Supporting Information for

Catalytic active centers beyond transition metals: atomically dispersed alkaline-earth metals for electroreduction of nitrate to ammonia

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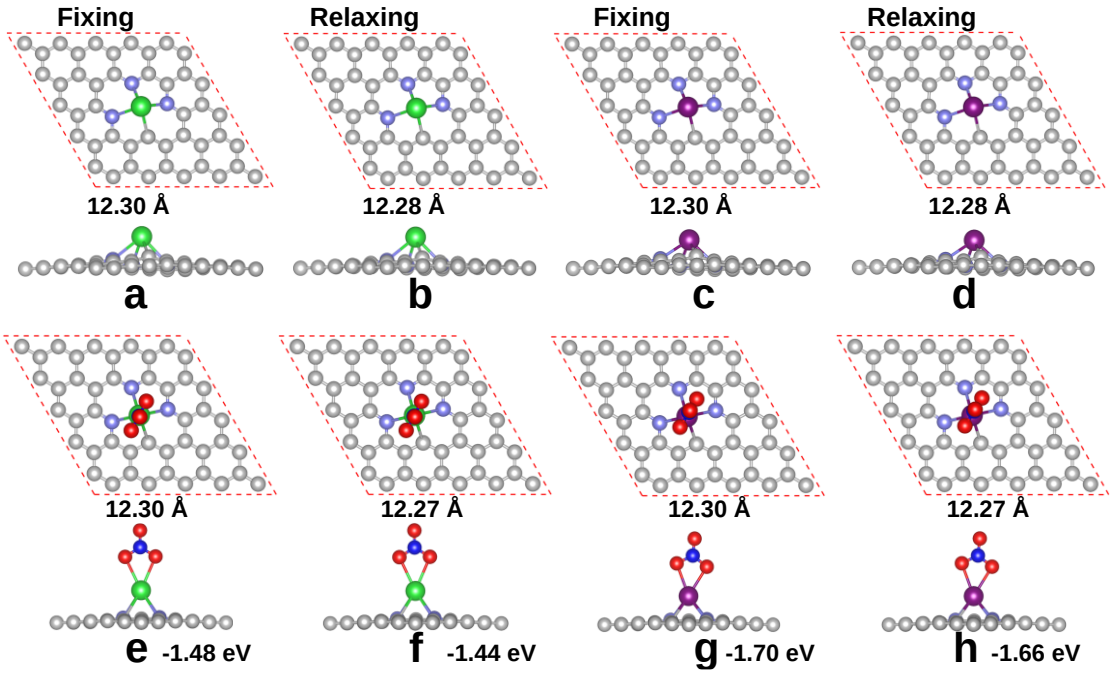

Fig. S1. Top and side views of optimized configurations for DV-BaN_3C (a)-(b) and DV-SrN_3C (c)-(d) systems, and the adsorbed *NO_3 on DV-BaN_3C (e)-(f) and DV-SrN_3C (g)-(h) systems by fixing (a), (c), (e), (g) or relaxing (b), (d), (f), (h) the lattice parameters, together with their corresponding lattice parameters and *NO_3 adsorption free energies.

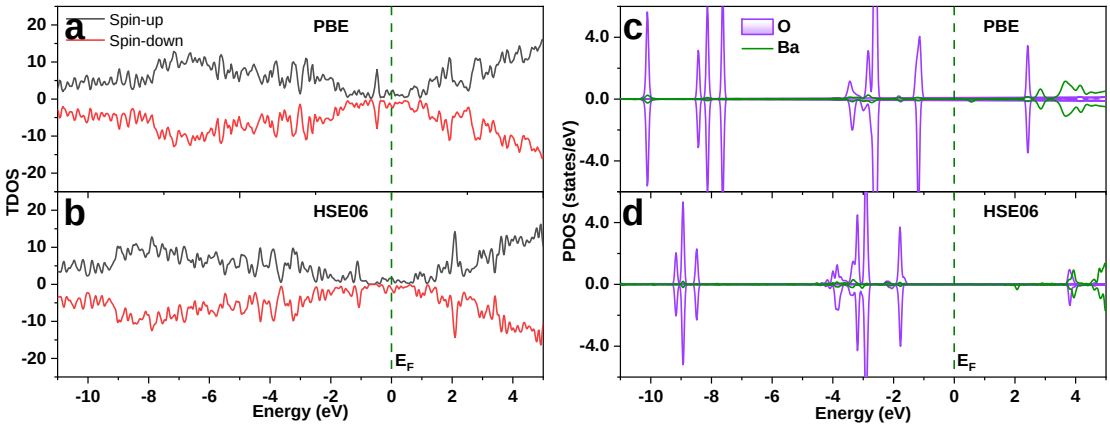

Fig. S2. The calculated TDOS of DV-BaN_3C system with PBE (a) and HSE06 (b) functionals, and PDOS of *NO_3 on DV-BaN_3C with PBE (c) and HSE06 (d) functionals. The Fermi level (E_F) is labeled by vertical dash line and set to 0 eV.

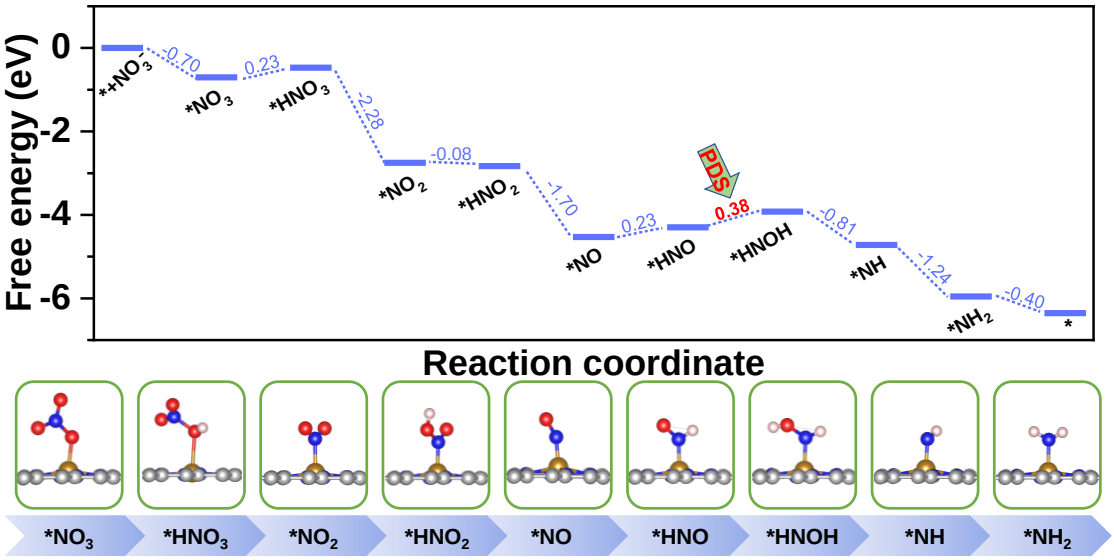

Fig. S3. Free energy diagram together with corresponding intermediate configurations for eNO_3RR on DV-FeN_4.

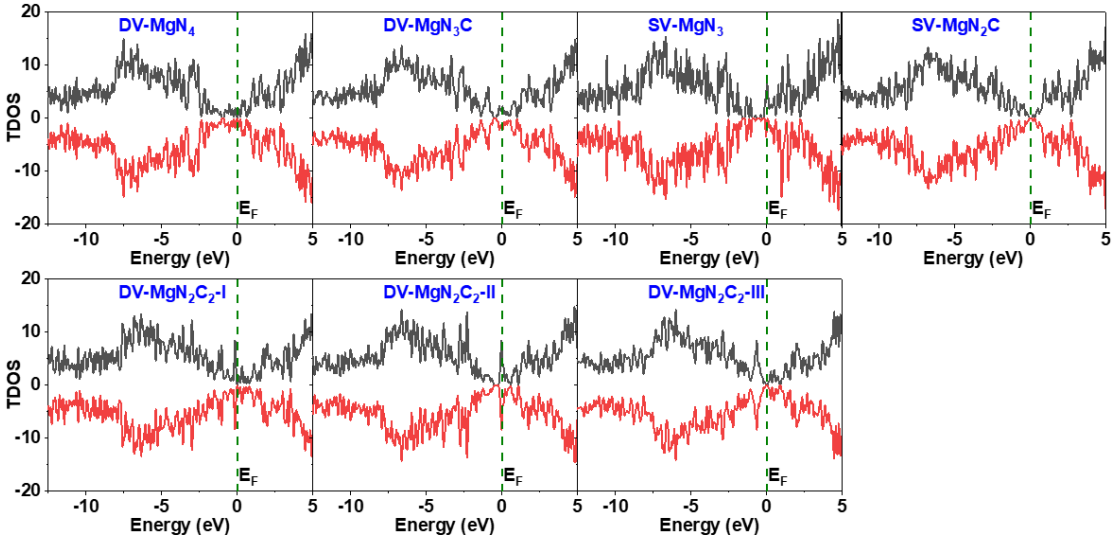

Fig. S4. Total density of states (TDOS) of Mg-based SACs. The Fermi level (E_F) is labeled by vertical dash line and set to 0 eV. The positive and negative values of TDOS correspond to the spin-up and spin-down states, respectively.

