Supplementary Materials

Nitrate reduction reaction on Zr-doped TiO_2 (101) surfaces investigated by first-principles calculations

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Contents

1. Free energies for gas molecules and gas phase correction

2. Calculation of the Gibbs free energy for nitrate adsorption by a thermodynamic cycle

3. Electronic structure of undoped and Zr-doped TiO_2

4. The molecular orbital (MO) of nitrate

5. Gibbs free energy (G) for each elementary step on the (101) surfaces of TiO_2, Zr-TiO_2-S and Zr-TiO_2-B

6. Comparison of the Gibbs free energy (G) in the thermodynamically favored reaction pathways on the (101) surfaces of TiO_2, Zr-TiO_2-S and Zr-TiO_2-B models

1. Free energies for gas molecules and gas phase correction

Table S1 The calculated free energies of free gas molecules.

Molecules	E_{DFT} / eV	E_{ZPE} / eV	TS / eV	G / eV
H_2(g)	-6.773	0.293	0.409	-6.889
O_2(g)				-9.948*
H_2O(g, 0.035 atm)	-14.235	0.582	0.670	-14.324
N_2(g)	-16.647	0.154	0.599	-17.093
NO(g)	-12.258	0.121	0.654	-12.791
NO_2(g)	-18.372	0.234	0.745	-18.883
NH_3(g)	-19.540	0.920	0.600	-19.320
HNO_3(g)	-28.656	-0.697	0.830	-28.789

* G for O_2(g) was calculated from the energy (4.92 eV) released from the reaction $2H_2 + O_2 \rightarrow 2H_2O$ at standard condition.

The formation energy of HNO_3(g) calculated from the free energies of H_2(g), N_2(g), O_2(g) and HNO_3(g) was -1.875 eV, and the experimental value was -0.77 eV [1]. Therefore, a correction of 1.105 eV was applied to HNO_3(g). The correction value is close to those reported by previous studies, i.e., 1.12 eV [2] and 1.08 eV [3].

2. Calculation of the Gibbs free energy for nitrate adsorption by a thermodynamic cycle

The Gibbs free energy for nitrate adsorption from $NO_3^-(l)$ to *NO_3 was calculated by a thermodynamic cycle (Fig.S1) according to

$$\Delta G(*NO_3) = \Delta G_{ads}(*NO_3) - (-0.075) - (-0.317) \quad \text{(S1)}$$

where -0.075 eV and -0.317 eV represented the liquefaction energy from HNO_3(g) to HNO_3(l) at standard condition, and the dissociation energy from HNO_3(l) to $NO_3^-(l)$ + H^+, respectively.

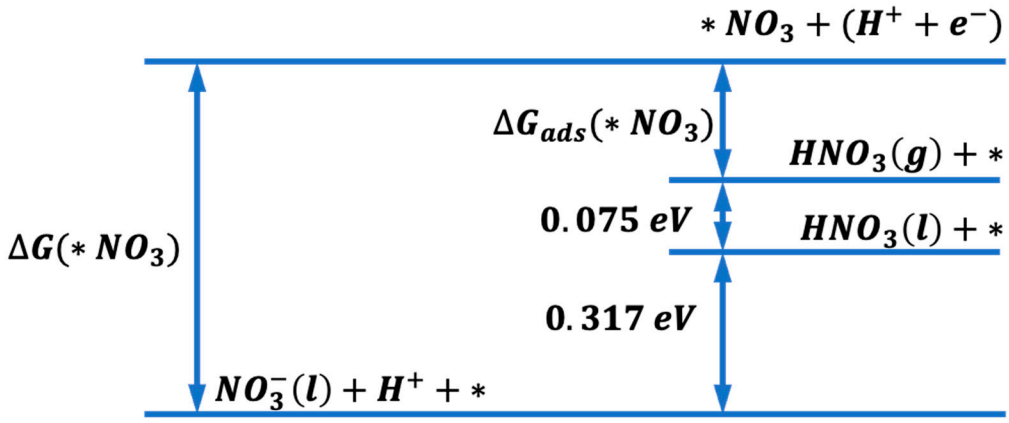


Figure S1. The thermodynamic cycle for calculating the nitrate adsorption energy in aqueous solution. The figure is replotted from Ref.[2].

