

Supporting Information

Towards Efficient Nitrite-to-Ammonia Conversion: DFT-Guided Design of Single-Atom Catalysts on Defective Boron Phosphide

AoXue Hu^a, Zhepei Yan^a, Yongfan Zhang^a, Shuping Huang^{a,*}, Jiehua Hu^{b*}

^a College of Chemistry, Fujian Provincial Key Laboratory of Electrochemical Energy Storage
Materials, Fuzhou University, Fuzhou, 350116, China

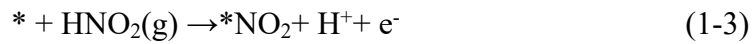
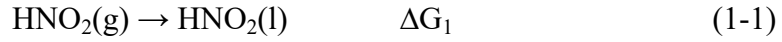
^b School of Marine Biology, Xiamen Ocean Vocational College, Applied Technology Engineering
Center of Fujian Provincial Higher Education for Marine Resource Protection and Ecological
Governance, Xiamen 361100, China

*Corresponding authors

E-mail addresses: huangshp@fzu.edu.cn(S. Huang), pthjh1027@163.com (J. Hu)

1. The details of the adsorption energy calculation of NO_2^-

To avoid direct calculation of the energy of the charged ion NO_2^- , the energy of the nitrite ion was derived from the thermodynamic cycle using the neutral gaseous HNO_2 as a reference (Fig. S1).



where * indicates the substrate.

The adsorption of NO_2^- on the substrate can be described as:



Accordingly, the approximate Gibbs free energy change of nitrate adsorbed on the electrode surface in aqueous solution ($\Delta G_{* \text{NO}_2^-}$) is as follows:

$$\Delta G_{* \text{NO}_2^-} = G_{* \text{NO}_2} - G_* - G_{\text{HNO}_2(\text{g})} + 0.5G_{\text{H}_2} + \Delta G_{\text{correct}} \quad (1-5)$$

$$\Delta G_{\text{correct}} = -\Delta G_1 - \Delta G_2 = -0.007 \text{ eV} \quad (1-6)$$

$$\Delta G_{* \text{NO}_2^-} = G_{* \text{NO}_2} - G_* - G_{\text{HNO}_2(\text{g})} + 0.5G_{\text{H}_2} - 0.007 \quad (1-7)$$

The Gibbs free energy of NO_2 adsorbed on the catalyst, H_2 , and HNO_2 gas phase molecules, and the catalyst are shown by the symbols $G_{* \text{NO}_2}$, G_{H_2} , $G_{\text{HNO}_2(\text{g})}$, and G_* , respectively. The CRC Handbook of Chemistry and Physics[1] states that $\Delta G_{\text{correct}}$ is equal to -0.007 eV.

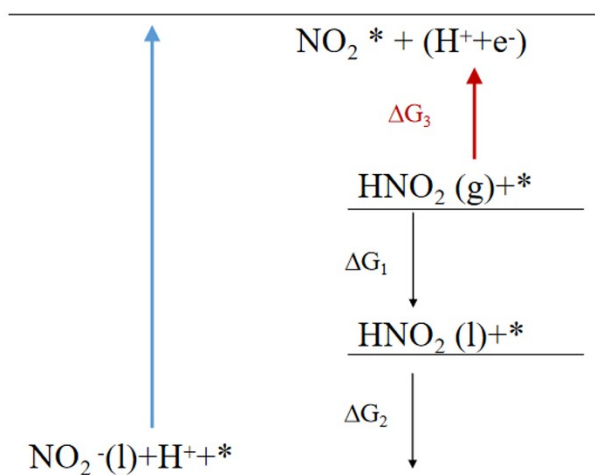
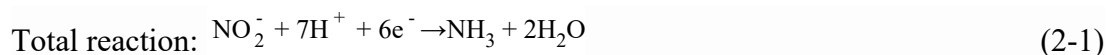
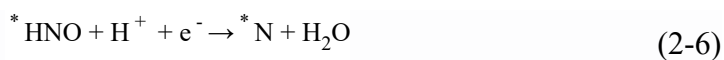
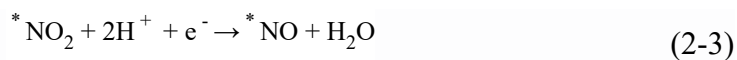


Fig. S1. The thermodynamic cycle for finding the energy of the nitrite ion.