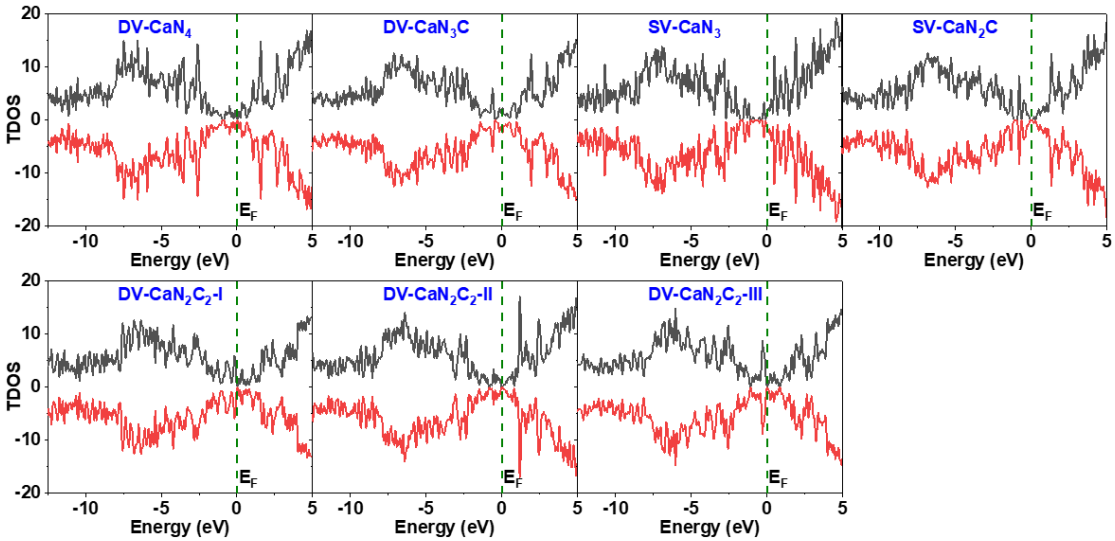

Fig. S5. Total density of states (TDOS) of Ca-based SACs. The Fermi level (E_F) is labeled by vertical dash line and set to 0 eV. The positive and negative values of TDOS correspond to the spin-up and spin-down states, respectively.

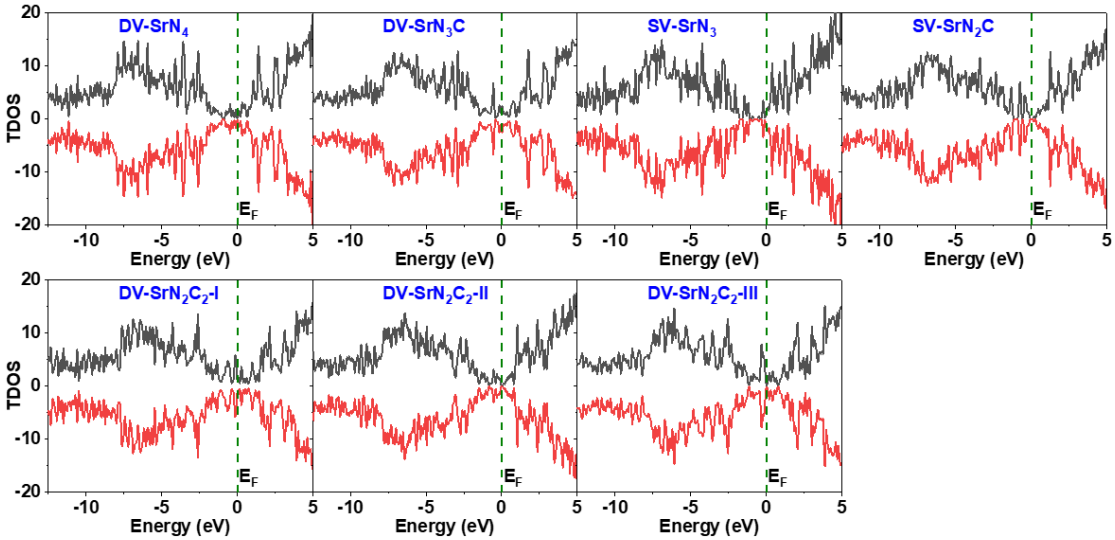

Fig S6. Total density of states (TDOS) of Sr-based SACs. The Fermi level (E_F) is labeled by vertical dash line and set to 0 eV. The positive and negative values of TDOS correspond to the spin-up and spin-down states, respectively.

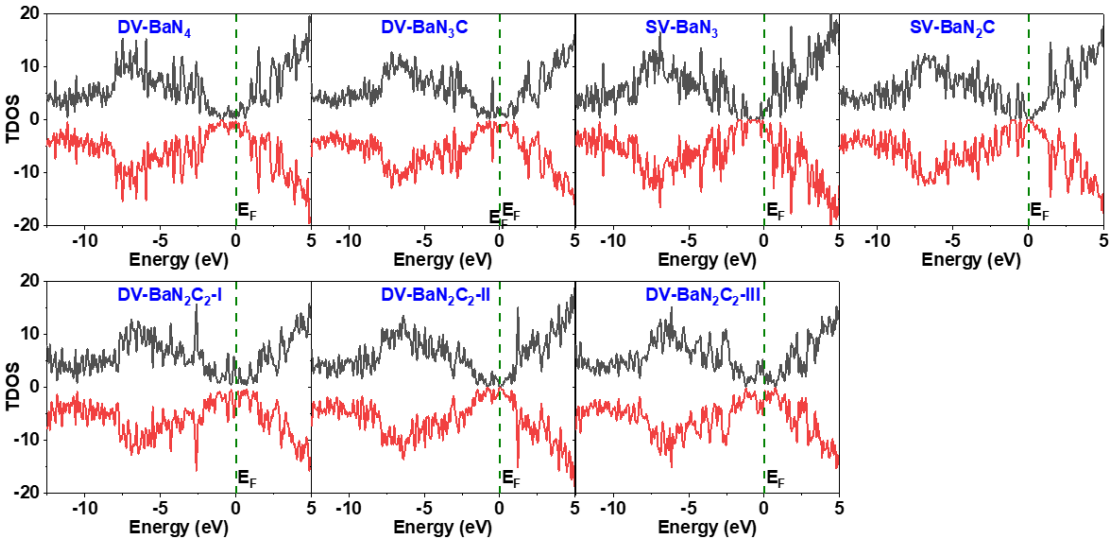

Fig. S7. Total density of states (TDOS) of Ba-based SACs. The Fermi level (E_F) is labeled by vertical dash line and set to 0 eV. The positive and negative values of TDOS correspond to the spin-up and spin-down states, respectively.

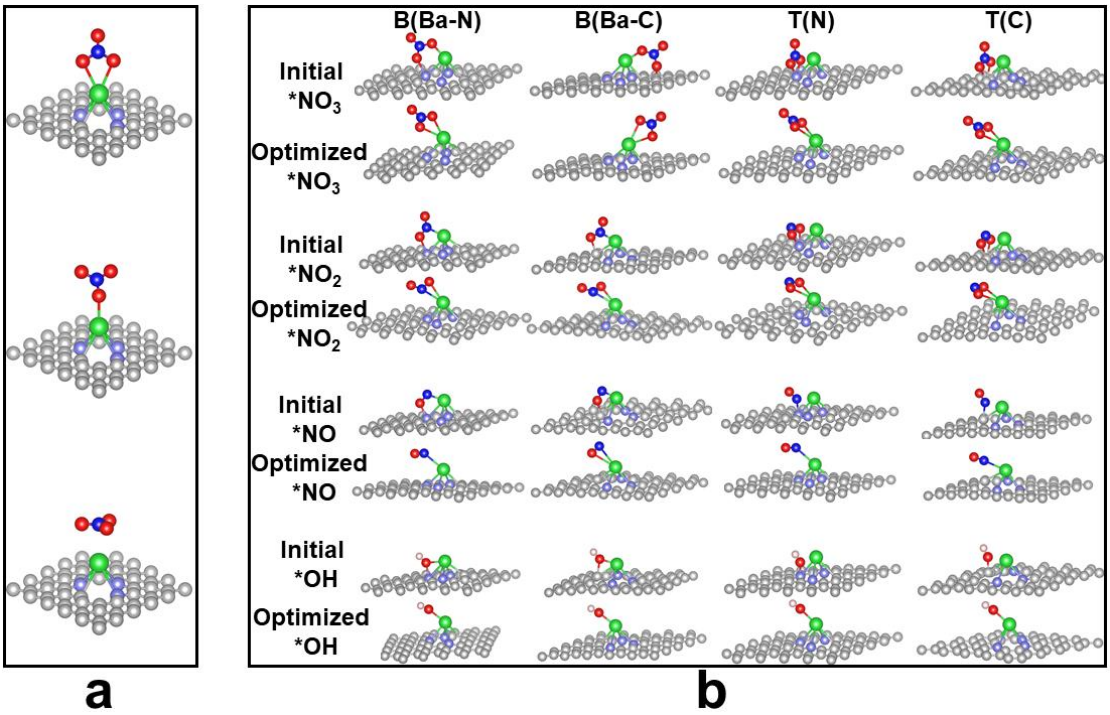

Fig. S8. (a) The possible adsorption configurations of $*NO_3$ on the AE-SAC systems. (b) The initial and optimized configurations of $*NO_3$, $*NO_2$, *NO, and *OH on DV-BaN_3C system, where the B(Ba-N/C) denotes the bridge sites between Ba and N/C atoms and T(N/C) represents the on-top sites of N/C atoms.

