Black phosphorus-hosted single-atom catalyst for electrocatalytic nitrogen reduction

Xiaoyun Lin¹, Lulu Li¹, Xin Chang¹, Chunlei Pei^{1,2}, Zhi-Jian Zhao^{1,2*} and Jinlong Gong^{1,2,3}

ABSTRACT Designing highly selective and efficient single-atom electrocatalysts is essential for ammonia production under ambient conditions. This paper describes a density functional theory study on exploring the performance trends of transition metal complexes with P-based ligands in nitrogen reduction reaction (NRR) and further develops a design principle for high-performance single-atom catalysts (SACs) of NRR. Among the explored catalysts, W@BP (0.40 eV), Ta@BP (0.47 eV), and Nb@BP (0.53 eV) are identified as remarkable candidates with low free energy change in the potential-limiting step, high stability and high electrical conductivity for NRR. It is worth noting that almost all SACs with P-based ligands exhibit high NRR selectivity, due to the fact that they adsorb $\ast\text{N}_2$ more strongly than $\ast\text{H}$. The adsorption free energy of $\ast\text{N}_2\text{H}$ can be considered as a descriptor for the intrinsic activity trends in NRR. Furthermore, by constructing a volcano plot of the activity against the electronic charge on metal centers, it is demonstrated that the metal center with a moderate amount of positive charge can promote the catalytic performance of NRR.

Keywords: nitrogen reduction reaction, electrocatalysts, single-atom catalysts, density functional theory (DFT), black phosphorus

INTRODUCTION

As a basic raw material for agriculture and industry, ammonia (NH_3) plays an important role in the global economy [1,2]. Nowadays, ammonia synthesis is mainly carried out through the Haber-Bosch process under high temperature and high pressure, which suffers from excessive energy consumption and CO_2 emission [3]. Therefore, searching for an environment-friendly alternative route has drawn increasing attention recently [4].

After 20 years of development [5–8], electrochemical nitrogen reduction reaction (NRR) has become a hot field since it proceeds under ambient conditions [9]. Considering the remarkable chemical inertness of the N_2 molecule, a desirable NRR electrocatalyst must be able to activate the $\text{N}\equiv\text{N}$ bond [10,11]. Certain transition metals (TM) have an advantageous combination of unoccupied and occupied d orbitals, favorable for N_2 binding and activation [12]. However, the unoccupied d orbitals of TM are also known to strengthen hydrogen adsorption, facilitating the competing hydrogen evolution reaction (HER) [13,14] and leading to a poor selectivity of NRR [15–19].

Previous studies inspired by the enzyme nitrogenase [20] and molecular catalyst complexes [21] provided evidence that the coordination between a metal center and ligands is able to promote NRR [22]. Among various ligands commonly used in molecular NRR catalysts, electron rich P-based ligands could stabilize the metal center and enhance the catalytic performance [1,23–25]. For instance, Mo coordinated by PPP-type (PPP = bis(di-tert-butylphosphinoethyl)phenylphosphine) ligands can produce up to 63 equivalents of ammonia on the Mo atom under ambient conditions [26]. Moreover, it has been discovered recently that elemental P in the form of nanosheets can be active for NRR. Zhang *et al.* [27] successfully applied few-layer thick black phosphorus (BP) to catalyze NRR, achieving a high NH_3 yield of $31.37 \mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat}}$. However, only special edge sites of BP nanosheets were found to serve as active centers, whereas regular sites are inactive, being a limiting factor for the NRR catalytic performance.

To alleviate this issue, single-atom catalysts (SACs), in which isolated metal atoms are doped onto supports [28],

¹ Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China

² Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300350, China

³ Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Fuzhou 350207, China

* Corresponding author (email: zjzhao@tju.edu.cn)

can increase the number as well as intrinsic activity of active sites due to their unique geometrical structures and electronic properties [29]. Excellent performance of SACs has been demonstrated in various reactions, making them a very promising emerging novel class of catalysts, since they can afford the maximum atom utilization efficiency and offer much higher selectivity toward the target products [30–32]. Thanks to selectivity similar to that of molecular catalysts combined with the high durability of heterogeneous catalysts [33–35], SACs have been theoretically and experimentally identified as highly active and selective catalysts for NRR [19,36–42]. SACs can efficiently suppress the HER due to the lack of an “ensemble effect” [38] and stronger binding N_2 owing to favorable “electronic effect” [43]. By combining different metal centers with various types of supports, many recent theoretical studies have mainly focused on the screening of effective SACs and on the exploration of NRR mechanisms [39,44,45]. Mo [34,43,46] and W [41,47] have been reported as promising metal centers with low overpotential and high selectivity for NRR. In addition, the catalytic performance for NRR can be adjusted by controlling the coordination environment of metal centers [39,43].