2. The total reaction and elementary reactions of nitrite reduction to ammonia



Elementary reactions:



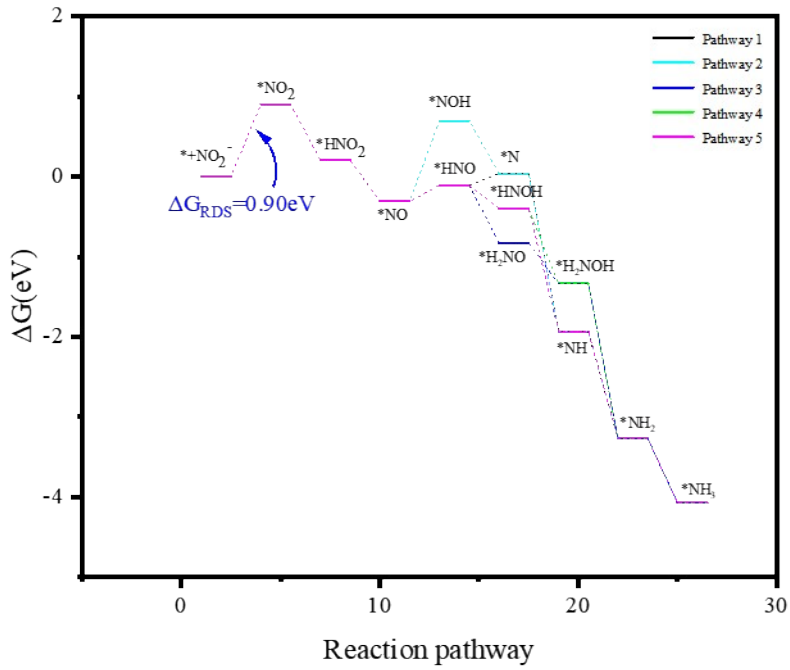
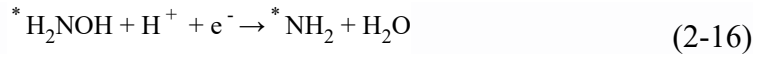
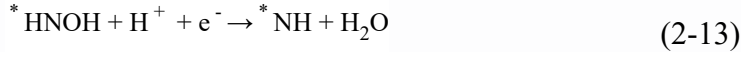


Fig. S2. Plots of the Gibbs free energy changes of the NO_2RR on BP.

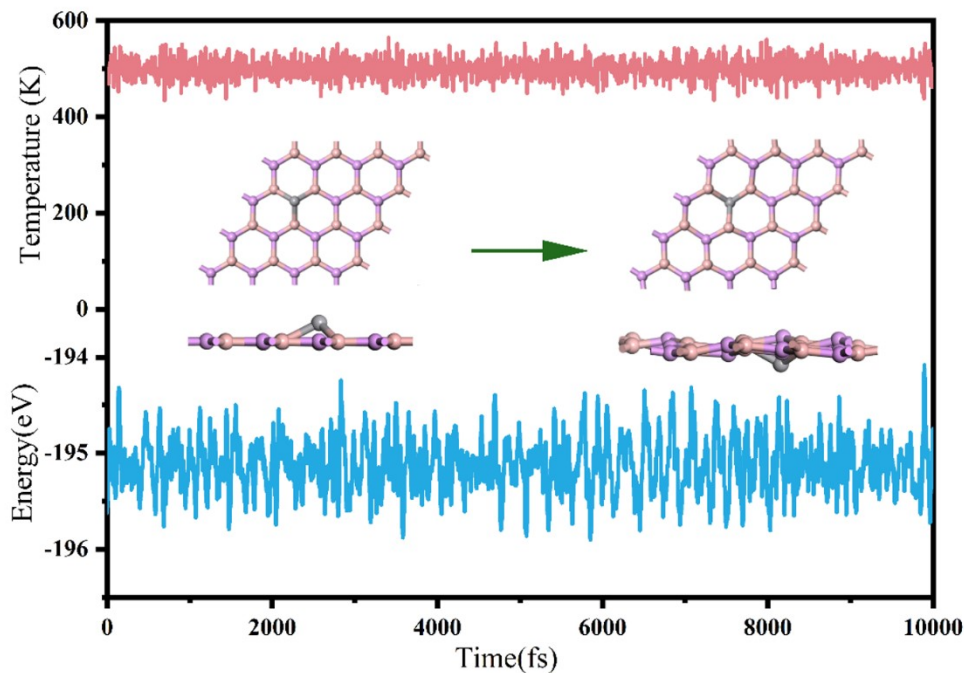


Fig. S3. The total energy fluctuations and temperature fluctuations from 0 to 10 ps of V-B₃ during AIMD at 500K.

Table S1. The formation energies (E_f , eV) and solvation potentials (U_{diss} , V) of 17 M-B₃ configurations and M-P₃ configurations.

