A DFT Study on the Mechanism of Photocatalytic Nitrogen Reduction

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Highlights

- Photocatalytic nitrogen reduction.
- Revealing the ground state and excited state mechanism of photocatalytic nitrogen reduction.
- DFT calculations were performed to study ammonia synthesis over Ru-doped TiO_2 clusters.

1. Introduction

Photocatalytic nitrogen activation holds the promise of producing ammonia in an environmentally friendly way, reducing the carbon footprint and operating at mild conditions [1]. Titanium dioxide (TiO_2) is a promising photocatalyst for ammonia synthesis due to its non-toxicity, high stability and good photocatalytic activity [1,2]. The aim of our study was to elucidate the nitrogen reduction mechanism in the ground state and the lowest excited state over Ru-doped TiO_2 nanoclusters.

2. Methods

Density Functional Theory (DFT) calculations were performed in the GPAW within the Projector-Augmented Wave (PAW) method [3]. The Perdew-Burke-Ernzerhof (PBE) functional and the plane-wave (PW) or local atomic orbitals (LCAO) basis set were chosen for all simulations. We set the cutoff energy to 500 eV and the Fermi-Dirac smearing to 0.01 eV. We also included DFT-D3 correction to account for van der Waals interactions. Ground state calculations were performed using the PW basis set and the above parameters, while excited state calculations were performed using the maximum overlap method (MOM) [4] as implemented in GPAW.

3. Results and discussion

The activation of nitrogen was studied on pristine and Ru-doped $(TiO_2)_{1\text{-}12}$ nanoclusters. The formation energies and calculated optical properties of the clusters showed higher stability and thus lower reactivity of larger clusters. In addition, the adsorption energies calculated for the adsorption of N_2, NH_3, H and 2H over pristine and Ru-doped $(TiO_2)_{3,\ 6\ \text{and}\ 12}$ clusters showed the most promising adsorption on smaller clusters. The obtained results also showed a significant role of Ru atom, as we observed that Ru atom improves the optical properties of the clusters and binds nitrogen molecule more tightly, which is important for nitrogen activation and consequent reduction [5].

Based on the obtained results of cluster properties and promising nitrogen adsorption modes, we selected Ru-$(TiO_2)_6$ cluster as a promising cluster for nitrogen activation and reduction. The main aim of our study was to investigate which of the possible nitrogen reaction pathways predominates over the Ru-$(TiO_2)_6$ cluster in the lowest excited state. Based on the obtained nitrogen adsorption modes, we excluded the associative enzymatic pathway and focused on dissociative nitrogen reduction, associative distal and associative alternating nitrogen reduction.

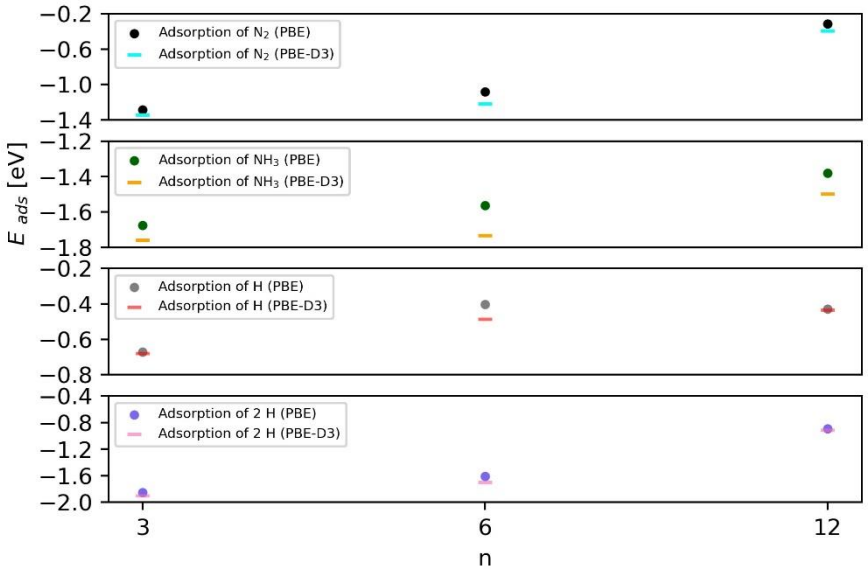

Figure 1. Adsorption energies of N_2, NH_3, H and 2H on Ru-doped $(TiO_2)_{3,\ 6\ and\ 12}$ clusters [5].

4. Conclusions

Photocatalytic nitrogen reduction is a promising route to environmentally friendly ammonia production. In our study, we have shown which of the proposed reaction pathways (dissociative, associative distal and associative alternating pathways) is the most promising for photocatalytic nitrogen reduction over Ru-$(TiO_2)_6$ cluster. A first principles nitrogen reduction mechanism allows the construction of a multiscale model by studying the kinetics of this reaction using microkinetic modelling.

References

[1] K. Ithisuphalap, H. Zhang, L. Guo, Q. Yang, H. Yang, G. Wu, Small Methods 3 (2019) 1–20
[2] I. Ali, M. Suhail, Z. A. Alothman, A. Alwarthan, RSC Adv. 8 (2018) 30125–30147
[3] J. J. Mortensen, L. B. Hansen, K. W. Jacobsen, Phys. Rev. B - Condens. Matter Mater. Phys. 71 (2005) 1–11
[4] A. T. B. Gilbert, N. A. Besley, P. M. W. Gill, J. Phys. Chem. A. 112 (2008) 13164–13171
[5] T. Žibert, B. Likozar, M. Huš, Fuel 334 (2023) 1–11

Keywords
nitrogen reduction; reaction mechanism; density functional theory; photocatalysis