Considering the unique role of P-ligands in molecular complexes and the limitations of using pristine BP in electrocatalytic NRR, this paper describes NRR electrocatalytic properties of twenty-nine TM-SACs supported on BP (TM@BP) through density functional theory (DFT) calculations. W@BP, Ta@BP and Nb@BP are predicted as the most promising materials towards NRR. Our study revealed the origin of NRR activity trends by analyzing the bonding/antibonding interactions between metal centers and $*N_2H$ and proposed a design principle for BP-based NRR catalysts: metal centers with a moderate amount of positive charge show the highest NRR activity.

COMPUTATIONAL DETAILS

First-principles calculations were done within the framework of DFT, as implemented in the Vienna *Ab initio* Simulation Package (VASP) [48,49]. All calculations, including geometry optimizations and electronic properties, were performed using spin-polarized approach. The projector-augmented-wave (PAW) pseudo-potential was utilized to describe valence electrons and the ionic core interactions [50]. We used the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [51] and considered the van der Waals correction employing the DFT-D₃ scheme [52]. The 400-eV cutoff energy was set for all

calculations and the reciprocal space was sampled with the $4 \times 4 \times 1$ k -points for geometry optimization. The model of monolayer BP was simulated by a (2×2) periodic supercell and all the atoms were relaxed until the force on each atom was less than $0.02 \text{ eV } \text{\AA}^{-1}$. The vacuum layer with $15 \text{ \AA}$ thickness was set to avoid interaction between periodic units. We also tested the Hubbard U correction [53] for Fe, Co, and Ni 3d with the U value of 2.5 eV [54] and we found that the Hubbard correction had little effect on our calculated adsorption free energy and reaction free energy (Table S1). After the geometry optimization, the finer $6 \times 6 \times 1$ k -points mesh was employed for the crystal orbital Hamilton population (COHP) and Bader charge analysis. The hybrid functional (HSE06) method was used for the electronic bandgap calculation.

We utilized the computational hydrogen electrode (CHE) model [55] to calculate the free energy diagrams. In this model, one-half of the chemical potential of gaseous H_2 at equilibrium (0 V vs. standard hydrogen electrode) can be used as a reference to calculate the free energy of the electron-proton pair ($H^+ + e^-$). The free energy for each intermediate state was defined as $G = E_{\text{tot}} + E_{\text{ZPE}} + \delta H_0 - TS$, where E_{tot} is the total energy, E_{ZPE} is the zero-point energy (ZPE), δH_0 is the integrated heat capacity, T is the reaction temperature ($T = 298.15 \text{ K}$), and S is the entropy. The calculated ZPE correction, enthalpy correction, and entropy correction of different adsorption species and gas molecules are listed in Table S2.

The transition states were determined by the climbing-image nudged elastic band method [56]. The activation barrier was defined as $\Delta E = E_{\text{TS}} - E_{\text{IS}}$, where E_{IS} and E_{TS} are the energy of the preceding lowest energy intermediate and the transition state, respectively.

RESULTS AND DISCUSSION

Doping structures of SACs with P-based ligands

Two potential doping states of metal atoms on one-layer BP have been proposed [57,58], including (i) the possibility of one metal atom to replace one or two P atoms respectively (Rep1 and Rep2), or (ii) the possibility of one metal atom to adsorb on the surface (Ads) (Fig. 1a). Our calculations showed that for the replaced states, the Rep1 structure was more thermodynamically stable (Table S3). Thus, we used the formula $\Delta E = E_{\text{Rep1}} + E_{\text{BP}}/N_{\text{P}} - E_{\text{Ads}}$ to further identify the relative thermodynamic stability of replaced and adsorbed doping structures (Fig. 1b). Here, E_{Rep1} , E_{BP} , and E_{Ads} represent the total energy of the structure Rep1, pristine BP, and structure Ads, respec-

