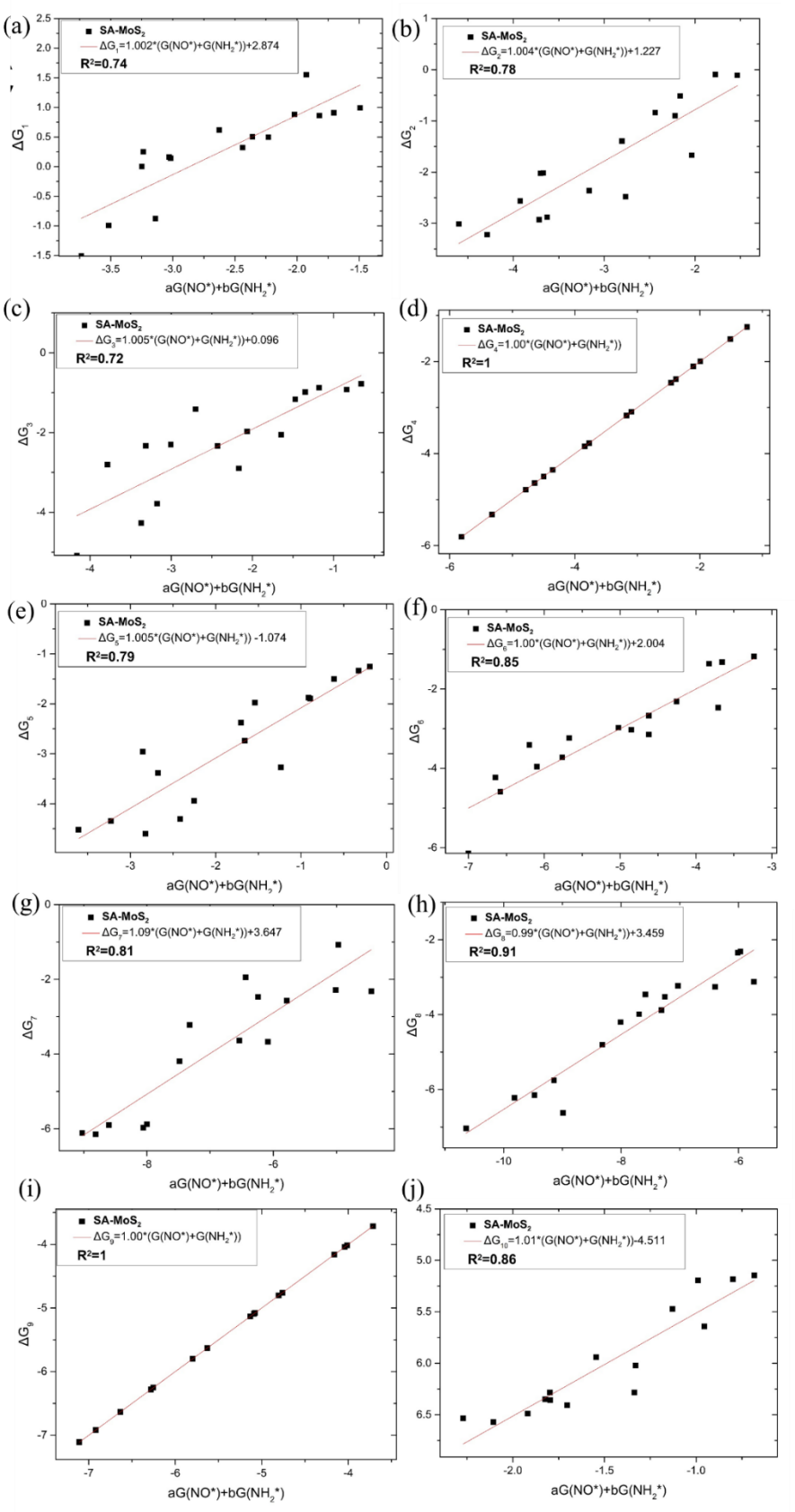
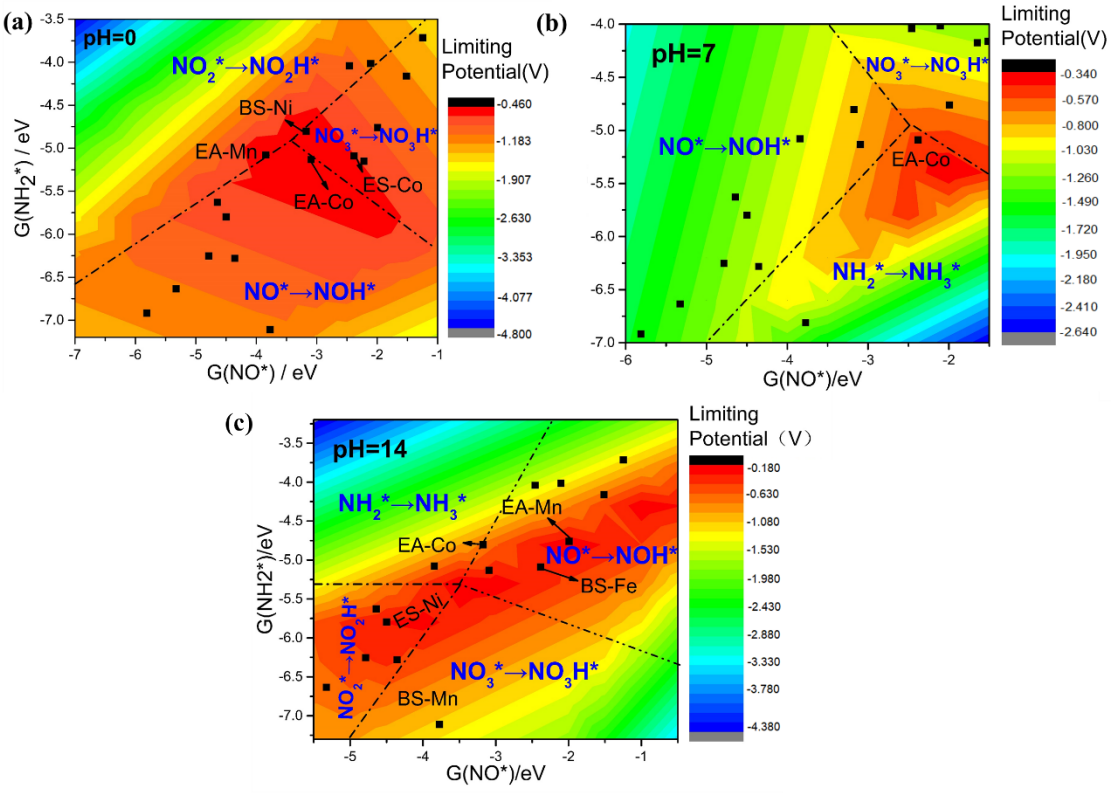


