Supplementary Material for "Multi-Orbital Engineering of Single-Atom Catalysts: Unlocking High-Efficiency Nitrate Reduction"

Chun Wu [a,†], Yanqing Shen [a,c,†,*], Lingling Lv [a], Xianghui Meng [a], Xin Yang [a], Xinyu Wang [a], Xiangqian Jiang [a], Qing Ai [b,*], Yong Shuai [b,*], Zhongxiang Zhou [a,c]

a School of Physics, Harbin Institute of Technology, Harbin 150001, PR China

b School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, PR China

c Heilongjiang Provincial Key Laboratory of Plasma Physics and Application Technology, Harbin Institute of Technology, Harbin 150001, PR China

† Contributed equally to this work

* Corresponding authors: Yanqing Shen. E-mail: shenyanqing2004@163.com

Qing Ai, E-mail: hitaiqing@hit.edu.cn

Yong Shuai, E-mail: shuaiyong@hit.edu.cn

The whole reaction process of the electrochemical reduction of NO_3^- to NH_3 can be summarized as $NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O$. Nine protons and eight electrons are transferred in the process. The basic reaction steps of the N-end pathway are described as

$$*+NO_3^- \rightarrow *NO_3 + e^- \quad (5)$$
$$*NO_3 + H^+ + e^- \rightarrow *NO_3H \quad (6)$$
$$*NO_3H + H^+ + e^- \rightarrow *NO_2 + H_2O \quad (7)$$
$$*NO_2 + H^+ + e^- \rightarrow *NO_2H \quad (8)$$
$$*NO_2H + H^+ + e^- \rightarrow *NO + H_2O \quad (9)$$
$$*NO + H^+ + e^- \rightarrow *NOH \quad (10)$$
$$*NOH + H^+ + e^- \rightarrow *N + H_2O \quad (11)$$
$$*N + H^+ + e^- \rightarrow *NH \quad (12)$$
$$*NH + H^+ + e^- \rightarrow *NH_2 \quad (13)$$
$$*NH_2 + H^+ + e^- \rightarrow *NH_3 \quad (14)$$
$$*NH_3 \rightarrow *+NH_3 \quad (15)$$

In addition, the production of NO, the production of NO_2, and the formation of NO dimers may lead to the production of byproduct N_2 by a pathway that can be described as

$$*NO + *NO \rightarrow *N_2O_2 \quad (16)$$
$$*N_2O_2 + H^+ + e^- \rightarrow *N_2O_2H \quad (17)$$
$$*N_2O_2H + H^+ + e^- \rightarrow *N_2O + H_2O \quad (18)$$
$$*N_2O + H^+ + e^- \rightarrow *N_2OH \quad (19)$$
$$*N_2OH + H^+ + e^- \rightarrow *N_2 + H_2O \quad (20)$$
$$*N_2 \rightarrow *+N_2 \quad (21)$$
$$*NO_2 \rightarrow *+NO_2 \quad (22)$$
$$*NO \rightarrow *+NO \quad (23)$$
$$*NO + H^+ + e^- \rightarrow *HNO \quad (24)$$
$$*HNO + H^+ + e^- \rightarrow *NHOH \quad (25)$$
$$*NOH + H^+ + e^- \rightarrow *NHOH \quad (26)$$
$$*NHOH + H^+ + e^- \rightarrow *NH_2OH \quad (27)$$
$$*NH_2OH + H^+ + e^- \rightarrow * +NH_2OH \quad (28)$$

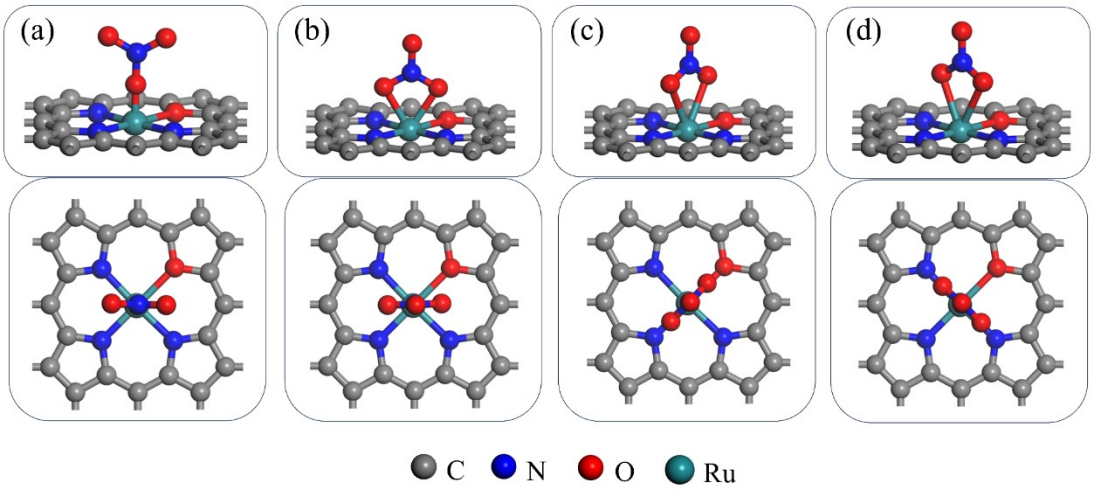


Figure S1. Four possible configurations of NO_3^-, namely, (a)1-O pattern (one oxygen atom adsorbed on TM-N_3X) , (b)2-O pattern (two oxygen atoms adsorbed on TM-N_3X), (c)2-OO pattern (oxygen of NO_3^- closed to O of base), and (d)2-ON pattern (oxygen of NO_3^- closed to N of base). Ru-N_3O is taken as a representative.

