Single vs double atom catalyst for N₂ activation in nitrogen reduction reaction: A DFT perspective

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Funding information
U.S. Department of Energy, Grant/Award Number: DE-SC0019019; Priority Academic Program Development of Jiangsu Higher Education Institutions; Base for Introducing Talents of Discipline to Universities, Grant/Award Number: National 111 Project; Collaborative Innovation Center of Suzhou Nano Science & Technology (NANO-CIC); Jiangsu Planned Projects for Postdoctoral Research Funds, Grant/Award Number: 1701051A; National Natural Science Foundation of China, Grant/Award Number: 51772199

Abstract
Ammonia synthesis through electrochemical reduction of nitrogen molecules is a promising strategy to significantly reduce the energy consumption in traditional industrial process. Detailed mechanism study of multistep complex nitrogen reduction reaction is prerequisite for the design of highly efficient catalyst. Stable atomically dispersed catalyst with unique geometric and electronic structure is suitable for the mechanism clarification of such a complex reaction. In this study, d-block transition-metal (TM) anchored C₂N single layer catalyst is investigated by the density functional theory (DFT) calculation. Both single TM-anchored single atom catalyst (SAC) and double TM-anchored double atom catalyst (DAC) exhibit good thermodynamic stability in atomically dispersed catalyst. In the case of SACs, IVB metals (Ti, Zr, Hf) exhibit the highest reactivity and lowest overpotential. While in the case of DACs, Cr─Cr system leads to the NH₃ formation, but V─V system leads to the N₂H₄ formation. The SACs show much lower overpotential and stronger activation of N₂ molecule than the DACs due to the different activation mechanisms: traditional σ-donation/π-backdonation N₂ activation mechanism is found in SACs, while a new π-donation/π-backdonation N₂ activation mechanism is found in the DACs. The present work demonstrates that the different catalytic effect for NRR between SAC and DAC and their corresponding electronic structure origin, which gives more insight into the single atom catalyst.

KEYWORDS
backdonation, double-atom catalyst, nitrogen reduction reaction, single-atom catalyst
1 | INTRODUCTION

Ammonia is an important material for chemical industry and agriculture. The current ammonia synthesis employs a high temperature and high pressure Haber-Bosch process invented more than a century ago. Such a synthesis method consumes 2 to 3% world energy supply and 2 to 5% natural gas supply, in addition to producing 3% of global CO₂ emission. It is urgent to find alternative ways to replace the energy and carbon intensive Haber-Bosch process. For the last several decades, various strategies have been proposed to solve this challenge, such as electrochemical and photochemical methods, plasma, chemical looping and so on. Among the proposed strategies, electrochemical reduction of the nitrogen molecule is one of the most promising methods in consideration of energy consumption and sustainability. However, the performance of the electrocatalyst is far away from expectation, and the lacking of efficient catalyst is the main obstacle in ammonia synthesis.

Transition metal (TM) compounds are widely used as catalyst for a long history in nitrogen reduction reaction (NRR). The electrons from the occupied σ bond of N₂ overlap with the empty d orbital of TM, and the occupied d orbital of TM overlaps with the empty π* bond of N₂, resulting in the injection of electron to the antibonding π* bond of N₂ and activation of N₂ through the π bond back-donation mechanism.

There are mainly two strategies to increase the catalytic efficiency: increase the number of active sites and increase the intrinsic activity. Downsizing the TM from nanoparticle to nanocrystal or hetero-nano framework has been proven to be a useful strategy to boost the activity of the catalyst. Single atom catalysts (SACs), which exhibit the potential of well-dispersed single-atom active sites to maximize the atomic utilization, have attracted intensive attention after the first report in 2011 and is now a new frontier in heterogeneous catalysis. More importantly, the special geometric and electronic structure make the SACs exhibiting unique activity, selectivity and stability, which are quite different from its nanoparticle counterpart. The uniform dispersion of atomic catalyst with high density of active sites and stability is a major challenge in SAC research. The whole scientific research community have tried various kinds of methods both theoretically and experimentally to understand and solve this challenge.