Figure 1 (a) Potential structure of TM@BP SACs. Yellow, blue, and orange spheres represent P, replacing, and adsorbing TM, respectively. (b) Stability comparison of the two doping structures.

tively. N_P is the total number of P atoms in pristine BP. For the elements located at the right end of the periodic table's d-block (Zn, Cd, and Hg), only replaced states (Rep1 and Rep2) exist. According to this figure, the ΔE values show an increase through the periodic table's periods. The ΔE values are negative for most metals, suggesting general higher stability of Rep structure than Ads structure. Therefore, in this paper, we mainly investigated the NRR performance of the SACs with Rep structure.

Reaction mechanism and free energy for NRR on SACs with P-based ligands

To examine the intrinsic activity of electrocatalysts, four possible NRR pathways have been considered: distal, hybrid, alternating, and enzymatic (Fig. 2a) [59]. It is recognized that the N_2 adsorption is the first step in NRR, and the structure of N_2 (end-on and side-on mode) can determine the subsequent reaction pathway [34]. Firstly,

it has been shown that N_2 cannot chemisorb on P atoms adjacent to the metal center, indicating that only metal centers are active sites for NRR [60]. Secondly, N_2 cannot chemisorb on those metals with fully filled d-shell (Cu, Zn, Pd, Ag, Cd, Au, and Hg). Therefore, these catalysts are not qualified for NRR. Furthermore, the side-on mode of N_2 adsorption is thermodynamically unstable (Table S4), suggesting that the enzymatic pathway is not feasible. Only the distal, hybrid and alternating pathways have been considered in the following study.

ΔG values of the six elementary steps in NRR ($N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$) have been computed and the free energy change of the potential-limiting step ($\Delta G_{\max}$) has been chosen to evaluate the overall performance, which is often used to identify the overpotential and limiting potential of NRR (Fig. 2b) [34,61,62]. Interestingly, elements with small $\Delta G_{\max}$ are all located in the middle of 4d and 5d blocks (i.e., Nb (0.53 eV) for 4d metal, Ta (0.47 eV), and W (0.40 eV) for 5d metal). These catalysts could be effective candidates with excellent activity towards NRR. It is worth noting that Mo@BP exhibits relatively small $\Delta G_{\max}$ (0.56 eV), which is consistent with previous reports finding a remarkable intrinsic activity for Mo performance in NRR in biological nitrogen fixation [1, 20] and homogeneous catalysis [23,26]. The $\Delta G_{\max}$ of the majority of TM@BP SACs is lower than that of Ru(0001) (1.08 eV), which is generally recognized to offer the highest catalytic activity among bulk metals [16], indicating that as a substrate, BP holds great potential for catalytic NRR. The potential-limiting step on all catalysts is the first protonation step. In previous reports, however, the last protonation step was also often considered as a potential-limiting step, because of the strong interaction between $*NH_2$ and the catalyst surface [34,38]. However, for the catalysts analyzed in this study, the last protonation step was demonstrated to be exothermic, suggesting that SACs with P-based ligands could destabilize the $*NH_2$ species. Given that $*NH_3$ might be desorbed easily to form NH_4^+ in solution, here we did not consider the free energy of NH_3 desorption [38,62]. Furthermore, we explored the reaction mechanism *via* the favorable pathways of W@BP, Ta@BP, and Nb@BP (Fig. 2c–e). These intermediate structures are shown in Fig. S1 and the free energy diagrams *via* the remaining possible pathways are shown in Fig. S2. At the second protonation step, there are two possible intermediates, $*NHNH$ and $*NNH_2$. For these three models, the formation of $*NHNH$ is endothermic while $*NNH_2$ is formed in an exothermic process. Hence, for all three metals the formation of $*NNH_2$ intermediate is preferred. In the third step, both

Figure 2 (a) Schematic depiction of four NRR pathways on TM@BP SACs. M represents the metal center and P represents the P-ligands on SACs. (b) Calculated ΔG_{max} on 22 TM@BP SACs. Blue and orange represent SACs with ΔG_{max} below and above 0.6 eV, respectively. The horizontal dashed line represents ΔG_{max} of Ru(0001) as a reference. Free energy diagrams *via* the favorable pathways of (c) W@BP, (d) Ta@BP, and (e) Nb@BP, respectively. The reference temperature and pressure are set to 298.15 K and 1 atom, respectively.

