Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Electronic Supplementary Information

# Oxotitanium-porphyrin for Selective Catalytic Reduction of NO by $NH_3$: A Theoretical Mechanism Study

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**Table of Contents**

**Table S1.** Adsorption energies with corrected ZPE (kcal/mol) by M06L/6-31G** and LANL2DZ and M06L/6-311G** and LANL2DZ method of calculations

| | Adsorption energies with corrected ZPE (kcal/mol) | |
|---|---|---|
| | **M06L/6-31G** and LANL2DZ** | **M06L/6-311G** and LANL2DZ** |
| TiO-NO | -3.9 | -4.9 |
| TiO-$N_2O$ | -4.0 | -5.2 |
| TiO-$NO_2$ | -4.7 | -6.3 |
| TiO-$N_2$ | -2.4 | -3.1 |
| TiO-$NH_3$ | -4.5 | -5.2 |
| TiO-$H_2O$ | -7.6 | -8.7 |

**Table S2.** Step A reaction energies with corrected ZPE (kcal/mol) by M06L/6-31G** and LANL2DZ and M06L/6-311G** and LANL2DZ method of calculations

| **Step A** | **TiO** | **TiO-NO** | **TS1** | **Ti-$NO_2$** |
|---|---|---|---|---|
| M06L/6-31G** and LANL2DZ | 0.0 | -3.9 | 15.3 | 7.3 |
| M06L/6-311G** and LANL2DZ | 0.0 | -4.9 | 17.3 | 7.4 |

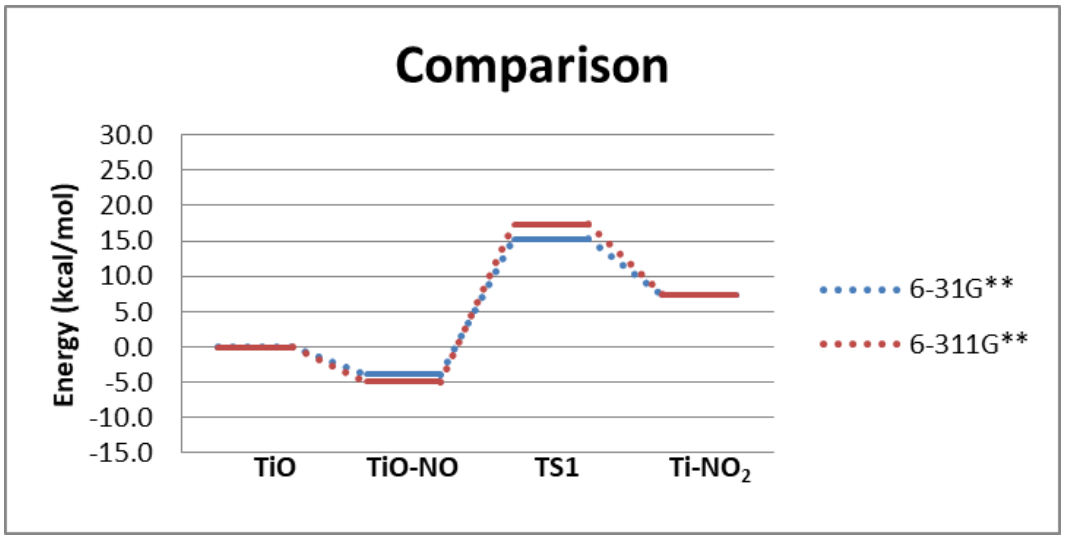


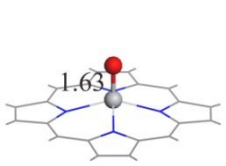
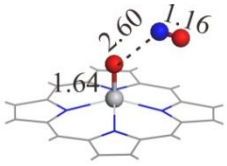
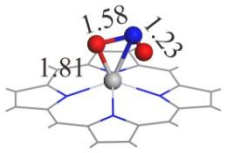
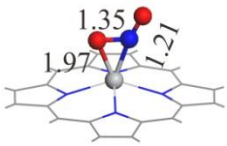
**Table S3.** Activation energies for NO decomposition along the reaction pathways of the low- and high-spin states TiO-por catalyst and the imaginary frequencies.