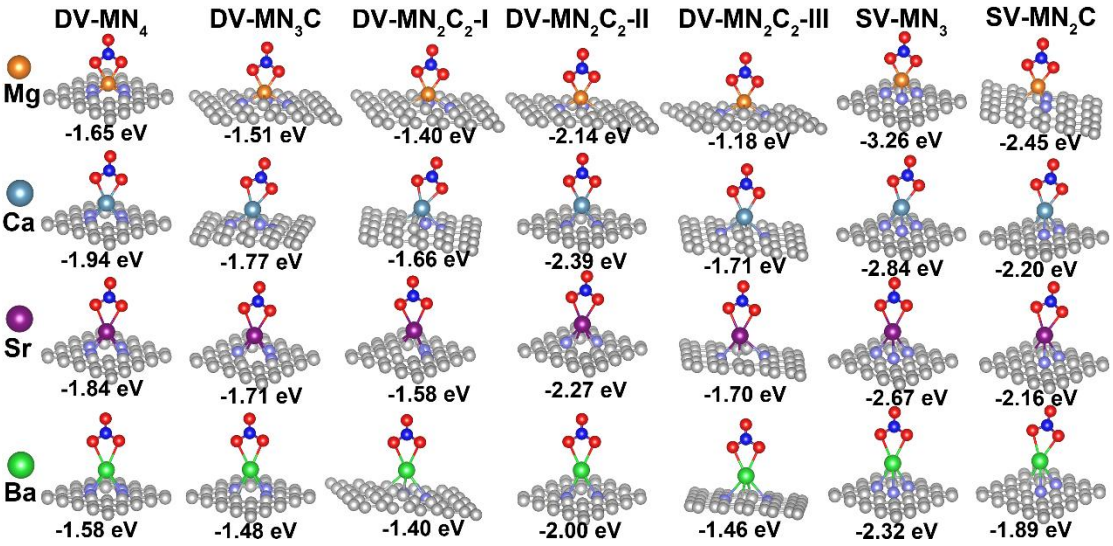

Fig. S9. The most stable configurations and corresponding adsorption free energies (black numbers in the bottom) of NO_3^- adsorption on the AE-SAC systems.

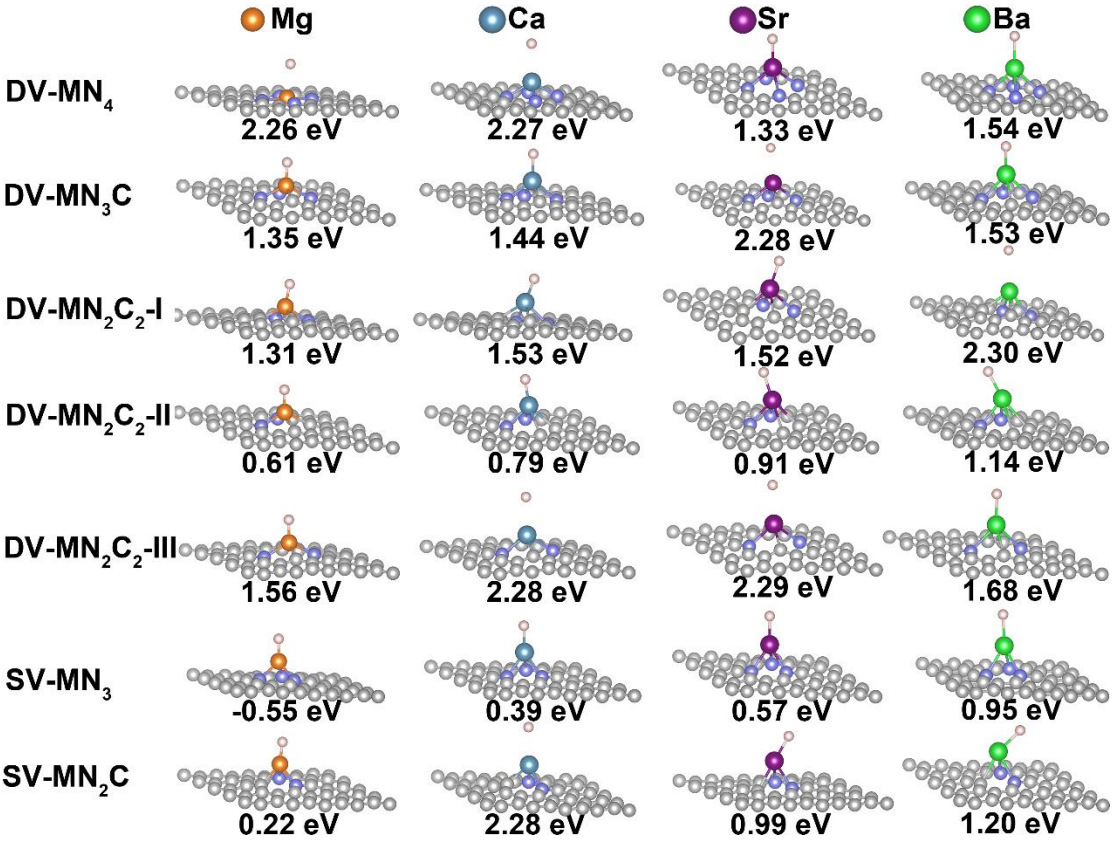

Fig. S10. The most stable configurations and corresponding adsorption free energies (black numbers in the bottom) of H atoms adsorption on the AE-SAC systems.

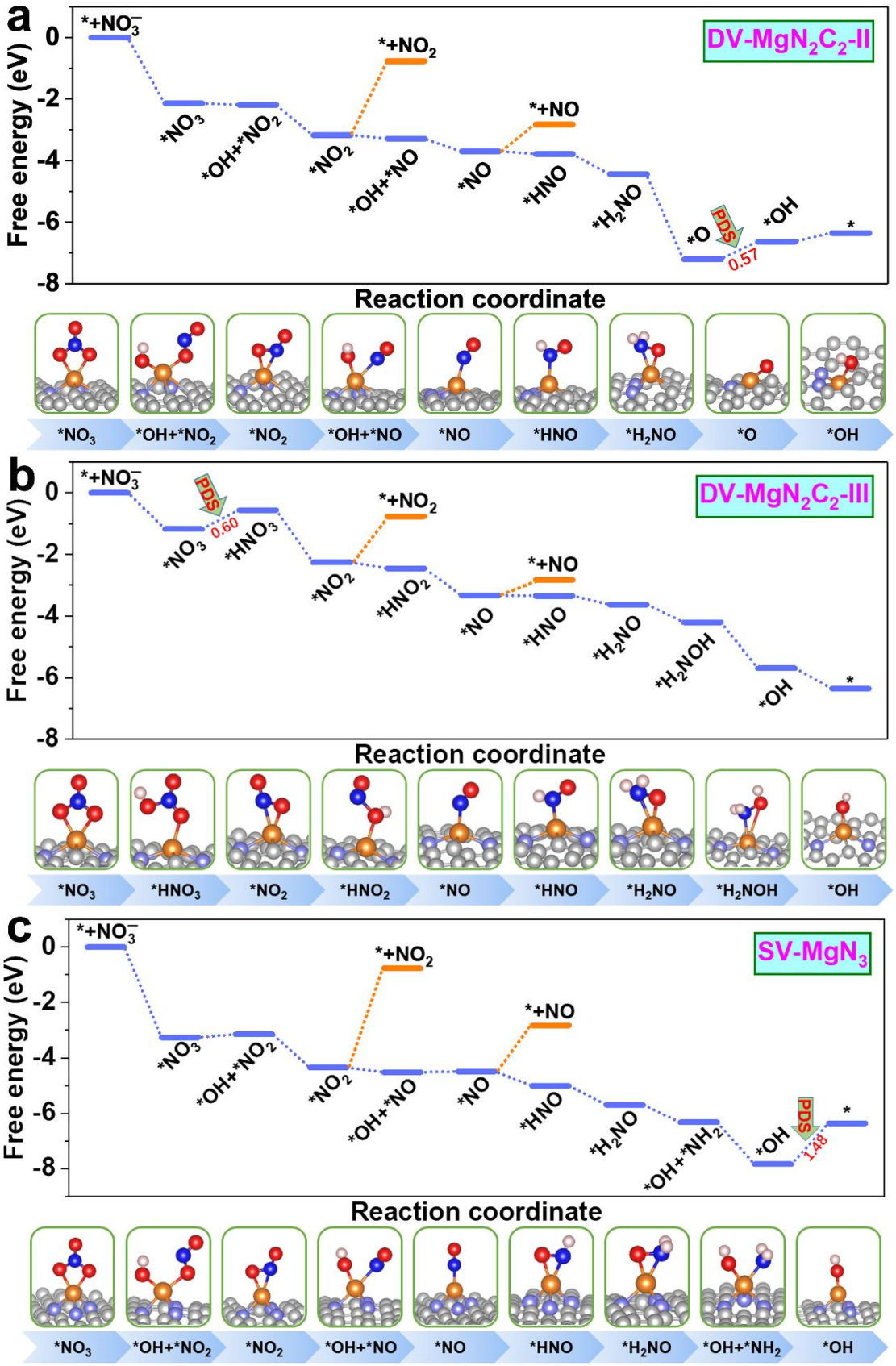

Fig. S11. Free energy diagrams together with corresponding intermediate configurations for eNO_3RR on DV-MgN_2C_2-II (a), DV-MgN_2C_2-III (b) and SV-MgN_3 (c) under the potentials of 0 V. The U_L is highlighted by red number.