$*N + NH_3$ and $*NHNH_2$ are possible intermediates, following the distal and hybrid pathway, respectively. For the W@BP and Nb@BP surfaces, the distal pathway is preferred with the minimum Gibbs free energy potential, whereas the NRR on the Ta@BP surface is favorable *via* a hybrid pathway. The free energy diagrams *via* the favorable pathways of the other TM@BP are shown in Fig. S3.

The selectivity of SACs with P-based ligands

Poor selectivity is a fundamental issue in NRR because of the competing HER. To effectively suppress the HER, the adsorption free energy of $*N_2$ on a desirable catalyst should be stronger than that of $*H$ [10,38]. The sufficiently strong binding of $*N_2$ could result in a higher surface concentration of $*N_2$ compared with the undesirable $*H$ adsorption on active sites [36]. In this case, the protons and electrons would prefer to attack $*N_2$, which is in favor of further NRR [19]. Our calculation showed that the adsorption free energies of $*H$ on all SACs are weaker than that on Ru(0001), and that nearly all SACs are located in the $*N_2$ dominant region, indicating high NRR selectivity (Fig. 3). Previous studies revealed that $*H$ prefers to adsorb on bridge or hollow

sites rather than on the atop site. The weak $*H$ adsorption of our catalysts is attributed to the fact that only the atop site is available on single metal atoms [38]. Interestingly, Pt@BP still show relatively strong $*H$ adsorption ($\Delta G(*H)$ of -0.1 eV), indicating that it is a remarkable candidate for HER, which is consistent with the intrinsic high activity of the Pt atom. Furthermore, five SACs with ΔG_{max} below 0.6 eV have been chosen to compare the energy required for HER and NRR (Table S5). Accordingly, Ta@BP, Nb@BP, and Re@BP showed a comparable or even more positive limiting potential for NRR, suggesting that they may suppress the HER effectively [43,61].

Origin of the NRR activity trends on different metal centers

Since the potential-limiting step of NRR on all SACs is the formation of $*N_2H$ from $*N_2$, $*N_2H$ is the key intermediate for the whole reaction. As shown in Fig. 4a, there is a linear relationship between the adsorption free energy of $*N_2H$ ($\Delta G(*N_2H)$) and ΔG_{max} , which means $\Delta G(*N_2H)$ can be considered as a descriptor to reflect the inherent NRR activity of these catalysts. Bader charge on $*N_2H$ was calculated to further analyze the relationship between the activity and the electronic environment of $*N_2H$, as

Figure 3 Calculated $\Delta G(*H)$ and $\Delta G(*N_2)$ on 22 TM@BP SACs and Ru (0001) as a reference. Dashed line indicates $\Delta G(*H) = \Delta G(*N_2)$.

Figure 4 COHP curve of the metal center from La to Pt and the proximal N adatom of $*N_2H$ interaction.

shown in Fig. 4b. Our calculations revealed that the electron transfer between $*N_2H$ and the metal atom is vital for $*N_2H$ adsorption and activation. Such an electron transfer process assumes that the d electrons of the TM atom are donated into the antibonding orbital of the N–N

bond, leading to the repulsive interaction between the two N atoms. It can be inferred that a desirable catalyst with excellent NRR performance should have a high capability of transferring electrons to $*N_2H$.

In order to explore the trends in the computed $\Delta G(*N_2H)$ values for different metal centers and to correlate them with the nature of the M– N_2H bond, we screened a series of 5d block metals and analyzed the interactions between metal centers and hydrogen free N atom of $*N_2H$ by using COHP (Fig. 5). For Ta, W and Re with relatively high activity, the lack of antibonding interactions below the Fermi level (E_f) implies strong adsorption of $*N_2H$ on these centers. Although there are also only tiny or even no antibonding interactions below E_f for La and Hf, their bonding features are not as broad as in the case of Ta, W and Re. For Os, Ir and Pt, the lower binding strength of $*N_2H$ is illustrated by the higher antibonding interactions present below E_f . Fig. 6a shows a linear relationship between the integrated COHP (ICOHP) and $\Delta G(*N_2H)$, which quantitatively confirms that bonding/antibonding interactions of different metal centers with $*N_2H$ are a key factor determining the value of $\Delta G(*N_2H)$.