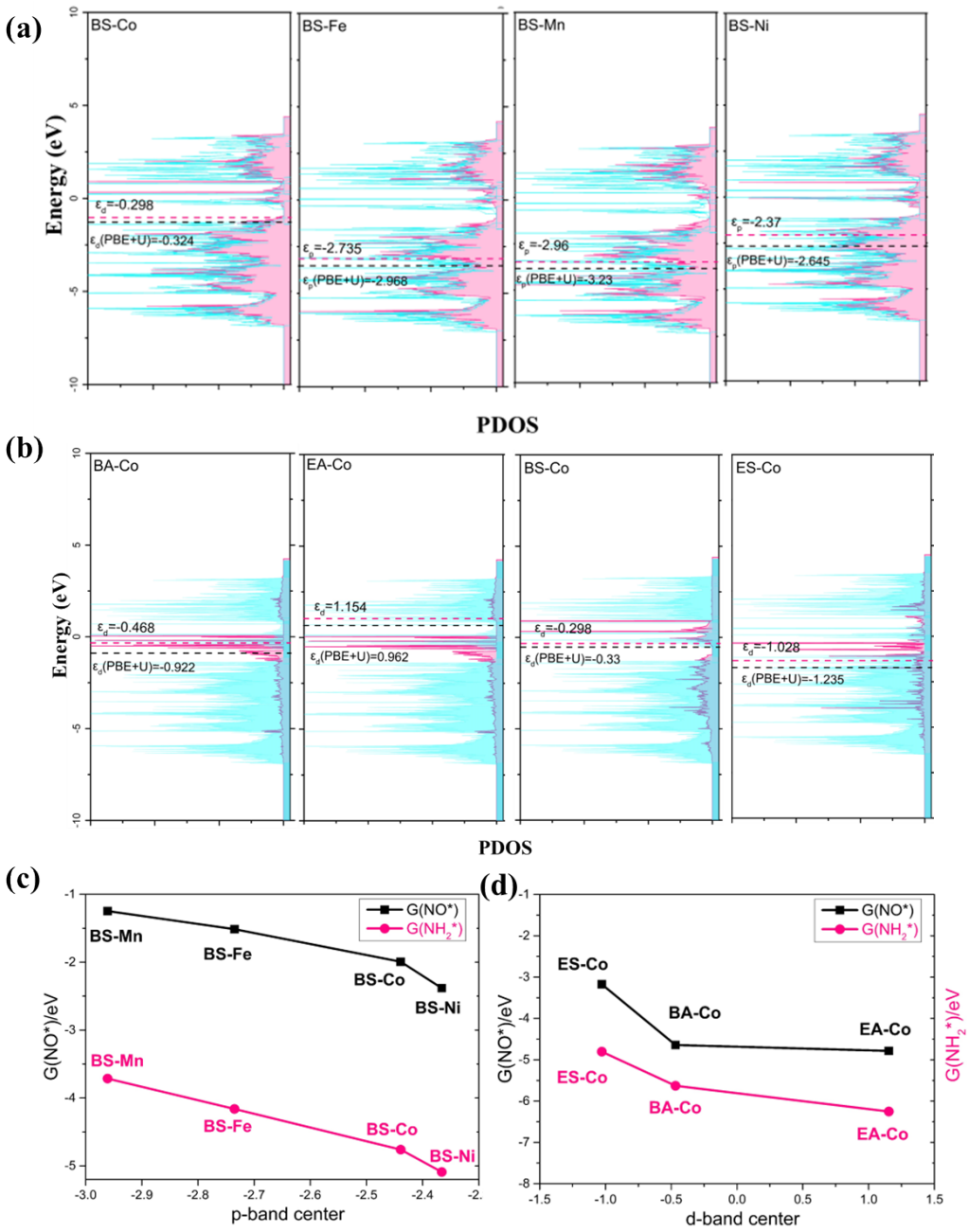
Figure S9. Free energies diagram of NO_3RR on EA-Co derived from PBE+U method. Four kinds of NO_3RR pathways at (a) pH = 0, (b) pH = 7, and (c) pH = 14.



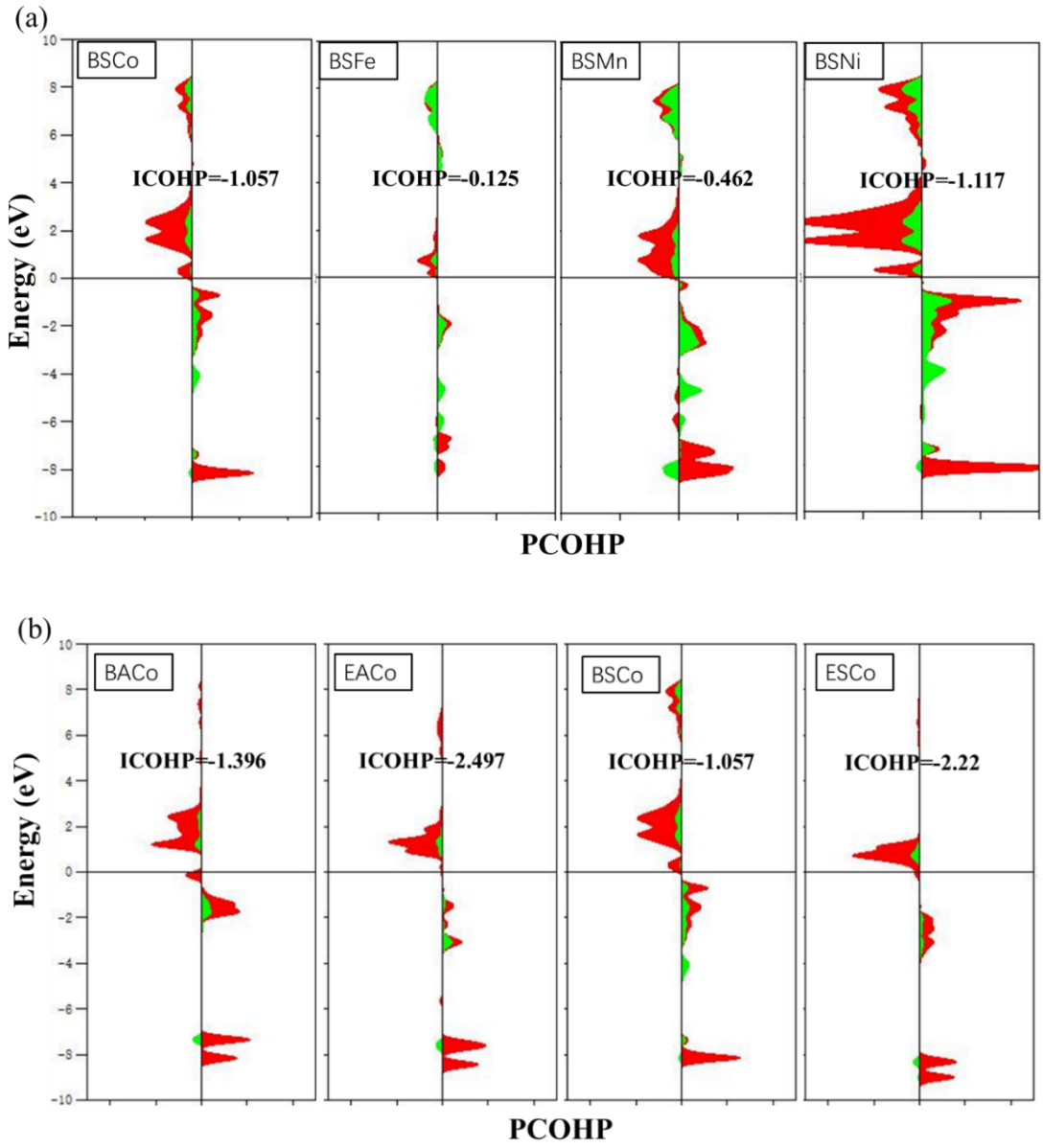
Supplementary Figure 10. The determined BEP scaling relations between (G_{NO*}, G_{NH2*}) and $\Delta G_{1\text{-}10}$ for the nitrate reduction process. The parameters of the linear fits are provided.



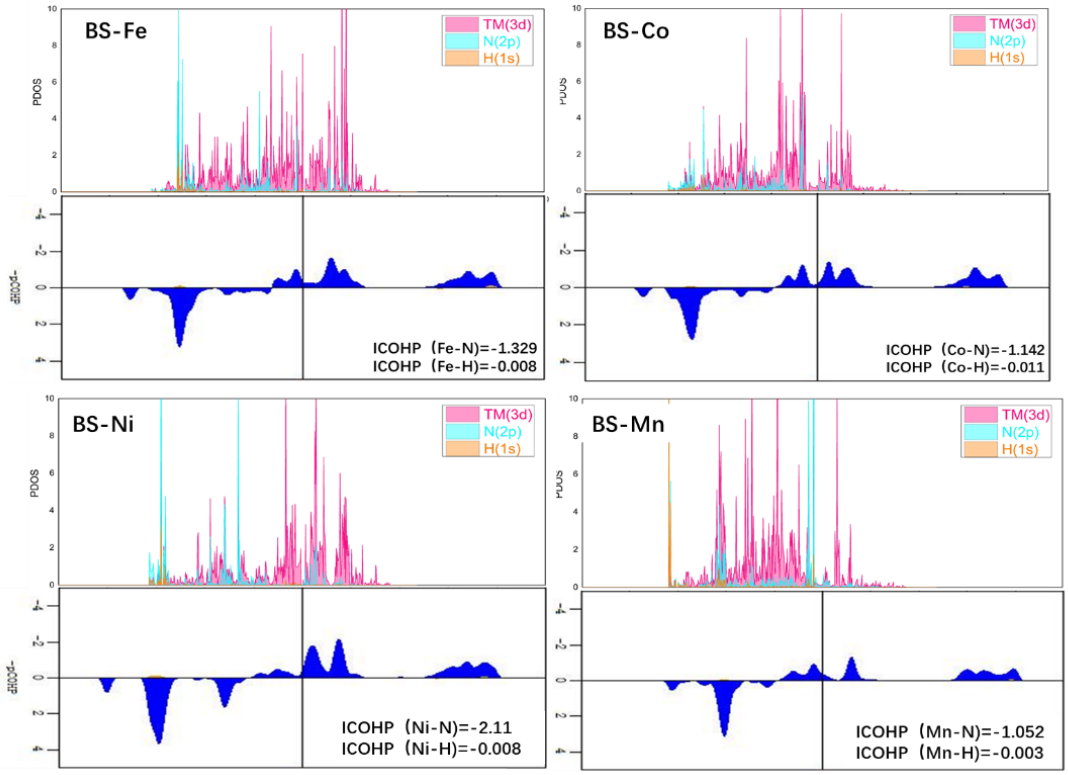
Supplementary Figure 11. Contour plot of limiting potential (v.s. RHE) as a function of the Gibbs adsorption free energy of *NO (G(NO*)) and *NH_2 (G(NH_2*)) at (b) pH = 0, (c) pH = 7, and (d) pH = 14.