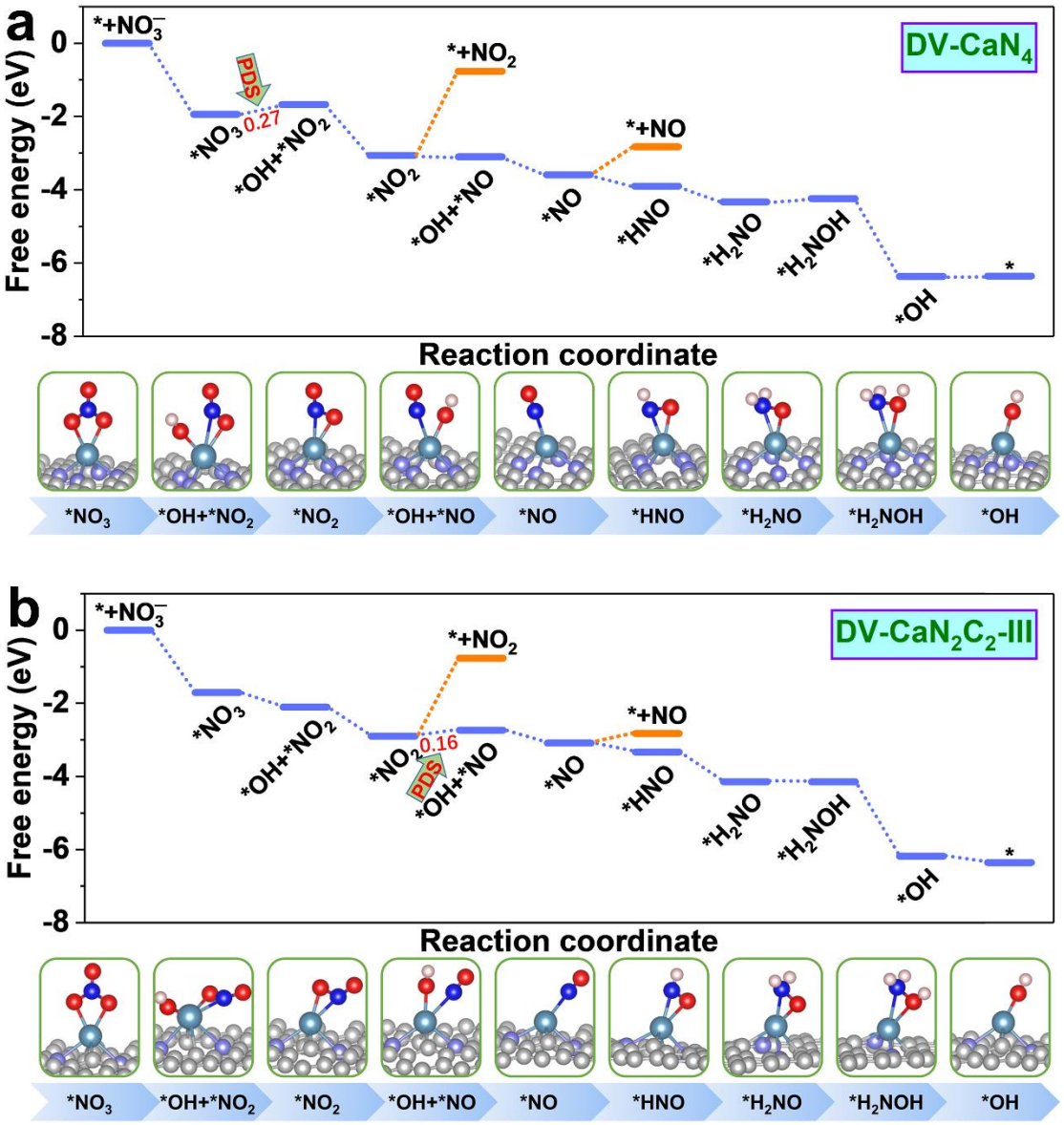

Fig. S12. Free energy diagrams together with corresponding intermediate configurations for eNO_3RR on DV-CaN_4 (a) and DV-CaN_2C_2-III (b) under the potentials of 0 V. The U_L is highlighted by red number.

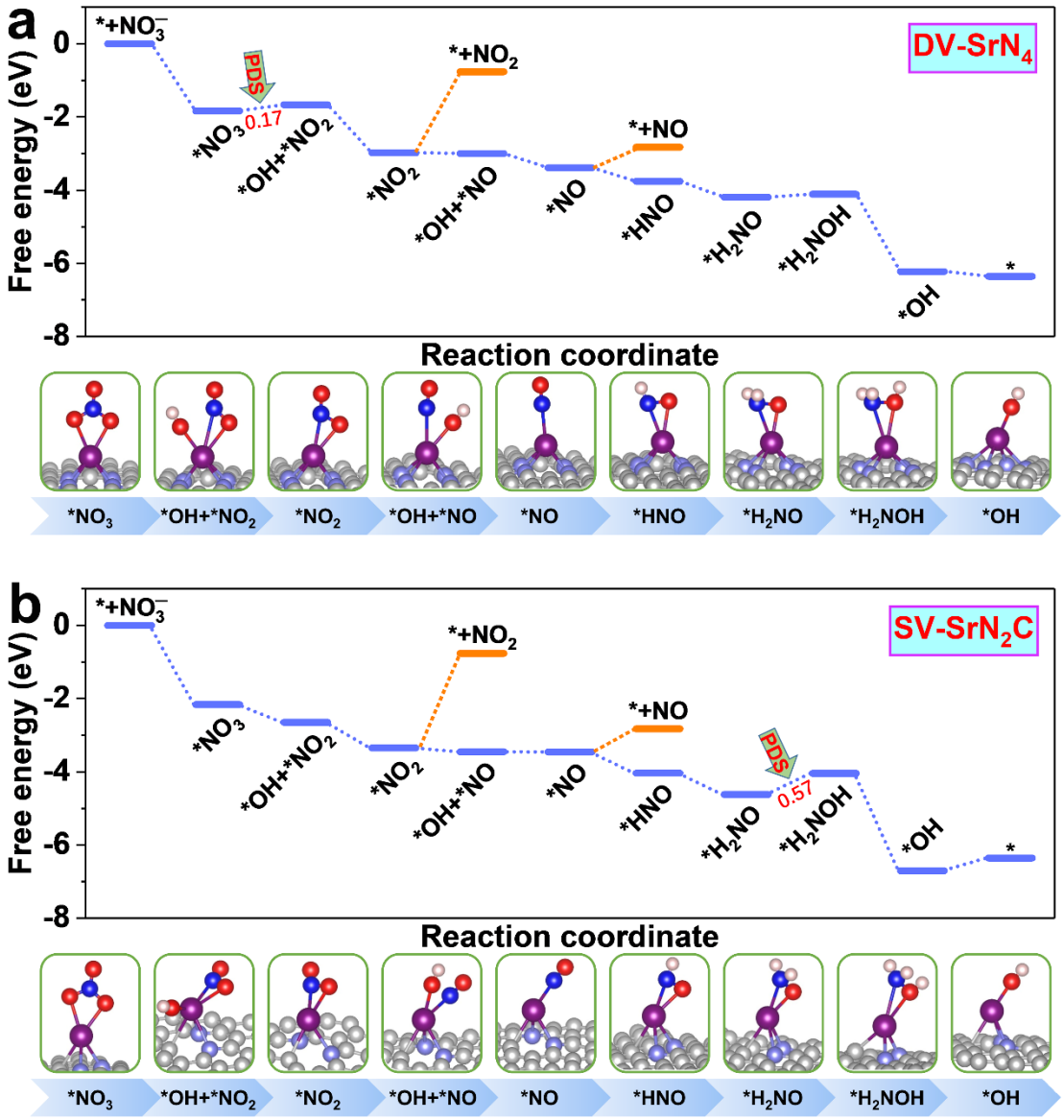

Fig. S13. Free energy diagrams together with corresponding intermediate configurations for eNO_3RR on DV-SrN_4 (a) and SV-SrN_2C (b) under the potentials of 0 V. The U_L is highlighted by red number.