| | **Activation energy ($E_a$) in kcal/mol** | | | | **Imaginary frequency ($cm^{-1}$)** | |
|---|---|---|---|---|---|---|
| | **Low spin** | | **High spin** | | **Low spin** | **High spin** |
| | **E** | **E+ZPE** | **E** | **E+ZPE** | | |
| **TS1** | 18.8 | 19.2 | 19.7 | 20.3 | 285*i* | 279*i* |
| **TS2** | 24.7 | 21.5 | 23.6 | 21.1 | 827i | 762*i* |
| **TS3** | 0.9 | 0.8 | 10.5 | 8.4 | 164*i* | 129*i* |
| **TS4** | 34.9 | 32.2 | 35.0 | 31.8 | 1644*i* | 1655*i* |
| **TS5** | 25.3 | 19.6 | 23.9 | 19.0 | 1685*i* | 1144*i* |
| **TS6** | 19.8 | 16.8 | 19.4 | 16.5 | 633*i* | 615*i* |
| **TS7** | 2.5 | 2.3 | 26.0 | 24.7 | 287*i* | 180*i* |
| **TS8** | 39.6 | 36.2 | 34.4 | 30.0 | 1543*i* | 1621*i* |
| **TS9** | 31.9 | 29.5 | 1.5 | -0.4 | 1442*i* | 1163*i* |

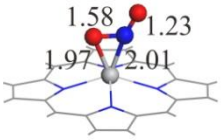
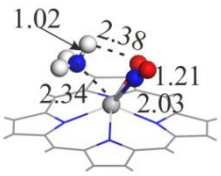
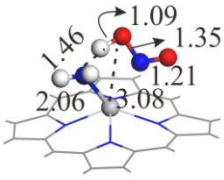
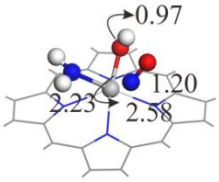
We systematically studied the reaction mechanisms for both low and high spin states, the information of the high-spin state catalyst is provided here; following by step A to step G.

**Figure S1.** Optimized structures and their relative energies of the high-spin state TiO-por catalyst for step A to step G.

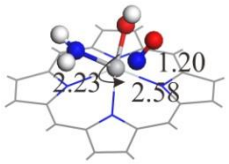
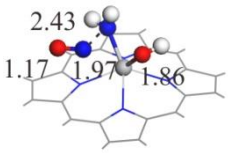
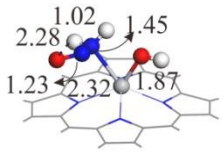
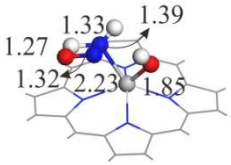
***Step A***

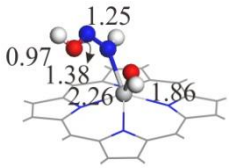
| |  |  |  |  |
|---|---|---|---|---|
| | **TiO** | **TiO-NO** | **TS1** | **Ti-$NO_2$** |
| E (kcal/mol) | 40.8 | 37.0 | 56.7 | 47.4 |
| E + ZPE | 37.5 | 34.1 | 54.4 | 45.4 |

***Step B***

| |  |  |  |  |
|---|---|---|---|---|
| | **Ti-$NO_2$** | **Ti-$NO_2$-$NH_3$** | **TS2** | **Ti-NOOH-$NH_2$** |
| E (kcal/mol) | 47.4 | 35.1 | 58.7 | 36.9 |
| E + ZPE | 45.4 | 36.5 | 57.6 | 37.9 |

***Step C***

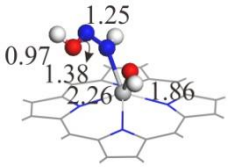
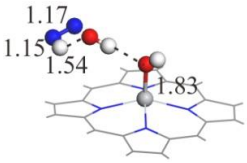
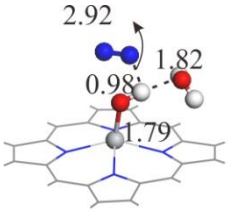
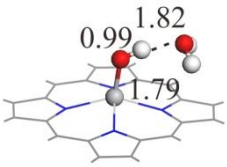
| |  |  |  |  |
|---|---|---|---|---|
| | **Ti-NOOH-$NH_2$** | **TS3** | **TiOH-$NH_2NO$** | **TS4** |
| E (kcal/mol) | 36.9 | 47.4 | 40.6 | 75.5 |
| E + ZPE | 37.9 | 46.3 | 41.5 | 73.3 |