By analyzing the electronic charge of the metal centers supported on the BP surface, we found that metal centers with a moderate amount of positive charge exhibit the most promising activity performance, which presents a guideline for the design of SACs for NRR. Previous studies indicated because N_2 is a weak Lewis base, creating a positive charge on the metal center (which can be realized by electron transfer to a ligand atom) is favorable for the N_2 adsorption [38,62]. However, if the metal center carries too strongly positive charge, it is not beneficial for transferring electrons to reaction intermediates, and will also inhibit the NRR activity. As seen from Fig. 6b, there is a volcano-like relationship between ΔG_{max} and the metal center-to-substrate electron transfer. To further understand how the chemical environment of the metal center affects the NRR activity, we investigated the relationship between Bader charge of the $*N_2H$ inter-

Figure 5 The correlation between ΔG_{max} on 22 TM@BP SACs with (a) $\Delta G(*N_2H)$ and (b) Bader charge of $*N_2H$ intermediate.

Figure 6 (a) The correlation between ICOHP and $\Delta G(\text{*N}_2\text{H})$ on 22 TM@BP SACs. (b) The correlation between ΔG_{max} on 22 TM@BP SACs with Bader charge of the metal center.

mediate and metal center-to-substrate electron transfer. The volcano-like plot (Fig. S4) reveals that only a metal center with a moderate amount of positive charge leads to a greater ability to inject electrons into $\text{*N}_2\text{H}$, ultimately resulting in excellent NRR activity. If a metal center transfers too much charge to P-ligands, its ability to further inject electrons into $\text{*N}_2\text{H}$ decreases. If a metal center withdraws electrons from P-ligands, the electronic interaction between $\text{*N}_2\text{H}$ and the metal is weak, so is the ability for the electron-transfer into $\text{*N}_2\text{H}$. These predictions for the two limiting cases can also be confirmed by the volcano-like relationship between $\Delta G(\text{*N}_2\text{H})$ and the metal center-to-substrate electron transfer (Fig. S5). Despite the same coordination environment, the amount of charge transferred from metal centers varies with their electronegativity, resulting in different performance of the catalytic activities.

Stability and electrical conductivity of SACs with P-based ligands

As the particle size decreases, the surface free energy of metals increases prominently [35]. Therefore, single metal atoms might aggregate on the substrate, which can reduce

the catalytic activity and stability. To assess the stability of these SACs, we first doubled the (2×2) unit cell to (2×4) unit cell to model the structure of two sufficiently separated single atoms on the substrate (S) and then we brought the two single metal atoms together to model their dimerization (D). The dimers of metal atoms on the substrate surface mainly have three geometries (Fig. S6). Furthermore, we compared the energy (E_S) of thermodynamically favorable structure S with structure D (E_D) by using the formula $\Delta E_{\text{stability}} = E_S - E_D$, as shown in Fig. S7. The results demonstrated that the dimerization of metal atoms is thermodynamically favorable for most metals. However, considering that these SACs might be kinetically stable, we calculated the activation barriers of W, Ta and Nb dimerization. Our calculation revealed that the dimerization barriers are as high as 2.12 eV for W, 2.81 eV for Ta, and 1.18 eV for Nb (Fig. 7 and Fig. S8), revealing a kinetically hindered process. In consequence, these three catalysts are predicted to be stable as single atoms resistant to agglomeration. Besides, W@BP has been chosen as a representative to verify the stability of these catalysts by performing *Ab Initio* Molecular Dynamics (AIMD) simulations at 300 K. The results showed that W atom is well doped in BP during the simulation (Fig. S9), indicating that the catalysts should be sufficiently stable in the electrolyte.