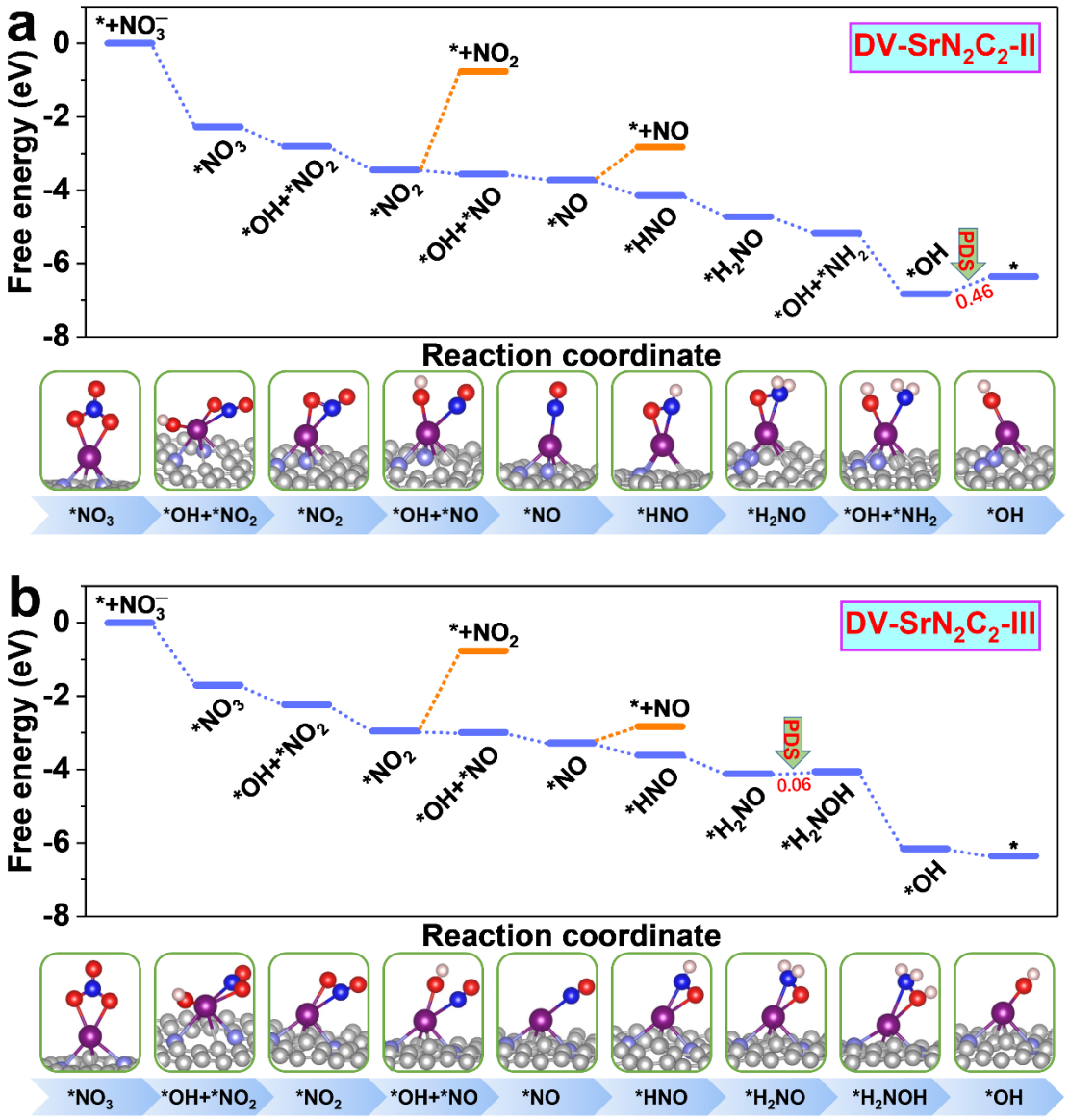

Fig. S14. Free energy diagrams together with corresponding intermediate configurations for eNO_3RR on DV-SrN_2C_2-II (a) and DV-SrN_2C_2-III (b) under the potentials of 0 V. The U_L is highlighted by red number.

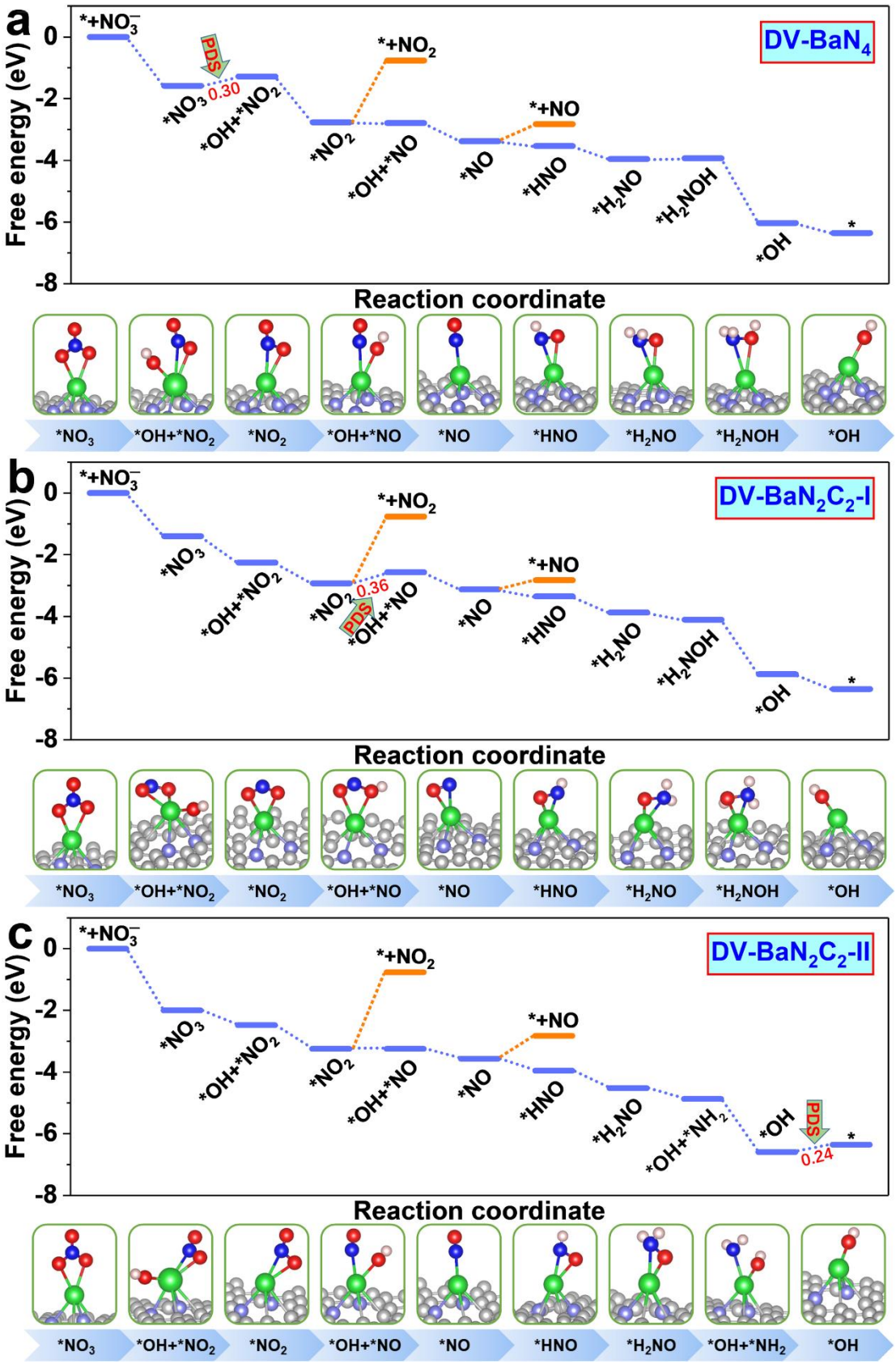

Fig. S15. Free energy diagrams together with corresponding intermediate configurations for eNO_3RR on DV-BaN_4 (a), DV-BaN_2C_2-I (b), and DV-BaN_2C_2-II (c) under the potentials of 0 V. The U_L is highlighted by red number.

