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Mo-decorated triazine based covalent organic framework for enhanced nitrogen reduction reaction

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INTRODUCTION

Ammonia (NH_3) is a vital chemical feedstock for fertilizers and an emerging carbon-neutral energy carrier. However, its industrial production via the Haber–Bosch process requires high temperature and pressure, consuming substantial energy and generating significant amounts of CO_2. Electrocatalytic nitrogen reduction reaction (NRR) under ambient conditions offers a promising and sustainable alternative route for ammonia synthesis. The main challenge in NRR lies in activating the chemically inert N≡N triple bond, which possesses a high bond dissociation energy of 941 kJ mol^{-1}. Transition metal-based catalysts, particularly those incorporating molybdenum (Mo), have shown potential to overcome this limitation through effective π-back-donation into N_2 antibonding orbitals.[1] Covalent Organic Frameworks (COFs), owing to their ordered porous structure, high surface area, and tunable electronic environment, serve as ideal catalysts for NRR by stabilizing atomically dispersed metal active sites.[2]

In this work, density functional theory (DFT) calculations were employed to investigate the N_2 activation and reduction mechanism on a Mo-decorated triazine based COF (Mo-COF). The optimized unit cell of the triazine based COF and the Mo-COF is shown in Figure 1. Five possible sites were examined for Mo decoration on the COF surface. Among these, site 2 (on the pore of the middle aromatic ring) was found to be the most stable configuration, with the highest binding energy (**E_b = 6 eV**), indicating strong interaction between the Mo atom and the COF. This strong binding prevents metal aggregation.

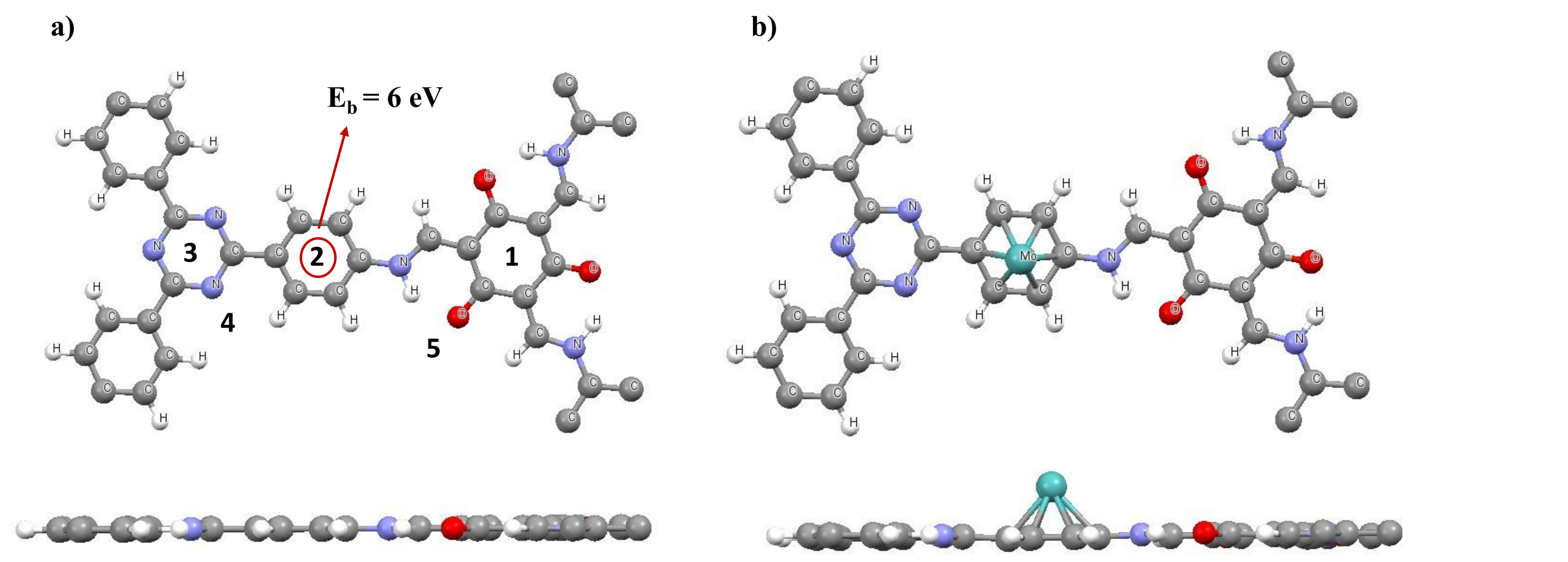


Figure 1. Top and side view of optimized structure of a) the studied COF and b) Mo-decorated triazine based COF (Mo-COF). The numbers indicate the possible sites for Mo atom decoration and E_b represents the binding energy of Mo atom decorated at site 2.