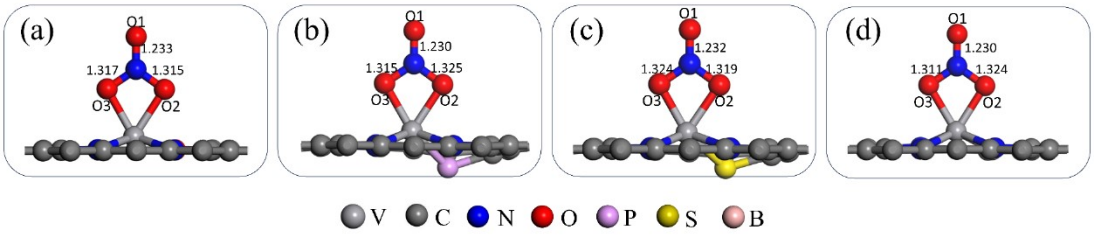
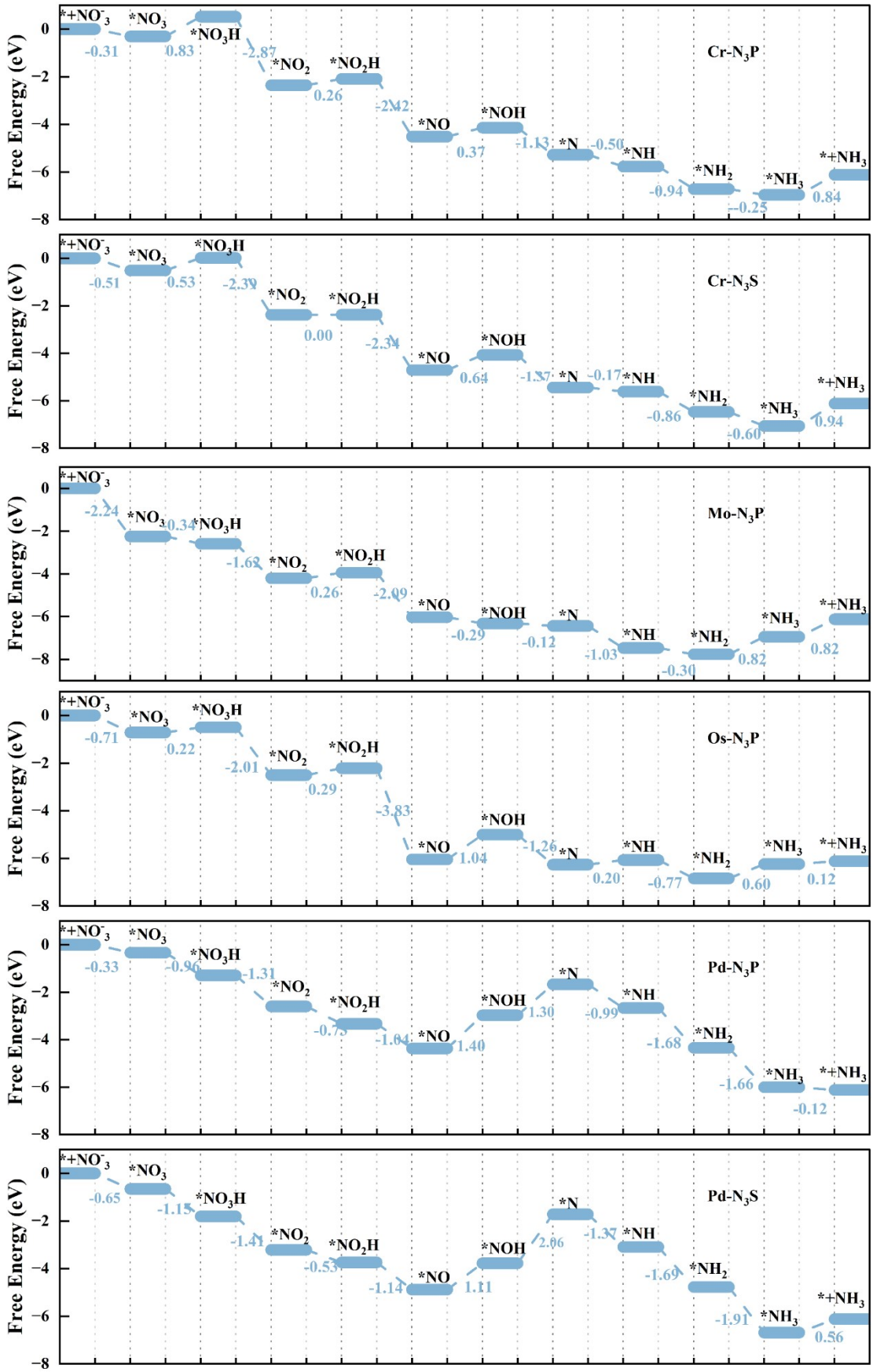
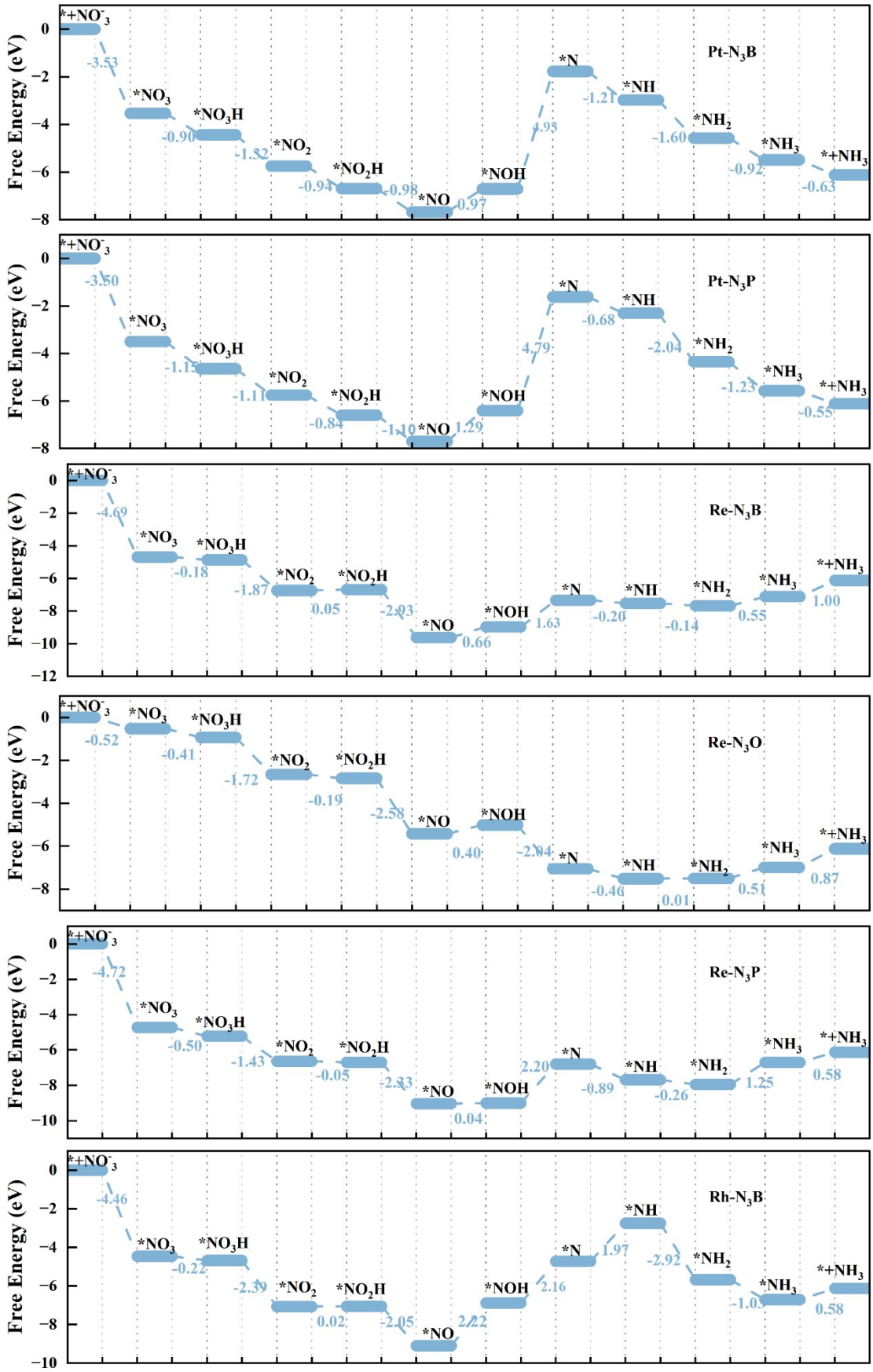
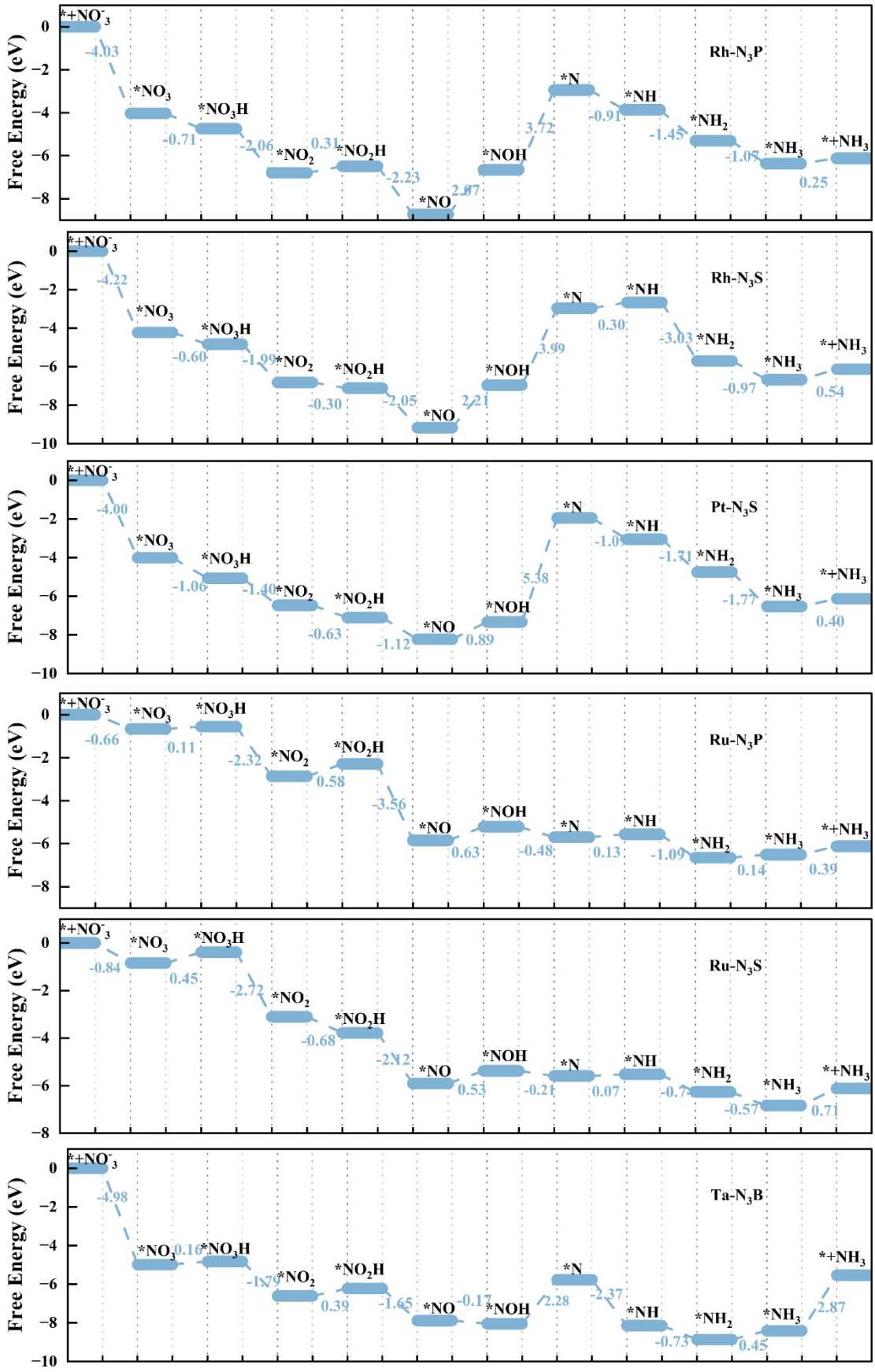
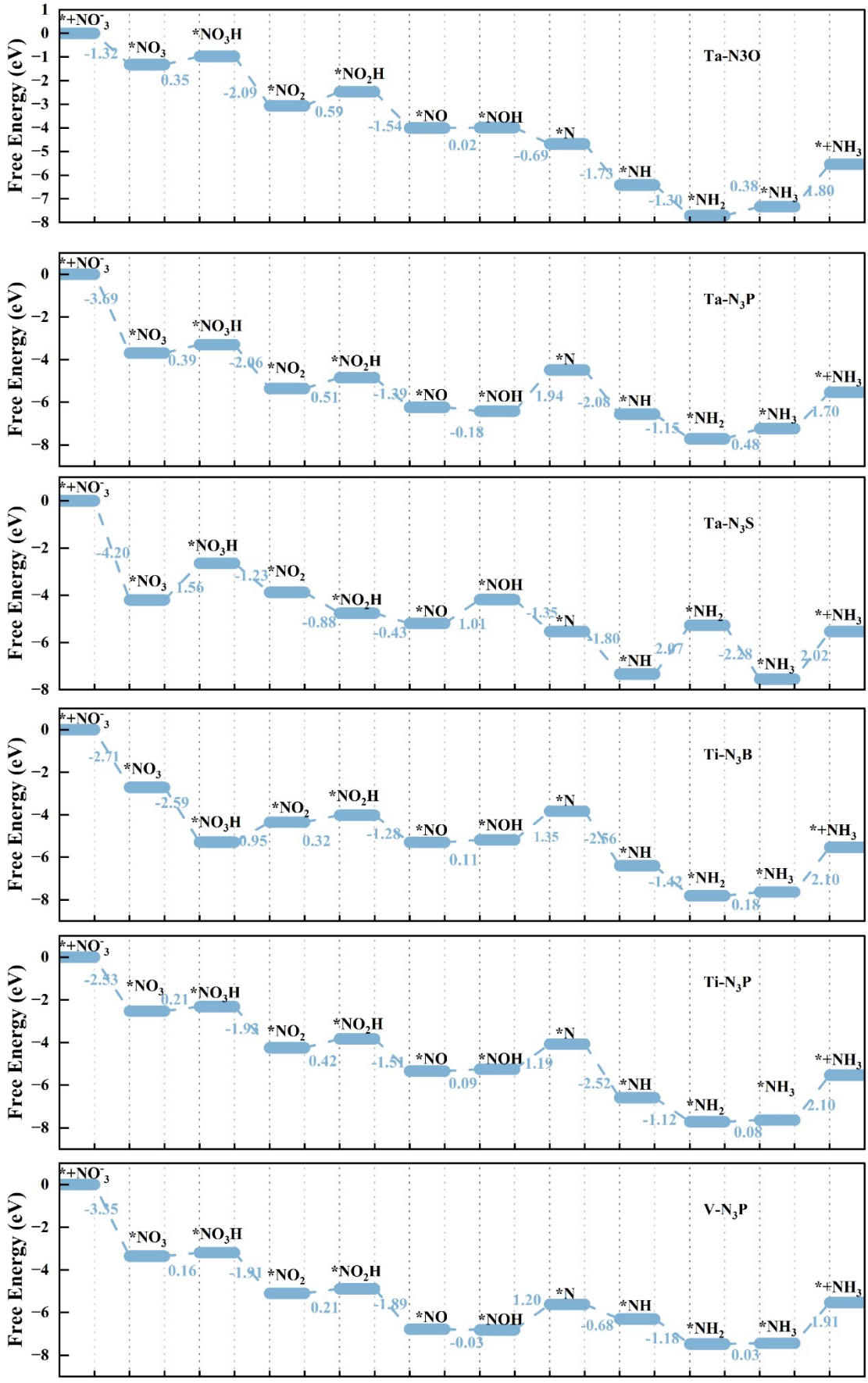