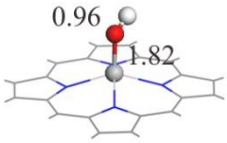



**TiOH-NHNOH**

| | |
|---|---|
| E (kcal/mol) | 43.8 |
| E + ZPE | 43.9 |

***Step D***

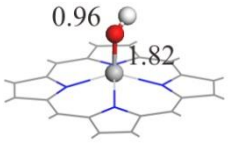
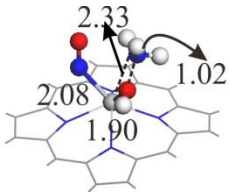
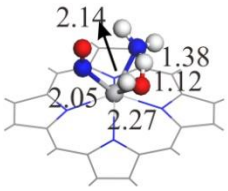
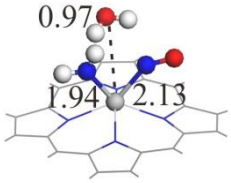
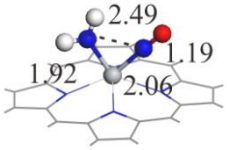
| |  |  |  |  |
|---|---|---|---|---|
| | **TiOH-NHNOH** | **TS5** | **TiOH-$N_2$-$H_2O$** | **TiOH-$H_2O$** |
| E (kcal/mol) | 43.8 | 67.7 | -28.3 | -24.1 |
| E + ZPE | 43.9 | 62.9 | -30.1 | -26.7 |



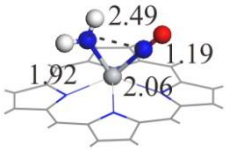
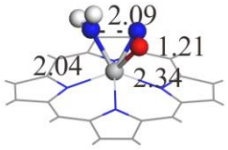
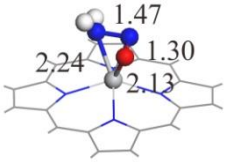
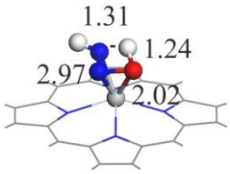
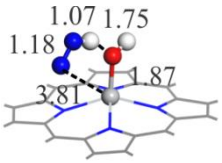

**TiOH**

| | |
|---|---|
| E (kcal/mol) | -12.5 |
| E + ZPE | -17.9 |

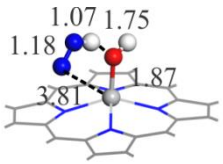
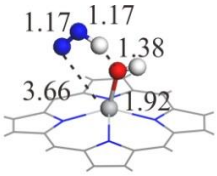
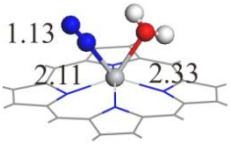
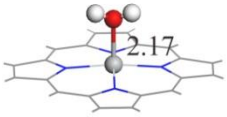
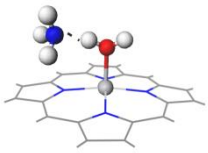
***Step E***

| | | | | |
|---|---|---|---|---|
| |  |  |  |  |
| | **TiOH** | **TiOH-NO** | **TiOH-NO-$NH_3$** | **TS6** |
| E (kcal/mol) | 40.9 | -13.8 | -27.2 | -7.8 |
| E + ZPE | 37.5 | -11.3 | -21.6 | -5.1 |
| |  |  | | |
| | **$TiNH_2$-NO-$H_2O$** | **$TiNH_2$-NO** | | |
| E (kcal/mol) | -11.6 | -5.1 | | |
| E + ZPE | -7.6 | -2.7 | | |