M-B ₃	E_f	U_{diss}	M-B ₃	E_f	U_{diss}	M-B ₃	E_f	U_{diss}
V	-1.20	1.21	Nb	-1.47	0.33	Ta	-1.09	0.68
Cr	-1.58	1.64	Mo	-1.13	1.02	W	-0.46	0.95
Mn	-2.11	1.75	Ru	-2.72	2.94	Re	-1.31	1.49
Fe	-1.90	2.16	Rh	-4.04	3.88	Os	-2.27	1.39
Co	-2.70	2.66	Pd	-3.35	3.67	Ir	-4.05	3.33
Ni	-2.14	2.36				Pt	-4.09	4.49
M-P ₃	E_f	U_{diss}	M-P ₃	E_f	U_{diss}	M-P ₃	E_f	U_{diss}
V	-1.84	1.53	Nb	-1.48	0.33	Ta	-0.55	0.5
Cr	-1.71	1.71	Mo	-0.97	0.96	W	0.17	0.74
Mn	-1.45	1.41	Ru	-1.91	2.54	Re	-0.34	1.16
Fe	-1.44	1.93	Rh	-2.3	3.01	Os	-1.06	1.24
Co	-1.74	2.18	Pd	-1.86	2.92	Ir	-1.93	2.62
Ni	-1.58	2.08				Pt	-2.28	3.59

Table S2. Adsorption energies (eV) of three adsorption models for NO₂⁻.

*NO ₂ ⁻	N-end	O-end	NO-side
V-B ₃	\	-1.46	-1.65
Cr-B ₃	\	-0.83	-0.92
Mn-B ₃	\	-0.89	-0.88
Fe-B ₃	\	-0.73	-0.88
Co-B ₃	\	-0.38	-0.37
Ni-B ₃	-1.03	-0.98	-0.89
Nb-B ₃	\	-1.39	-1.61
Mo-B ₃	\	-1.15	-1.34
Ru-B ₃	-0.71	-0.40	\
Rh-B ₃	0.09	0.15	\
Pd-B ₃	-0.43	-0.68	\
Ta-B ₃	\	-1.69	-1.80
W-B ₃	\	-1.69	-1.69
Re-B ₃	\	-0.96	-1.11
Os-B ₃	-0.89	-0.59	\
Ir-B ₃	-0.14	-0.15	\
Pt-B ₃	-0.45	-0.79	\

Table S3. Adsorption energies (eV) of three adsorption models for NO.

ΔG^*_{NO}	N-end	O-end	NO-side
V-B ₃	-2.52	-1.51	-2.37
Cr-B ₃	-2.83	-0.78	-1.89
Mn-B ₃	-2.37	-1.05	\
Fe-B ₃	-2.45	-1.17	\
Co-B ₃	-1.68	-0.64	\
Ni-B ₃	-1.70	-0.82	-1.21
Nb-B ₃	-2.06	-1.22	-2.17
Mo-B ₃	-3.25	-2.24	-2.54
Ru-B ₃	-2.28	-0.80	\
Rh-B ₃	-1.01	-0.08	\
Pd-B ₃	-1.04	-0.41	\
Ta-B ₃	-2.27	-1.45	-2.32
W-B ₃	-3.38	-1.39	-2.45
Re-B ₃	-3.04	-1.08	-2.43
Os-B ₃	-2.56	-0.89	\
Ir-B ₃	-1.25	-0.25	\
Pt-B ₃	-1.18	-0.35	\

Table S4. Adsorption energies (eV) of H atom on M-B₃.

	ΔG^*_{H}		ΔG^*_{H}		ΔG^*_{H}
V-B ₃	0.17	Nb-B ₃	0.17	Ta-B ₃	-0.15
Cr-B ₃	0.47	Mo-B ₃	0.07	W-B ₃	-0.3
Mn-B ₃	0.35	Ru-B ₃	-0.74	Re-B ₃	-0.15
Fe-B ₃	-0.32	Rh-B ₃	0.65	Os-B ₃	-0.41
Co-B ₃	0.48	Pd-B ₃	0.25	Ir-B ₃	0.19
Ni-B ₃	-0.77			Pt-B ₃	-0.15

Table S5. The Gibbs free energy changes (eV) of reactions in all five paths for NO₂RR on M-B₃.