Figure S2. Taking V-N3X as an example, the N-O2 and N-O3 bond lengths of activated *NO_3 increased significantly from 1.264 Å in the gaseous state to 1.311 ~ 1.325 Å.


Free Energy (eV)
0
−2
−4
−6
−8
*+NO3
*NO3
*NO3H
*NO2
*NO2H
*NO
*NOH
*N
*NH
*NH2
*NH3
*+NH3
-0.31
0.83
-2.87
0.26
-2.42
0.37
-1.13
-0.50
-0.94
-0.25
0.84
Cr-N3P
-0.51
0.53
-2.39
0.00
-2.34
0.64
-1.37
-0.17
-0.86
-0.60
0.94
Cr-N3S
-2.24
0.34
-1.62
0.26
-2.09
-0.29
-0.12
-1.03
-0.30
0.82
0.82
Mo-N3P
-0.71
0.22
-2.01
0.29
-3.83
1.04
-1.26
0.20
-0.77
0.60
0.12
Os-N3P
-0.33
-0.96
-1.31
-0.75
-1.64
1.40
1.30
-0.99
-1.68
-1.66
-0.12
Pd-N3P
-0.65
-1.15
-1.41
-0.53
-1.14
1.11
2.06
-1.37
-1.69
-1.91
0.56
Pd-N3S


Free Energy (eV)
Pt-N3B
*+NO3-
-3.53
*NO3
-0.90
*NO3H
-1.32
*NO2
-0.94
*NO2H
-0.98
*NO
0.97
*NOH
4.93
*N
-1.21
*NH
-1.60
*NH2
-0.92
*NH3
-0.63
*+NH3
Pt-N3P
*+NO3-
-3.50
*NO3
-1.13
*NO3H
-1.11
*NO2
-0.84
*NO2H
-1.10
*NO
1.29
*NOH
4.79
*N
-0.68
*NH
-2.04
*NH2
-1.23
*NH3
-0.55
*+NH3
Re-N3B
*+NO3-
-4.69
*NO3
-0.18
*NO3H
-1.87
*NO2
0.05
*NO2H
-2.93
*NO
0.66
*NOH
1.63
*N
-0.20
*NH
-0.14
*NH2
0.55
*NH3
1.00
*+NH3
Re-N3O
*+NO3-
-0.52
*NO3
-0.41
*NO3H
-1.72
*NO2
-0.19
*NO2H
-2.58
*NO
0.40
*NOH
-2.94
*N
-0.46
*NH
0.01
*NH2
0.51
*NH3
0.87
*+NH3
Re-N3P
*+NO3-
-4.72
*NO3
-0.50
*NO3H
-1.43
*NO2
-0.05
*NO2H
-2.33
*NO
0.04
*NOH
2.20
*N
-0.89
*NH
-0.26
*NH2
1.25
*NH3
0.58
*+NH3
Rh-N3B
*+NO3-
-4.46
*NO3
-0.22
*NO3H
-2.39
*NO2
0.02
*NO2H
-2.05
*NO
2.22
*NOH
2.16
*N
1.97
*NH
-2.92
*NH2
-1.05
*NH3
0.58
*+NH3