For achieving high performance, it is important for an electrocatalyst to have a good electrical conductivity [41]. Since BP is a semiconductor and previous theoretical studies have shown that the substitutional doping of different metals can change the bandgap of BP [54], it is necessary for us to estimate the electrical conductivity of W@BP, Ta@BP and Nb@BP by calculating their band structures. According to the layer-dependent bandgap

Figure 7 The dimerization barriers of W@BP, Ta@BP and Nb@BP and the dimerization structure of Ta@BP. Yellow and orange spheres represent P and Ta, respectively.

property of BP, one-layer and three-layer BP were screened [63]. The bandgaps of pristine BP, W@BP, Ta@BP and Nb@BP with HSE06 are listed in Table S6. For pristine BP, the calculated bandgaps (1.70 eV for one-layer and 1.05 eV for three-layer) are consistent with the experimental values previously reported (1.73 eV for one-layer and 0.83 eV for three-layer) [64]. According to Table S6, the bandgaps of one-layer and three-layer BP are all reduced with the substitutional doping of W, Ta and Nb, which reflects that their electrical conductivity may be stronger than pristine BP. Therefore, these catalysts can be used in electrocatalysis. Moreover, it is worth noting that limiting the electron transfer rate may be a promising way to improve NRR selectivity, which can be realized by requiring electrons to tunnel through a thin insulator to the catalyst [10].

CONCLUSIONS

In summary, we employed DFT calculations to systematically explore twenty-nine TM-SACs supported on BP, with the aim to screen excellent NRR electrocatalysts theoretically. Among these catalysts, W@BP, Ta@BP and Nb@BP are considered as most promising candidates, offering remarkable activity ($\Delta G_{\max}$ of 0.40, 0.47 and 0.53 eV, respectively), selectivity, electrical conductivity, and long stability. *N_2H intermediate is identified as the key intermediate for the whole reaction and $\Delta G(^*N_2H)$ is a descriptor reflecting the intrinsic activity of these SACs. By analyzing electron transfer between *N_2H and metal atoms, we revealed that a good ability for metal centers to inject electrons into *N_2H intermediate is essential for high NRR activity. Additionally, the revealed dependence of $\Delta G(^*N_2H)$ on the metal nature is strongly related to the strength of bonding/antibonding interactions of metal centers with *N_2H , which uncovers the origin of NRR activity trends for different metal centers. Finally, a guideline for SACs with P-based ligands design is developed: The metal center with a moderate amount of positive charge for both *N_2H adsorption and electron-transfer into *N_2H ultimately result in excellent NRR activity. This theoretical study systematically verified that P-ligands attached to a TM is a promising building block for electrocatalytic NRR, paving the way to design and discover more effective TM-SACs for further NRR studies.

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Supplementary information Supporting data are available in the online version of the paper.

Xiaoyun Lin is currently a MSc candidate at the School of Chemical Engineering and Technology, Tianjin University. She received her BSc degree from Beijing University of Chemical Technology in 2018. Her current interest lies in the molecular level understanding of electrocatalytic reactions.

Zhi-Jian Zhao received his BSc and MSc degrees in chemistry from Zhejiang University and his PhD degree from Technische Universität München in 2012. After working as a Postdoc with Prof. Greeley in Purdue University and with Dr. Studt and Prof. Nørskov at Stanford University, now he is a professor at Tianjin University. His current research focuses on mechanistic studies on heterogeneous catalysts using multi-scaling simulation methods.

黑磷负载的单原子催化剂用于电催化 N_2 还原

林晓韵¹, 李璐璐¹, 常鑫¹, 裴春雷^{1,2}, 赵志坚^{1,2*}, 巩金龙^{1,2,3}

摘要 设计和开发高选择性、高活性的单原子电催化剂是实现在常规环境条件下合成氨的关键。本论文利用密度泛函理论对P配体在 N_2 还原反应(NRR)中的应用前景进行了预测,并且提出了一种高性能NRR单原子催化剂的设计准则。理论计算结果显示, W@BP (0.40 eV)、Ta@BP(0.47 eV)和Nb@BP(0.53 eV)由于具有低反应自由能、高稳定性和导电性,在高效电催化NRR中潜力巨大。特别是,几乎所有金属中心对 $*N_2$ 中间体的吸附能力都比 $*H$ 更强,这表明以P为配体的单原子催化剂具有较强的NRR选择性,且 $*N_2H$ 中间体的吸附自由能可作为描述符,反映这一系列催化剂的催化活性。此外,计算结果显示,金属中心向P配体转移的电子数目与NRR活性存在着火山关系,带有适度正电荷的金属中心具有优异的电催化NRR活性。该发现为高性能单原子催化剂的设计提供了理论指导。