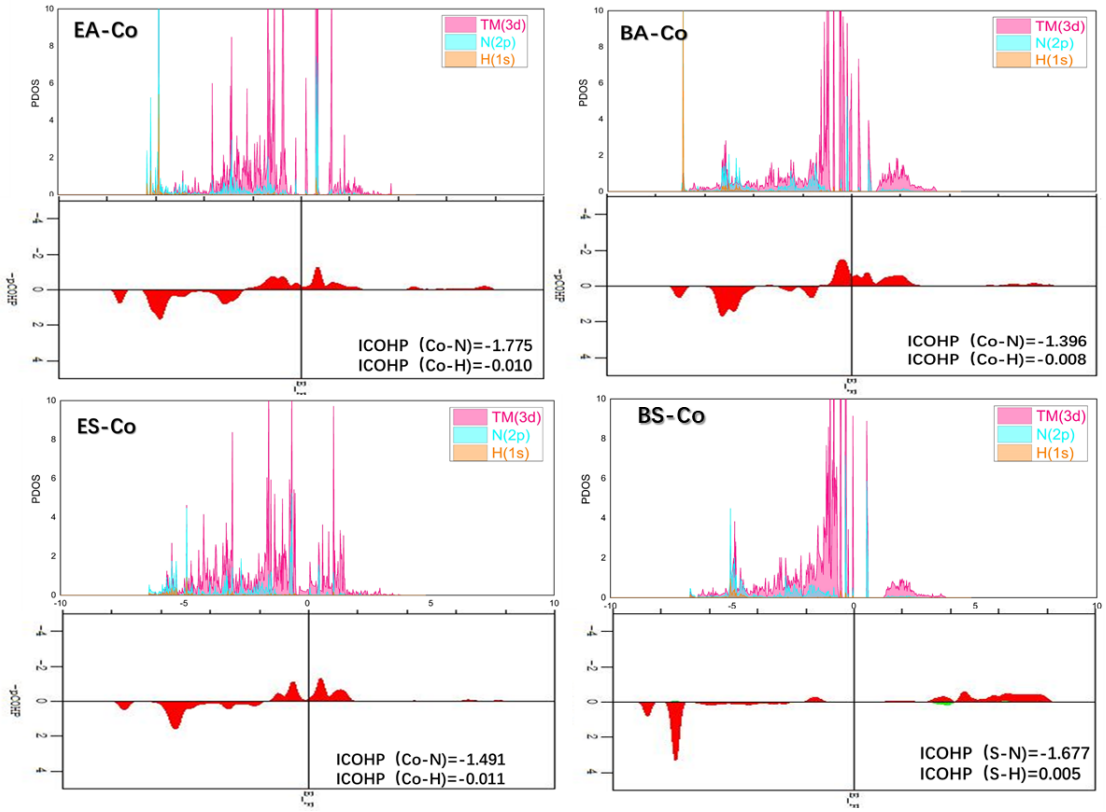
Supplementary Figure 12. a) The computed partial density of states (PDOS) of p-orbitals of S atom in BS-TM (TM=Fe, Co, Ni, Mn). b) The computed partial density of states (PDOS) of d-orbitals of Co atom in ES, BS, BA, EA-Co. c) Correlation between the p-band center of S atoms for BS-TM and G(NO*), G(NH_2*). The computed partial density of states (PDOS) by PBE and PBE+U methods are depicted by pink and blue, respectively. d) Correlation between the d-band center of Co single atoms on diverse support sites and G(NO*), G(NH_2*).



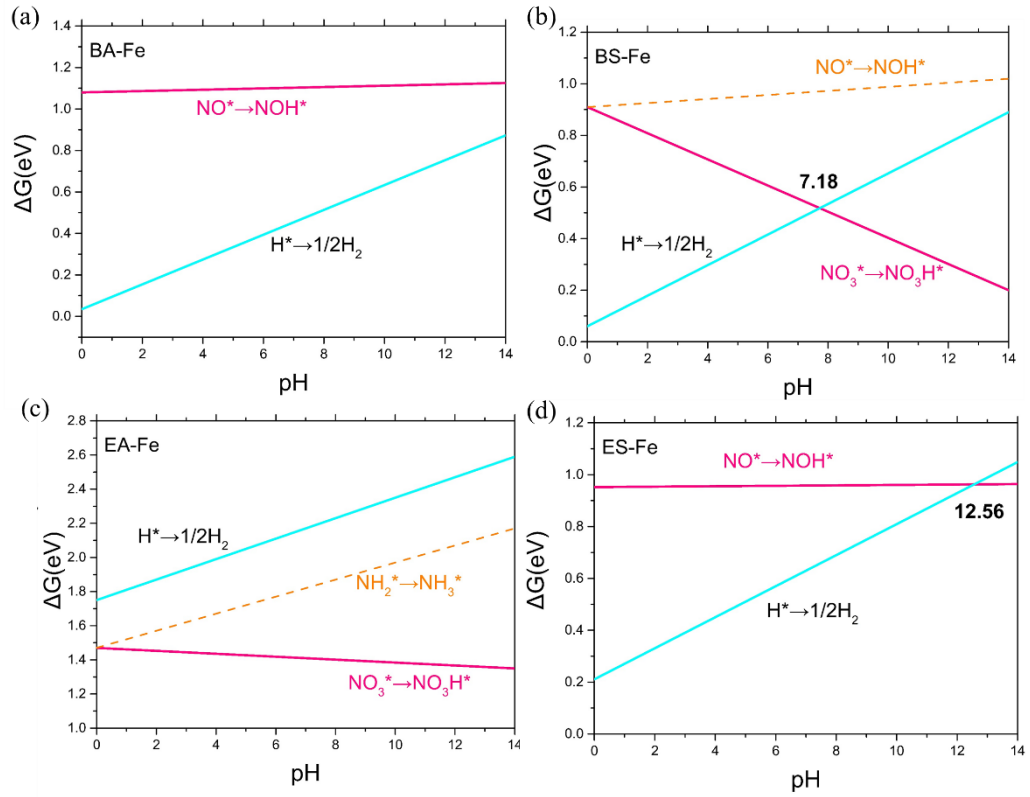
Supplementary Figure 13. The crystal orbital Hamilton populations (COHPs) of NO* in BS-TM (TM=Fe, Co, Ni, Mn) and ES, BS, BA, EA-Co. The bonding contribution of N and O in COHP are depicted by red and green, respectively.