Single transition-metal atom or atom clusters supported on N-doped graphene (Figure 1A) show good NRR activity. But it is challenging for large-scale application in terms of affordable cost to create sufficient sites for the supporting TM with good uniformity and high density. Metal-polypyridines and metalloporphyrin derivatives (Figure 1B) have a long history being widely used in organic synthesis and electrocatalyst, because of their flexible geometry and electronic tunability. However, they typically serve as molecular homogenous catalyst with poor electronic conductivity that slows down the reactivity kinetics. Moreover, it is challenging to construct chemically robust, well-defined three-dimensional porphyrin cages. Thus, it is highly desirable to find a supporting substrate with low/zero band gap and high metal supporting site density.

Recent investigations have shown that the C₂N crystals may be used as supporting substrate towards various catalytic reactions. The structure of C₂N layer possesses uniformly distributed pore with six sp³ N locating at the pore boundary, which can be used to trap the metal by strong coordinating bond. Such a structure can be viewed as the combination of graphene and polypyridine-based metal complexes. It is also highly resembles the covalent organic framework (COF) and metal organic framework (MOF). Mahmood et al reported a layered two-dimensional C₂N stoichiometry network structure that possesses evenly distributed pores and nitrogen atoms in its basal plane. When hybridized with graphene material, the resultant material exhibits moderate band gap of around 2 eV, similar to that of MoS₂. The computational work from Zhang et al predicted that several single or double anchored C₂N shows high activity towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Mahmood et al reported that C₂N supported Ru nanocrystal showed good HER effect across a broad pH range. Zhao et al calculated the copper dimer supported on C₂N for efficient reduction of CO₂. Li et al reported double anchored C₂N for the ORR by DFT calculation. In their investigation, nonnoble metals such as Cu—Cu, Co—Co and Ni—Ni exhibited both high adsorption and low activation barrier for ORR. Ji et al reported B-doped C₂N for NRR. Chen et al reported some double TM anchored C₂N for NRR. But these reports have not yet payed enough attentions to the stability issue of the catalysts. Here we used Density Functional Theory (DFT) method to give thorough study of the TM anchored C₂N material with address on stability and selectivity of the catalysts during NRR. A possible π-donation/π-backdonation mechanism is found in double anchored C₂N, but single anchored IVB elements on C₂N are more efficient for N₂ activation due to stronger σ-donation/π-backdonation mechanism.

2 | RESULTS AND DISCUSSION

Almost all d-block elements have been investigated except for Tc and Hg (Figure S1). A three-step strategy...
was employed to give a thorough study of the NRR activity of the catalysts based on TM-anchored C\textsubscript{2}N monolayer. First, stability calculation was carried out, because the stability of the catalyst is a major concern for SACs. Second, NRR activity was screened using adsorption energy of the most important intermediates of N\textsubscript{2}H and NH\textsubscript{2}. Third, calculation on the competition between HER and NRR was carried out to highlight the catalysts which are able to suppress the HER while maintaining high Faradic efficiency. The possible TM anchoring configuration in C\textsubscript{2}N are presented in Figure 1 for the single atom with different coordination number (Figure 1C) and double atoms (Figure 1D). We also noticed that the triple atomic doping was previous reported on the other substrate.\textsuperscript{36} However, the pores in C\textsubscript{2}N are not big enough to accommodate triple atoms. The calculation of the metal–metal bond length in double-anchored C\textsubscript{2}N indicated that the maximum number of anchored atoms was two for a stable configuration. It is worth noticing the different definition of single site catalyst and single atom catalyst.\textsuperscript{37} In this study, the double-anchored system contained two atoms as the active sites, while the single-site heterogeneous catalyst (SSHC) was more suitable for both the single and double-anchored system. The prerequisite for the catalyst was that it should be thermodynamically stable to withstand in various acidic or alkaline condition during the electrochemical processes. Decreasing the size of the particles, the coordination number decreased and the surface energy increased, which would result in severe metal agglomeration.\textsuperscript{38} Such effect was especially prominent for the atomic dispersed catalyst. The stability of SAC catalyst is one of the biggest challenges in real application.\textsuperscript{39} Here only the thermodynamic stability of TM anchored C\textsubscript{2}N was considered (see Data S1 for the detail of the calculation). Figure 2 shows the structural stability relative to the bulk crystal. Most of the single anchored TM atoms exhibited a lower binding energy than their bulk state, implying that such kind of anchoring state is unstable. Only Hf, La, Sc, Ti, Y, and Zr showed strong binding with C\textsubscript{2}N monolayer, but there were still some single binding elements with smaller relative binding energy, such as Cd, Mn and Zn. A threshold of 0.5 eV was selected as the upper limit for a stable binding energy of single anchored C\textsubscript{2}N in case of the kinetic confined local geometry. For single-anchored system, Cd, Hf, La, Mn, Sc, Ti, Y, Zn, and Zr were selected as potential candidates for further detailed calculation. For the double-anchored system, Cd, Cr, Sc, Ti, V, Y, Zn, and Zr were thermodynamically stable on the C\textsubscript{2}N monolayer. The calculation showed