NRR CATALYTIC ACTIVITY AND SELECTIVITY

As shown in Figure 2, the adsorption of N_2 on Mo-COF was examined in two possible configurations: end-on and side-on. In the end-on configuration, single N atom of N_2 bonded with Mo, but, in the side-on configuration both nitrogen atoms were bonded with the Mo. For the Mo-COF, both end-on and side-on configurations are found to be equally favourable, as their N_2 adsorption energies differ by only about 0.2 eV. The hydrogen evolution reaction (HER) is the main competing process during NRR, reducing Faradaic efficiency by consuming proton–electron pairs that would otherwise form ammonia. Strong H adsorption on active sites blocks N_2 activation and N_xH_y hydrogenation. Hence, an ideal NRR catalyst should suppress HER by exhibiting stronger N_2 adsorption and weaker H adsorption, ensuring preferential N_2 activation and efficient ammonia formation. As shown in Figure 2, the studied Mo-COF exhibits relatively weak adsorption of H atoms on the Mo site indicating that H adsorption is thermodynamically less favourable than N_2 adsorption. This behaviour suggests effective suppression of the competing HER and enhanced selectivity toward the NRR.

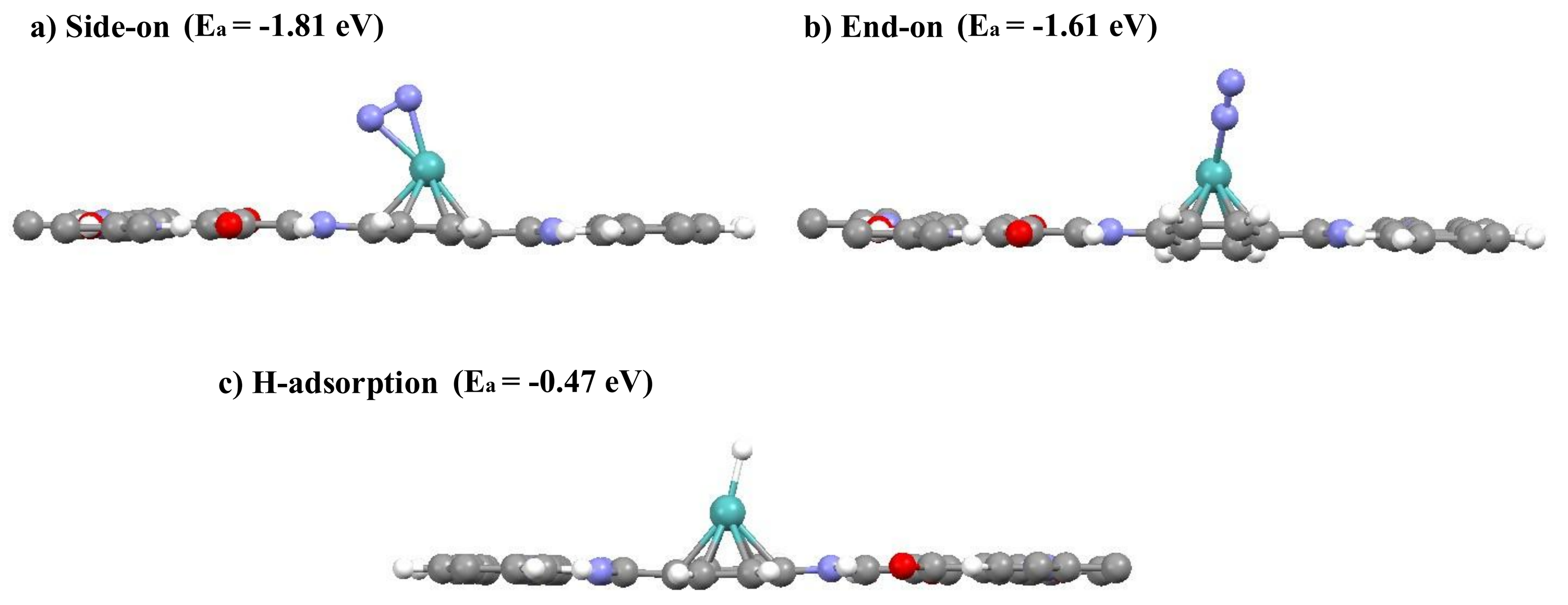
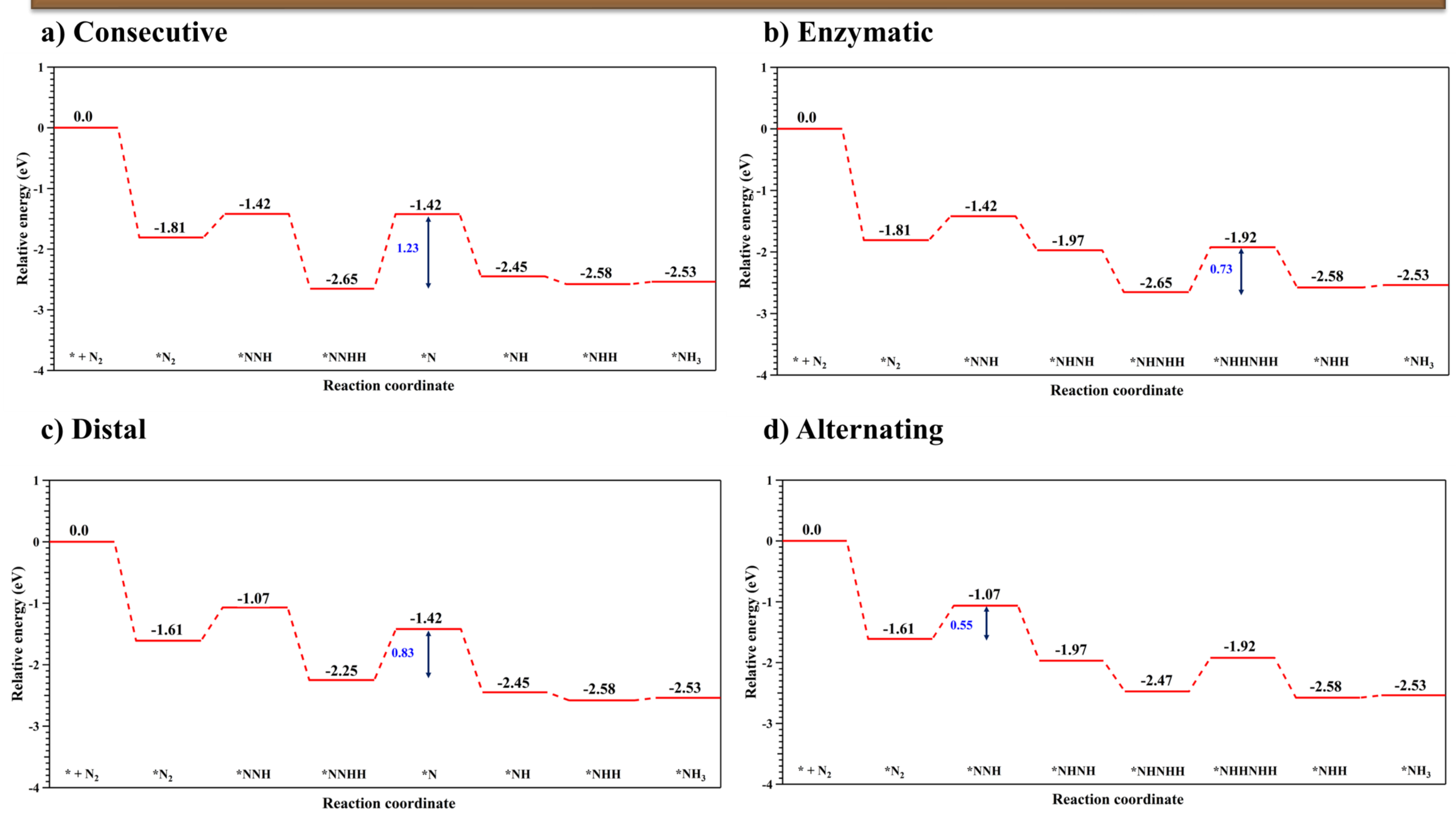