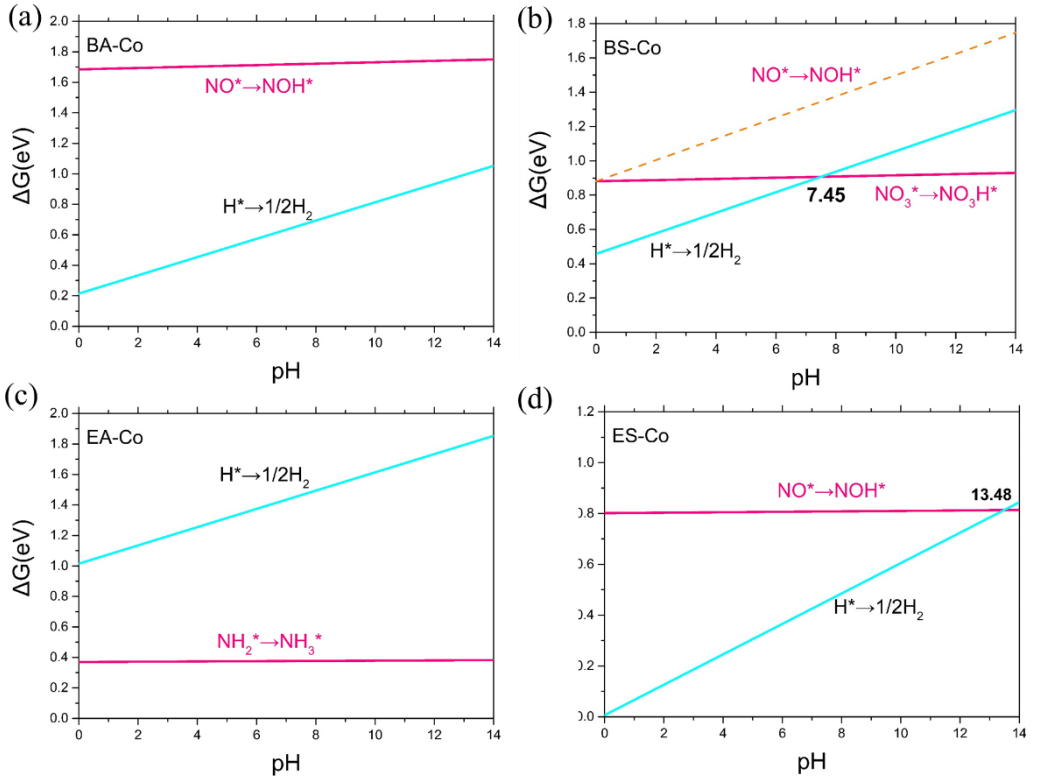
Supplementary Figure 14. The computed partial density of states (PDOS) and the crystal orbital Hamilton populations (COHPs) of NH_2* in BS-TM (TM=Fe, Co, Ni, Mn). The bonding contribution of N and H in COHP are depicted by blue and orange, respectively.



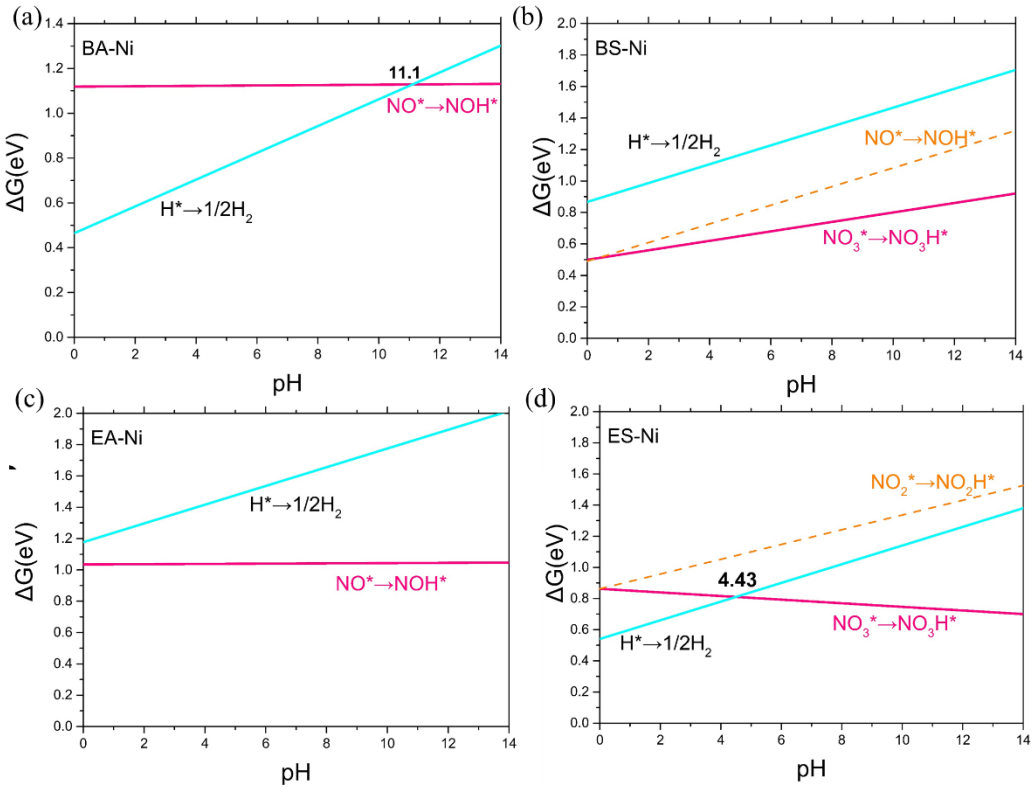
Supplementary Figure 15. The computed partial density of states (PDOS) and the crystal orbital Hamilton populations (COHPs) of NH_2* in EA, BA, ES, BS-Co. The bonding contribution of N and H in COHP are depicted by red and green, respectively.



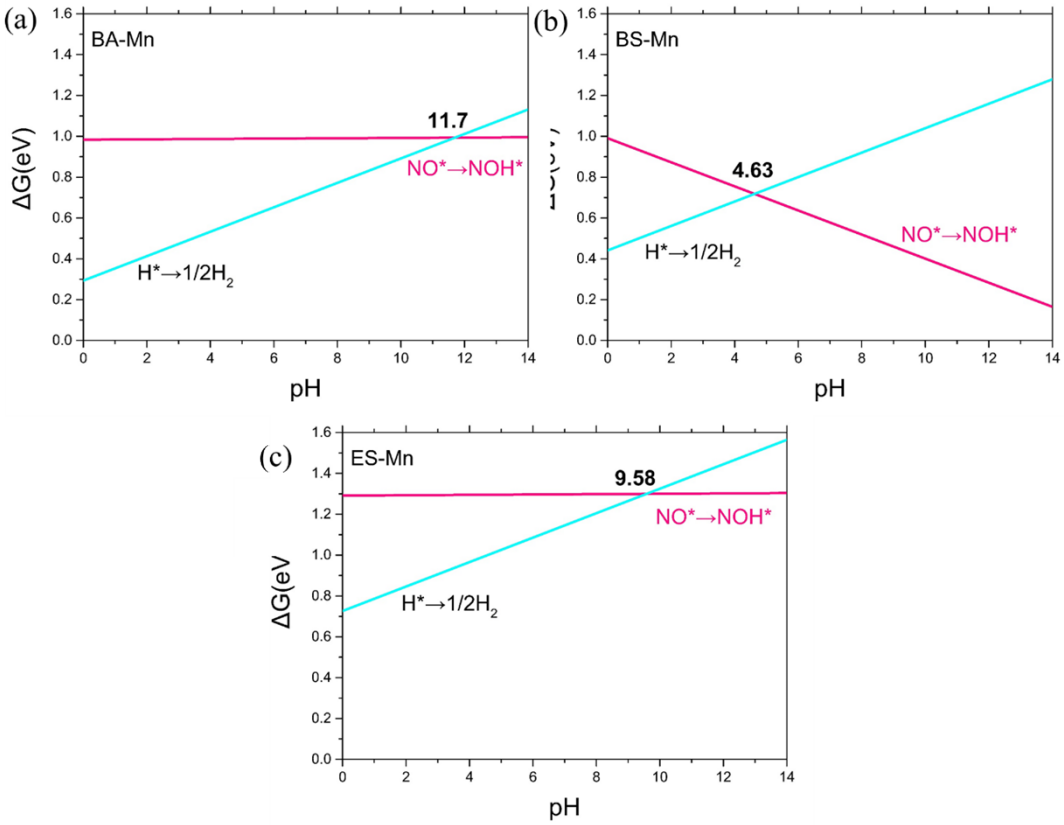
Supplementary Figure 16. Competing relationship between NO_3RR and HER on (a) BA-Fe, (b) BS-Fe, (c) EA-Fe and (d) ES-Fe.