**FIGURE 1** TM coordinated to the graphene, A, and metalloporphyrin, B. The structure of single, C. and double, D, anchored C\textsubscript{2}N monolayer. The purple atom is in the armchair site, and the pink and purple circles are in the zig-zag and central site, respectively

**FIGURE 2** Cohesive energy relative to the bulk crystal of the selected d block elements anchored on C\textsubscript{2}N monolayer. $E_{\text{SAC/DAC}}$ is the binding energy of TM anchored on C\textsubscript{2}N, and $E_{\text{bulk}}$ is the bulk cohesive energy of transition metal
that the COF-like C2N monolayer and TM metal exhibited strong metal substrate interaction by forming TM2N4 and TMN2, which keep the SSHC/SAC/DAC stable and uniformly dispersed, and prevent the TM atoms from agglomeration. The present study enriched the target elements reported the previous calculation,33,40,41 and have stronger potential for practical application.

The first protonation of adsorbed N2 to form N2H was the most difficult step towards NRR and was considered as the rate determine step.42 Usually NH2 was another important intermediate, which is destabilized from the catalyst after adopting another proton and releasing the active site. Therefore the N2H and NH2 adsorption could be used for further selection of suitable candidates43,44 as summarized in Figure 3A,B. The adsorption of N2H should be strong enough to ensure the activity of NRR, and the adsorption of NH2 should be weak enough to diffuse away and then release the active site. We set the threshold adsorption energy of N2H at 1.5 eV, below which the anchored system could be treated as active for NRR, similar with the strategy used in other calculation.42 For the NH2 adsorption the threshold was set to -2.5 eV. Above this threshold, the system could be treated as effective NRR catalyst, while below this threshold, the active site might be blocked by the strong NH2 adsorption. In aqueous solution, hydrogen binding to TM metals is another commonly occurred issue in addition to the N2 binding to the TM atom. The hydrogen adsorption competes not only for the active site in the NRR process, but also for the electron which results in the low activity and low Faradic efficiency. Therefore, detailed calculation comparing the HER and NRR should be considered for the design of efficiency NRR catalyst. The comparison of H adsorption and N2 adsorption was previously employed to determine the selectivity between HER and NRR on metal oxide and nitride surface.36,43,45 Here we also did such kind of comparison as shown in Figure 3C-E. The elements below the dash line had stronger adsorption of N2 than that of H, thus favoring the NRR process. For the single anchored system, NRR seemed highly preferable than the HER, except Zn. Large amount of double anchored systems preferred HER than NRR, but there were still some double anchored system, such as Cd, La, Sc, Ti, V, Y, and Zr, showing a stronger selection for the