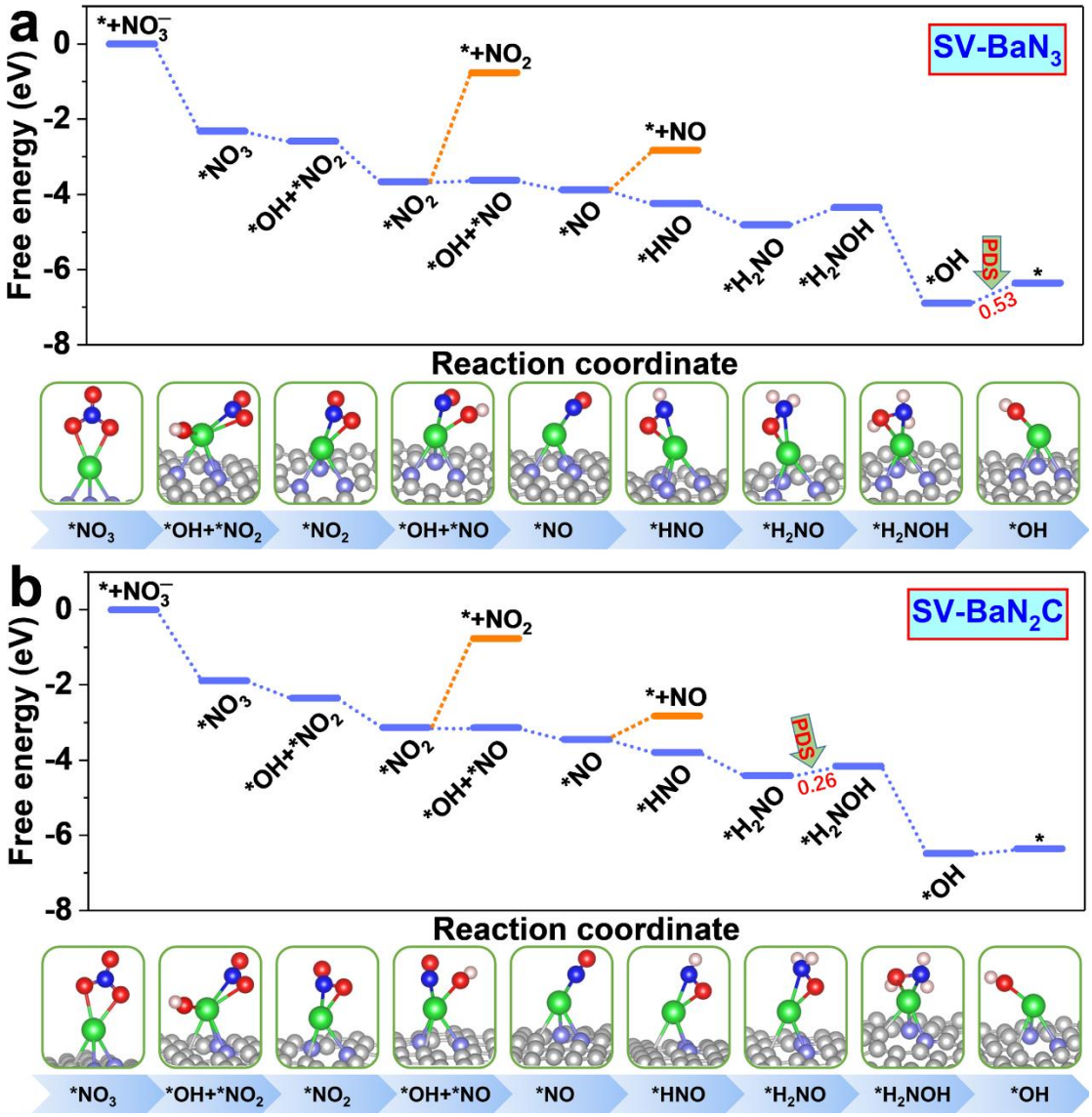

Fig. S16. Free energy diagrams together with corresponding intermediate configurations for eNO_3RR on SV-BaN_3 (a) and SV-BaN_2C (b) under the potentials of 0 V. The U_L is highlighted by red number.

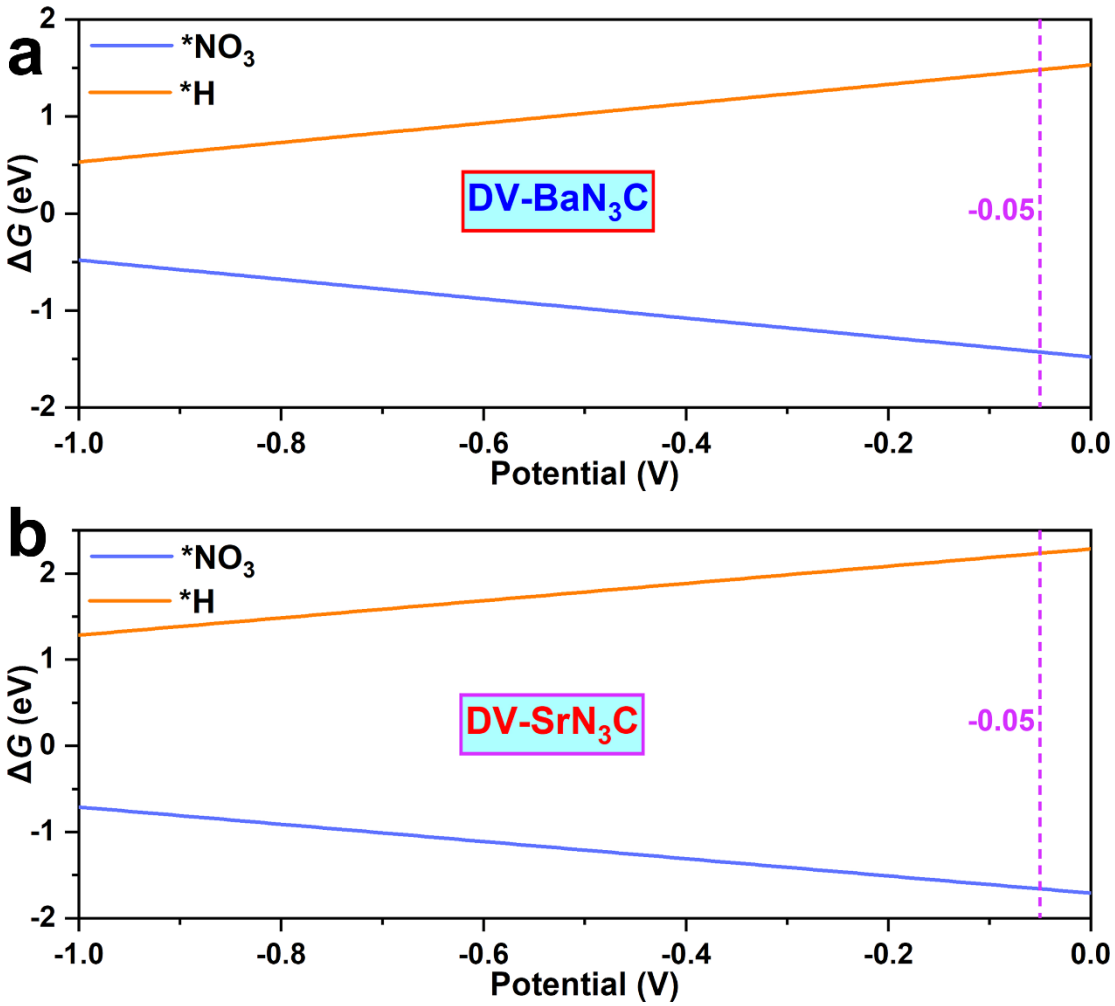

Fig. S17. The adsorption free energies of NO_3^- and H versus electrode potential from –1.0 to 0 V on DV-BaN_3C (a) and DV-SrN_3C (b), respectively. The U_L are labeled with dash lines.

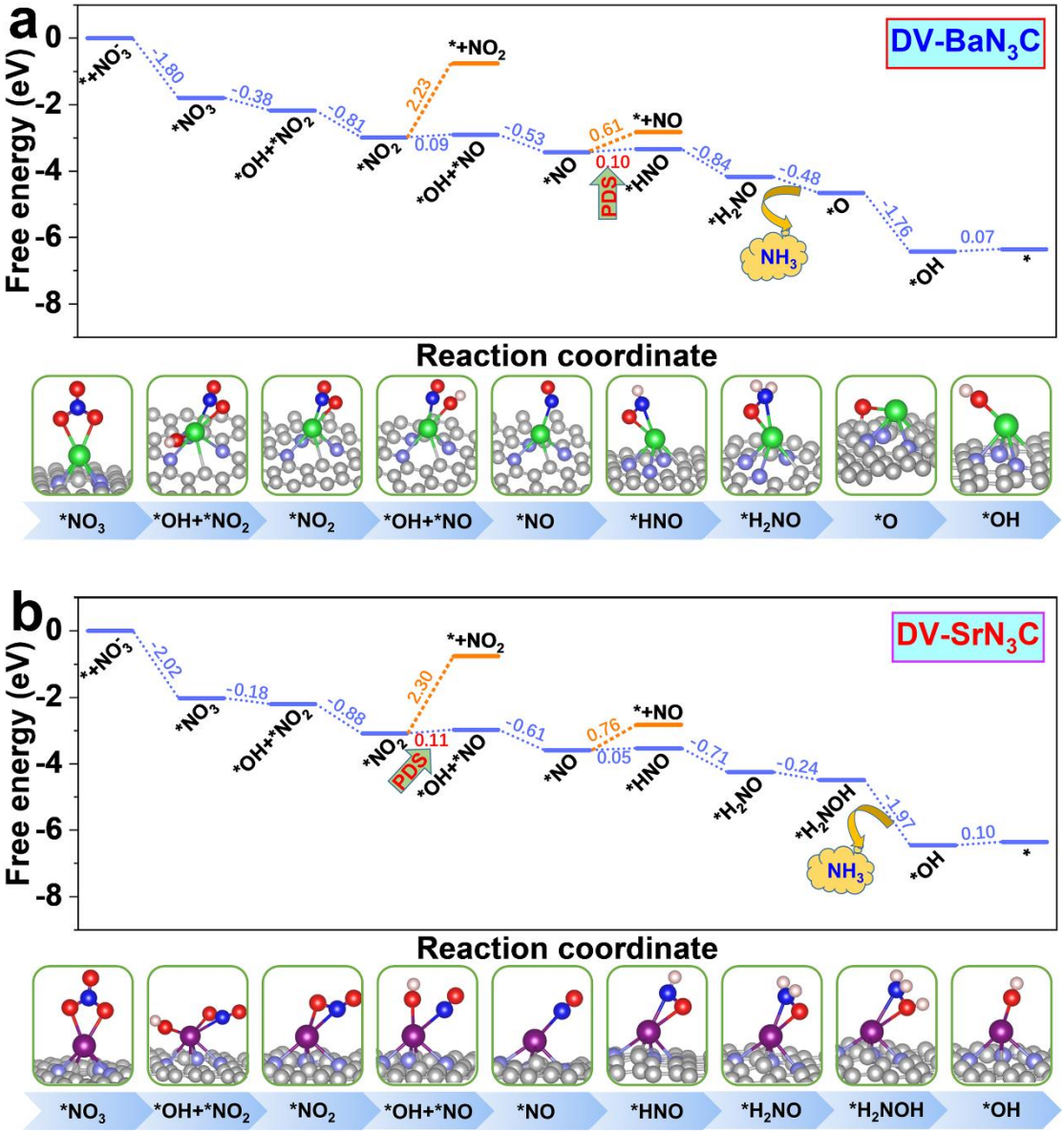

Fig. S18. Free energy diagrams together with corresponding intermediate configurations for eNO_3RR under the potentials of 0 V on DV-BaN_3C (a) and DV-SrN_3C (b) with consideration of the solvation effect. The U_L is highlighted by red number.