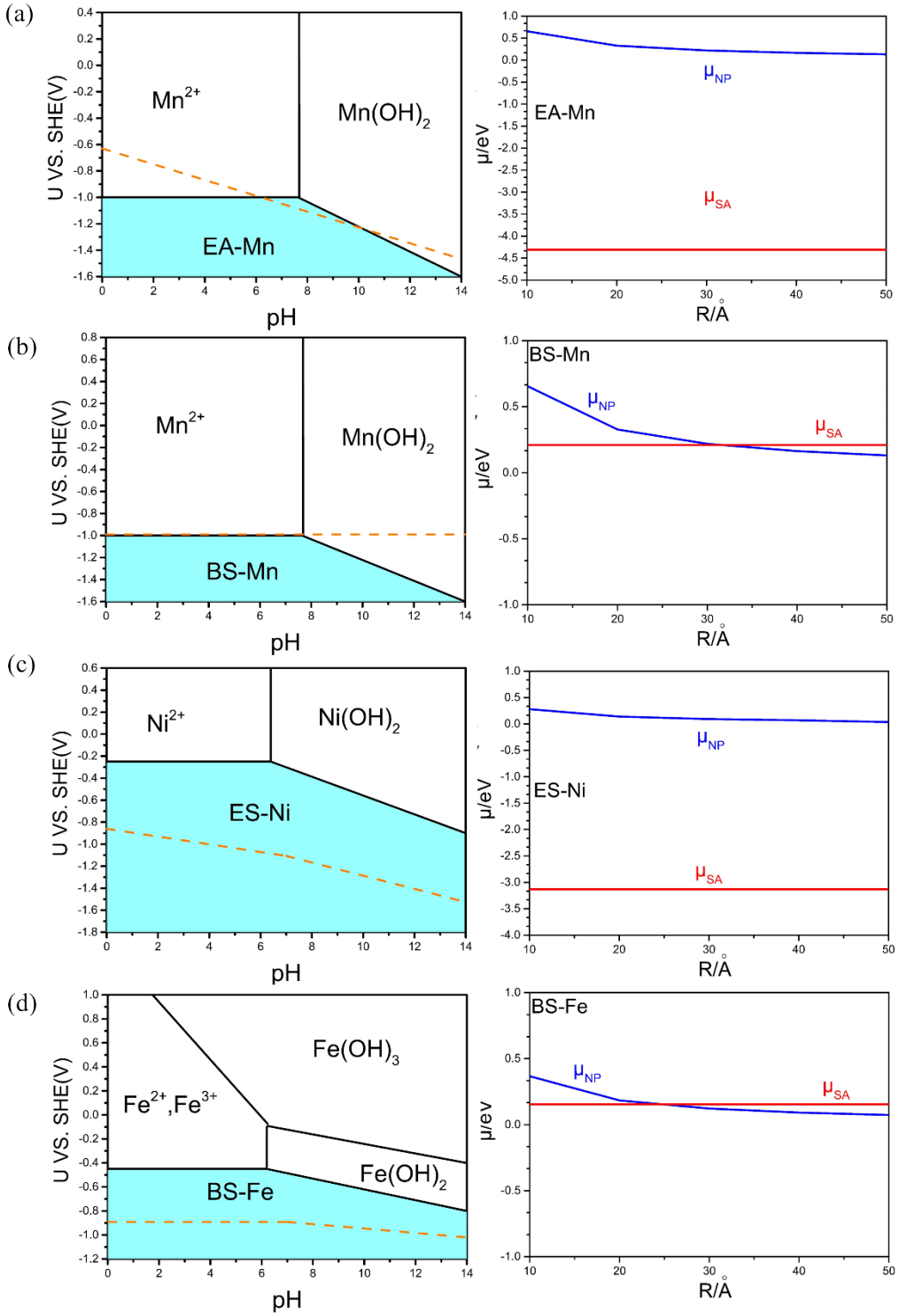
Supplementary Figure 17. Competing relationship between NO_3RR and HER on (a) BA-Co, (b) BS-Co, (c) EA-Co and (d) ES-Co.



Supplementary Figure 18. Competing relationship between NO_3RR and HER on (a) BA-Ni, (b) BS-Ni, (c) EA-Ni and (d) ES-Ni.



Supplementary Figure 19. Competing relationship between NO_3RR and HER on (a) BA-Mn, (b) BS-Mn, and (c) ES-Mn.



Supplementary Figure 20. Pourbaix diagram for the electrochemical dissolution process of SA-MoS_2, at 25°C. The orange dotted line represents the limiting potential of SA-MoS_2 at different pH. Comparison between chemical potential of NPs, $\mu_{NP}(R)$, and that of SAs, μ_{SA}, with respect to curvature of NPs. Black line, $\mu_{NP}(R)$; colored lines, μ_{SA} of SA-MoS_2.

PART III. Supplemental Tables

Supplementary Table 1. Formation energy of different substitution of TM-Basal MoS_2.

Substitution Atom	***Mo***	***S***
Fe-E_{form}/eV	3.509	4.939
Co-E_{form}/eV	4.139	4.373
Ni-E_{form}/eV	-2.213	-0.254
Mn-E_{form}/eV	2.363	5.322

Supplementary Table 2. Formation energy of different adsorption sites of TM-Basal MoS_2.

Adsorption site	***Top-Mo***	***Top-S***	***Bridge-Mo***	***Bridge-S***
Fe-E_{form}/eV	3.123	4.069	7.459	3.304
Co-E_{form}/eV	2.621	4.275	7.458	2.630
Ni-E_{form}/eV	1.958	3.609	5.809	1.961
Mn-E_{form}/eV	4.310	4.331	12.690	4.312

Supplementary Table 3. Formation energy of different S-coverage of TM-Edge MoS_2.

S-Coverage	***12.5%***	***25%***	***37.5%***	***50%***
Fe-E_{form}/eV	-2.7093	-5.5274	-6.1308	-8.3711
Co-E_{form}/eV	-2.5667	-2.7220	-5.8470	-6.4967
Co-E_{form} (PBE+U)/eV	-1.3767	-1.5239	-4.6237	-5.0468
Ni-E_{form}/eV	-3.2107	-3.8616	-5.8078	-6.2296
Mn-E_{form}/eV	-3.1241	-4.3467	-6.0229	-6.5569

Supplementary Table 4. The values of U-J parameters for PBE+U calculations

3d	***Mn***	***Fe***	***Co***	***Ni***
U-J	3.06	3.29	3.42	3.4

Supplementary Table 5. The adsorption energy of NO_3 and NO_3H on SA-MoS_2.

	ΔG(NO_3*)/eV	***ΔG(NO_3H*)/eV***
BA-Fe	0.182	0.164
BS-Fe	1.020	0.910
EA-Fe	1.623	1.551
ES-Fe	0.784	0.620
BA-Co	0.149	0.142
BS-Co	0.991	0.881
EA-Co	0.113	0.001
ES-Co	0.623	0.505
BA-Ni	0.565	0.322
BS-Ni	0.692	0.499

EA-Ni	0.369	0.251
ES-Ni	0.986	0.863
BA-Mn	-0.684	-0.991
BS-Mn	1.201	0.991
EA-Mn	-0.528	-0.876
ES-Mn	-0.944	-1.510

Supplementary Table 6. Computed adsorption energies, zero-point energies and entropy of reaction intermediates on Fe.