**FIGURE 3** A, B, Adsorption energy of N2H and NH2 on selected TM anchored C2N layer. The comparison of hydrogen adsorption energy and N2H adsorption energy on SAC and DAC anchored system: C, parallel adsorption (DAC-P); D, vertical adsorption (DAC-V); E, adsorption on the SAC
NRR process. As indicated in Figure 3A,B, all the selected elements exhibited NRR activity without strong NH\textsubscript{2} adsorption to block the active site. An exception was found in double anchored Zn, where there is no N\textsubscript{2}H adsorption. During the simulation of the NRR process, it was facile for the adsorbed intermediate to destroy the structure and lead the TM atom detach from the C\textsubscript{2}N for double Cd and La anchored systems. The stability comparison of double anchored and single anchored C\textsubscript{2}N cases listed in Figure 2 was further conducted from the material synthetic aspects for experimentally realizing the most promising catalysts. Thus, the double anchored Cr and V were left and for the single anchored case: Hf, La, Mn, Sc, Ti, Y, and Zr were left for further detailed study.

Figure 4 shows the free energy profile for the reaction process of NRR. For the DAC in Figure 4A,B, the parallel and vertical N\textsubscript{2} molecule adsorption showed completely different reactivity and selectivity. The overpotential for parallel adsorption case was 0.66 and 0.88 eV for Cr and V, respectively. While the vertical N\textsubscript{2} adsorption has much higher overpotential with 1.75 and 1.60 eV for Cr and V, respectively. For parallel N\textsubscript{2} adsorption (Figure S2), Cr led to the formation of NH\textsubscript{3}, while V led to the formation of N\textsubscript{2}H\textsubscript{4} (Figure 4D). For the vertical N\textsubscript{2} adsorption, they all led to the formation of NH\textsubscript{3} (Figure 4E). The reactivity of the SACs in Figure 4C could be categorized into three groups: (a) IIIB series (Sc, Y, La); (b) IVB series (Ti, Zr, Hf), and (c) Mn. As summarized in Table 1, IIIB series showed higher

**FIGURE 4** The adsorption energy of various intermediate along the reaction pathway. A and B, N\textsubscript{2} parallel (DAC-P) and vertical (DAC-V) adsorption case for TM double anchored DAC. C, The TM single anchored SAC case. D and E, The corresponding reaction pathway for DAC and SAC
overpotential above 2 eV, the IVB series exhibited lower overpotential around 1.0 eV, and Mn possessed a moderate overpotential of 1.41 eV. The free energy change of elementary step of NRR process show the potential limiting step (PLS) are N2H2 ➞ N and NH3 desorption for IIIB series and IVB series, respectively (Table S1). Moreover, IVB series anchored C2N had the highest adsorption energy for N2, which means the IVB series anchored C2N has much higher reactivity than the IIIB series and Mn anchored C2N. The SAC showed stronger N2 activation, especially the IVB series SACs were more efficient than the DACs. To the best of our knowledge, this is the first study to compare the effectiveness between SAC and DAC for NRR. The optimized geometric structure of the double anchored monolayer is shown in Figure S3. Combined with the parameters shown in Table 1, it could be seen that for DAC, Cr and V occupied zigzag site with 3 N ligands, V—V bond was slightly larger than the Cr—Cr bond, indicating a weaker metal—metal bonding in V—V DAC. The ligand—metal bond of V was slightly smaller than that of Cr, which would lead to slightly different crystal field splitting strength of the d orbital manifolds. In the case of SAC, the coordinate environment was the same with metal—ligand bond length slightly different. The crystal field was almost the same except for the case of La and different splitting strength of d orbital. Bader charge analysis was also carried out to demonstrate the charge transfer (CT) between metal and substrate C2N, overpotential of NRR (η) and potential limiting step (PLS).