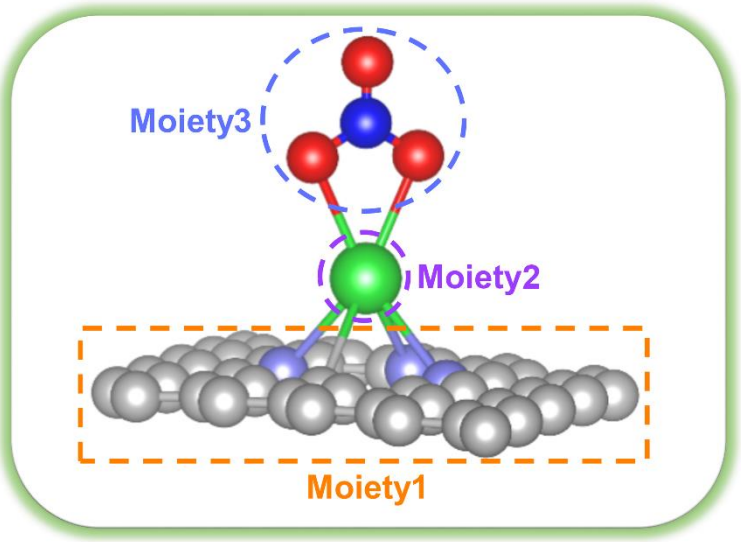

Fig. S19. Schematic diagram of three moieties of NO_3^- adsorption on DV-BaN_3C, for example. (moiety1: DV-N_3C support; moiety2: Ba atom; moiety3: adsorbed NO_3 species)

Table S1. The calculated zero-point energy (E_{ZPE}) and the product (T*S*) of the temperature (298.15 K) and entropy of various species along the reaction pathways for eNO_3RR on the AE-SAC systems, where * represents the active site.

Species	E_{ZPE} (eV)	T*S* (eV)
$*NO_3$	0.40	0.24
$*OH+*NO_2$	0.55	0.39
$*NO_2$	0.25	0.21
*OH+*NO	0.48	0.35
*NO	0.13	0.13
*HNO	0.41	0.13
$*H_2NO$	0.78	0.18
$*H_2NOH$	1.09	0.23
*O	0.09	0.04
OH	0.32	0.16

Table S2. The zero-point energy (E_{ZPE}) and the product (TS) of the temperature (298.15 K) and entropy for relevant free molecules, and their free energy correction referenced to the experimental formation energy, $\Delta G_{correct}$.

Species	E_{ZPE} (eV)	TS (eV)	$\Delta G_{correct}$ (eV)
HNO_3 (g)	0.70	0.83	1.06
NO_2 (g)	0.23	0.74	0.93
NO (g)	0.12	0.65	0.18
NH_3 (g)	0.89	0.60	0.18
H_2 (g)	0.27	0.40	--
H_2O (g)	0.56	0.67	--

Table S3. The key parameters of the AE-SAC systems: distance between AE metal and its bonded N/C atoms, d(AE–N/C); net charge of AE metal, ΔQ; spin magnetic moment of the whole system, M; formation energy, E_f; and binding energy, E_b.

Systems	d(AE–N/C) (Å)				ΔQ (e)	M (μ_B)	E_f (eV)	E_b (eV)
DV-MgN_4	1.97	1.97	1.97	1.97	1.58	0.00	-0.25	-5.59
DV-CaN_4	2.26	2.26	2.26	2.26	1.48	0.00	-0.36	-6.05
DV-SrN_4	2.41	2.41	2.41	2.41	1.52	0.00	-0.65	-5.50
DV-BaN_4	2.56	2.56	2.56	2.56	1.50	0.00	-0.05	-5.68
DV-MgN_3C	2.01	1.99	2.03	2.01	1.59	0.00	1.89	-5.11
DV-CaN_3C	2.33	2.29	2.29	2.29	1.44	0.00	1.78	-5.56
DV-SrN_3C	2.48	2.43	2.47	2.44	1.46	0.00	2.02	-5.02
DV-BaN_3C	2.64	2.61	2.63	2.57	1.42	0.00	2.00	-5.27
DV-MgN_2C_2-I	2.06	2.06	2.04	2.04	1.57	0.00	4.15	-4.64
DV-CaN_2C_2-I	2.35	2.35	2.34	2.34	1.40	0.00	3.96	-5.17
DV-SrN_2C_2-I	2.51	2.51	2.49	2.49	1.42	0.00	4.19	-4.64
DV-BaN_2C_2-I	2.69	2.69	2.64	2.64	1.36	0.00	4.14	-4.92
DV-MgN_2C_2-II	2.02	2.02	2.06	2.06	1.56	0.87	4.16	-3.43
DV-CaN_2C_2-II	2.23	2.23	2.51	2.51	1.46	0.00	3.69	-4.24
DV-SrN_2C_2-II	2.38	2.38	2.66	2.66	1.49	0.00	3.72	-3.92
DV-BaN_2C_2-II	2.54	2.54	2.82	2.82	1.48	0.00	3.55	-4.32
DV-MgN_2C_2-III	2.09	2.09	2.02	2.02	1.57	0.00	**4.02**	-4.66
DV-CaN_2C_2-III	2.40	2.40	2.30	2.30	1.40	0.00	4.02	-5.00
DV-SrN_2C_2-III	2.55	2.55	2.43	2.43	1.41	0.00	4.26	-4.47
DV-BaN_2C_2-III	2.72	2.72	2.72	2.72	1.35	0.00	4.17	-4.79
DV-MgN_1C_3	2.04	2.09	2.23	2.03	1.55	1.00	6.19	-3.13
DV-Ca N_1C_3	2.27	2.47	2.68	2.29	1.40	0.00	5.75	-3.91
DV-Sr N_1C_3	2.40	2.67	2.81	2.43	1.42	0.00	5.80	-3.56
DV-Ba N_1C_3	2.57	2.85	2.95	2.55	1.38	0.00	5.57	-4.03
DV-MgC_4	2.39	2.39	2.39	2.39	1.14	0.00	8.61	-0.87
DV-CaC_4	2.47	2.47	2.47	2.47	1.43	0.00	7.15	-2.66
DV-SrC_4	2.63	2.63	2.63	2.63	1.47	0.00	6.92	-2.60
DV-BaC_4	2.81	2.81	2.81	2.81	1.43	0.00	6.47	-3.28
SV-MgN_3	2.00	2.00	2.00	--	1.20	0.56	1.64	-3.40
SV-CaN_3	2.19	2.19	2.18	--	1.45	0.00	0.76	-4.62
SV-SrN_3	2.33	2.33	2.33	--	1.50	0.00	0.86	-4.23
SV-BaN_3	2.49	2.49	2.49	--	1.49	0.00	0.67	-4.65
SV-MgN_2C	1.96	1.96	1.99	--	1.51	0.00	3.35	-3.10
SV-CaN_2C	2.22	2.22	2.26	--	1.37	0.00	2.41	-4.37
SV-SrN_2C	2.36	2.36	2.40	--	1.41	0.00	2.54	-3.96
SV-BaN_2C	2.53	2.53	2.53	--	1.39	0.00	2.32	-4.40
SV-$MgNC_2$	1.98	2.06	2.06	--	1.44	1.00	5.54	-1.62
SV-Ca NC_2	2.21	2.31	2.30	--	1.36	1.00	4.41	-3.09
SV-Sr NC_2	2.35	2.45	2.44	--	1.40	1.00	4.46	-2.75
SV-Ba NC_2	2.52	2.59	2.59	--	1.37	1.00	4.18	-3.26
SV-MgC_3	2.12	2.13	2.13	--	1.29	2.00	7.64	-1.78
SV-CaC_3	2.34	2.34	2.34	--	1.33	1.95	6.52	-3.24

SV-SrC_3	2.48	2.50	2.48	--	1.38	2.00	6.49	-2.97
SV-BaC_3	2.62	2.67	2.62	--	1.35	2.00	6.15	-3.55

Table S4. The key parameters for NO_3^- adsorption on the AE-SAC systems: distance between AE metal and its bonded O atoms, d(AE–O); net charge of AE metal, ΔQ(M-NO_3) and *NO_3, ΔQ(NO_3); and adsorption free energy of NO_3^-, ΔG(*NO_3).