Free Energy (eV)
Rh-N3P
*+NO3-
-4.03
*NO3
-0.71
*NO3H
-2.06
*NO2
0.31
*NO2H
-2.23
*NO
2.87
*NOH
3.72
*N
-0.91
*NH
-1.45
*NH2
-1.07
*NH3
0.25
*+NH3
Rh-N3S
*+NO3-
-4.22
*NO3
-0.60
*NO3H
-1.99
*NO2
-0.30
*NO2H
-2.05
*NO
2.21
*NOH
3.99
*N
0.30
*NH
-3.03
*NH2
-0.97
*NH3
0.54
*+NH3
Pt-N3S
*+NO3-
-4.00
*NO3
-1.06
*NO3H
-1.40
*NO2
-0.63
*NO2H
-1.12
*NO
0.89
*NOH
5.38
*N
-1.09
*NH
-1.71
*NH2
-1.77
*NH3
0.40
*+NH3
Ru-N3P
*+NO3-
-0.66
*NO3
0.11
*NO3H
-2.32
*NO2
0.58
*NO2H
-3.56
*NO
0.63
*NOH
-0.48
*N
0.13
*NH
-1.09
*NH2
0.14
*NH3
0.39
*+NH3
Ru-N3S
*+NO3-
-0.84
*NO3
0.45
*NO3H
-2.72
*NO2
-0.68
*NO2H
-2.12
*NO
0.53
*NOH
-0.21
*N
0.07
*NH
-0.74
*NH2
-0.57
*NH3
0.71
*+NH3
Ta-N3B
*+NO3-
-4.98
*NO3
0.10
*NO3H
-1.79
*NO2
0.39
*NO2H
-1.65
*NO
-0.17
*NOH
2.28
*N
-2.37
*NH
-0.73
*NH2
0.45
*NH3
2.87
*+NH3


Free Energy (eV)
Ta-N3O
*+NO3-
-1.32
*NO3
0.35
*NO3H
-2.09
*NO2
0.59
*NO2H
-1.54
*NO
0.02
*NOH
-0.69
*N
-1.73
*NH
-1.30
*NH2
0.38
*NH3
1.80
*+NH3
Ta-N3P
*+NO3-
-3.69
*NO3
0.39
*NO3H
-2.06
*NO2
0.51
*NO2H
-1.39
*NO
-0.18
*NOH
1.94
*N
-2.08
*NH
-1.15
*NH2
0.48
*NH3
1.70
*+NH3
Ta-N3S
*+NO3-
-4.20
*NO3
1.56
*NO3H
-1.23
*NO2
-0.88
*NO2H
-0.43
*NO
1.01
*NOH
-1.35
*N
-1.80
*NH
2.07
*NH2
-2.28
*NH3
2.02
*+NH3
Ti-N3B
*+NO3-
-2.71
*NO3
-2.59
*NO3H
0.95
*NO2
0.32
*NO2H
-1.28
*NO
0.11
*NOH
1.35
*N
-2.56
*NH
-1.42
*NH2
0.18
*NH3
2.10
*+NH3
Ti-N3P
*+NO3-
-2.53
*NO3
0.21
*NO3H
-1.98
*NO2
0.42
*NO2H
-1.51
*NO
0.09
*NOH
1.19
*N
-2.52
*NH
-1.12
*NH2
0.08
*NH3
2.10
*+NH3
V-N3P
*+NO3-
-3.55
*NO3
0.16
*NO3H
-1.91
*NO2
0.21
*NO2H
-1.89
*NO
-0.03
*NOH
1.20
*N
-0.68
*NH
-1.18
*NH2
0.03
*NH3
1.91
*+NH3

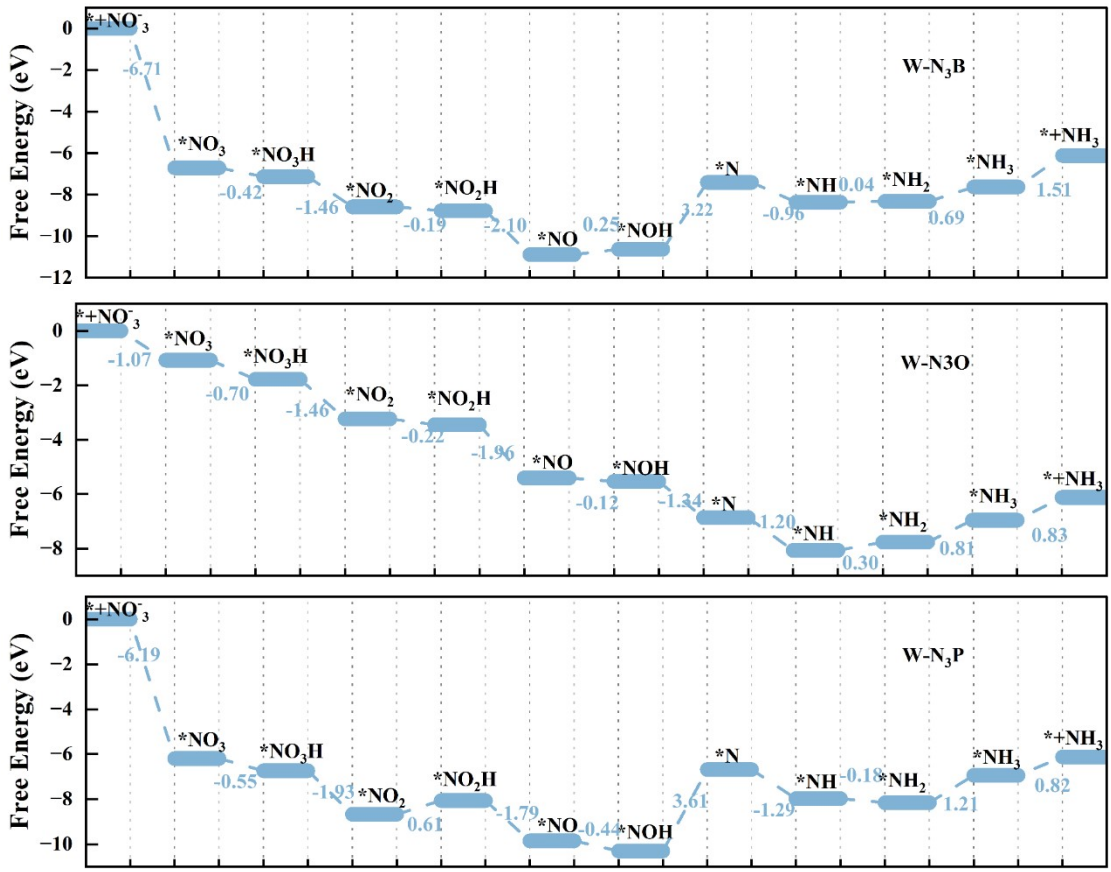


Figure S3. Gibbs Free energy diagrams of NO_3RR on Ta-N_3O, W-N_3O, Re-N_3O, Ti-N_3P, V-N_3P, Cr-N_3P, Mo-N_3P, Ru-N_3P, Rh-N_3P, Pd-N_3P, Ta-N_3P, W-N_3P, Re-N_3P, Os-N_3P, Pt-N_3P, Cr-N_3S, Ru-N_3S, Rh-N_3S, Pd-N_3S, Ta-N_3S, Pt-N_3S, Ti-N_3B, Rh-N_3B, Ta-N_3B, W-N_3B, Re-N_3B, Pt-N_3B.