### Table 1

| Elements | V | Cr | Mn | Sc | Y | La | Ti | Zr | Hf |
|----------|---|----|----|----|---|----|----|----|----|
| TMNC     | 3 | 3  | 2  | 2  | 2 | 2  | 2  | 2  | 2  |
| d_{TMN} (Å) | 2.28 | 2.35 | 2.14 | 2.20 | 2.45 | 2.71 | 2.10 | 2.25 | 2.18 |
| d_{TM} (Å) | 1.644 | 1.51 |
| MLCT (e/site) | 0.78 | 0.86 | 1.27 | 1.69 | 2.09 | 2.06 | 1.56 | 1.93 | 1.78 |
| η (V) | 0.88 | 0.66 | 1.41 | 2.28 | 2.47 | 2.16 | 1.56 | 1.93 | 1.78 |
| PLS | N2H2 ➞ N2H4 | N2 ➞ N2H | N2 ➞ N2H | N2H2 ➞ N | N2H2 ➞ N | N2H2 ➞ N | NH3 | NH3 | NH3 |

**Figure 5** N2 molecule activation mechanism for the DAC, A, and SAC, B and C. The π (left) and σ (right) splitting of LOL for N2 adsorption on the double anchored V, D, single anchored Sc, E, and Ti, F, respectively.
and they were almost $\text{TM}^{2+}$, except for the magnetic case of Mn anchored system. The occupation of the split $d$ orbital was the main difference in both SAC and DAC systems. Different occupation of $d$ orbital would lead to different frontier orbital binding between TM and $\text{N}_2$ molecules, thus leading to different reactivity and selectivity.

When the overlap between the frontier orbital of $\text{N}_2$ with the split $d$ orbitals was different, the strength of the bonding would be different. This is consistent with the calculated adsorption energy shown in Figure 4A,B. More importantly, the different adsorption strength between the intermediates on the reaction process led to completely different selectivity and products. In the SAC case, the metal–ligand bond lengths were similar, except for Y and La with large ionic radius. But IVB series had one additional electron, which leads to the different orbital occupation, and the overlap between $\text{N}_2$ and $d$ orbitals with strong head to head overlap in SAC cases as show in Figure 5. Thus, the SAC exhibited stronger $\text{N}_2$ activation and fast reaction kinetics. Similar with previous observation in various kind of metal–metal bond,47 Cr–Cr and V–V bonded to C$_2$N and formed stable dimer, which leads to the different selectivity compared with SACs. The $\text{N}_2$ molecule activation mechanism was further explored by the inspection of the $d$ orbital and $\text{N}_2$ molecular orbital alignment. In double anchored DAC case, for $\text{N}_2$ parallel adsorption, the occupied $\sigma$ bonding orbital of $\text{N}_2$ molecular lied shoulder-to-shoulder to the empty $d$-orbit, then formed $\pi$ bond between $\text{N}_2$ and TM-TM and resulted in the $\pi$-donation. The calculated Localized-orbital locator (LOL) showed stronger $\pi$ bonding than the $\sigma$ bonding characteristic as show in Figure 5A,D. The bonding between $\text{N}_2$ and catalyst should be strong enough to activate the triple bond of $\text{N}_2$. Such $\pi$-donation was less likely to activate the $\text{N}_2$ molecule than the $\sigma$-donation. And this might be the reason that all previously reported TM-based catalysts followed the $\sigma$-donation mechanism. For $\text{N}_2$ vertical adsorption, only one N atom contacted with TM atoms. The occupied $\sigma$ bonding orbital of $\text{N}_2$ molecular lied head-to-head with the empty $d$-orbit, which forms strong $\sigma$ bond between $\text{N}_2$ and TM-TM, and results in the $\sigma$-donation. The $\sigma$ bond was much stronger than the $\pi$ bond, and this was the reason why $\text{N}_2$ vertical adsorption was much stronger than the $\text{N}_2$ parallel adsorption. In SAC case, $\text{N}_2$ had no parallel adsorption site. Thus, it was similar to the vertical adsorbed $\text{N}_2$ in DAC case with a stronger $\text{N}_2$ adsorption energy as show in Figure 5B,C. The calculated LOL showed stronger $\sigma$ bonding than the $\pi$ bonding, as shown in Figure 5E,F. Besides, from the point view of crystal field, for the IVB series atoms, there was one more electron occupying the $d_{z^2}$ orbital, but the $d_{xy}$ orbital was empty for IIIB series elements. However, $\text{N}_2$ molecule had stronger overlap with $d_{z^2}$ orbital than $d_{xy}$ orbital though they all belonged to $\sigma$-donation. This should be the reason for the strong binding and activation of $\text{N}_2$ molecule on IVB series SACs.