3. Electronic structure of undoped and Zr-doped TiO_2

The projected density of states (PDOS) of the three models are shown in Fig.S2. For the undoped TiO_2 (101) surface (Fig.S2a), the conduction band is predominated by the Ti 3*d* orbital with minor contribution from O 2*p*. On the contrary, the valence band adopts a larger contribution from the O 2*p* orbital than Ti 3*d*. PDOS for the Zr-TiO_2-S model (Fig.S2b) show similar features as those for undoped TiO_2. The Zr 4*d* orbital (inset figure in Fig.S2b) has very small contribution to the total DOS due to the low doping level of Zr (~ 2.8%). For the Zr-TiO_2-B model, as the Zr-doping level is significantly increased to 25%, contribution from the Zr 4*d* orbital to the total DOS, especially to the conduction band, becomes notable (Fig.S2c). Comparison of the total DOS for the three models (Fig.S2d) shows that Zr-doping neither

introduces any additional energy level to the forbidden band nor changes the band gap. All the three models show identical band gap values ~ 2.15 eV. Therefore, it can be expected that Zr-doped TiO_2 is semiconducting with similar electrical conductivity as undoped TiO_2.

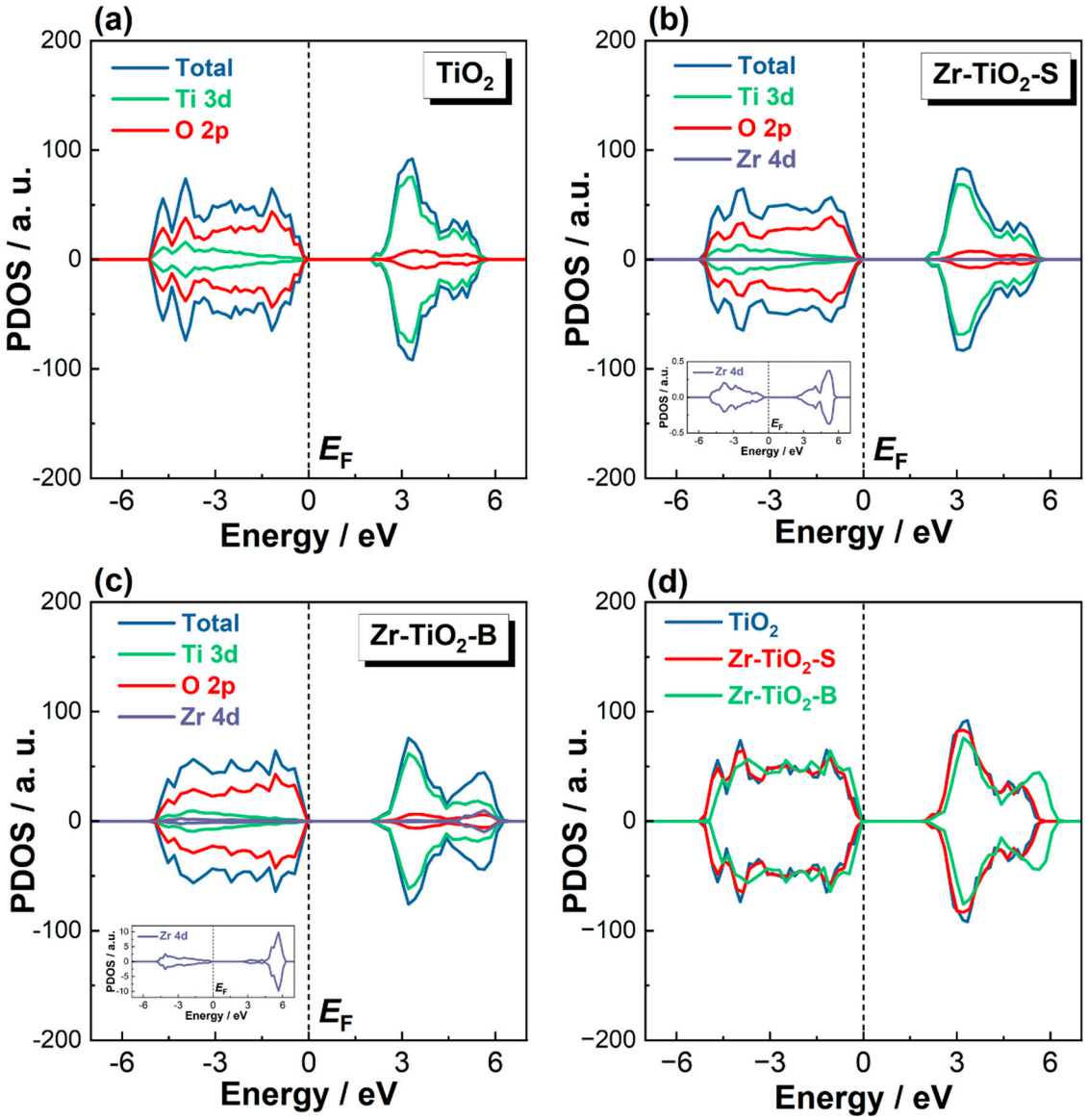


Figure S2. (a)-(c) PDOS of undoped TiO_2, Zr-TiO_2-S and Zr-TiO_2-B, respectively. (d) Comparison of the total DOS of the three models. The inset figures in (b) and (c) are the expanded views of the PDOS for the Zr 4d orbital in Zr-TiO_2-S and Zr-TiO_2-B, respectively.