ΔG	V	Cr	Mn	Fe	Co	Ni
NO ₂ ⁻ →*NO ₂	-1.65	-0.92	-0.88	-0.88	-0.37	-0.98
*NO ₂ →*HNO ₂	0.11	0.14	-0.00	-0.21	-0.43	0.31
*HNO ₂ →*NO	-1.27	-2.34	-1.78	-1.65	-1.17	-1.32
*NO→*HNO	-0.26	0.79	0.58	0.62	0.19	0.07
*NO→*NOH	0.12	1.08	1.04	0.98	0.14	0.07
*NOH→*N	-0.24	-1.55	-1.30	-1.01	-1.94	-4.63
*HNO→*N	0.11	-1.27	-0.83	-0.65	-1.99	-4.63
*N→*NH	-1.79	-0.28	-0.54	-0.62	1.18	2.14
*NH→*NH ₂	-0.61	-0.80	-1.29	-1.30	-1.58	-0.17
*NH ₂ →*NH ₃	-0.04	-0.62	-0.57	-0.65	-1.13	-0.40
*HNO→*HNOH	0.11	-0.08	-0.19	-0.35	-0.24	-0.34
*HNOH→*NH	-1.78	-1.46	-1.18	-0.91	-0.55	-2.15
*HNO→*H ₂ NO	-0.69	-0.75	-0.86	-0.74	-0.55	-0.88
*HNOH→*H ₂ NOH	0.39	-0.09	-0.21	-0.08	-0.46	0.21
*H ₂ NO→*H ₂ NOH	1.18	0.59	0.46	0.30	-0.16	0.75
*H ₂ NOH→*NH ₂	-2.78	-2.19	-2.26	-2.12	-1.68	-2.53
ΔG	Nb	Mo	Ru	Rh	Pd	
NO ₂ ⁻ →*NO ₂	-1.61	-1.34	-0.71	0.09	-0.68	
*NO ₂ →*HNO ₂	0.35	0.08	-0.06	-0.46	0.52	
*HNO ₂ →*NO	-1.20	-2.28	-1.81	-0.93	-1.18	
*NO→*HNO	-0.56	0.51	0.67	0.20	-0.05	
*NO→*NOH	0.14	0.97	1.25	0.95	0.64	
*NOH→*N	-0.41	-1.62	-0.83	-0.15	0.35	
*HNO→*N	0.29	-1.16	-0.25	0.61	1.04	
*N→*NH	-1.75	-0.33	-0.84	-1.31	-1.67	
*NH→*NH ₂	-0.85	-0.60	-1.25	-1.76	-2.07	
*NH ₂ →*NH ₃	0.12	-0.13	-0.89	-1.32	-0.62	
*HNO→*HNOH	0.11	0.16	-0.27	-0.33	-0.28	
*HNOH→*NH	-1.58	-1.66	-0.82	-0.38	-0.35	

*HNO→*H ₂ NO	-0.83	-0.61	-0.31	-0.51	-0.78	
*HNOH→*H ₂ NOH	0.02	0.43	-0.18	-0.77	-0.31	
*H ₂ NO→*H ₂ NOH	0.97	1.21	-0.14	-0.59	0.18	
*H ₂ NOH→*NH ₂	-2.45	-2.70	-1.88	-1.38	-2.11	
ΔG	Ta	W	Re	Os	Ir	Pt
NO ₂ ⁻ →*NO ₂	-1.81	-1.69	-1.11	-0.89	-0.14	-0.79
*NO ₂ →*HNO ₂	0.54	0.39	-0.14	-0.14	-0.34	0.59
*HNO ₂ →*NO	-1.35	-2.14	-2.08	-1.82	-1.07	-1.27
*NO→*HNO	-0.64	0.21	0.64	0.57	0.15	-0.11
*NO→*NOH	-0.01	0.64	0.40	0.99	0.84	0.61
*NOH→*N	-0.14	-1.48	-0.91	-0.84	-0.42	-0.02
*HNO→*N	0.49	-1.05	-1.15	-0.42	0.27	0.70
*N→*NH	-2.07	-0.31	-0.55	-0.81	-1.24	-1.53
*NH→*NH ₂	-0.81	-0.77	-0.62	-1.16	-1.67	-2.03
*NH ₂ →*NH ₃	0.27	0.17	-0.30	-0.60	-0.96	-0.24
*HNO→*HNOH	0.12	0.28	-0.06	-0.17	-0.34	-0.35
*HNOH→*NH	-1.70	-1.64	-1.64	-1.05	-0.63	-0.49
*HNO→*H ₂ NO	-0.73	-0.51	-0.51	-0.18	-0.48	-0.74
*HNOH→*H ₂ NOH	0.55	0.58	0.21	-0.17	-0.43	-0.04
*H ₂ NO→*H ₂ NOH	1.40	1.36	0.66	-0.05	-0.29	0.34
*H ₂ NOH→*NH ₂	-3.06	-2.98	-2.48	-2.15	-1.86	-2.48

Reference

- [1] CRC Handbook of Chemistry and Physics, 2009–2010, 90th ed, J. Am. Chem. Soc., 131 (2009) 12862-12862, 10.1021/ja906434c, 2009/09/09.