***Step F***

| | | | | |
|---|---|---|---|---|
| |  |  |  |  |
| | **$TiNH_2$-NO** | **TS7** | **$TiNH_2NO$** | **TS8** |
| E (kcal/mol) | -5.1 | 20.9 | 14.4 | 48.8 |
| E + ZPE | -2.7 | 22.0 | 17.1 | 47.1 |
| |  | | | |
| | **TiNHNOH** | | | |
| E (kcal/mol) | -13.8 | | | |
| E + ZPE | -14.1 | | | |

***Step G***

| | | | | |
|---|---|---|---|---|
| |  |  |  |  |
| | **TiNHNOH** | **TS9** | **Ti-$N_2$-$H_2O$** | **Ti-$H_2O$** |
| E (kcal/mol) | -13.8 | -12.3 | -40.9 | -32.6 |
| E + ZPE | -14.1 | -14.5 | -39.0 | -33.3 |
| |  | | | |
| | **Ti-$OH_2$-$NH_3$** | | | |
| E (kcal/mol) | -52.7 | | | |
| E + ZPE | -50.9 | | | |

**Catalyst regeneration**

The catalyst regeneration after Step D possibly occurs via oxidizing agents such as ammonia. In literature, it showed that during $NH_3$-SCR process $NH_3$ can adsorb on the Brønsted acid site to produce $NH_4^+$.[1-3] Thus this work we provided the possible catalytic regeneration as follows: **[Cat]**–$OH^-$ + $NH_3$ → **[Cat]**–O + $NH_4^+$ as shown in Figure S2. The catalyst regeneration is initially adsorbed $NH_3$ with adsorption energy of -8.9 kcal/mol. Then, the oxidation process requires a higher energy to surpass the barrier to form $NH_4^+$. This reaction is quite difficult to be obtained. Thus, the catalyst with Brønsted acid site would prefer to proceed the cycle II of the purpose reaction mechanism (Step E to G).

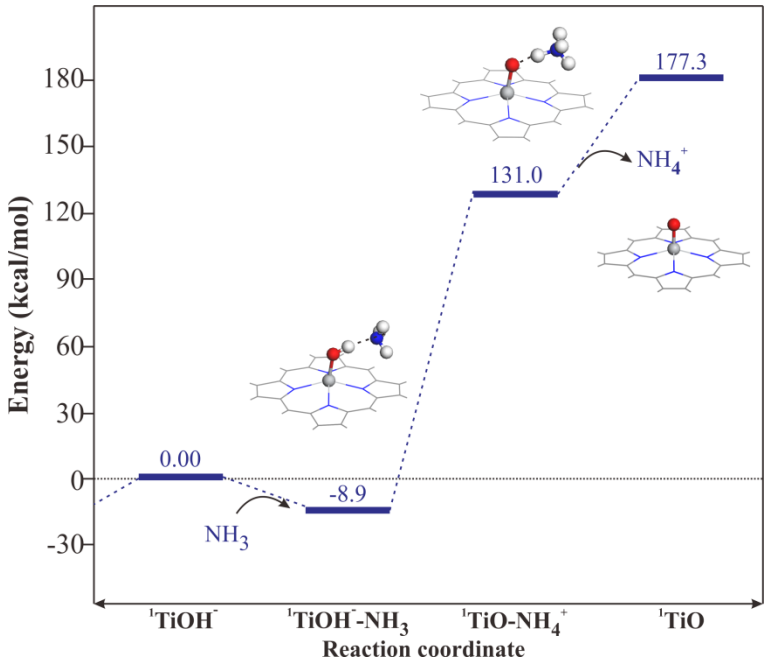



**Figure S2.** Catalyst regeneration by $NH_3$ reducing agent over the Brønsted site of TiOH intermediate calculated at the low-spin state.

**References**

(1) Busca, G.; Lietti, L.; Ramis, G.; Berti, F. *Applied Catalysis B: Environmental* 1998, *18*, 1.

(2) Yuan, R.-M.; Fu, G.; Xu, X.; Wan, H.-L. *Physical Chemistry Chemical Physics* 2011, *13*, 453.

(3) Calatayud, M.; Mguig, B.; Minot, C. *Surface Science Reports* 2004, *55*, 169.