4. The molecular orbital of nitrate

The molecular orbital of nitrate was determined by calculating the energy of each orbital using VASP, and then analyzing the degeneracy of each orbital based on group theory. The calculated MO of nitrate is shown in Fig.S3.

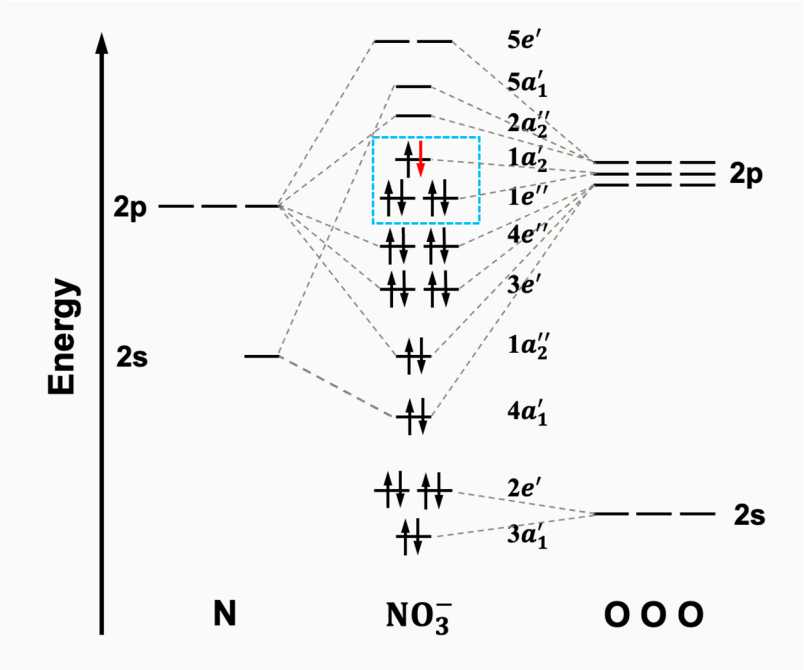


Figure S3. The molecular orbital (MO) of nitrate. The dashed rectangle represents for the non-bonding orbitals, and the red arrow indicates the extra electron in NO_3^-.

5. Gibbs free energy (*G*) for each elementary step on the (101) surfaces of TiO_2, Zr-TiO_2-S and Zr-TiO_2-B

Table S2 Calculated Gibbs free energy (*G*) for each step on the (101) surface of undoped TiO_2.

Reaction coordinate	N-end1		N-end2		O-end	
	Step	*G* / eV	Step	*G* / eV	Step	*G* / eV
1	*→NO_3	0.934	*→NO_3	0.934	*→NO_3	0.934
2	NO_3→NO_2	-2.012	NO_3→NO_2	-2.012	NO_3→NO_2	-2.012
3	NO_2→*NO	-1.582	NO_2→*NO	-1.582	NO_2→*ON	-1.455
4	*NO→*NHO	-0.095	*NO→*NOH	0.795	*ON→*ONH	-0.080
5	*NHO→*NH_2NO	-0.503	*NOH→*N	0.989	*ONH→*ONH_2	-1.109
6	*NH_2NO→*NH_2NOH	-1.220	*N→*NH	-1.674	*ONH_2→*ONH_3	-0.810
7	*NH_2NOH→*NH_2	-0.191	*NH→*NH_2	-2.119	*ONH_3→*OH	0.179
8	*NH_2→*NH_3	-2.225	*NH_2→*NH_3	-2.225	*OH→*	-2.121
9	*NH_3→*	0.417	*NH_3→*	0.417		

Table S3 Calculated Gibbs free energy (*G*) for each step on the (101) surface of Zr-TiO2-S.