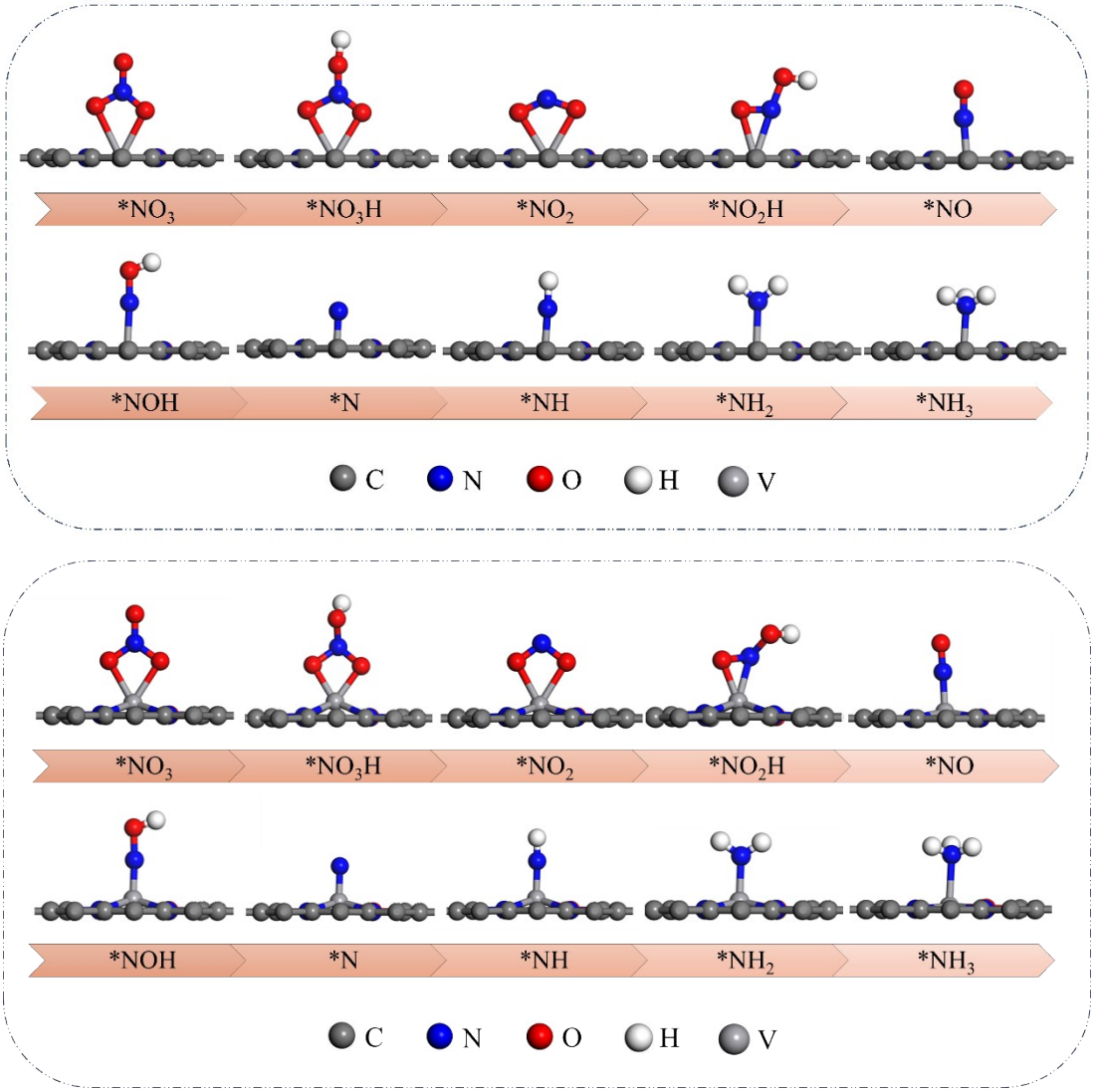


Figure S4. The changes of the adsorption configuration of V-N_3O during the entire reaction process before and after optimization, the path from *NO_3^- to *NH.

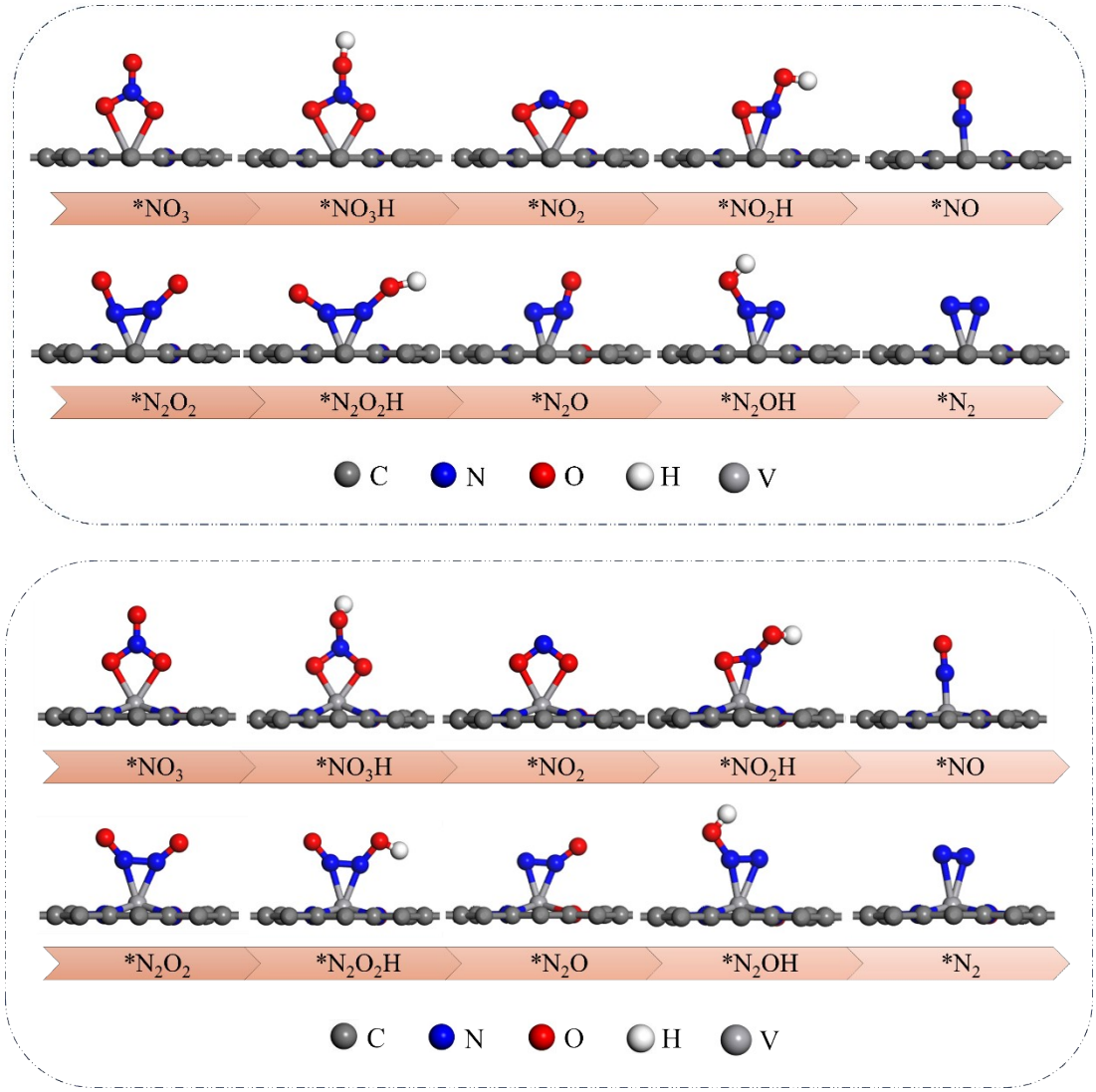


Figure S5. The changes of the adsorption configuration of V-N_3O during the entire reaction process before and after optimization, the path from *NO_3^- to *N_2.