Reaction Intermediates	***BA-Fe***			***BS-Fe***			***EA-Fe***			***ES-Fe***		
	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)
$*NO_3H$	0.164	0.685	0.201	0.910	0.700	0.275	1.472	0.660	0.263	0.620	0.700	0.271
NO_2*	-2.020	0.266	0.200	-0.094	0.256	0.223	-0.978	0.253	0.230	-2.458	0.274	0.166
O_2N*	-1.900	0.412	0.184	-0.082	0.443	0.146	-0.923	0.376	0.163	-2.361	0.389	0.152
$*NO_2H$	-3.738	0.512	0.215	-0.920	0.545	0.302	-2.132	0.594	0.189	-1.410	0.535	0.234
$*NO_2H_2$	-4.200	0.845	0.196	-1.400	0.865	0.200	-2.633	0.823	0.187	-1.980	0.869	0.223
*NO**	-4.498	0.200	0.149	-1.513	0.223	0.152	-2.538	0.214	0.135	-3.843	0.216	0.126
*ON**	-4.472	0.132	0.167	-1.421	0.139	0.188	-2.487	0.141	0.145	-3.565	0.136	0.158
*N*O**	-4.465	0.167	0.195	-1.324	0.168	0.186	-2.332	0.170	0.191	-3.262	0.169	0.210
*NOH	-3.385	0.455	0.206	-1.335	0.414	0.260	-3.352	0.475	0.150	-3.941	0.512	0.089
*NHOH	-3.721	0.531	0.074	-1.321	0.792	0.133	-1.362	0.785	0.168	-2.975	0.777	0.133
*N	-4.193	0.085	0.054	-2.289	0.086	0.056	-3.731	0.083	0.051	-3.640	0.085	0.058
*NH	-4.801	0.353	0.073	-3.258	0.372	0.069	-2.392	0.337	0.093	-3.881	0.304	0.069
$*NH_2$	-5.798	0.643	0.078	-4.161	0.698	0.090	-4.120	0.663	0.117	-5.079	0.658	0.126
$*NH_3$	-6.358	1.011	0.186	-5.184	0.944	0.279	-4.067	1.027	0.155	-5.940	1.035	0.137
$*NH_4^+$	-4.152	2.502	1.925	-4.188	2.609	1.896	-3.412	2.421	2.202	-5.323	2.532	2.001

Supplementary Table 7. Computed adsorption energies, zero-point energies and entropy of reaction intermediates on Co.

Reaction Intermediates	***BA-Co***			***BS-Co***			***EA-Co***			***ES-Co***		
	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)
$*NO_3H$	0.142	0.697	0.258	0.881	0.700	0.272	0.0006	0.696	0.246	0.863	0.704	0.250
NO_2*	-2.023	0.285	0.153	-0.515	0.300	0.227	-2.564	0.286	0.193	-1.670	0.294	0.155
O_2N*	-1.968	0.412	0.184	-0.441	0.443	0.146	-2.382	0.376	0.163	-1.994	0.389	0.152
$*NO_2H$	-2.330	0.569	0.261	-0.875	0.534	0.256	-4.267	0.581	0.251	-0.982	0.581	0.209
$*NO_2H_2$	-2.966	0.845	0.196	-1.369	0.865	0.200	-4.779	0.823	0.187	-1.365	0.869	0.223
*NO**	-4.642	0.204	0.151	-1.993	0.200	0.174	-4.785	0.194	0.158	-2.104	0.195	0.092
*ON**	-4.232	0.132	0.167	-1.758	0.139	0.188	-4.552	0.141	0.145	-1.951	0.136	0.158
*N*O**	-4.441	0.167	0.195	-1.748	0.168	0.186	-4.647	0.170	0.191	-2.001	0.169	0.210
*NOH	-2.958	0.452	0.198	-1.503	0.450	0.166	-4.597	0.484	0.139	-1.877	0.471	0.114
*NHOH	-3.235	0.755	0.178	-2.315	0.792	0.133	-3.410	0.785	0.168	-2.470	0.777	0.133
*N	-3.220	0.085	0.054	-2.572	0.086	0.056	-5.970	0.093	0.035	-1.075	0.086	0.045

**NH*	-4.198	0.300	0.033	-3.520	0.358	0.084	-6.623	0.378	0.058	-2.345	0.287	0.091
**NH$_2$*	-5.629	0.644	0.088	-4.760	0.701	0.091	-6.253	0.666	0.120	-4.015	0.618	0.077
**NH$_3$*	-6.348	1.023	0.185	-5.196	0.938	0.228	-6.489	1.033	0.165	-5.640	1.040	0.131
**NH$_4^+$*	-3.902	2.563	1.837	-4.770	2.597	1.874	-6.247	2.681	2.200	-3.716	2.558	1.967

Supplementary Table 8. Computed adsorption energies, zero-point energies and entropy of reaction intermediates on Ni.

Reaction Intermediates	***BA-Ni***			***BS-Ni***			***EA-Ni***			***ES-Ni***		
	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)
**NO$_3$H*	0.322	0.703	0.261	0.499	0.701	0.337	0.251	0.705	0.258	0.863	0.693	0.213
*NO$_2$**	-1.395	0.273	0.199	-0.836	0.306	0.219	-2.881	0.286	0.193	-1.670	0.294	0.161
*O$_2$N**	-1.330	0.412	0.184	-0.668	0.443	0.146	-2.632	0.376	0.163	-1.232	0.389	0.152
**NO$_2$H*	-1.969	0.573	0.202	-1.165	0.533	0.196	-2.336	0.581	0.251	-0.982	0.575	0.203
**NO$_2$H$_2$*	-2.359	0.845	0.196	-1.665	0.865	0.200	-2.669	0.823	0.187	-1.331	0.869	0.223
*NO**	-3.094	0.176	0.168	-2.382	0.166	0.189	-3.773	0.194	0.158	-2.105	0.164	0.183
*ON**	-2.787	0.132	0.167	-2.221	0.139	0.188	-3.520	0.141	0.145	-1.998	0.136	0.158
*N*O**	-2.889	0.167	0.195	-2.332	0.168	0.186	-3.002	0.170	0.191	-2.014	0.169	0.210
**NOH*	-1.975	0.461	0.193	-1.895	0.455	0.156	-2.738	0.463	0.185	-1.877	0.465	0.140
**NHOH*	-3.023	0.775	0.163	-2.672	0.796	0.128	-4.591	0.780	0.145	-2.470	0.787	0.139
**N*	-1.944	0.080	0.077	-2.471	0.085	0.057	-6.147	0.078	0.051	-1.075	0.082	0.063
**NH*	-3.459	0.272	0.071	-3.986	0.362	0.079	-7.032	0.377	0.057	-3.345	0.300	0.075
**NH$_2$*	-5.132	0.638	0.164	-5.090	0.696	0.111	-7.110	0.666	0.120	-4.015	0.643	0.092
**NH$_3$*	-6.293	1.024	0.186	-5.471	0.931	0.121	-6.408	1.033	0.165	-5.640	1.024	0.150
**NH$_4^+$*	-3.798	2.613	1.932	-5.161	2.595	1.918	-6.405	2.681	2.200	-3.716	2.406	2.137

Supplementary Table 9. Computed adsorption energies, zero-point energies and entropy of reaction intermediates on Mn.

Reaction Intermediates	***BA-Mn***			***BS-Mn***			***EA-Mn***			***ES-Mn***		
	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)	E_{ads}(eV)	ZPE(eV)	TS(eV)
**NO$_3$H*	-0.991	0.707	0.304	0.991	0.695	0.216	-0.876	0.658	0.259	-1.510	0.656	0.290
*NO$_2$**	-3.221	0.272	0.221	-0.109	0.256	0.231	-2.929	0.290	0.183	-3.014	0.286	0.171
*O$_2$N**	-2.987	0.412	0.184	0.002	0.443	0.146	-2.668	0.376	0.163	-2.875	0.389	0.152
**NO$_2$H*	-2.806	0.568	0.271	-0.775	0.534	0.141	-2.300	0.556	0.262	-5.082	0.669	0.315
**NO$_2$H$_2$*	-3.112	0.845	0.196	-1.023	0.865	0.200	-2.600	0.823	0.187	-5.368	0.869	0.223
*NO**	-5.325	0.196	0.156	-1.247	0.144	0.181	-4.354	0.195	0.095	-5.811	0.215	0.127
*ON**	-4.789	0.132	0.167	-1.023	0.139	0.188	-4.011	0.141	0.145	-5.623	0.136	0.158
*N*O**	-4.997	0.167	0.195	-1.234	0.168	0.186	-4.204	0.170	0.191	-5.741	0.169	0.210
**NOH*	-4.342	0.507	0.159	-1.255	0.394	0.168	-4.302	0.471	0.170	-4.519	0.464	0.140
**NHOH*	-4.228	0.775	0.163	-1.178	0.796	0.128	-3.955	0.780	0.145	-6.143	0.730	0.155
**N*	-5.901	0.080	0.077	-2.322	0.085	0.057	-5.880	0.078	0.051	-6.117	0.082	0.063
**NH*	-6.151	0.338	0.112	-3.117	0.366	0.077	-5.753	0.358	0.093	-6.219	0.345	0.096