Figure 2. Optimized structure of N_2 adsorbed and H atom adsorbed Mo-COF. E_a is the adsorption energy of the adsorbate.

REACTION MECHANISM



The stepwise hydrogenation on adsorbed N_2 to form NH_3 was investigated through **four distinct pathways,** namely **consecutive, enzymatic, distal and alternating pathway**. In the consecutive (end-on) and distal (side-on) pathways, hydrogenation occurs sequentially on one nitrogen atom before on the other, and in the enzymatic (end-on) and alternating (side-on) pathways, hydrogen addition occurs alternatively on the two nitrogen atoms. As shown in Figure 3, a significant difference in reaction energies among the various pathways is noted. For the consecutive and distal pathways, the elimination of the first NH_3 results in *N intermediate which is identified as the potential determining step (PDS). However, in the enzymatic and alternating pathways, the formation of *NNH intermediate is found to be the PDS.

Among all the investigated pathways, the side-on alternating pathway exhibits the lowest reaction energy with PDS of **0.55 eV**, confirming its thermodynamic favourability. The overall limiting potential (U_l) derived from the most endothermic step is lower for this pathway, suggesting that this pathway requires less external potential to drive the NRR process efficiently.

CONCLUSION

In summary, the studied Mo-decorated triazine-based COF exhibits strong N_2 adsorption and weak H adsorption, ensuring high selectivity toward NRR. The side-on alternating pathway is found to be the most favourable pathway with a lower limiting potential of -0.55 V, confirming Mo-COF as a promising and efficient catalyst for sustainable ammonia synthesis.

FUTURE WORK

In future work, CI-NEB calculations will be performed to determine the energy barrier for the $*NH_2 \rightarrow *NH_3$ conversion. Additionally, we will explore the effects of different transition metal decorations, functional group substitutions, and applied potentials to further tune the electronic properties and enhance NRR performance.

Reference

1 Bin Chang, H. Yuan, et.al, Enhancing electrochemical nitrogen fixation by mimicking π back-donation on laser-tuned Lewis acid sites in noble-metal-molybdenum carbide, Appl. Catal. B Environ., 2023, 320, 121777.

2 J. Feng, W. Zhang and Z. Gu, Covalent Organic Frameworks for Electrocatalysis: Design, Applications, and Perspectives, Chempluschem, DOI:10.1002/cplu.202400069.