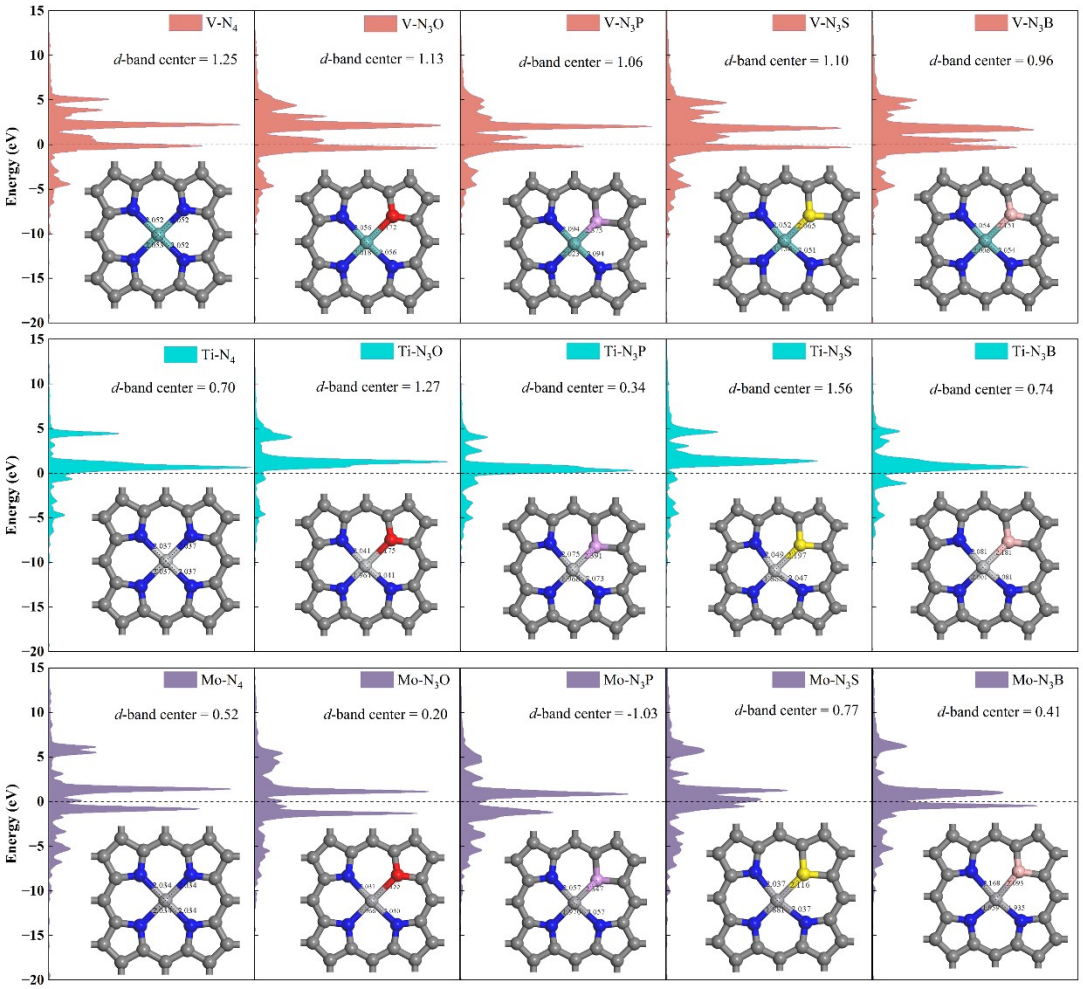


Figure S6. Changes in *d*-band center and bond length of V, Ti and Mo under different coordination environments.

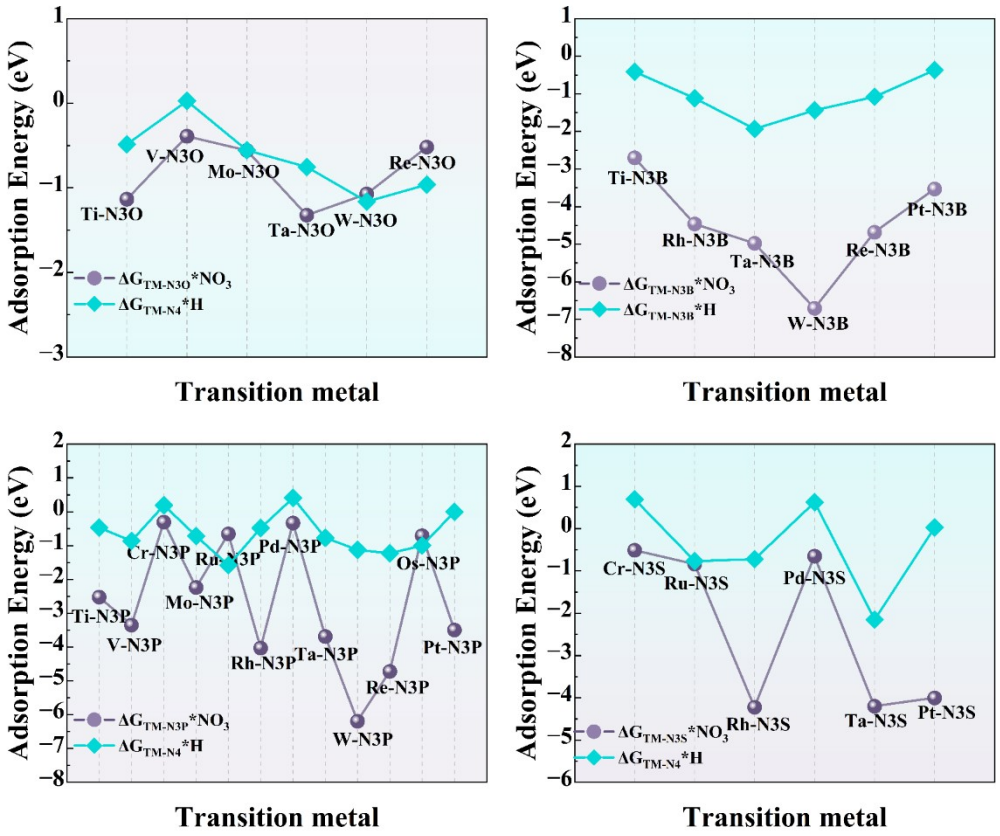


Figure S7. Adsorption energy of 30 TM-N_3X catalysts for NO_3^- and H^+ adsorption in corresponding modes.

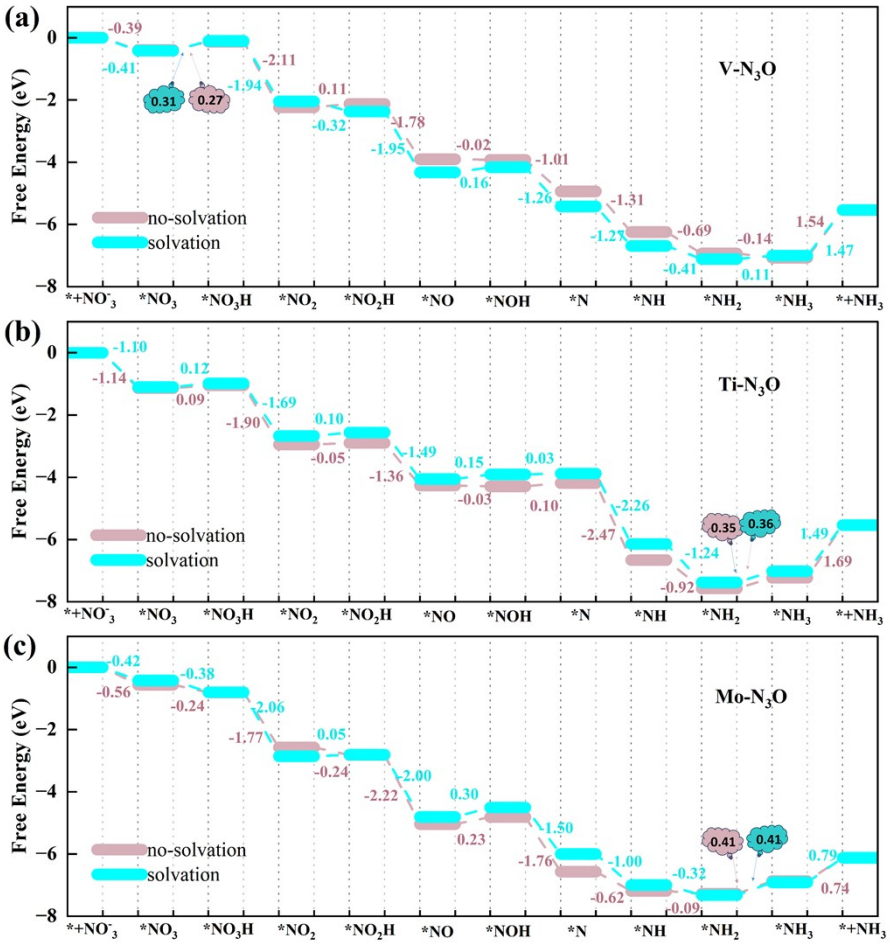


Figure S8. Free energy diagrams of NO_3RR on (a) V-N_3O, (b) Ti-N_3O, (c) Mo-N_3O. Purple represents the result without considering the solvation effect, and blue represents the result with considering the solvation effect.