3 | CONCLUSION

In summary, the calculation of $d$-block anchored C$_2$N monolayer for NRR process shows that both SAC and DAC exhibit good thermodynamic stability. Many of them show activity for NRR but suffering from the competition of HER. Through sophisticated calculation comparing the competition between HER and NRR, single anchored Sc, Y, La, Ti, Zr, Hf SACs and double anchored Cr, V DACs are selected as promising NRR catalyst. Among these elements, Cr and V form strong metal–metal bond, and the other elements tend to exist as single dopant to form the SACs. The different occupation of the $d$ orbital leads to the different reactivity and selectivity for SACs and DACs. For SACs, they all lead to the formation of the final NH$_3$ products. But IVB series have stronger $\text{N}_2$ activation capability and lower overpotential than the IIIB series originating from the heavier overlap between the frontier orbitals of the TM atom and $\text{N}_2$ molecule. A new $\pi$-donation/$\pi$-backdonation $\text{N}_2$ molecule activation mechanism is found in double dopant DACs. The present work uses C$_2$N to show that the COF like material has strong potential to stabilize the well dispersed atomic catalyst. Both SAC and COF are all at the infancy stage, and we expect the merge of these two fields to form a new platform for the clearer and deeper mechanistic understanding of the atomic dispersed catalyst such as SAC or DAC. More novel and exciting new findings will be discovered in the future to boost the fundamental scientific understanding and real application of SAC in various electrochemical fields, such as NRR, HER, ORR, OER and so on.

4 | EXPERIMENTAL SECTION

The first principles calculations based on DFT were performed within spin-polarized generalized gradient approximation (GGA). Core electron states were represented by the projector augmented-wave method as implemented in the Vienna ab initio simulation package (VASP). The Perdew-Burke-Ernzerhof exchange correlation functional and a plane wave representation for the wave function with a cut-off energy of 450 eV were used. Lattice parameters were fully relaxed, geometry of crystal is fully optimized before the electron structure...
and total energy calculation. The convergence criterion for the residual force and energy was set to 0.01 eV/Å and 10⁻⁵ eV, respectively, during the structure relaxation. Supercells consisting of 2 × 1 × 1 C₂N unit cells were used and the Brillouin zones were sampled by a Monkhorst-Pack k-point mesh with a 1 × 1 × 1 k-point grid. A vacuum space exceeds 15 Å was employed to avoid the interaction between two periodic layers.

ACKNOWLEDGEMENTS

G.Y. acknowledges the financial support from the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0019019. Y.Q., Y.Z. and X.Z. acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 51772199); the Jiangsu Planned Projects for Postdoctoral Research Funds (Grant No. 1701051A); the Collaborative Innovation Center of Suzhou Nano Science & Technology (NANO-CIC) and the Base for Introducing Talents of Discipline to Universities (National 111 Project), and the Priority Academic Program Development of Jiangsu Higher Education Institutions. The authors also acknowledge the Texas Advanced Computing Center (TACC) at The University of Texas at Austin for providing HPC resources that have contributed to the research results reported within this article. URL: http://www.tacc.utexas.edu

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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**How to cite this article:** Qian Y, Liu Y, Zhao Y, Zhang X, Yu G. Single vs double atom catalyst for N2 activation in nitrogen reduction reaction: A DFT perspective. *EcoMat*. 2020;1-9. [https://doi.org/10.1002/eom2.12014](https://doi.org/10.1002/eom2.12014)