Systems	d(AE–O_1) (Å)	d(AE–O_2) (Å)	ΔQ(M-NO_3) (e)	ΔQ(NO_3) (e)	ΔG(*NO_3) (eV)
DV-MgN_4	2.13	2.13	1.65	-0.88	-1.65
DV-CaN_4	2.36	2.37	1.55	-0.86	-1.94
DV-SrN_4	2.52	2.52	1.61	-0.88	-1.84
DV-BaN_4	2.70	2.70	1.62	-0.88	-1.58
DV-MgN_3C	2.12	2.12	1.63	-0.89	-1.51
DV-CaN_3C	2.36	2.38	1.53	-0.86	-1.77
DV-SrN_3C	2.51	2.50	1.61	-0.86	-1.71
DV-BaN_3C	2.69	2.67	1.62	-0.86	-1.48
DV-MgN_2C_2-I	2.11	2.11	1.63	-0.88	-1.40
DV-CaN_2C_2-I	2.35	2.37	1.53	-0.85	-1.66
DV-SrN_2C_2-I	2.50	2.52	1.58	-0.87	-1.58
DV-BaN_2C_2-I	2.66	2.68	1.57	-0.86	-1.40
DV-MgN_2C_2-II	2.09	2.10	1.64	-0.88	-2.14
DV-CaN_2C_2-II	2.33	2.33	1.55	-0.84	-2.39
DV-SrN_2C_2-II	2.48	2.49	1.62	-0.86	-2.27
DV-BaN_2C_2-II	2.66	2.66	1.62	-0.86	-2.00
DV-MgN_2C_2-III	2.10	2.09	1.63	-0.88	-1.18
DV-CaN_2C_2-III	2.34	2.35	1.52	-0.85	-1.71
DV-SrN_2C_2-III	2.51	2.51	1.58	-0.87	-1.70
DV-BaN_2C_2-III	2.66	2.65	1.61	-0.85	-1.46
SV-MgN_3	2.06	2.08	1.64	-0.87	-3.26
SV-CaN_3	2.35	2.35	1.56	-0.85	-2.84
SV-SrN_3	2.51	2.51	1.63	-0.87	-2.67
SV-BaN_3	2.68	2.68	1.64	-0.87	-2.32
SV-MgN_2C	2.05	2.06	1.63	-0.87	-2.45
SV-CaN_2C	2.33	2.33	1.56	-0.83	-2.20
SV-SrN_2C	2.50	2.48	1.62	-0.85	-2.16
SV-BaN_2C	2.68	2.64	1.63	-0.85	-1.89

Table S5. The key parameters of H atoms adsorption on the AE-SAC systems: distance between AE metal and H atoms, d(AE–H); net charge of AE metal, ΔQ(M-H) and *H atoms, ΔQ(H); adsorption free energy of H atoms, ΔG(*H).

Systems	d(AE–H) (Å)	ΔG(*H) (eV)	ΔQ(M-H) (e)	ΔQ(H) (e)
DV-MgN_4	2.60	2.26	1.60	0.01
DV-CaN_4	2.98	2.27	1.47	0.01
DV-SrN_4	2.32	1.33	1.55	-0.59
DV-BaN_4	2.51	1.54	1.57	-0.57
DV-MgN_3C	1.78	1.35	1.43	-0.70
DV-CaN_3C	2.13	1.44	1.48	-0.59
DV-SrN_3C	3.17	2.28	1.46	0.01
DV-BaN_3C	2.40	1.53	1.51	-0.56
DV-MgN_2C_2-I	1.76	1.31	1.32	-0.68
DV-CaN_2C_2-I	2.11	1.53	1.47	-0.62
DV-SrN_2C_2-I	2.26	1.52	1.51	-0.59
DV-BaN_2C_2-I	3.42	2.30	1.37	0.00
DV-MgN_2C_2-II	1.76	0.61	1.56	-0.68
DV-CaN_2C_2-II	2.05	0.79	1.50	-0.71
DV-SrN_2C_2-II	2.21	0.91	1.54	-0.71
DV-BaN_2C_2-II	2.36	1.14	1.53	-0.68
DV-MgN_2C_2-III	1.78	1.56	1.55	-0.58
DV-CaN_2C_2-III	2.97	2.28	1.40	0.01
DV-SrN_2C_2-III	3.14	2.29	1.41	0.00
DV-BaN_2C_2-III	2.46	1.68	1.48	-0.53
SV-MgN_3	1.73	-0.55	1.55	-0.73
SV-CaN_3	2.08	0.39	1.52	-0.76
SV-SrN_3	2.26	0.57	1.55	-0.71
SV-BaN_3	2.45	0.95	1.58	-0.68
SV-MgN_2C	1.72	0.22	1.54	-0.72
SV-CaN_2C	2.96	2.28	1.37	0.01
SV-SrN_2C	2.20	0.99	1.53	-0.69
SV-BaN_2C	2.33	1.20	1.51	-0.67

Table S6. The potential-determining step (PDS) and corresponding limiting potential (U_L) for eNO_3RR on the AE-SAC systems.

Systems	PDS	U_L (V)
DV-MgN_4	$*NO_3 \rightarrow *OH + *NO_2$	-0.84
DV-CaN_4	$*NO_3 \rightarrow *OH + *NO_2$	-0.27
DV-SrN_4	$*NO_3 \rightarrow *OH + *NO_2$	-0.17
DV-BaN_4	$*NO_3 \rightarrow *OH + *NO_2$	-0.30
DV-MgN_3C	$*NO_3 \rightarrow *OH + *NO_2$	-0.84
DV-CaN_3C	$*NO_3 \rightarrow *OH + *NO_2$	-0.92
DV-SrN_3C	$*NO_2 \rightarrow *OH + *NO$	-0.05
DV-BaN_3C	$*NO \rightarrow *HNO$	-0.05
DV-MgN_2C_2-I	$*OH \rightarrow * + H_2O$	-0.63
DV-CaN_2C_2-I	$*NO_3 \rightarrow *OH + *NO_2$	-0.93
DV-SrN_2C_2-I	$*NO_3 \rightarrow *OH + *NO_2$	-0.88
DV-BaN_2C_2-I	$*NO_2 \rightarrow *OH + *NO$	-0.36
DV-MgN_2C_2-II	$*O \rightarrow *OH$	-0.57
DV-CaN_2C_2-II	$*OH \rightarrow * + H_2O$	-0.62
DV-SrN_2C_2-II	$*OH \rightarrow * + H_2O$	-0.46
DV-BaN_2C_2-II	$*OH \rightarrow * + H_2O$	-0.24
DV-MgN_2C_2-III	$*NO_3 \rightarrow *OH + *NO_2$	-0.60
DV-CaN_2C_2-III	$*NO_2 \rightarrow *OH + *NO$	-0.16
DV-SrN_2C_2-III	$*H_2NO \rightarrow *H_2NOH$	-0.06
DV-BaN_2C_2-III	$*NO_3 \rightarrow *OH + *NO_2$	-0.80
SV-MgN_3	$*OH \rightarrow * + H_2O$	-1.48
SV-CaN_3	$*OH \rightarrow * + H_2O$	-0.98
SV-SrN_3	$*OH \rightarrow * + H_2O$	-0.79
SV-BaN_3	$*OH \rightarrow * + H_2O$	-0.53
SV-MgN_2C	$*OH \rightarrow * + H_2O$	-0.69
SV-CaN_2C	$*H_2NO \rightarrow *H_2NOH$	-0.63
SV-SrN_2C	$*H_2NO \rightarrow *H_2NOH$	-0.57
SV-BaN_2C	$*H_2NO \rightarrow *H_2NOH$	-0.26

Table S7. The calculated adsorption free energy of *H_2O (ΔG_{*H2O}, in eV) and the free energy change of *OH → *H_2O ($\Delta G_{*OH \rightarrow *H2O}$, in eV) for the AE-SAC systems.

Systems	ΔG_{*H2O}				$\Delta G_{*OH \rightarrow *H2O}$			
	Mg	Ca	Sr	Ba	Mg	Ca	Sr	Ba
DV-MN_4	-0.23	-0.13	-0.02	0.15	-0.38	-0.13	-0.16	-0.17
DV-MN_3C	-0.23	-0.11	-0.07	-0.01	-0.57	-0.26	-0.38	-0.35
DV-MN_2C_2-I	-0.19	-0.05	0.05	-0.01	-0.56	-0.27	-0.24	-0.49
DV-MN_2C_2-II	-0.56	-0.21	-0.15	-0.16	-0.27	0.41	0.31	0.08
DV-MN_2C_2-III	-0.16	-0.19	-0.11	0.20	-0.82	-0.36	-0.31	-0.13
SV-MN_3	-0.51	-0.18	-0.06	-0.16	0.97	0.81	0.73	0.38
SV-MN_2C	-0.55	-0.11	-0.02	-0.19	0.14	0.30	0.33	-0.06