*NH_2	-6.635	0.666	0.122	-3.715	0.680	0.072	-6.281	0.667	0.113	-6.918	0.681	0.107
*NH_3	-6.573	1.021	0.189	-5.145	0.915	0.126	-6.283	1.108	0.121	-6.534	1.107	0.109
*NH_4^+	-6.425	2.649	1.919	-0.167	2.595	1.918	-6.188	2.496	2.112	-7.519	2.498	1.900

Supplementary Table 10. Calculated Gibbs free energies change of elementary step in NO_3RR on BA-Fe at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.164	0.164	0.164
NO_3H→O_2N	-2.184	-1.765	-1.346
O_2N*→*NO_2H	-1.762	-1.343	-0.924
NO_2H→ON	-0.716	-0.297	0.122
ON*→*NOH	1.113	1.532	1.951
*NOH→*NHOH	-0.337	0.083	0.502
*NHOH→*NH	-1.080	-0.660	-0.241
NH→NH_2	-0.997	-0.578	-0.159
NH_2→NH_3	-0.560	-0.141	0.278
NH_3→NH_4^+	2.201	2.201	/

Supplementary Table 11. Calculated Gibbs free energies change of elementary step in NO_3RR on BS-Fe at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.910	0.910	0.910
NO_3H→O_2N	-1.004	-0.585	-0.166
O_2N*→*NO_2H	-0.825	-0.406	0.013
NO_2H→ON	-0.594	-0.175	0.244
ON*→*NOH	0.179	0.598	1.017
*NOH→*NHOH	-0.954	-0.535	-0.116
*NHOH→*NH	-0.969	-0.550	-0.131
NH→NH_2	-0.903	-0.484	-0.065
NH_2→NH_3	-1.023	-0.604	-0.185
NH_3→NH_4^+	0.996	0.996	/

Supplementary Table 12. Calculated Gibbs free energies change of elementary step in NO_3RR on EA-Fe at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	1.472	1.472	1.472
NO_3H→O_2N	-2.449	-2.030	-1.611
O_2N*→*NO_2H	-1.154	-0.735	-0.316
NO_2H→ON	-0.407	0.012	0.413
ON*→*NOH	-0.814	-0.395	0.024
*NOH→*NHOH	-0.378	0.041	0.460
*NHOH→*NH	1.339	1.758	2.177
NH→NH_2	-1.729	-1.310	-0.891
NH_2→NH_3	0.053	0.472	0.891
NH_3→NH_4^+	0.655	0.655	/

Supplementary Table 13. Calculated Gibbs free energies change of elementary step in NO_3RR on ES-Fe at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.620	0.620	0.620
NO_3H→O_2N	-2.981	-2.562	-2.143
O_2N*→*NO_2H	0.952	1.371	1.790
NO_2H→ON	-2.433	-2.014	-1.595
ON*→*NOH	-0.098	0.321	0.740
*NOH→*NHOH	0.301	0.720	1.139
*NHOH→*NH	-0.241	0.178	0.597
NH→NH_2	-1.198	-0.779	-0.360
NH_2→NH_3	-0.861	-0.442	-0.023
NH_3→NH_4^+	0.617	0.617	/

Supplementary Table 14. Calculated Gibbs free energies change of elementary step in NO_3RR on BA-Co at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.142	0.142	0.142
NO_3H→O_2N	-2.165	-1.746	-1.327
O_2N*→*NO_2H	-0.307	0.112	0.531
NO_2H→ON	-2.312	-1.893	-1.474
ON*→*NOH	1.684	2.103	2.522
*NOH→*NHOH	-0.277	0.142	0.561
*NHOH→*NH	-0.964	-0.545	-0.126
NH→NH_2	-1.431	-1.012	-0.593
NH_2→NH_3	-0.719	-0.300	0.119
NH_3→NH_4^+	2.446	2.446	/

Supplementary Table 15. Calculated Gibbs free energies change of elementary step in NO_3RR on BS-Co at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.881	0.881	0.881
NO_3H→O_2N	-1.395	-0.976	-0.138
O_2N*→*NO_2H	-0.360	0.059	0.897
NO_2H→ON	-1.118	-0.699	0.139
ON*→*NOH	0.490	0.909	1.747
*NOH→*NHOH	-0.812	-0.393	0.445
*NHOH→*NH	-1.205	-0.786	0.052
NH→NH_2	-1.240	-0.821	0.018
NH_2→NH_3	-0.436	-0.017	0.082
NH_3→NH_4^+	-1.069	-1.069	/

Supplementary Table 16. Calculated Gibbs free energies change of elementary step in NO_3RR on EA-Co at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.0006	0.0006	0.0006
NO_3H→O_2N	-2.565	-2.146	-1.727

$O_2N^*\rightarrow{}^*NO_2H$	-1.703	-1.284	-0.865
$^*NO_2H\rightarrow ON^*$	-0.518	-0.099	0.320
$ON^*\rightarrow{}^*NOH$	0.188	0.607	1.026
$^*NOH\rightarrow{}^*NHOH$	-1.373	-0.954	-0.535
$^*NHOH\rightarrow{}^*NH$	-0.653	-0.234	0.185
$^*NH\rightarrow{}^*NH_2$	0.370	0.789	1.208
$^*NH_2\rightarrow{}^*NH_3$	-0.0236	0.183	0.602
$^*NH_3\rightarrow{}^*NH_4^+$	0.242	0.242	/

Supplementary Table 17. Calculated Gibbs free energies change of elementary step in NO_3RR on ES-Co at different pH.

	pH=0	***pH=7***	***pH=14***
$^*\rightarrow{}^*NO_3H$	0.505	0.505	0.505
$^*NO_3H\rightarrow O_2N^*$	-2.984	-2.565	-2.146
$O_2N^*\rightarrow{}^*NO_2H$	-0.418	0.001	0.420
$^*NO_2H\rightarrow ON^*$	-0.277	0.142	0.561
$ON^*\rightarrow{}^*NOH$	0.802	1.221	1.640
$^*NOH\rightarrow{}^*NHOH$	-0.772	-0.353	0.066
$^*NHOH\rightarrow{}^*NH$	-0.084	0.335	0.754
$^*NH\rightarrow{}^*NH_2$	-1.574	-1.155	-0.736
$^*NH_2\rightarrow{}^*NH_3$	-1.219	-0.800	-0.381
$^*NH_3\rightarrow{}^*NH_4^+$	0.519	0.519	/

Supplementary Table 18. Calculated Gibbs free energies change of elementary step in NO_3RR on BA-Ni at different pH.

	pH=0	***pH=7***	***pH=14***
$^*\rightarrow{}^*NO_3H$	0.322	0.322	0.322
$^*NO_3H\rightarrow O_2N^*$	-1.717	-1.298	-0.879
$O_2N^*\rightarrow{}^*NO_2H$	-0.573	-0.154	0.265
$^*NO_2H\rightarrow ON^*$	-1.125	-0.706	-0.287
$ON^*\rightarrow{}^*NOH$	1.119	1.538	1.957
$^*NOH\rightarrow{}^*NHOH$	-1.051	-0.632	-0.213
$^*NHOH\rightarrow{}^*NH$	-0.434	-0.015	0.404
$^*NH\rightarrow{}^*NH_2$	-1.673	-1.254	-0.835
$^*NH_2\rightarrow{}^*NH_3$	-1.151	-0.732	-0.313
$^*NH_3\rightarrow{}^*NH_4^+$	2.485	2.485	/

Supplementary Table 19. Calculated Gibbs free energies change of elementary step in NO_3RR on BS-Ni at different pH.

	pH=0	***pH=7***	***pH=14***
$^*\rightarrow{}^*NO_3H$	0.499	0.499	0.499
$^*NO_3H\rightarrow O_2N^*$	-1.336	-0.917	-0.498
$O_2N^*\rightarrow{}^*NO_2H$	-0.328	0.091	0.510
$^*NO_2H\rightarrow ON^*$	-1.217	-0.798	-0.379
$ON^*\rightarrow{}^*NOH$	0.487	0.906	1.325
$^*NOH\rightarrow{}^*NHOH$	-0.778	-0.359	0.060
$^*NHOH\rightarrow{}^*NH$	-1.313	-0.894	-0.475