Table S1. The formation energy (E_{form}) and dissolution potential (U_{diss}) of 52 TM-N_3X catalysts.

	E_{form}(eV)	U_{diss}(V)
Ti-N_3O	-3.66	0.20
V-N_3O	-3.30	0.47
Cr-N_3O	-3.22	0.70
Nb-N_3O	-1.62	-0.56
Mo-N_3O	-0.99	0.13
Ru-N_3O	-0.94	0.93
Rh-N_3O	-2.15	1.68
Pd-N_3O	-2.56	2.23
Ta-N_3O	-1.99	0.06
W-N_3O	-0.41	0.24
Re-N_3O	-0.09	0.33
Os-N_3O	-0.14	0.86
Pt-N_3O	-2.34	2.35
Ti-N_3P	-4.46	0.60
V-N_3P	-2.45	0.04
Cr-N_3P	-3.48	0.83
Nb-N_3P	-2.63	-0.22
Mo-N_3P	-1.02	0.14
Ru-N_3P	-1.88	1.40
Rh-N_3P	-2.19	1.70
Pd-N_3P	-3.44	2.67
Ta-N_3P	-2.60	0.27
W-N_3P	-0.25	0.18
Re-N_3P	-0.12	0.34
Os-N_3P	-1.52	1.03
Pt-N_3P	-2.67	2.52
Ti-N_3S	-3.15	-0.06
V-N_3S	-1.85	-0.25
Cr-N_3S	-2.96	0.57
Nb-N_3S	-1.49	-0.60
Mo-N_3S	0.35	-0.32
Ru-N_3S	-1.28	1.10
Rh-N_3S	-1.25	1.23
Pd-N_3S	-2.93	2.42
Ta-N_3S	-1.96	0.05
W-N_3S	1.12	-0.27
Re-N_3S	0.70	0.07
Os-N_3S	0.20	0.81
Pt-N_3S	-2.07	2.21

Ti-N_3B	-4.52	0.63
V-N_3B	-2.04	-0.16
Cr-N_3B	-3.49	0.84
Nb-N_3B	-1.78	-0.51
Mo-N_3B	0.07	-0.22
Ru-N_3B	-1.73	1.32
Rh-N_3B	-2.45	1.83
Pd-N_3B	-4.24	3.07
Ta-N_3B	-2.73	0.31
W-N_3B	-0.22	0.17
Re-N_3B	-0.56	0.49
Os-N_3B	-1.24	1.00
Pt-N_3B	-3.64	3.00

Table S2. The adsorption energies of all 40 TM-N_3X for NO_3^- adsorption.

	ΔG^*NO_3		ΔG^*NO_3
Ti-N_3O	-1.14	Ti-N_3P	-2.53
V-N_3O	-0.39	V-N_3P	-3.35
Cr-N_3O	0.64	Cr-N_3P	-0.31
Mo-N_3O	-0.56	Mo-N_3P	-2.24
Ru-N_3O	0.76	Ru-N_3P	-0.66
Rh-N_3O	1.24	Rh-N_3P	-4.03
Pd-N_3O	1.87	Pd-N_3P	-0.33
Ta-N_3O	-1.32	Ta-N_3P	-3.69
W-N_3O	-1.07	W-N_3P	-6.19
Re-N_3O	-0.52	Re-N_3P	-4.72
Os-N_3O	0.93	Os-N_3P	-0.71
Pt-N_3O	2.02	Pt-N_3P	-3.50
Ti-N_3B	-2.71	Cr-N_3S	-0.51
Cr-N_3B	-0.73	Ru-N_3S	-0.84
Ru-N_3B	-1.59	Rh-N_3S	-4.22
Rh-N_3B	-4.46	Pd-N_3S	-0.65
Pd-N_3B	-0.37	Ta-N_3S	-4.20
Ta-N_3B	-4.98	Pt-N_3S	-4.00
W-N_3B	-6.71		
Re-N_3B	-4.69		
Os-N_3B	-1.85		
Pt-N_3B	-3.53		

Table S3. Gibbs free energy variation in the reaction process (step 1 to 6) of TM-N_3O systems, ΔG-n representing the gibbs free energy change in the n-step (n = 1 to 6), corresponding to equation S5 to S10.

	ΔG-1	ΔG-2	ΔG-3	ΔG-4	ΔG-5	ΔG-6
	-1.14	0.09	-1.90	0.05	-1.36	-0.02
V-N_3O	-0.39	0.27	-2.11	0.11	-1.78	-0.02
Mo-N_3O	-0.56	-0.24	-1.77	-0.24	-2.22	0.23
Ta-N_3O	-1.32	0.35	-2.09	0.59	-1.54	0.02
W-N_3O	-1.07	-0.70	-1.46	-0.22	-1.96	-0.12
Re-N_3O	-0.52	-0.41	-1.72	-0.19	-2.58	0.40

Table S4. Gibbs free energy variation in the reaction process (step 7 to 11) of TM-N_3O systems, ΔG-n representing the gibbs free energy change in the n-step (n = 7 to 11), corresponding to equation S11 to S15.

	ΔG-7	ΔG-8	ΔG-9	ΔG-10	ΔG-11
Ti-N_3O	0.10	1.37	-2.47	-0.92	0.35
V-N_3O	-1.01	1.25	-1.31	-0.69	-0.14
Mo-N_3O	-1.76	-0.17	-0.62	-0.09	0.41
Ta-N_3O	-0.69	1.56	-1.73	-1.30	0.38
W-N_3O	-1.34	3.70	-1.20	0.30	0.81
Re-N_3O	-2.04	1.93	-0.46	0.01	0.51

Table S5. Gibbs free energy variation in the reaction process (step 1 to 6) of TM-N_3P systems, ΔG-n representing the gibbs free energy change in the n-step (n = 1 to 6), corresponding to equation S5 to S10.

	ΔG-1	ΔG-2	ΔG-3	ΔG-4	ΔG-5	ΔG-6
Ti-N_3P	-2.53	0.21	-1.93	0.42	-1.51	0.09
V-N_3P	-3.35	0.16	-1.91	0.21	-1.89	-0.03
Cr-N_3P	-0.31	0.83	-2.87	0.26	-2.42	0.37
Mo-N_3P	-2.24	-0.34	-1.62	0.26	-2.09	-0.29
Ru-N_3P	-0.66	0.11	-2.32	0.58	-3.56	0.63
Rh-N_3P	-4.03	-0.71	-2.06	0.31	-2.23	2.07
Pd-N_3P	-0.33	-0.96	-1.31	-0.73	-1.04	1.40
Ta-N_3P	-3.69	0.39	-2.06	0.51	-1.39	-0.18
W-N_3P	-6.19	-0.55	-1.93	0.61	-1.79	-0.44
Re-N_3P	-4.72	-0.50	-1.43	-0.05	-2.33	0.04
Os-N_3P	-0.71	0.22	-2.01	0.29	-3.83	1.04
Pt-N_3P	-3.50	-1.15	-1.11	-0.84	-1.10	1.29

Table S6. Gibbs free energy variation in the reaction process (step 7 to 11) of TM-N_3P systems, ΔG-n representing the gibbs free energy change in the n-step (n = 7 to 11), corresponding to equation S11 to S15.