Reaction coordinate	N-end1		N-end2		O-end	
	Step	*G* / eV	Step	*G* / eV	Step	*G* / eV
1	*→NO_3	0.796	*→NO_3	0.796	*→NO_3	0.796
2	NO_3→NO_2	-1.425	NO_3→NO_2	-1.425	NO_3→NO_2	-1.425
3	NO_2→*NO	-1.956	NO_2→*NO	-1.956	NO_2→*ON	-1.035
4	*NO→*NHO	0.396	*NO→*NOH	1.214	*ON→*ONH	-0.412
5	*NHO→*NH_2NO	-0.501	*NOH→*N	1.190	*ONH→*ONH_2	-1.388
6	*NH_2NO→*NH_2NOH	-1.322	*N→*NH	-1.908	*ONH_2→*ONH_3	-1.062
7	*NH_2NOH→*NH_2	-0.264	*NH→*NH_2	-2.187	*ONH_3→*OH	0.289
8	*NH_2→*NH_3	-2.236	*NH_2→*NH_3	-2.231	*OH→*	-2.238
9	*NH_3→*	0.036	*NH_3→*	0.031		

Table S4 Calculated Gibbs free energy (*G*) for each step on the (101) surface of Zr-TiO2-B.

Reaction coordinate	N-end1		N-end2	
	Step	*G* / eV	Step	*G* / eV
1	*→NO_3	0.693	*→NO_3	0.693
2	NO_3→NO_2	-1.368	NO_3→NO_2	-1.368
3	NO_2→*NO	-1.689	NO_2→*NO	-1.689
4	*NO→*NHO	-0.120	*NO→*NOH	0.847
5	*NHO→*NH_2NO	-0.299	*NOH→*N	0.618
6	*NH_2NO→*NH_2NOH	-1.194	*N→*NH	-1.419
7	*NH_2NOH→*NH_2	-0.390	*NH→*NH_2	-2.049
8	*NH_2→*NH_3	-2.176	*NH_2→*NH_3	-2.176
9	*NH_3→*	0.067	*NH_3→*	0.067

6. Comparison of the Gibbs free energy (*G*) for each step in the thermodynamically favored reaction pathways on the (101) surfaces of TiO_2, Zr-TiO_2-S and Zr-TiO_2-B

Table S5 Comparison of the Gibbs free energy (*G*) for each step in the thermodynamically favored reaction pathways on the (101) surfaces of TiO_2, Zr-TiO2-S and Zr-TiO_2-B models

Reaction coordinate	Step	*G* / eV		
		TiO_2	Zr-TiO_2-S	Zr-TiO_2-B
1	$*\rightarrow NO_3$	0.934	0.796	0.693
2	$NO_3\rightarrow NO_2$	-2.012	-1.425	-1.368
3	$NO_2\rightarrow *NO$	-1.582	-1.956	-1.689
4	$*NO\rightarrow *NHO$	-0.095	0.396	-0.120
5	$*NHO\rightarrow *NH_2NO$	-0.503	-0.501	-0.299
6	$*NH_2NO\rightarrow *NH_2NOH$	-1.220	-1.322	-1.194
7	$*NH_2NOH\rightarrow *NH_2$	-0.191	-0.264	-0.390
8	$*NH_2\rightarrow *NH_3$	-2.225	-2.236	-2.176
9	$*NH_3\rightarrow *$	0.417	0.036	0.067

Reference

[1] M. W. Chase, NIST-JANAF Thermochemical Tables 2 Volume-Set, Journal of Physical and Chemical Reference Data Monographs. (1998).

[2] Y. Guo, X. Cai, S. Shen, G. Wang and J. Zhang, "Computational prediction and experimental evaluation of nitrate reduction to ammonia on rhodium", Journal of Catalysis 402 (2021) 1-9.

[3] F. Calle-Vallejo, M. Huang, J. B. Henry. M. T. M. Koper and A. S. Bandarenka, "Theoretical design and experimental implementation of Ag/Au electrodes for the electrochemical reduction of nitrate", Physical Chemistry Chemical Physics 15 (2013) 3196-3202.