NH→NH_2	-1.104	-0.685	-0.266
NH_2→NH_3	-0.381	0.038	0.457
NH_3→NH_4^+	0.310	0.310	/

Supplementary Table 20. Calculated Gibbs free energies change of elementary step in NO_3RR on EA-Ni at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.251	0.251	0.251
NO_3H→O_2N	-3.132	-2.713	-2.293
O_2N*→*NO_2H	0.545	0.964	1.383
NO_2H→ON	-1.437	-1.018	-0.599
ON*→*NOH	1.035	1.454	1.873
*NOH→*N	-3.409	-2.990	-2.571
*N→*NH	-0.885	-0.466	-0.047
NH→NH_2	-0.078	0.341	0.760
NH_2→NH_3	0.702	1.121	-1.540
NH_3→NH_4^+	0.003	0.003	/

Supplementary Table 21. Calculated Gibbs free energies change of elementary step in NO_3RR on ES-Ni at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.863	0.863	0.863
NO_3H→O_2N	-2.533	-2.114	-1.694
O_2N*→*NO_2H	0.688	1.107	1.526
NO_2H→ON	-1.123	-0.704	-0.285
ON*→*NOH	0.227	0.646	1.066
*NOH→*NHOH	-0.593	-0.174	0.245
*NHOH→*NH	0.125	0.544	0.963
NH→NH_2	-1.670	-1.251	-0.832
NH_2→NH_3	-1.625	-1.206	-0.787
NH_3→NH_4^+	1.924	1.924	/

Supplementary Table 22. Calculated Gibbs free energies change of elementary step in NO_3RR on BA-Mn at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	-0.991	-0.991	-0.991
NO_3H→O_2N	-2.231	-1.812	-1.393
O_2N*→*NO_2H	0.415	0.834	1.253
NO_2H→ON	-2.519	-2.100	-1.681
ON*→*NOH	0.984	1.403	1.822
*NOH→*N	-1.560	-1.141	-0.722
*N→*NH	-0.250	0.170	0.590
NH→NH_2	-0.484	-0.065	0.354
NH_2→NH_3	0.062	0.484	0.901
NH_3→NH_4^+	0.148	0.148	/

Supplementary Table 23. Calculated Gibbs free energies change of elementary step in NO_3RR on BS-Mn at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	0.991	0.991	0.991
NO_3H→O_2N	-1.100	-0.681	-0.262
O_2N*→*NO_2H	-0.666	-0.247	0.173
NO_2H→ON	-0.472	-0.053	0.366
ON*→*NOH	-0.009	0.411	0.830
*NOH→*N	-1.063	-0.644	-0.225
*N→*NH	-0.799	-0.38	0.040
NH→NH_2	-0.600	-0.179	0.241
NH_2→NH_3	-1.431	-1.012	-0.593
NH_3→NH_4^+	1.088	1.088	/

Supplementary Table 24. Calculated Gibbs free energies change of elementary step in NO_3RR on EA-Mn at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	-0.875	-0.875	-0.875
NO_3H→O_2N	-2.054	-1.635	-1.216
O_2N*→*NO_2H	0.629	1.148	1.467
NO_2H→ON	-2.054	-1.635	-1.216
ON*→*NOH	0.052	0.471	0.890
*NOH→*N	-1.578	-1.159	-0.740
*N→*NH	0.127	0.546	0.965
NH→NH_2	-0.528	-0.109	0.310
NH_2→NH_3	-0.001	0.418	0.837
NH_3→NH_4^+	0.094	0.094	/

Supplementary Table 25. Calculated Gibbs free energies change of elementary step in NO_3RR on ES-Mn at different pH.

	pH=0	***pH=7***	***pH=14***
→NO_3H	-1.510	-1.510	-1.510
NO_3H→O_2N	-1.504	-1.085	-0.666
O_2N*→*NO_2H	-2.069	-1.650	-1.231
NO_2H→ON	-0.728	-0.309	0.110
ON*→*NOH	1.292	1.711	2.130
*NOH→*NHOH	-1.624	-1.205	-0.786
*NHOH→*NH	-0.076	0.343	0.762
NH→NH_2	-0.699	-0.280	0.139
NH_2→NH_3	0.384	0.803	1.222
NH_3→NH_4^+	-0.985	-0.985	/

Supplementary Table 26. The parameters of aG(NO*)+bG(NH_2*) and the parameter of linear fits in Figure 4a.

	ΔG_1	ΔG_2	ΔG_3	ΔG_4	ΔG_5	ΔG_6	ΔG_7	ΔG_8	ΔG_9	ΔG_{10}
Intercept	0.696	0.826	1.190	0	0.917	0.837	1.40	0.771	0	0.715
Slope	1.002	1.004	1.005	1	1.005	1	1.09	0.99	1	1.01
R^2	0.71	0.77	0.70	1	0.78	0.84	0.80	0.90	1	0.72

Supplementary Table 27. The parameters of aG(NO*)+bG(NH_2*) and the parameter of linear fits in Figure S8.

	G(NO_3H*)	G(NO_2*)	G(NO_2H*)	G(NO*)	G(NOH*)	G(NHOH*)	G(N*)	G(NH*)	G(NH_2*)	G(NH_3*)
a	0.275	0.503	0.843	1	0.934	0.281	0.212	-0.252	0	0.178
b	0.311	0.245	-0.104	0	-0.261	0.778	1.128	1.629	1	0.326
Intercept	2.874	1.227	0.096	0	-1.074	2.004	3.647	3.459	0	-4.511
Slope	1.002	1.004	1.005	1	1.005	1	1.09	0.99	1	1.01

Supplementary Table 28. Calculated Faraday efficiencies for NO_3RR on SA-MoS_2 and MoS_2 substrates.

	MoS_2	BA-Fe	BS-Fe	EA-Fe	ES-Fe	BA-Co	BS-Co	EA-Co	ES-Co
FE	0	0	0	0	0	0	0	100%	0
	BA-Ni	*BS-Ni*	*EA-Ni*	*ES-Ni*	*BA-Mn*	*BS-Mn*	*EA-Mn*	*ES-Mn*	
FE	0	99.9%	99.5%	0	0	0	0	0	

Supplementary Table 29. Formation energy (E_f) and dissolution potential (U_{diss}) of metals. For comparison, the standard dissolution potential ($U°_{diss}$) of metal atoms are also listed.

		Metal ion		Metal Hydroxide	
Metal	**E_f(eV)**	**$U°_{diss}$(V)**	**U_{diss}(V)**	**$U°_{diss}$(V)**	**U_{diss}(V)**
BS-Fe	3.509	-0.450	-2.205	-0.045	-1.799
EA-Co	-6.497	-0.280	2.968	-0.730	2.519
ES-Ni	-14.257	-0.260	6.869	0.490	7.619
BS-Mn	2.356	-1.190	-2.368	-1.470	-2.648
EA-Mn	-6.557	-1.190	2.088	-1.470	1.8085

Reference

[1] LIU J, RICHARDS D, SINGH N, et al. Activity and Selectivity Trends in Electrocatalytic Nitrate Reduction on Transition Metals [J]. ACS Catalysis, 2019, 9(8): 7052-7064.

[2] VALDÉS A, QU Z W, KROES G J. Oxidation and photo-oxidation of water on TiO2 surface [J]. 2008, 112(26): 9872–9879.

[3] LIU X, JIAO Y, ZHENG Y, et al. Building Up a Picture of the Electrocatalytic Nitrogen

Reduction Activity of Transition Metal Single-Atom Catalysts [J]. J Am Chem Soc, 2019, 141(24): 9664-9672.

[4] GUO X, GU J, LIN S, et al. Tackling the Activity and Selectivity Challenges of Electrocatalysts toward the Nitrogen Reduction Reaction via Atomically Dispersed Biatom Catalysts [J]. J Am Chem Soc, 2020, 142(12): 5709-5721.

[5] LIU J, WANG Y, LI J. Toward Rational Design of Oxide-Supported Single-Atom Catalysts: Atomic Dispersion of Gold on Ceria [J]. Journal of the American Chemical Society, 2017, 139(17): 6190-6199.