	ΔG-7	ΔG-8	ΔG-9	ΔG-10	ΔG-11
Ti-N_3P	1.19	1.37	-2.52	-1.12	0.08

V-N_3P	1.20	-0.68	-1.18	0.03	1.91
Cr-N_3P	-1.13	-1.56	-0.50	-0.94	-0.25
Mo-N_3P	-0.12	-0.17	-1.03	-0.30	0.82
Ru-N_3P	-0.48	-0.10	0.13	-1.09	0.14
Rh-N_3P	3.72	4.12	-0.91	-1.45	-1.07
Pd-N_3P	1.30	2.34	-0.99	-1.68	-1.66
Ta-N_3P	1.94	1.56	-2.08	-1.15	0.48
W-N_3P	3.61	3.70	-1.29	-0.18	1.21
Re-N_3P	2.20	1.93	-0.89	-0.26	1.25
Os-N_3P	-1.26	-0.66	0.20	-0.77	0.60
Pt-N_3P	4.79	-0.68	-2.04	-1.23	-0.55

Table S7. Gibbs free energy variation in the reaction process (step 1 to 6) of TM-N_3S systems, ΔG-n representing the gibbs free energy change in the n-step (n = 1 to 6), corresponding to equation S5 to S10.

	ΔG-1	ΔG-2	ΔG-3	ΔG-4	ΔG-5	ΔG-6
Cr-N_3S	-0.51	0.53	-2.39	0.00	-2.34	0.64
Ru-N_3S	-0.84	0.45	-2.72	-0.68	-2.12	0.53
Rh-N_3S	-4.22	-0.60	-1.99	-0.30	-2.05	2.21
Pd-N_3S	-0.65	-1.15	-1.41	-0.53	-1.14	1.11
Ta-N_3S	-4.20	1.56	-1.23	-0.88	-0.43	1.01
Pt-N_3S	-4.00	-1.06	-1.40	-0.63	-1.12	0.89

Table S8. Gibbs free energy variation in the reaction process (step 7 to 11) of TM-N_3S systems, ΔG-n representing the gibbs free energy change in the n-step (n = 7 to 11), corresponding to equation S11 to S15.

	ΔG-7	ΔG-8	ΔG-9	ΔG-10	ΔG-11
Cr-N_3S	-1.37	-1.56	-0.17	-0.86	-0.60
Ru-N_3S	-0.21	-0.10	0.07	-0.74	-0.57
Rh-N_3S	3.99	4.12	0.30	-3.03	-0.97
Pd-N_3S	2.06	2.34	-1.37	-1.69	-1.91
Ta-N_3S	-1.35	1.56	-1.80	2.07	-2.28
Pt-N_3S	5.38	5.59	-1.09	-1.71	-1.77

Table S9. Gibbs free energy variation in the reaction process (step 1 to 6) of TM-N_3B systems, ΔG-n representing the gibbs free energy change in the n-step (n = 1 to 6), corresponding to equation S5 to S10.

	ΔG-1	ΔG-2	ΔG-3	ΔG-4	ΔG-5	ΔG-6
Cr-N_3B	-2.71	-2.59	0.95	0.32	-1.28	0.11
Ru-N_3B	-4.46	-0.22	-2.39	0.02	-2.05	2.22
Rh-N_3B	-4.98	0.16	-1.79	0.39	-1.65	-0.17
Pd-N_3B	-6.71	-0.42	-1.46	-0.19	-2.10	0.25
Ta-N_3B	-4.69	-0.18	-1.87	0.05	-2.93	0.66
Pt-N_3B	-3.53	-0.90	-1.32	-0.94	-0.98	0.97

Table S10. Gibbs free energy variation in the reaction process (step 7 to 11) of TM-N_3B systems, ΔG-n representing the Gibbs free energy change in the n-step (n = 7 to 11), corresponding to equation S11 to S15.

	ΔG-7	ΔG-8	ΔG-9	ΔG-10	ΔG-11
Cr-N_3B	1.35	1.37	-2.56	-1.42	0.18
Ru-N_3B	2.16	4.12	1.97	-2.92	-1.03
Rh-N_3B	2.28	1.56	-2.37	-0.73	0.45
Pd-N_3B	3.22	3.70	-0.96	0.04	0.69
Ta-N_3B	1.63	1.93	-0.20	-0.14	0.55
Pt-N_3B	4.93	5.59	-1.21	-1.60	-0.92

Table S11. The Mulliken population for *NOH → *N and *NO_2H → *NO.

	*NO_2H(N-O)	length	*NO(N-O)	length	*NOH(N-O)	length
Ti-N3O	0.29	1.46249	0.75	1.22731	0.42	1.36359
V-N3O	0.29	1.45233	0.77	1.22587	0.44	1.35335
Mo-N3O	0.3	1.45875	0.79	1.23142	0.45	1.35275
Ta-N3O	0.35	1.38593	0.71	1.23589	0.43	1.36294
W-N3O	0.31	1.46037	0.77	1.23648	0.45	1.35347
Re-N3O	0.28	1.46916	0.8	1.2295	0.46	1.34665
Ti-N3P	0.37	1.38824	0.75	1.2262	0.42	1.36473
V-N3P	0.37	1.38413	0.78	1.22677	0.44	1.35446

Cr-N3P	0.31	1.42179	0.82	1.22229	0.45	1.34995
Mo-N3P	0.35	1.40714	0.77	1.23348	0.42	1.36986
Ru-N3P	0.28	1.41268	0.83	1.21649	0.41	1.37807
Rh-N3P	0.27	1.42627	0.79	1.20855	0.35	1.35671
Pd-N3P	0.27	1.43721	0.75	1.20228	0.36	1.33946
Ta-N3P	0.35	1.39237	0.72	1.23444	0.39	1.38155
W-N3P	0.32	1.44151	0.75	1.23714	0.42	1.37093
Re-N3P	0.37	1.42014	0.8	1.22477	0.44	1.37638
Os-N3P	0.25	1.43388	0.82	1.22125	0.43	1.35236
Pt-N3P	0.26	1.44334	0.77	1.20564	0.32	1.3556
Cr-N3S	0.34	1.44943	0.82	1.223	0.46	1.34921
Ru-N3S	0.37	1.4419	0.84	1.21282	0.41	1.37674
Rh-N3S	0.31	1.4449	0.8	1.20645	0.35	1.35213
Pd-N3S	0.27	1.43102	0.74	1.20402	0.35	1.34966
Ta-N3S	0.25	1.45992	0.68	1.20031	0.38	1.32335
Pt-N3S	0.26	1.42515	0.73	1.2042	0.34	1.35291
Ti-N3B	0.37	1.3891	0.74	1.22452	0.42	1.36473
Rh-N3B	0.3	1.45488	0.78	1.21189	0.34	1.35673
Ta-N3B	0.35	1.39494	0.74	1.22955	0.42	1.36799
W-N3B	0.38	1.40266	0.79	1.2312	0.44	1.35985
Re-N3B	0.37	1.42147	0.81	1.22742	0.44	1.35477
Pt-N3B	0.27	1.44347	0.78	1.19832	0.34	1.35129

Table S12. The limiting potentials(U_L) of 30 TM-PP catalysts are listed. The U_L is defined by $U_L = -(\Delta G_{max} / e)$.

	Limiting Potentials		Limiting Potentials
Ti-N_3O	-0.35	Ti-N_3P	-1.19
V-N_3O	-0.27	V-N_3P	-1.20
Mo-N_3O	-0.41	Cr-N_3P	-0.83
Ta-N_3O	-0.59	Mo-N_3P	-0.82
W-N_3O	-0.81	Ru-N_3P	-0.63
Re-N_3O	-0.51	Rh-N_3P	-3.72
Ti-N_3B	-1.35	Pd-N_3P	-1.40
Rh-N_3B	-2.22	Ta-N_3P	-1.94
Ta-N_3B	-2.28	W-N_3P	-3.61
W-N_3B	-3.22	Re-N_3P	-2.20
Re-N_3B	-1.63	Os-N_3P	-1.04
Pt-N_3B	-4.93	Pt-N_3P	-4.79
		Cr-N_3S	-0.64
		Ru-N_3S	-0.53
		Rh-N_3S	-3.99
		Pd-N_3S	-2.06
		Ta-N_3S	-2.07
		Pt-N_3S	-5.38